Chapter 10
Polymeric Materials for Special Applications

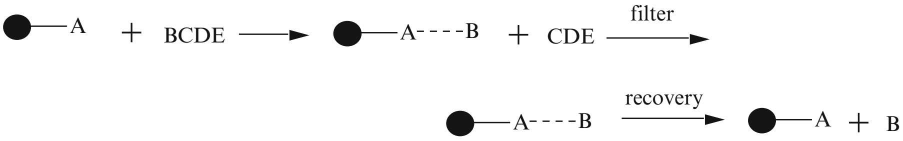
10.1 Polymer Supports for Reagents, Catalysts, and Drug Release

Supports are materials that are used for immobilization of various reagents, catalysts, drugs for release. Many of them are specially prepared macromolecules. Reagents and catalysts on support find applications in organic syntheses, biochemical reactions, special separations, and analyses. They also find uses in medicine for drug release, etc. An advantage of immobilized polymeric reagents in chemical reactions is that they can be separated, often easily by filtration, from the products of these reaction. Cross-linked polymeric reagents have an additional advantage in that several different polymeric reagents can be used simultaneously without the functional groups being accessible to each other for interaction. Reactions of some compounds in solution require high dilutions. Immobilization, however, may permit the same reactions to be carried out at relatively high concentrations. Immobilization can also be very useful in syntheses that consist of many steps, where the undesired by-products from each step can simply be washed away. This avoids lengthy isolation and purification procedures [2]. Also, by immobilizing on a polymer, the macromolecule may provide microenvironmental effects to the attached species for the reactions. These may include special electronic and steric conditions that could be different from those existing in bulk or in solution.

The chemical uses of polymeric reagents were originally classified by Patchornik according to the general type of reaction [1].

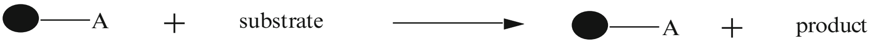
These are as follows:

1. Polymer-attached reagents are used in ***special separations*** to selectively bind one or a few species out of complex mixtures:



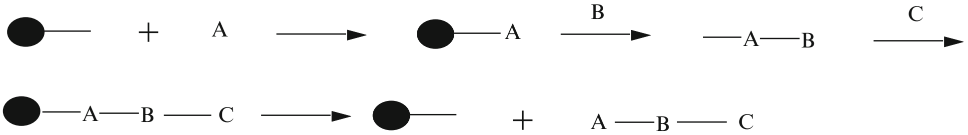
The polymer-bound compound is separated from the mixture and then released.

2. The polymer with a ***catalyst*** attached. Such catalysts can be enzymes, inorganic compounds, or organometallic compounds:



A. Ravve, *Principles of Polymer Chemistry*, DOI 10.1007/978-1-4614-2212-9_10,

3. The polymeric reagent can also be used as ***transfer agents***. Low molecular weight reactants transfer the functional moiety with the aid of the polymeric agent. This leaves the products in pure form after filtration and solvent removal.
4. The polymers are used as ***carriers*** or **as *blocking groups*** in syntheses [1]:

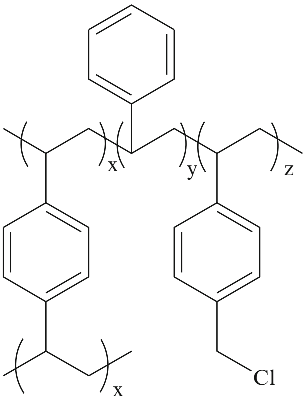


10.1.1 Support Materials

Many different support materials were developed [3, 4] since the original use by Merrifield of a polystyrene-based support material for polypeptide synthesis [5]. The work of Merrifield is described in Chap. 8 (see section on proteins). Beads of copolymers of styrene with divinyl benzene are available commercially and have been widely used as supports for many reactions. Many other polymeric materials are also used. These can be various other type of copolymers of styrene or with other polymers. The list includes cellulose, starch, polyalkanes, polyamides, poly(glycidyl methacrylate), polyisobutylene, polynorbornene, polyacrylamide, and others. In some instances, even glass was used. The more prominent support materials are presented below.

10.1.1.1 Materials Based on Polystyrene

Cross-linked polystyrene (copolymer with divinyl benzene) was the original support material used by Merrifield for polypeptide syntheses. The material is actually a terpolymer of styrene, chloromethyl styrene, and divinyl benzene.



Copolymers of styrene and divinyl benzene supports have since received many uses and have undergone many chemical modifications for various reactions as reagents and catalysts. The material can be functionalized in many ways. Thus, it can be nitrated, chloromethylated, sulfonated, lithiated, carboxylated, and acylated. The greatest use has been made of the chloromethylated and lithiated derivatives. These two derivatives can react with nucleophilic and electrophilic reagents, respectively, resulting in a wide range of functionalized polymers. For various modification reactions of polystyrene, see Chap. 9.

Two types of cross-linked polystyrene are often favored. One is a polymer that is cross-linked by only 1–2% of divinyl benzene. The material, though fairly strong mechanically, swells and expands significantly in volume when dispersed in proper solvents. It is called ***micro porous***. A copolymer with up to 20% divinyl benzene is the second type. It is prepared in the presence of large quantities of diluents to retain the products in expanded form. As a result, the structures are ***macro porous*** or ***macro reticular***. The advantages of micro porous over macro porous structures are faster reactions, less fragility, and easier handling. Although, macro reticular supports are less often used, they have the advantage of being useful in almost any solvent.

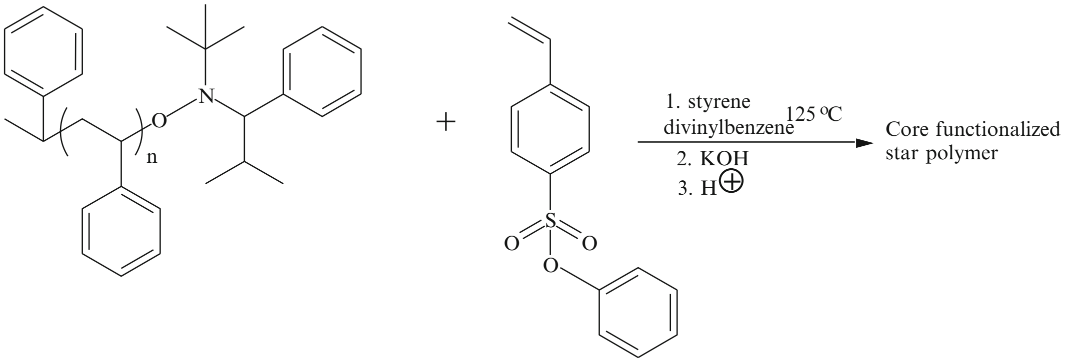
As a variation of the process, Fréchet and coworkers introduced ***reactive filtration*** [6]. In place of beads, they used discs of cross-linked polystyrene that were cut from a rod of the material. On the surface of these discs, they grafted 2,2-dimethylazlactone. These discs were then used in a filtration to efficiently scavenge excess amines from a reaction mixture. Subsequently, Frechet and coworkers also used such discs in a flow through acylation reaction [7].

To improve the access to the functional groups, Lee and coworkers developed a process of placing most of the functional groups on the outer surface of the polystyrene beads [7]. This was done by surface aminomethylation of preformed cross-linked commercially available polystyrene beads. Such bead usually range in size from 100 to 400 mesh (in.) in diameter and can be functionalized by surface reactions or by surface grafts. This yielded materials with a lower number of functional groups, but with the majority of them being accessible. Lee and coworkers then utilized the beads in a solid peptide synthesis [7].

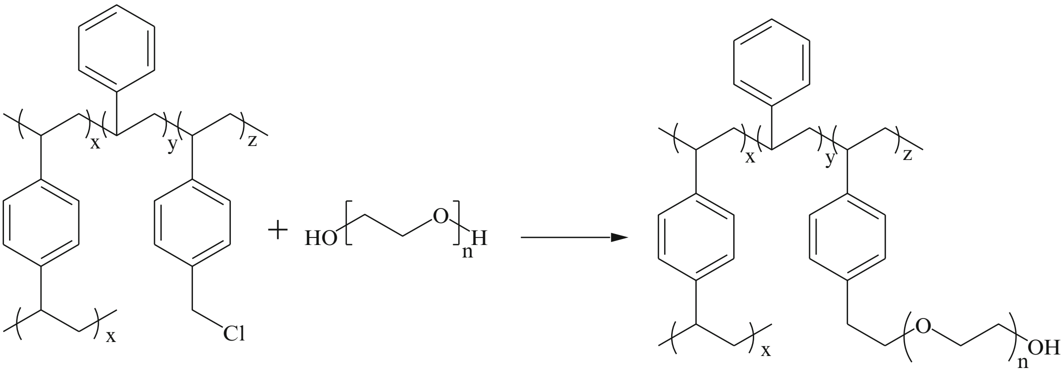
Lee and coworkers also prepared beads with *N*-heterocyclic carbene ligands located on the outer shell. In this preparation, they used beads formed in a suspension polymerization [8, 9].

Fréchet and coworkers [7] reported a variation of the strategy by attaching functional groups to cross-linked polystyrene in the interior of a soluble star polymer matrix. In this process, the catalytic groups are core-confined through the use of low molecular weight macroinitiators that form the surface of the final polymer. Presumably, this allows using simultaneous incompatible reagents, like acids and bases, because they are physically isolated from one another.

Lu and Toy [10] illustrated a similar approach: by showing how core-functionalized star polymers are prepared to form sulfonic acid-functionalized core material:

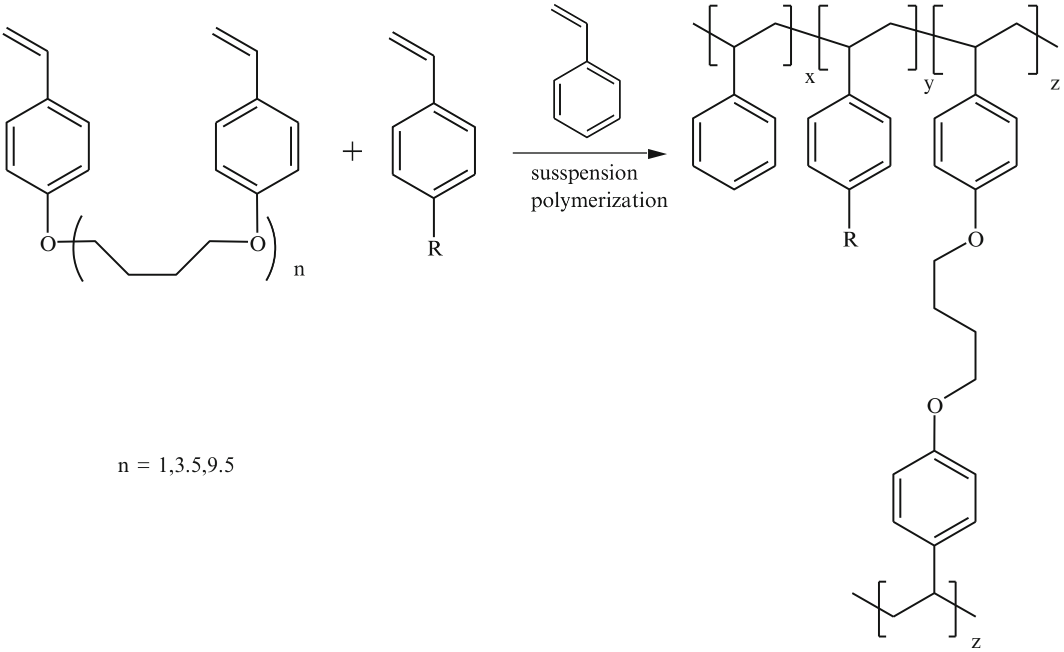


There is a drawback, however, of using the polymer described above, because many functional groups end up imbedded inside the resin and access to them requires the type of solvents that can thoroughly swell the resin. Many polar solvents, however, fail to swell cross-linked polystyrene adequately, yet may be required for specific reactions. That led to modifications, such as, the use of polar cross-linking materials, like oligomers of glycols. One example is a cross-linked polystyrene-poly(ethylene glycol) composite, known as ***Tentagel*** [10]. It can be illustrated as follows:



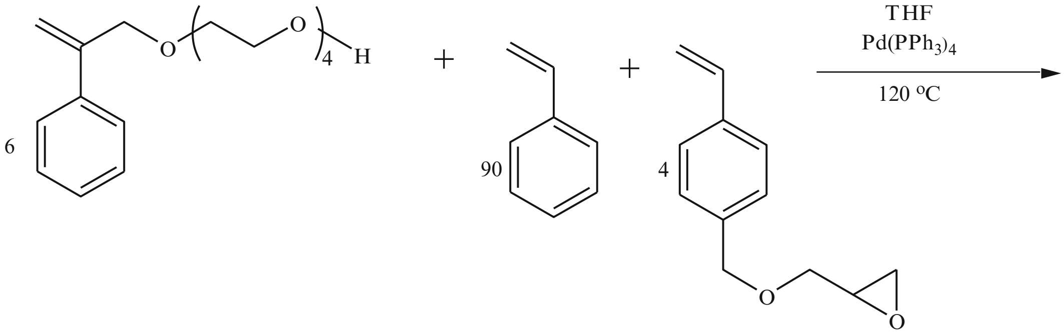
Another example is work by Bradley and coworkers who incorporated short oligomer (polyethylene glycol) groups into the backbone of the cross-linked polystyrene [11]. The oligomer poly (ethylene glycol) in this preparation also acts as a spacer to separate the polystyrene backbone from locations of the reactions. The material was used efficiently in a solid phase peptide synthesis.

Toy et al. [12] demonstrated that by replacing divinyl benzene with more flexible compounds usually increases their mechanical stability and allows them to absorb more solvent. In addition, when the cross-linked compounds contain oligomers of such materials as ethylene glycol, the compatibility with polar solvents increases. Subsequently, Janda and coworkers used polytetrahydrofuran in suspension polymerization of styrene to prepare general solid support resins for organic syntheses [13].



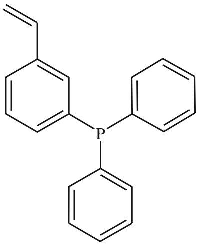
The material became known as **Janda Gel** [13]. The preparation of this gel with *n* equal to one is illustrated above [14].

An interesting application of cross-linked styrene resins that are similar to the Janda gel was developed by Kobayashi and coworkers, who used such materials to encapsulate metal catalysts [15]. The technique used was to first entrap the metal catalysts by coacervation with linear polystyrene that was functionalized both by epoxide groups and oligo poly(ethylene glycol). The polymer becomes cross-linked upon heating through reaction of the epoxide groups with polyethylene glycol entrapping the metal:

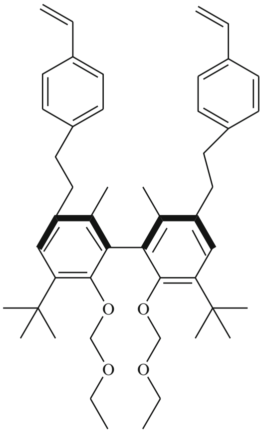


The above solid catalysts were used successfully to catalyze various reactions, like the Suzuki–Miyura reaction [15], such as aminocarbonylation, amidation, and the Heck reactions [16]. Polymers containing scandium triflate, ruthenium, platinum, or gold were prepared to perform Mukayama aldol, alcohol, and sulfide oxidation, hydrogenation, and indole syntheses [17].

Incorporation of some of the metals, like palladium, is improved by incorporating phosphine ligands into the polymer. One such ligand can be illustrated as follows [19]:

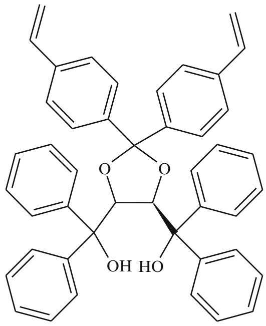


Hoveyda, Schrock, and coworkers [19] reported using chiral cross-linking compounds immobilized on heterogeneous polystyrene resins. The chiral moiety was then used as a ligand in asymmetric catalyses. In one application, they used the material to prepare a recyclable chiral molybdenum olefin metathesis catalyst that was used in enantioselective ring opening and ring-closing metathesis reactions. The material can be illustrated as follows:



The products that were isolated possessed only slightly lower enantiomeric excess than those obtained with the corresponding small molecule catalyst.

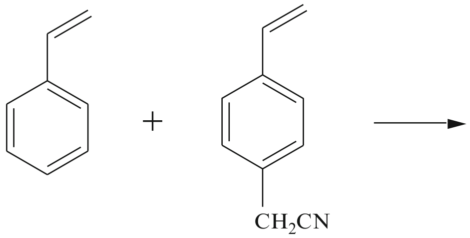
In a similar manner, Sellner et al. [20] prepared a variety of polystyrene beads with embedded α,α,α,α-tertiaryl-l,3-dioxolane-4,5-dlmethanol groups. They were subsequently used to form an immobilized catalyst with recyclable chiral titanium Lewis acid for addition of Bu_2Zn to benzaldehyde.

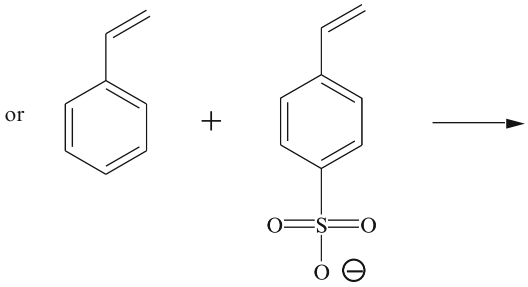


They also reported preparations of various cross-linkers containing tertiary aryl groups with polymerizable carbon-carbon double bonds [20].

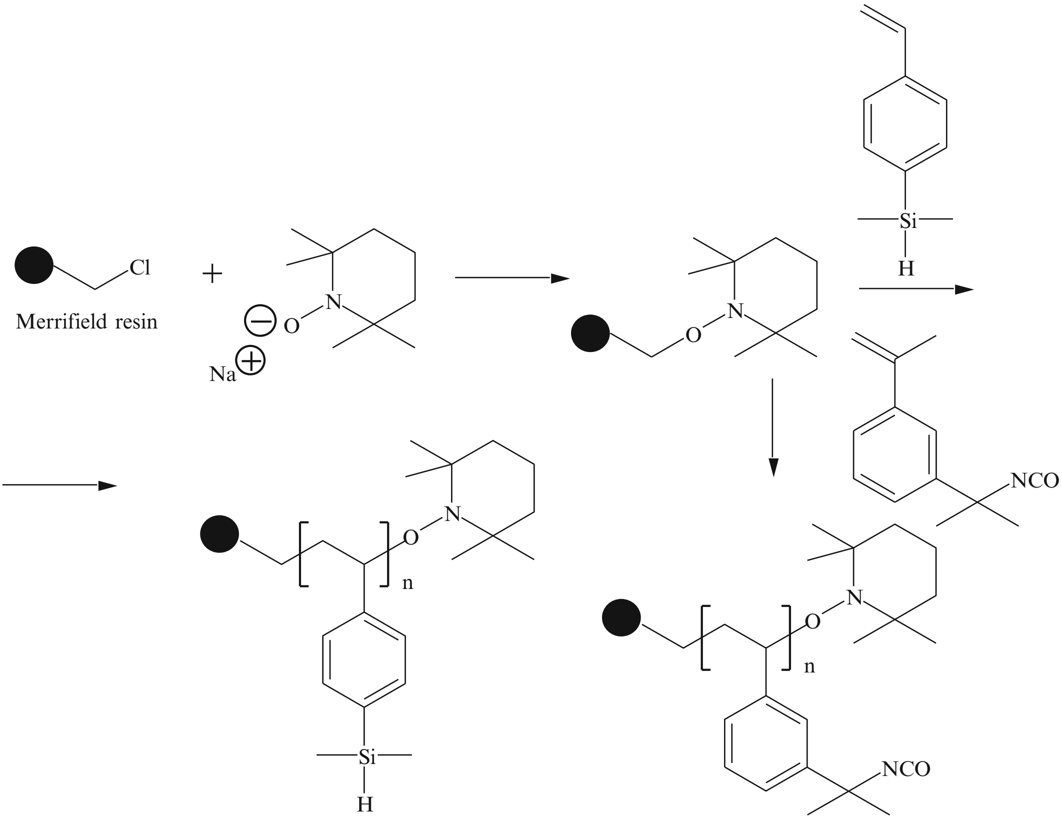
Itsuno et al. [21] synthesized a cross-linked polymer support with a chiral 1,2-diamine for enantioselective ruthenium transfer hydrogenation catalysis of aromatic ketones.

A variation on the process was to functionalize polystyrene by incorporating groups like hydroxy, acetoxy, or nitrile onto the backbone of polystyrene, through copolymerization of monomers [22]. Following are two examples:



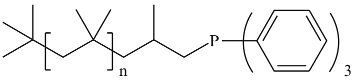


Similar to the work by Frechet who grafted functional groups to heterogeneous polystyrene (see above), Hodges used living free-radical polymerization to prepare what he referred to as **Rasta resin** [23]. The Merrifield resin was first functionalized with reduced TEMPO to form a resin core. With the help of Rhodamine dye, it was confirmed that the grafts and associated functional groups were located on the exterior of the resin beads [2]. The product was then used in free-radical polymerization with various styrene monomers [4]. It was also shown that such resins could be prepared efficiently using microwave-initiated polymerization [22]. Fontaine extended this concept by using atom transfer radical polymerization initiators to attach poly(2-vinyl-4,4-dimethyl-5-oxazollne) to form grafts that are efficient nucleophilic scavenging [25, 26]. Preparation of Rasta resin can be illustrated as follows:

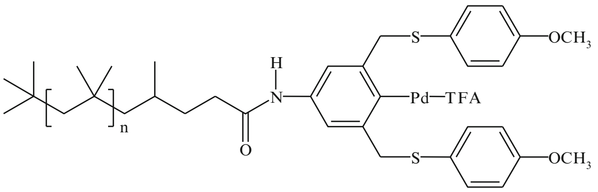


10.1.1.2 Support Materials Other Than Polystyrene

Barett et al. [27] as well as Hanson and coworkers [28] used low molecular weight polyisobutylene to form polyisobutylene-supported catalysts:

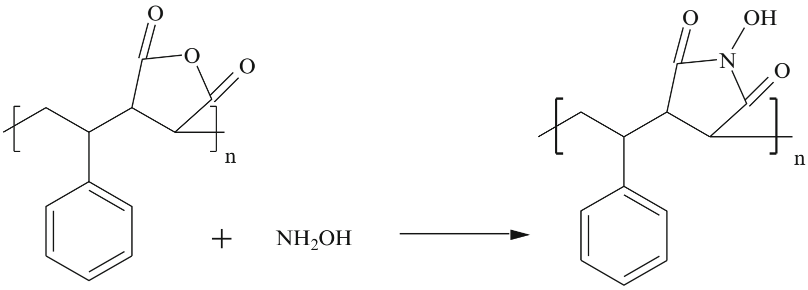


and

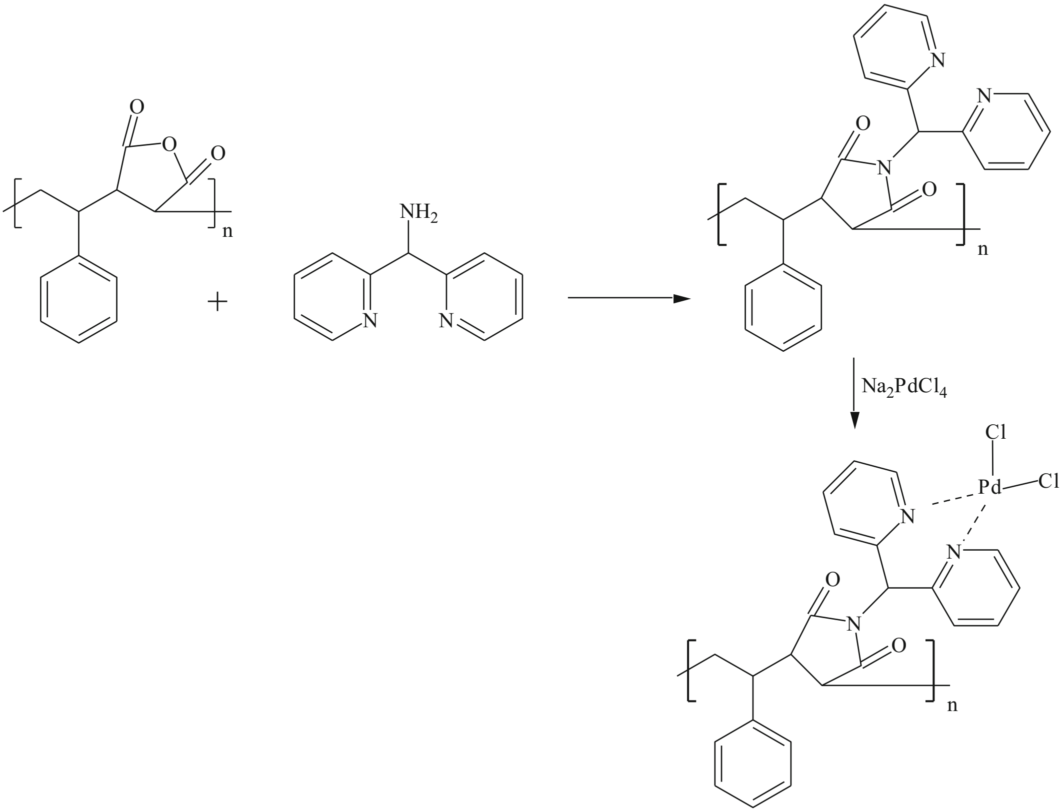


An advantage of using polyisobutylene is solubility in a variety of nonpolar solvents at ambient temperatures. Also, the terminal double bond of polyisobutylene can be readily transformed into various useful groups for attachment of catalysts or reagents. Thus, polyisobutylene was used as a catalyst support for anchoring a sulfur-cation-sulfur Pd(II), as shown above. These catalysts were used to perform allylic substitution, Heck, and Sonogashira reactions [26]. Polyisobutylene was also used to support chiral bisoxazoline ligands for copper-catalyzed cyclopropanation reactions [27]. Other uses included catalysis of self-separating atom transfer radical polymerization [28], RCM catalysis [29], and catalysis of a chromium-based polycarbonate polymerization [30]. It is important to note that these polyisobutylene-supported catalysts exhibited close to or similar activity to their unanchored counterparts. In addition, they were readily recovered and reused without appreciable loss of activity.

Nájera and coworkers [34] used a commercial poly(styrene-*alt*-maleic anhydride) copolymer as support material. The copolymer was first reacted with hydroxylamine and then converted to a polymer-supported *N*-hydroxy succinimide. The product was then used in a peptide-coupling reactions. Low levels of racemization were reported. Addition of hexane allowed the removal of the polymeric material by filtration.

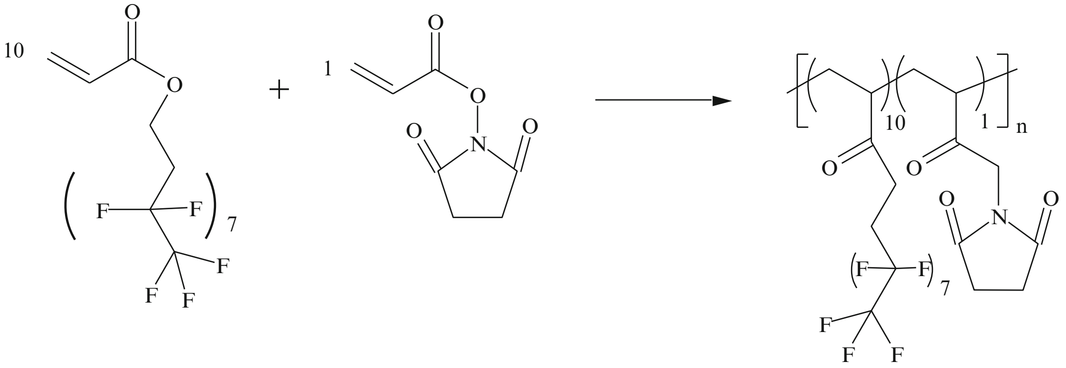


The polymeric imide could then be reacted with primary amines or ammonia to form ammonium salts for a subsequent reactions with a carboxylic acid in the presence of a coupling reagent. It could then be converted to amides or functionalized as a uranium salt for use as polymer-supported peptide coupling. In addition, the anhydride was also reacted with di(2-pyrldyl)methylamine and formed a recoverable palladium catalyst for cross-coupling reactions that could take place in water.

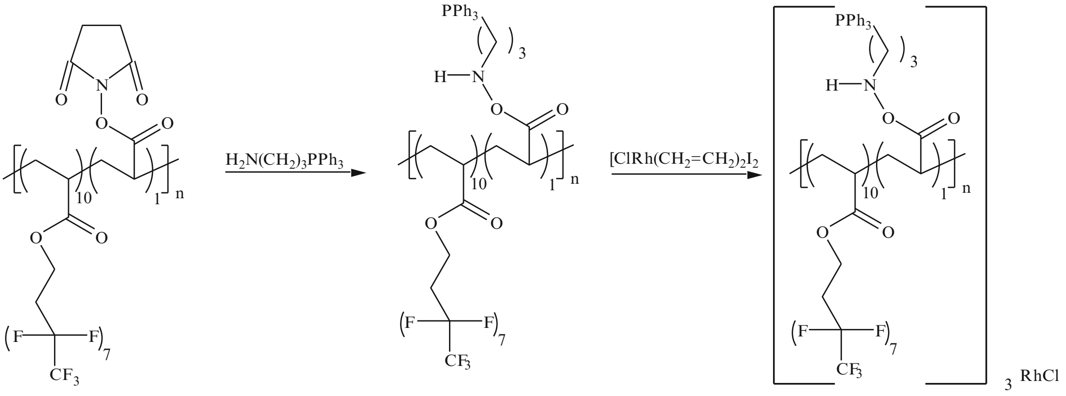


Acrylic Polymers as Support Materials

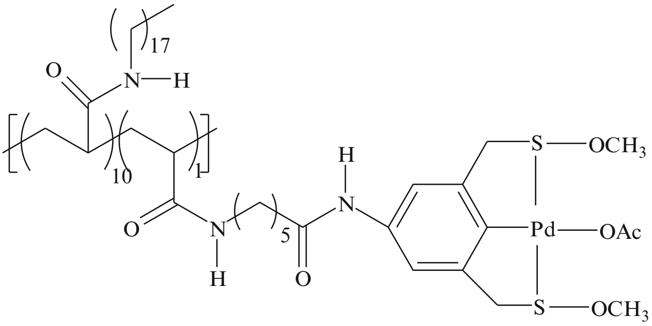
Various acrylic polymers and copolymers are also utilized as support materials. For instance, a copolymer of a fluoroacrylate monomers was prepared by Bergbreiter and coworkers to form a support material that is selectively soluble in fluorinated solvents [28–32].



The resulting polymer was then converted to a rhodium hydrogenation catalyst:



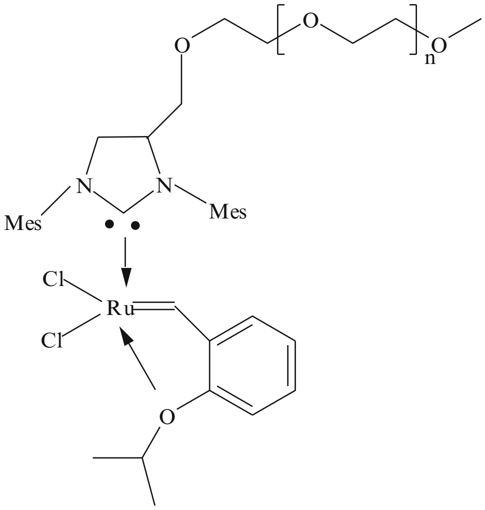
Numerous papers were also published on use of polyacrylamide and copolymers as support materials. Following is an example [33–36].



Bergbreiter reported using this material in mechanistic studies of the Heck reaction [33].

Polyether-Based Supports

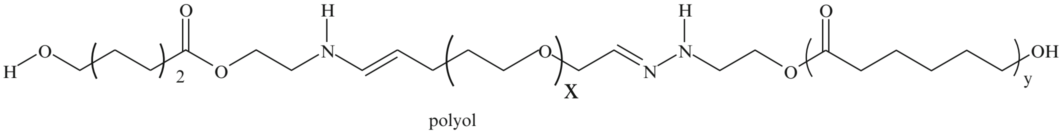
Tentagel, described above, is in wide use today in solid phase syntheses. Polyethylene glycol has also been attached to various other polymers to form support resins. For instance, Fréchet and coworkers [37] used cross-linked methacrylate esters of ethylene glycol oligomers in a suspension polymerization to synthesize hydroxyl group functionalized beads. These beads swell well in a variety of polar solvents. Another example is that of Grubbs attaching a ruthenium metathesis catalyst to polyethylene [38]:



10.1.2 Special Gels for Drug Release

Metyjaszewski et al. reported [39] preparation of nanostructured hybrid hydrogels for tissue engineering and drug delivery applications. They incorporate poly(oligo (ethylene oxide) monomethyl ether methacrylate) nanogels of size 100–200 nm into a larger 3D matrix, such as hyaluronic acid gel. The macroscopic hydrogel acts as a 3D matrix regulator for the drug release. In this work, polymerizable poly(oligo (ethylene oxide) monomethyl ether methacrylate) nanogels were covalently incorporated into a 3D network via a photo-polymerization process. The introduction of disulfide moieties into the polymerizable groups resulted in releasable nanogels from cross-linked 3D network under reducing environment.

Tan, Fu, and coworkers [40] reported preparation of a pH-sensitive biodegradable polyurethane for drug release:



A series of pH-sensitive polyurethanes were synthesized using pH-sensitive macrodiol, shown above, and a tripeptide chain extender. The obtained polyurethane had a number average molecular weights of 4,500–6,200. The material cleaves in acid media (pH 4–6) and degrades in enzymatic solution.

McCormick and coworkers [41] reported the synthesis of a temperature-responsive triblock copolymer, consisting of α-methoxypropyl (ethylene oxide)-*b*-poly(*N*-(3-aminopropyl)methacrylamide)-*b*-poly(*N*-isopropylacrylamide). At room temperature, the polymer is hydrophilic and exists as individual molecule in aqueous solution. Increasing the solution temperature above a lower critical solution temperature leads to self-assembly into micelles. The PAPMA portions were cross-linked with terephthaldicarboxaldehyde at pH 9.0 to generate shell cross-linked micelles with cleavable imine linkages. The release of a model hydrophobic drug, prednisolone 21-acetate, was studied at specific pH and temperature conditions. The drug was released at pH 6.0 as hydrolytic cleavage of the imine cross-links within the swollen micelles occurred.

10.1.3 Utilization of Support Materials

Following are examples of more prominent utilizations of support materials.

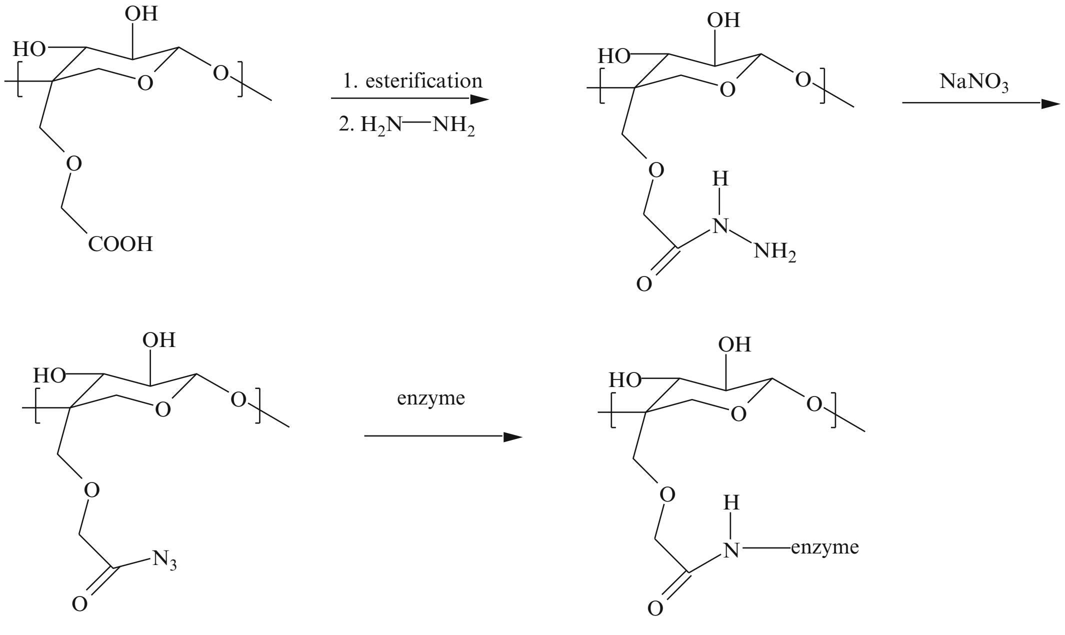
10.1.3.1 Immobilized Catalysts

It may be more accurate to refer to many of them as catalysts attached to polymers. Such catalysts can be inorganic compounds, like, for instance, Lewis acids attached to organic polymers. They can also be organic or biochemical catalysts. Perhaps the biggest group among such attached catalysts are *immobilized enzymes*. They are used in industrial processes as well as in research laboratories. Immobilization often improves stability, and in some rare cases, activity over a broader range of pH and temperatures. Another advantage is elimination of enzyme contamination of waste streams. On the other hand, immobilized enzymes can often be less active after immobilization.

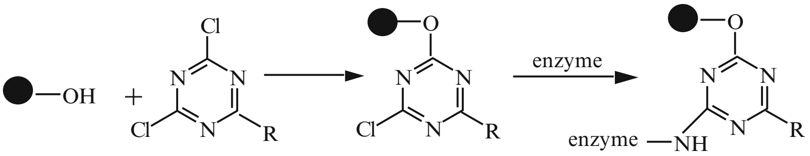
Immobilized Enzymes

Several major techniques of enzyme immobilization are used. One important one is covalent bonding of the enzyme to a support material. Such attachment usually consists of reacting some functional group of the enzyme, not active in the enzymatic process, with a functional group on another polymer that is the carrier. Hydrophilic groups are preferred for reactions with enzymes in aqueous media.

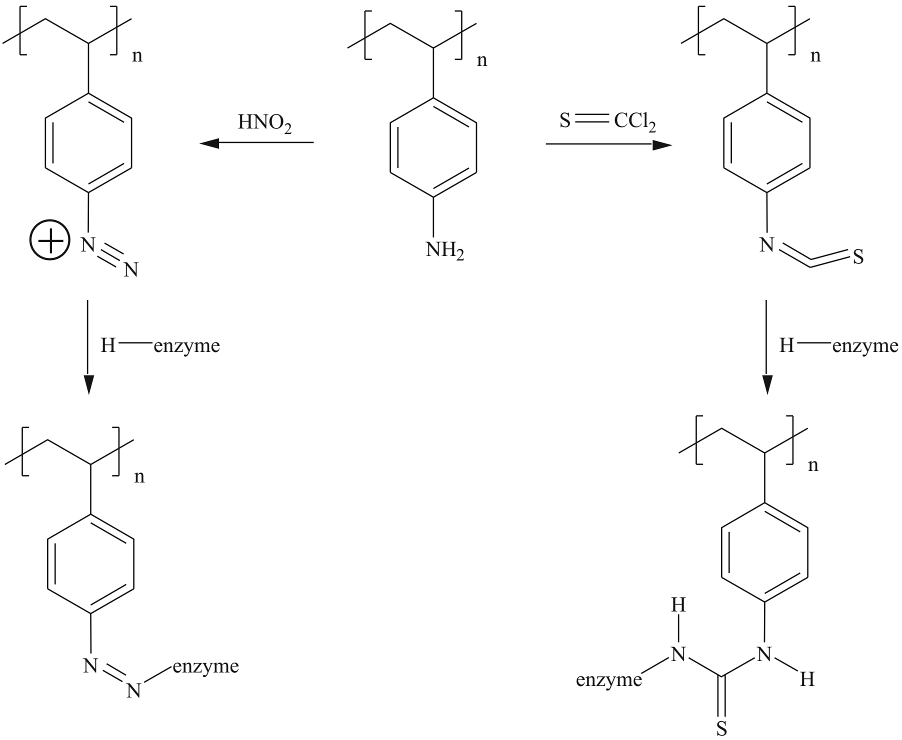
An immobilization of an enzyme on cellulose with azide groups [42] attached can serve as an illustration. Carboxymethyl cellulose is the starting material:



In other techniques, the protein may be bound by some copolymer of maleic anhydride, where the anhydride groups react with some available amine groups on the enzyme [42]. Other techniques may utilize cyanuric chloride attached to polysaccharides for immobilization [42]:



Polyaminostyrene can be diazotized or treated with thiophosgene and then used in enzyme immobilization [43]:

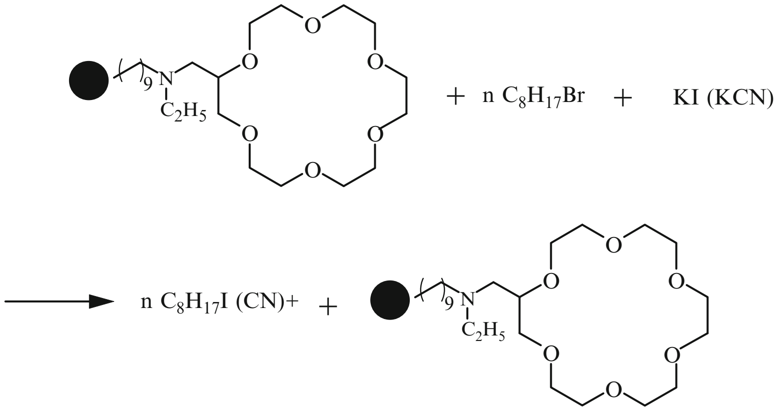


Because epoxy groups on carrier molecules are capable of reacting with an amine or a carboxylic acid groups of the enzymes, they can be used in enzyme immobilization. A variation on the technique is to react a vinyl monomer that contains an epoxy groups, like glycidyl methacrylate or glycidyl acrylate, with the enzyme first. The product is then polymerized or copolymerized through the vinyl portion [44]. As stated earlier, in many cases, immobilization of enzymes is accompanied by some loss of activity. In some instance, the loss in activity can be severe. A special technique, however, was developed [45], where the enzyme called protease is immobilized on a polymer with amino glucose units to form covalently bonded carbohydrate-protein conjugates. In aqueous solution, the conjugated enzymes show about the same catalytic activity as native enzymes. At elevated temperatures, however, they exhibit enhanced stability. In addition, they are capable of catalyzing reactions in organic solvents that denature and inactivate the native enzymes [45].

Hiroshi et al. reported [46] a high-performance immobilized lipase catalyst for polyester synthesis. A porous polypropylene was found to be a good support for immobilization of *Candida antarctica* lipase (enzyme). The immobilized lipase on polypropylene efficiently catalyzes ring opening polymerization of 15-pentadecanolide, polycondensation of divinyl sebacate, and 1,8-octanediol.

10.1.3.2 Immobilized Nonenzymatic Catalysts

There are also many uses for special nonenzymatic polymeric catalysts. For instance, polymer-bound crown ethers, cryptates, and channel compounds can be immobilized to act as polymeric phase-transfer catalysts. The catalytic activity is based on selective complex formation. An example is a use of polystyrene-attached oxygen heterocycles [18]-crown-6 or a cryptand[222] to catalyze replacements of bromine in *n*-octyl bromide by an iodine or by a cyanide group [47]:



A 95% yield is achieved. The catalytic activity, as a result of the complexation of the cations, results in an increased nucleophilicity of the anions.

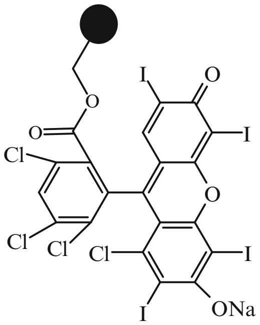
Interactions of ions and ion pairs with vinyl polymers of crown ethers were shown to be considerably more efficient than such interactions with unattached crown ethers [48]. Also, studies of diazo-4,7,13,16-tetraoxacyclooctadecane bound to polyacrylamide gel show an enhancement of cationic complexation when compared to ligands that are not bound to polymers [49]. On the other hand, polymer-bound crown ethers do not offer any advantage over unbound ligands in the Koening–Knorr reaction [50].

The catalytic properties and solute-binding capabilities of the pendant crown ethers and glyme ligands apparently depend on the spacing between the ligands. They also depend upon the structure and length of the chains connecting the ligand bound ions and the solvent [51]. In low polarity solvents, the ligands activate anionic reactants through modification of their ion pair structures.

Ion exchange resins have been used for a long time now to catalyze some reactions. This is mentioned, for instance, in Chap. 7 in the section on epoxy resins. Basic ion exchange resins can also be used in condensations of furfural with aliphatic aldehydes [52].

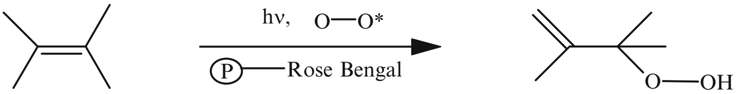
A still different kind of polymeric catalyst is one that has pendant photosensitizers attached. To be effective, the sensitizer portion must absorb light and undergo a transition from a singlet to a longer lived triplet state (see Sect. 10.4). It must then, without emitting radiation, activate a substrate molecule and return to the ground state. Some dyes function in this manner. An example is Rose Bengal. When it is attached to cross-linked polystyrene [53], it can be used to produce singlet oxygen.

The excited oxygen in turn hydroperoxidizes olefins. The structure of polymer-bound Rose Bengal can be illustrated as follows:

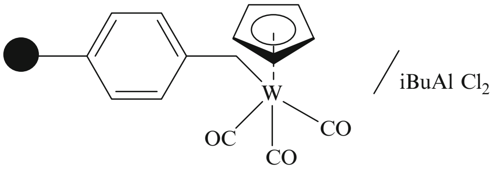


polymer bound Rose Bebgal

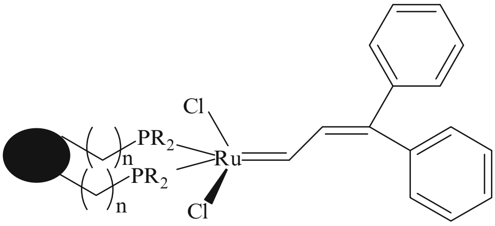
The photosensitized hydroperoxidation reaction of olefins [53] can be shown as follows:



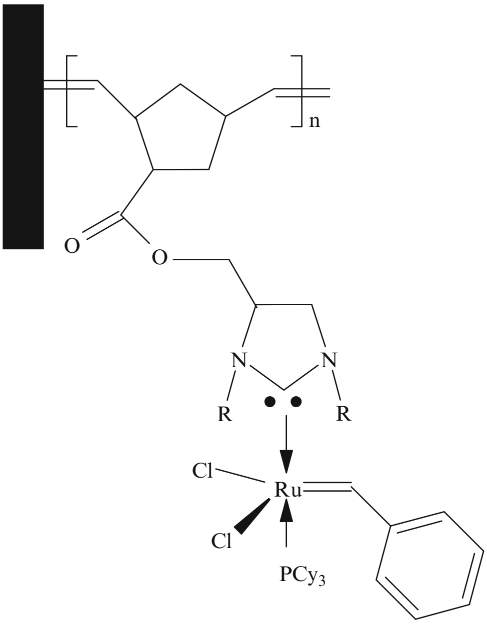
Metathesis catalysts including Grubbs ruthenium catalyst (see Chap. 5) are hard to separate from the reaction products. Chemists therefore sought ways to overcome this problem by immobilizing the catalyst on various supports. Buchmeister recently reviewed various polymer-supported metathesis catalysts [54]. A few are reported here. Early, Grubbs described a phosphine-derivatized polystyrene-supported catalyst [55]



Similarly, a Grubbs type ruthenium catalyst on a phosphine-derivatized polystyrene [56] can be illustrated as follows:

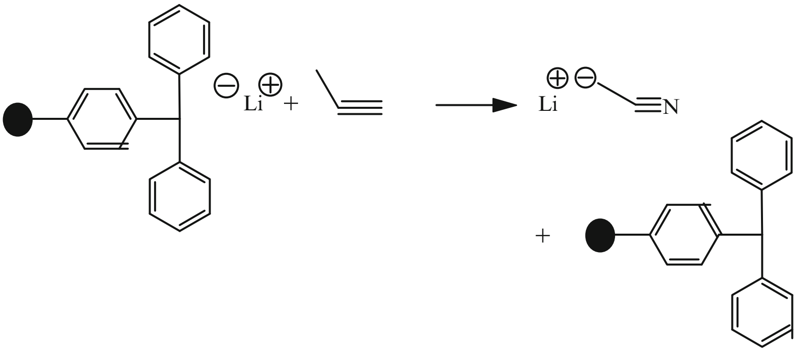


This catalyst, however, turned out to be considerably less active in ring opening metathesis polymerization of norborn-2-ene and in metathesis polymerization of *cis*-2-pentene. Better results were obtained when a ruthenium-based metathesis type catalyst was immobilized via an *N*-heterocyclic carbene [57]. Additional improvements in performance were obtained when the catalyst was immobilized on a monolithic silica rods:

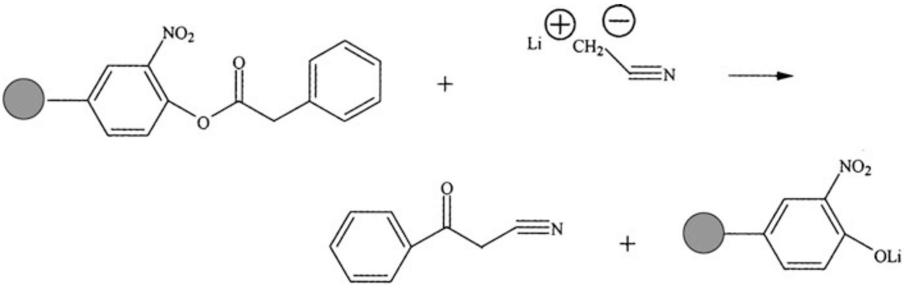


10.1.3.3 Immobilized Reagents

An example of such a reagent is use of immobilized triphenyl methyl lithium to transfer a charge and form a new carbanion:

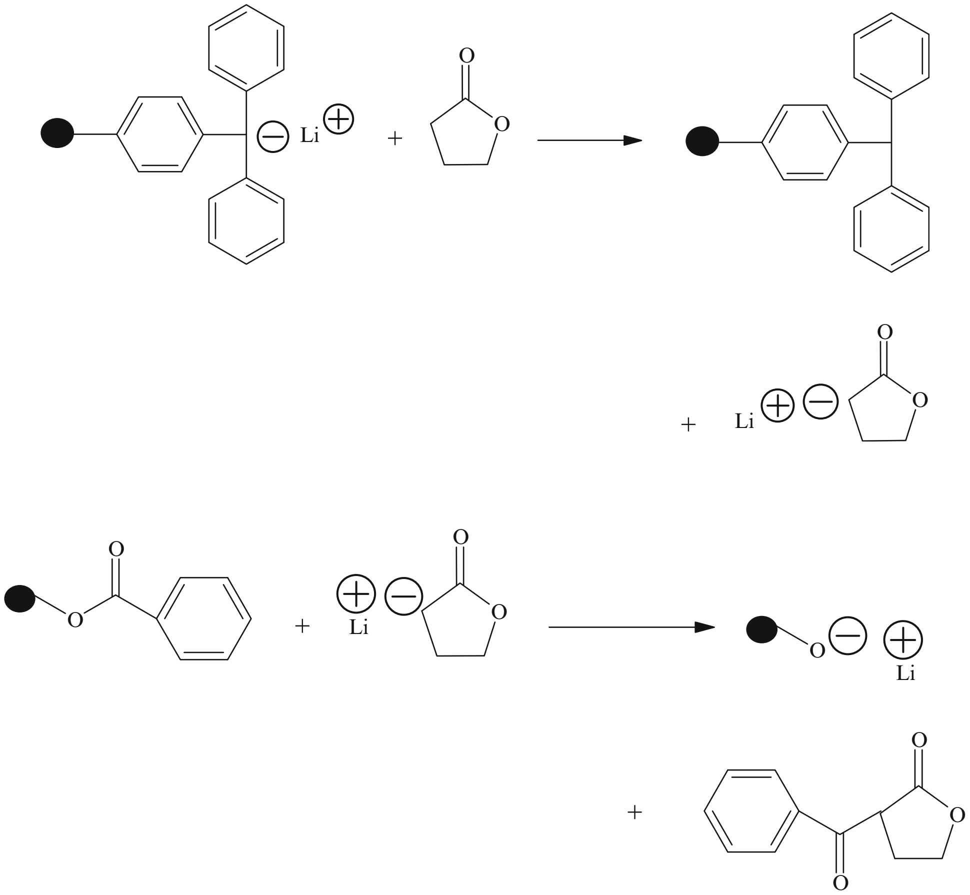


The carbanions in turn react with the ester groups and yielded the desired product:



The yield from the above reaction was found to be about 90%. This compares very favorably with a 27% yield obtainable without polymeric supports [58].

Another example is benzoylation of δ-butyrolactone. When an acylation reaction is being carried out on an ester in solution, the ester enolate must be completely formed before the acylating agent can be introduced. Otherwise, the acylating agent reacts with the base instead. During this period, however, the ester enolate can undergo self-condensation. Using polymer-attached reagents, however, benzoylation of δ-butyrolactone or similar compounds can be achieved in 95% yields [59]



By comparison, when the above reaction is performed in solution, without any support, the yield is only about 31% [59]. Patchornik termed the use of supports in this manner as "wolf and lamb chemistry" [58].

It appears unlikely that all organic reactions can benefit from use of polymeric reagents or catalysts. Nevertheless, such reagents and catalyst do appear to be promising for many applications. The fact that polymer-bound reagents and catalyst are more expensive, however, may preclude wider industrial utilization, except in special cases.

10.2 Electricity-Conducting Polymers

Most polymeric materials, as we usually know them, are insulators, yet conducting polymers were first prepared in 1862 by Letherby who formed polyaniline [60] by electro polymerization. It was only during the past 25–30 years, however, that organic polymers, capable of conducting electric current, created considerable interest [61]. Many polymeric materials were synthesized since. At present, it is not completely understood by what mechanism the electric current passes through them. We do know, however, that all conductive polymers, or intrinsically conducting polymers according to Inzelt [62], are similar in one respect. They all consist of extended π-conjugated systems, namely alternating single and double bonds along the chain.

One of the early known conductive polymers is polysulfurnitride $(SN)_x$, an inorganic material that tends to be explosive, but becomes superconducting at 0.3 K [63]. Since then many other conductive polymers evolved. The most investigated ones appear to be polyacetylene, polyaniline, polypyrrole, polythiophene, poly(phenylene sulfide), and poly(phenylene vinylene) and their derivatives. Many derivatives of these materials and other similar ones also been reported.

The mechanism of electro polymerization that is used to form many conductive polymers is also still not fully understood. According to Diaz et al. [64], the process involves a sequence of coupling steps, with each step being activated by two species. The polymer- forming process requires two electron per step It also includes partial oxidation of the polymer. Thus, the polymer formation and the polymer oxidation occur simultaneously. Diaz proposed a chain propagation process for the polymer formation. Although that is still accepted by many, his mechanism is now being questioned. Heinze et al. [65] suggest that the process of polymer formation consists of oligomer formation and oxidation followed by σ-coupling of chains.

All known conducting polymers have backbones of contiguous $\mathbf{sp}^2$-hybridized carbon centers. In each of these centers, one valence electron resides in a $\mathbf{p}_z$ orbital. It is orthogonal to the other three sigma bonds. When the material is oxidized or reduced, that removes some of the delocalized electrons. The electrons then obtain high mobility. As a result, the conjugated p-orbitals form a one-dimensional electronic band. The electrons within that band become mobile when it is partially emptied. Depending upon the chemical structure, some polymer can also be self-oxidizing or reducing.

Structural disorder in these polymer molecules interferes with electron mobility. Thus, for instance, polyacetylene exhibits conductivity of 0.1–10 kS/cm. Stretch-orienting this polyacetylene, a process that aligns the chains and removes much of the disorder, increases conductivity to 80 kS/cm [66].

Polyacetylene can be shaped into a silvery looking film. The polymer is more thermodynamically stable in the *trans* form and converts from *cis* to *trans* when heated above 150°C. Partial oxidation of the film, with iodine or other materials, transforms it and increases its conductivity 10^9-fold. The process of transforming a polymer to its conductive form through chemical oxidation or reduction is called **doping**.

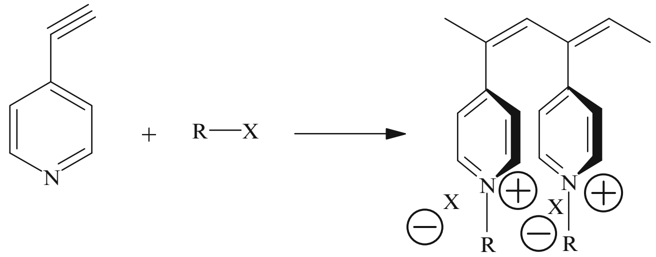
Two types of polyacetylene doping are possible:

$$(\mathrm{CH})_n + 1/2\mathrm{I}_2 \rightarrow (\mathrm{CH})_n^{\oplus}(\mathrm{I}_3)_{0.33}^{\ominus} \quad \text{oxidative doping (p - type)}$$

$$(\mathrm{CH})_n + x\mathrm{Na} \rightarrow (\mathrm{Na}^{\oplus})_x[(\mathrm{CH})_n^{\ominus}] \quad \text{reductive doping (n - type)}$$

The doping process can be reversed and conductive polymers can be undoped again by applying an electrical potential. It causes the dopant ions to diffuse in and out of the structure.

Improvements in preparations of polyacetylene came from several developments. One is the use of metathesis polymerization of cyclooctatetraene, catalyzed by a titanium alkylidine complex. The product has improved conductivity, though it is still intractable and unstable. By attaching substituents, it is possible to form soluble and more stable materials that can be deposited from solution on various substrates. Substitution, however, lowers the conductivity. This is attributed to steric factors introduced by the substituents that force the double bonds in the polymeric chains to twist out of coplanarity [67]. A family of substituted polyacetylenes were prepared [68] that were actually formed from ethynylpyridines by a polymerization reaction that takes place spontaneously by a quaternization process:



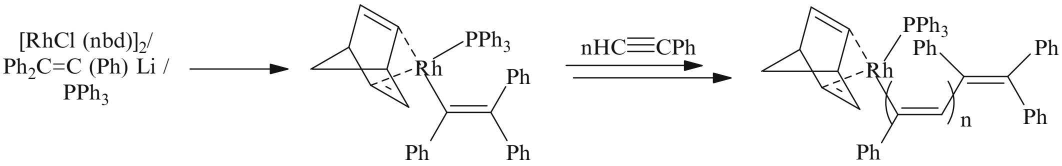
where X is a bromine or an iodine.

Like other substituted polyacetylenes, these materials are fairly stable in air and are soluble in polar solvents, also in water. The conductivity of these polymers is improved over previously reported substituted polyacetylenes to within the range of semiconductors.

Preparation of a highly conductive polyacetylene was achieved when Ziegler–Natta catalyst was used by Shirakawa in aged silicone oil at 150°C. It is believed that this reaction results in formation of polymers with less defects in the structures. The conductivity of these materials, when doped, actually approaches that of copper [62].

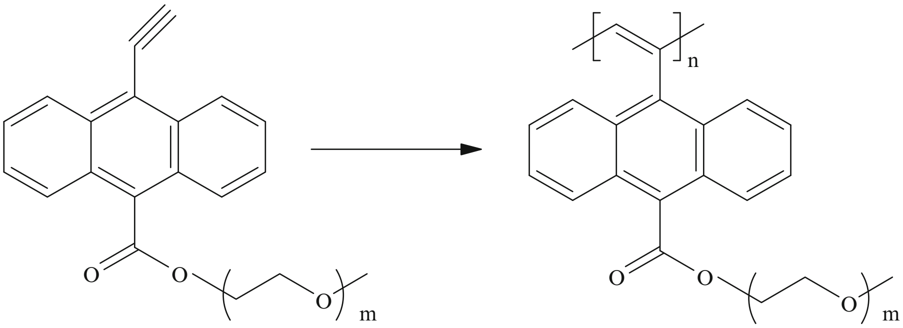
Considerable progress has been achieved in development of catalyst systems for living polymerization of various substituted acetylenes during the last 10 or 15 years [69]. Nowadays, there are available single-component catalysts based on stable carbene complexes and multicomponent catalysts based on $MoOCl_4$ and $WOCl_4$, both operating in metathesis mode, as well as Rh(diene) complexes operating in the Ziegler–Natta mode.

For instance, a living polymerization of phenyl acetylene and the synthesis of an end-functionalized poly(phenyl acetylene) by using Rh-based catalyst systems, $[RhCI(nbd)]_2/Ar_2C{=}C(Ph)Li/PPh_3$ (Ar = Ph, 4-Me_2-NC_6H_4), was reported [70]. Also, use of (triphenyl vinyl)lithium that has functional groups, such as the dimethylamino groups, results in formation of end-functionalized poly(phenyl acetylene)s, which quantitatively contained functional groups at the initiating chain end. The polymerization of phenyl acetylene by a catalyst prepared from $[RhCl(norbornadiene)]_2$, $Ph_2C{=}C(Ph)Li$, and PPh_3 proceeds smoothly in benzene to give quantitatively a yellow polymer with the number average molecular weight of 5,400 and the polydispersity ratio of 1.14. The reaction can be illustrated as follows:



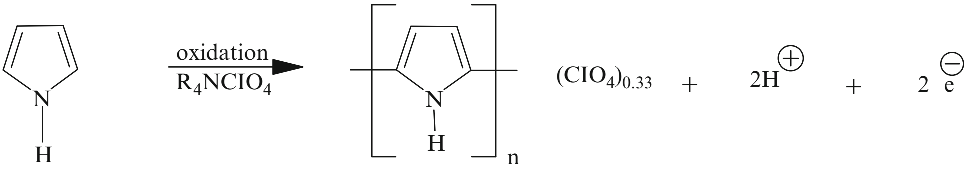
Masuda and colleagues reported [71] that they synthesized poly(anthryacetylenes)-bearing oligo oxyethylene units by using a transition metal catalyst, $WC1_6$, in 30 and 34% yields. The polymers were black solids. These polymers are soluble in chloroform, tetrahydrofuran, acetone, etc., but insoluble in alcohols, aliphatic hydrocarbons, etc. The UV–VS spectra of the polymers showed absorption maxima and band edges at around 570 and 750 nm, respectively, indicating that the polymer chains possess highly extended conjugation. These polymers exhibited blue emission

(emission maxima 470 nm) upon photo-excitation at 380 nm. One of the polymers ($n = 4$) showed a fairly large ionic conductivity (4.1 × 10 S/cm) at 80°C upon doping with $Li(CF_3SO_2)_2N$.

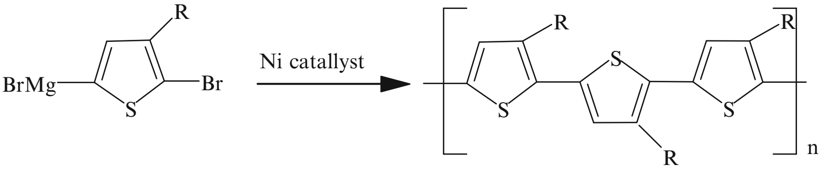


In 1979, it was demonstrated that **polypyrrole** can be formed as a film by electrochemical oxidative polymerization of the pyrrole monomer in acetonitrile. The polymers that form on the surface of the electrode can be peeled off as flexible, shiny blue-black films. Subsequently, in 1982 it was shown that thiophene can also be electro polymerized oxidatively at the anode. The method allows control over the oxidative potential during the polymerization, yielding doped films with optimized polymer properties. Both polypyrrole and **polythiophene** differ from polyacetylene in that both form during the polymerization in the doped form and that both are stable in air. They are, however, less conductive than the doped polyacetylene. The exact structures of polypyrrole and polythiophene prepared that way are still not fully established. The process of oxidative polymerization involves very reactive cation radical intermediates. Much of the coupling of the heterocyclic rings together is at the 2 and 5 positions. X-ray photoelectron spectroscopy shows that the polypyrrole formed in this manner has about 30% of the linkages at other than 2 and 5 positions. They might be in the 2 and 3 positions. This introduces "defects" into the hypothetically ideal chain and reduces the conjugation length and with it the conductivity.

The flexible films of polypyrrole that form upon electrochemical oxidation are not only stable in air and water, but may also be heated to 200°C without much change in electrical properties. The oxidative polymerization of pyrrole can be illustrated as follows:

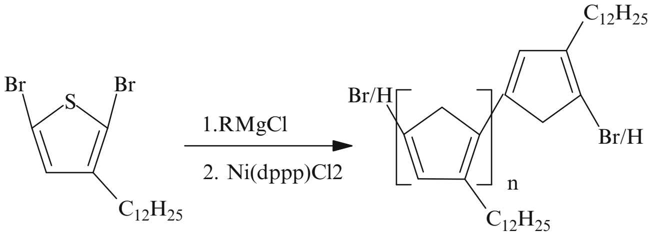


A regioselective synthesis of a highly conductive **poly(3-alkylthiophene)**s was reported [72]. Following synthetic procedure was used:



The iodine doped, unoriented poly(3-dodecyl thiophene)s exhibits average conductivity of 600 S/cm and a maximum conductivity of 1,000 S/cm [72].

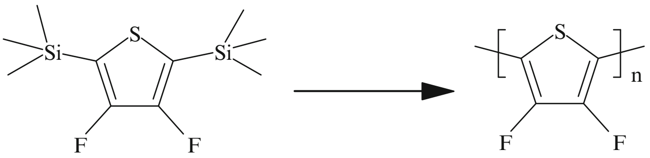
More recently, McCullough and coworkers [73] reported using the Grignard reaction to synthesize poly(3-dodecyl thiophene)



The molecular weights of the products were found by them to range from 10,000 to 50,000.

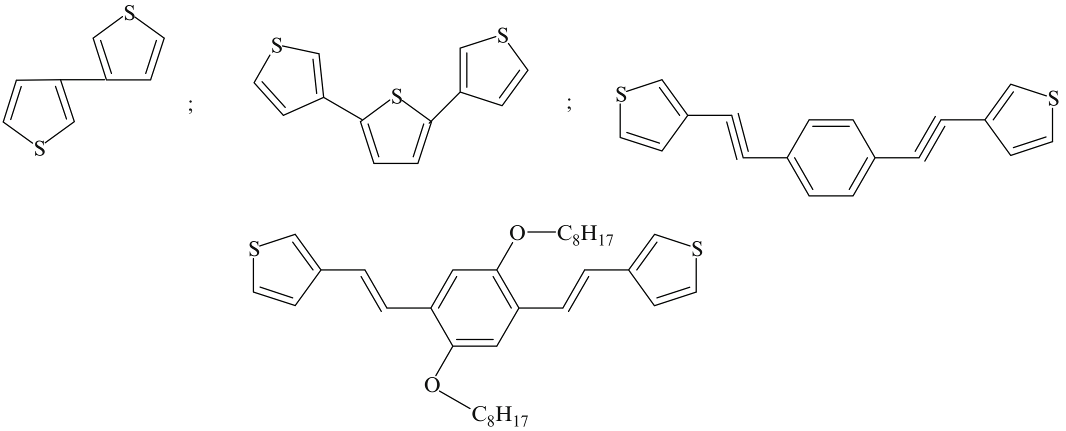
Earlier, McCullough et al. [74] reported that they have developed an end group functionalization method that enables the synthesis of many well-defined block copolymers that form nano wires with high electrical conductivity. They claim to have discovered that nickel-initiated regioregular polymerization of alkyl-thiophenes proceeds by a chain growth mechanism. They also observed that the degree of polymerization of poly(alkyl-thiophenes) increases with conversion and can be predicted by the molar ratio of monomer to nickel initiator. On the basis of their experimental results, they concluded that nickel-initiated cross-coupling polymerization is essentially a living system, with low polydispersities.

Irvin et al. [75] reported forming a poly(3,4-difluoro thiophene) by anodic polymerization:



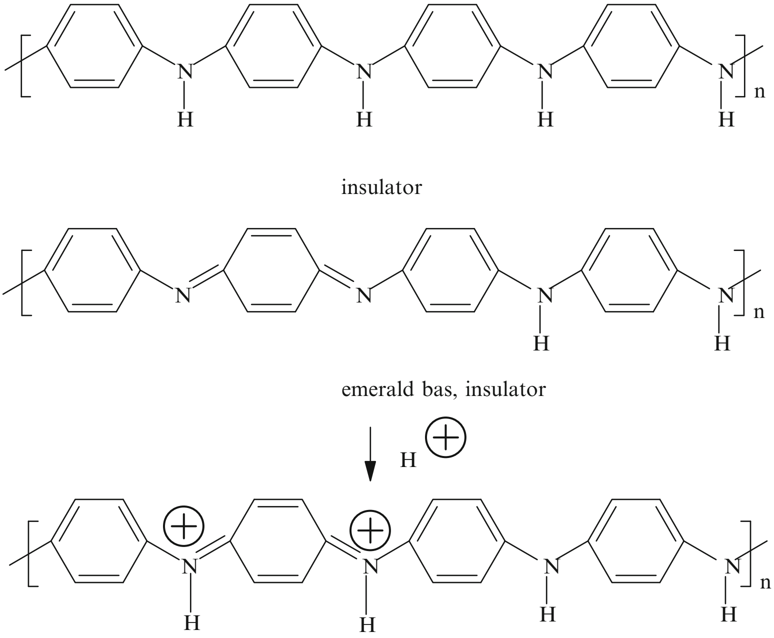
Because of the very electron-poor nature of the monomer, electro deposition could only be accomplished with a strong Lewis acid, BF_3EtO.

Mendez and Weder improved considerably the conductivity of poly(3,4-diethylene, dioxythiophene) by cross-linking [76]. The polymers were oxidatively synthesized in the presence of four different oxidative cross-linkers,



The cross-linking compounds were incorporated into the polymer in amounts of 0.5–2%. As a result, in a maximum case, the conductivity increased by as much 36%.

Polyaniline was first prepared at the beginning of the last century. Several oxidation states are known. The conductivity and the color of the material vary progressively with oxidation. Only one form, however, known as the emeraldine salt, is truly conducting. The material can be prepared readily by electrochemical or chemical oxidation of aniline in aqueous acid media. Common oxidants, such as ammonium peroxydisulfate, can be used. Flexible emeraldine films can be cast from solutions of *N*-methylpyrrolidone and made conductive by protonic doping. This is done by dipping the films in acid or by exposing them to acid vapors. The process results in protonation of the imine nitrogen atoms:

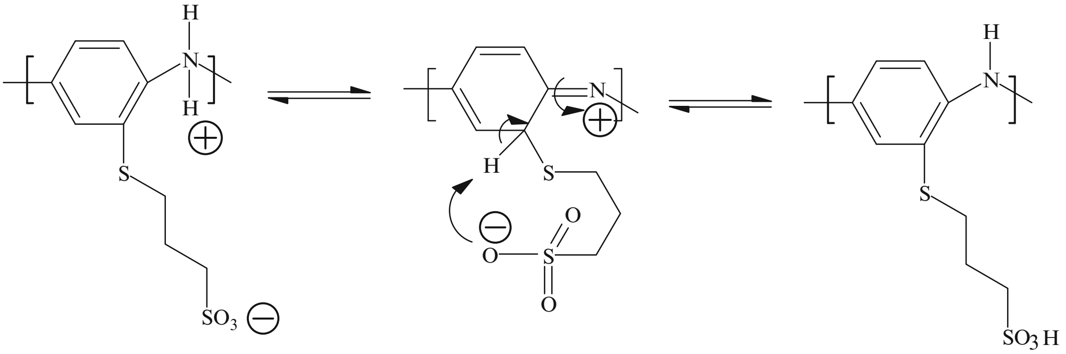


The conductivity of the emeraldine salt increases with decrease in pH of the acid used to dope it. In this respect, polyaniline, in its emeraldine form, differs from other conductive polymers because it does not require partial oxidation or reduction for doping. Protonation of the imine nitrogens is sufficient to make it a very conductive material.

A different method of synthesizing polyaniline was reported [77]. It uses an enzyme, horseradish peroxidase, in the presence of hydrogen peroxide to polymerize aniline. To prevent reactions at the *ortho* positions of the phenyl rings that yield insoluble branched materials, a polyelectrolyte template, like sulfonated polystyrene, was used. The polyelectrolyte aligns the monomers, dopes the polyaniline to the conducting form, and forms an irreversible complex with the polyaniline to keep it water-soluble [77]. The conductivity of the complex increases with increasing polyaniline to sulfonated polystyrene molar ratios. Conductivities of 0.005 S/cm are obtained with the pure complex and increase to 0.15 S/cm after additional doping by exposure to HCl vapor [77].

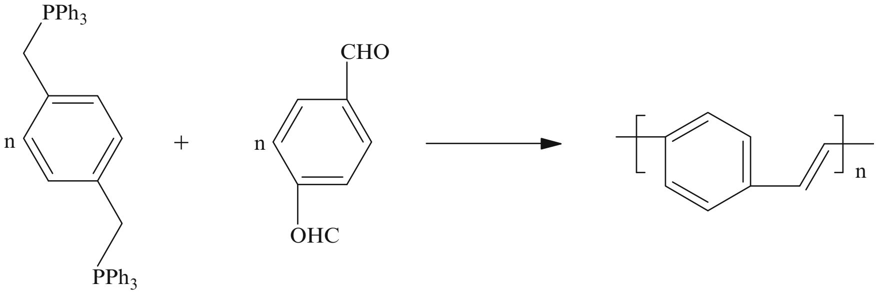
Lee reported [78] a new synthesis of polyaniline, where aniline hydrochloride monomer acts as a surfactant. The organic phase serves to diffuse water away from water-insoluble oligomers. As a result, the chains grow, because the monomer radicals can meet the active polymer chain ends at the organic aqueous interfaces. This results in formation of a polymer with high structural integrity. This enables the electrons or holes to travel in a perpendicular direction.

Han et al. [79] reported preparation of highly conductive and thermally stable, self doping propylthiosulfonated polyanilines. The polymer was illustrated as follows:

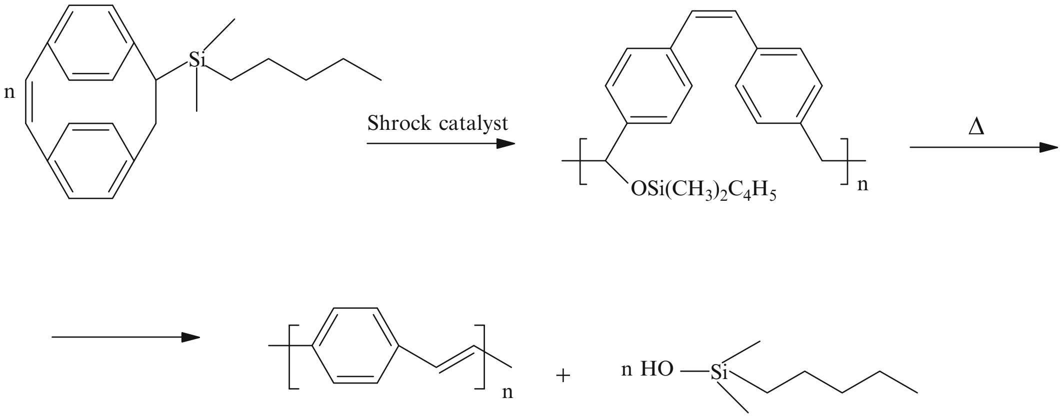


The material was found to be a better conductor than sulfonated polyaniline and more thermally stable.

Poly(phenyl vinylene) can be synthesized by several routes. One of them is step growth polymerization [80] by the Witting reaction:

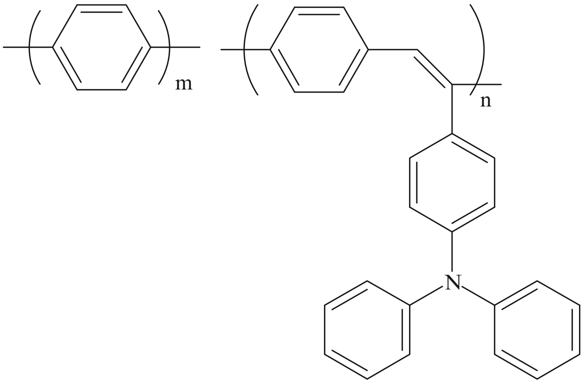


There are several other routes to poly(phenyl vinylene). One of them is through a metathesis ring opening polymerization:



The polymer can be doped with iodine, acids, and ferric chloride. Alkoxy-substituted poly(phenyl vinylene) is easier to oxidize and exhibits higher conductivity.

Natori et al. reported [81] the synthesis of a copolymer that consists of *p*-phenylene, *p*-phenylene vynelene, and styryl amine:



Orientation of the films yields large increases in conductivity. Thus, films of doped, oriented poly (phenylene vinylene) [81] not only have the strength of high-performance polymers, but also their conductivities measure as high as 10^4 S/cm. This is approximately 1,000 times greater than that of the unoriented films.

Another interesting material consists of the doped forms of covalently linked siloxane-phthalocyanin (Pc) complexes, $[\mathrm{Si(Pc)O}]_n$. In these polymers, the planar phthalocyanin units are apparently stacked face-to-face and form columns, due to the silicon-oxygen-silicon bonds. The polymers appear to be intrinsically metallic systems. The principal pathways of conductivity are perpendicular to the phthalocyanin planes. The extended π–π systems that form result from face to face are a pathway for the electron [67].

There are numerous applications for conducting polymeric materials. These applications include use in electronics, in organic solar cells that convert light to electricity and others.

10.3 Photonic Polymers

The term photonic polymer describes a wide variety of polymeric materials that respond to light in one manner or another. These can be rearrangement upon irradiation with light of a certain wavelength, or conductivity of electricity upon irradiation, or dimerization and others. What they all have in common is that they all required irradiation with light, often but not always of a specific wavelength to undergo a change. To understand the mechanism of these reactions, it is first necessary to look into the nature of light and how it reacts with matter.

10.3.1 The Nature of Light

Photochemical reactions involve interactions of light with matter. They either induce chemical changes, or they induce luminescence and conversions of electronic and other forms of energy into heat. For practical purposes, the photochemical reactions that are discussed here are limited to those that take place in the presence of light that ranges from ultra-violet to infra-red.

Light, independent of the source, travels in vacuum with a velocity equal to 2.9979×10^{10} cm/s. But that is only true in a vacuum. Within any medium, the light moves with a velocity of:

$$C' = C/(\varepsilon\mu)^{1/2}$$

where ε is the dielectric constant of the medium and μ is the magnetic permeability.

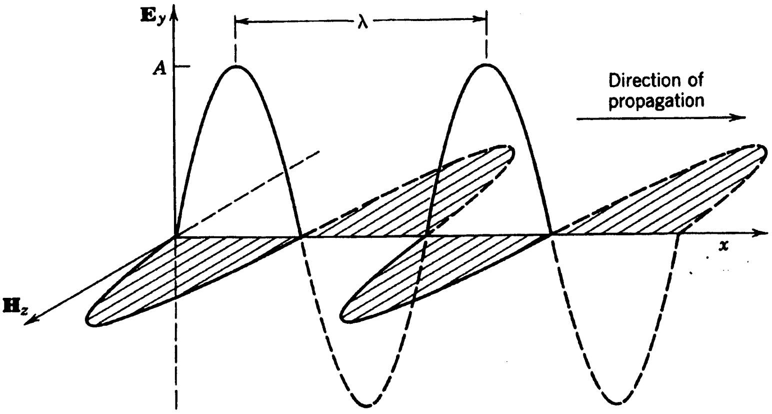


Fig. 10.1 The instantaneous electric, $\mathbf{E}_y$ and magnetic $\mathbf{H}_x$ field strength vectors of a light wave as a function of position along the axis of propagation (from Calvert and Pitts [82])

Our concept of light is that it also consists of packets of energy that travel in waves. In each packet, there is a range of energies. These energies cannot be represented by one wavelength, but rather by a whole spectrum of wavelengths. The energy of each particular wavelength in the wave-packet is a discrete unit, a *quantum*. Electromagnetic radiation is described in terms of a transverse plane wave involving associated electric and magnetic fields. Experimental data suggest that the electric vector **E** and magnetic vector **H** which describe the respective field strengths are aligned in planes at right angles to one another, with both planes perpendicular to the direction of propagation of the wave. This was illustrated by Calvin and Pitts [82], as shown in Fig. 10.1.

A convenient model for the variation of the field strength as a function of time K and distance x along the axis of propagation is one that can be described in Cartesian coordinates by the sinusoidal functions in the following equations:

$$\mathbf{E}_y = A \ \sin 2\pi(x/\lambda - vt)$$

$$\mathbf{H}_z = (\varepsilon\mu)^{1/2} A \ \sin 2\pi(x/\lambda - vt)$$

In these equations, $\mathbf{E}_y$ is the electric field strength vector lying in the xy plane and increasing along the y-axis, $\mathbf{H}_z$ is the magnetic field strength vector lying in the xz-plane and increasing along the z-axis, A is the amplitude of the electric vector (the *intensity* of the wave is proportional to A^2), ε is the dielectric constant, and μ is the magnetic permeability of the medium through which the light wave is transported. In a vacuum, $\varepsilon = \mu$ and they are approximately unity in air. The length of the wave, that is, the distance between adjacent maxima in the vectors measured at any instant along the direction of wave propagation (the x axis) is λ, while v is the frequency or number of complete cycles of vector position change per second. The relationship between λ and v is:

$$C/v = \lambda$$

where C is the velocity of the radiation. The frequency v is independent of the medium through which the radiation travels. Wavelength λ and velocity C, on the other hand, depend on ε and μ of the medium.

Ordinary light is not polarized. It consists of many electromagnetic vectors that are undulating in fixed, though randomly oriented with respect to each other, planes. When the light is polarized in a plane, it is believed that all the waves have their electric vectors oriented in the same direction. When the light is polarized elliptically, then it is believed that two plane waves of equal wavelength and frequency and with identical directions of propagation have the electric vectors perpendicular to one another and out of phase, as shown in Fig. 10.1.

The degree of polarization of light p is usually expressed by the equation

$$p = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}$$

where $I_{\|}$ and $I_{\perp}$ represent the intensities of light transmitted by an analyzer parallel and perpendicular to the plane of maximum polarization of ht incident light.

The above-described model is incomplete and even called naive by some. Mathematically, however, it can successfully account for many observations concerning light, and this theory has been used successfully to describe many phenomena associated with optics.

10.3.2 Quantum-Mechanical Description of Light

In order to better understand the emission and absorption of light by molecules, it is necessary to look at the quantum-mechanical concept of the nature of light. In this concept, light is considered to be a *beam of photons* whose energies are quantized. Detailed description of quantum mechanics and spectroscopy is beyond the scope of this book. Here will only be presented the major conclusions necessary for better understanding of light.

In the quantum theory of radiation [93], all electromagnetic radiation are considered to be beams of particles. As stated above, they are called photons. Each photon has an energy **E** that is defined by the Planck relationship,

$$\mathbf{E} = h\upsilon = hc/\lambda$$

where h is the proportionality constant, called Planck's constant. It is equal to 6.6256×10^{-27} erg s/quantum. The quantum theory has explained very many phenomena associated with interactions of light with matter. One of them is the photoelectric effect. This effect was discovered early by Hertz. He found that short wavelength radiation incident on a metal surface caused instantaneous emission of photoelectrons. The classical electromagnetic wave theory fails to explain these phenomena. Einstein, in 1905, derived an equation that is based on the phenomenon that, when a quantum of light of energy $h\upsilon$ is absorbed by the metal, an electron is emitted. This energy relationship is described by the following equation:

$$m_C\upsilon/2 = h\upsilon - \omega_0$$

where ω_0 is the minimum energy necessary to remove an electron, and $m_c\upsilon/2$ is the kinetic energy of the electron emitted.

10.3.3 Interaction of Light with Organic Molecules

If monochromatic light passes through a uniform thickness of an absorbing homogeneous medium with the absorbing centers acting independently of each other, then the energy of light that is absorbed follows the Lambert-Bouguer law. According to this law of physics, the light absorbed is independent of the intensity of the incident light and the intensity of radiation is reduced by the fraction that is proportional to thickness of the absorbing system. In addition, Beer's law states that absorption is proportional to the number of absorption centers. The two laws are usually combined and expressed as follows:

$$\mathrm{d}I/\mathrm{d}l = kcI$$

where I is the intensity of the radiation, l is the length of the optical path, through the absorbing medium, c is the concentration of the absorbing centers, and k is proportionality constant. While there are no know exceptions to the Lambert-Bouguer law, there are deviations from Beer's law due to partial ionization, molecular association and complexation, and fluorescence.

Portions of organic molecules or whole molecules that have π bonds can absorb light radiation, provided that it is of the right wavelength. Particular groupings or arrangements of atoms in molecules

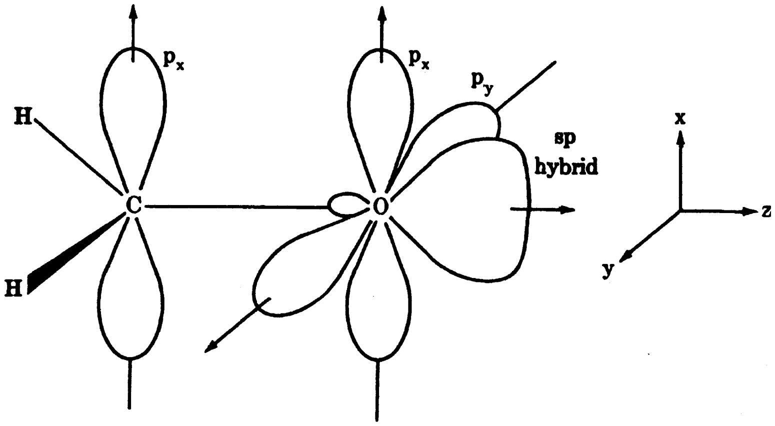


Fig. 10.2 The orbitals of formaldehyde (from Jaffe and Orchin)

give rise to characteristic absorption bands. Such groups of atoms, usually containing π bonds, are referred to as *chromophores*. Examples of such molecules with π bonds are compounds that contain carbonyl or nitro groups and aromatic rings. A molecule that serves as an example of carbonyl arrangement, one that is often referred to, is a molecule of the formaldehyde. In this molecule, the carbon atom is linked to two hydrogens and to one oxygen by σ bonds. The hybrid sp^2 orbitals bond one electron of carbon with one of oxygen in an sp orbital. In addition, there are two unbonded n electrons on oxygen that point away from the carbon atom. The orbitals of formaldehyde, the simplest of the carbonyl compounds, were illustrated by Orchin and Jaffe [88], as shown in Fig. 10.2.

As described above, the molecule has σ and π bonded skeleton, shown above. The carbon atom is attached to two hydrogen atoms by a single bond and to the oxygen atom by a double bond. This bonding of the carbon to the two hydrogens and one oxygen atoms is by means of sp^2 hybrid orbitals. The orbitals are approximately at 120° angles from each other. In the ground state of the molecules, the pair of electrons that form a bond is paired and has opposite or antiparallel spin. In this state, the formaldehyde molecule is planar. The Pauli exclusion principle [83] states that no two electrons can have identical quantum numbers. That means that if two electrons are in the same orbital and three of their quantum numbers are the same, the fourth quantum number, the spin quantum number, must be different. The total spin quantum number of a molecule is designated by a letter J and the sum of the spins of the individual electrons by a letter S. The spin quantum number of a molecule J is equal to $[2S] + 1$.

This arrangement of electrons in the p orbital can generate π bonding and π* antibonding orbitals. Absorption of light energy by a chromophore molecule results in formation of an excited state and an electronic transition from the ground state to an excited state. Such light may be in the ultraviolet or in the visible region of the electromagnetic spectrum, in the range of 200 μm to approximately 780 μm. Promotion of electrons out of the σ bonding orbitals to the excited states requires a large amount of energy and rupture of bonds in the process. On the other hand, the electronic transition to promote one of the n electrons on the oxygen atom in formaldehyde to the *antibonding* or the *nonbonding* orbital, $n \rightarrow \pi^*$ level requires the least amount of energy. The name, *antibonding*, as one might deduce, is a type of orbital where the electrons make no contribution to the binding energy of the molecule. In formaldehyde, this $n \rightarrow \pi^*$ transition to the excited state gives rise to an absorption band (at about 270 μm). This is a relatively weak band and it suggests that the transition is a forbidden one (forbidden does not mean that it never occurs, rather than it is highly improbable). It is referred to as a symmetry forbidden transition. The reason for it being forbidden is crudely justified by the fact that the π* is in the *xz* plane (see Fig. 10.2). The n electrons in the p orbital are in the *xz* plane and perpendicular to the π* orbital. Because the spaces of the two orbitals overlap so poorly, the likelihood of an electronic transition from one to the other is quite low. As stated above, in the ground (normal) state of the molecules, two electrons are paired. The pairing means that these electrons have opposite or anti-parallel spins. After absorbing the light energy, in the singlet excited

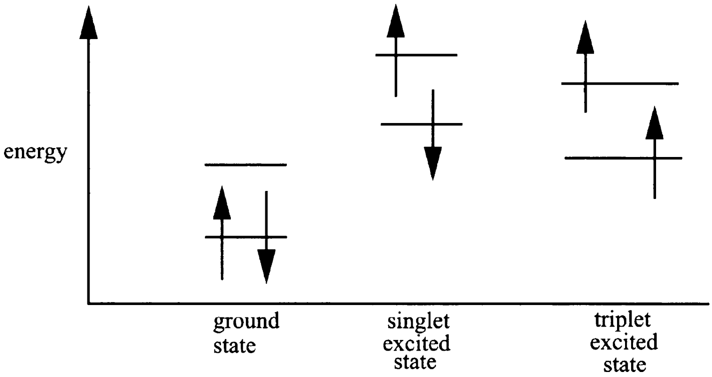


Fig. 10.3 Illustration of the singlet and the triplet states (from Ravve [91])

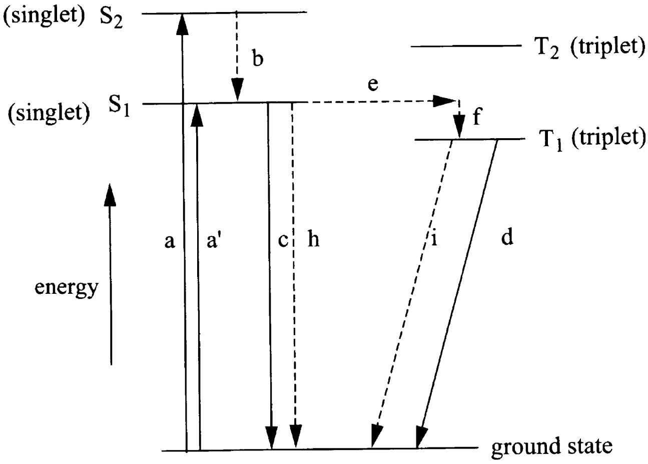


Fig. 10.4 Illustration of energy transitions (from Ravve [91])

state the two electrons maintain anti-parallel spins. The n → π* excitation, however, can lead to two excited state, a singlet (S_1) and a triplet (T_1) one with an absorption band (at about 250 μm). Intersystem crossing to a triplet state from the singlet results in a reversal of the spin of one of the electrons and an accompanying loss of some vibrational energy. This is illustrated in Fig. 10.3.

The intersystem crossing from the singlet to triplet states can occur with high efficiency in certain kinds of molecules, particularly in aromatic and carbonyl-containing compounds. Electron–electron repulsion in the triplet state is minimized because the electrons are farther apart in space and the energy is lower in that state than that of the corresponding excited singlet one. Solvents can exert a high influence on the n → π* transitions. While the intersystem crossing is a forbidden transition (see above), it can actually occur with high frequency in aromatic or carbonyl compounds.

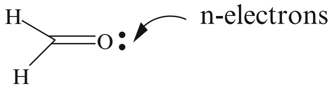
The chemical mechanism of photo-excitation of organic molecules has been fully described in various books on photochemistry [82, 84, 85, 87]. It will, therefore, be discussed here only briefly. The transitions are illustrated here in a very simplified energy diagram that shows the excited singlet state and the various paths for subsequent return to the ground state in Fig. 10.4.

The energy diagram (Fig. 10.4) represents energy states of a molecule that possesses both n and π* electrons. S_1 and S_2 are the singlet excited states. T_1 and T_2 are the excited **triplet** states. Solid lines represent electronic transitions. They are accompanied by absorption or emissions of photons. Radiationless transitions are represented by doted lines. The above diagram shows the lowest singlet state S_1, where the electrons are spin-paired, and the lowest triplet state T_1, where the electrons are spin-unpaired. The electron is excited by light of a particular wavelength into an upper singlet level, S_2. Relaxation follows via an internal conversion process to S level. The excess energy is dissipated by vibrational interactions giving rise to evolution of heat. At the S_1 level, there are three possible ways that the excited state becomes deactivated. The return to the ground state from the triplet one requires again an inversion of the spin. In Fig. 10.4, a and a' represent the energies of light absorbed, b, h, and I the energies of internal conversion, c represents return to the ground state by way of fluorescence, and d return by way of phosphorescence.

The Franck and Condon principle states that during an electronic transition the various nuclei in the molecule do not change their position or their moment [90]. What it means is that electronic transitions are much more rapid (10^{-15} s) than nuclear motions (10^{-12} s) so that immediately after the transitions the nuclei have nearly the same relative positions and velocities that they had just before the transitions. The energy of various bonding and antibonding orbitals increases for most molecules in the following order,

$$\sigma < \pi < \mathrm{n} < \pi^* < \sigma^*$$

In molecules with heteroatoms, such as oxygen or nitrogen, however, the highest filled orbitals in the ground state are generally nonbonding, essentially atomic, n orbitals. This, for instance, is a case with ketones and aldehydes. These molecules possess electrons that are associated with oxygen and are not involved in the bonding of the molecules. The n electrons in formaldehyde can be illustrated as follows:



As explained above, in the triplet state the spin of the excited electron becomes reversed. This results in both electrons having the same spin. From purely theoretical approach, such an electronic configuration is not allowed. Due to the fact that the excited electron cannot take up its original position in the ground state until it assumes the original spin, the triplet state is relative long-lived. For instance, in benzophenone at 77°C the lifetime can be 4.7×10^{-3} s. Orchin and Jaffe wrote [88] that the triplet state has a lifetime of 10^{-3} s. By comparison, the lifetime of a singlet state is about 10^{-8} to 10^{-7} s. Also, in the triplet state the molecule behaves as a free-radical and is very reactive. The carbon atom has a higher electron density in the excited state than in the ground state. This results in a higher localized site for photochemical activity at the orbital of the oxygen. Because the carbonyl oxygen in the excited state is electron-deficient, it reacts similarly to an electrophilic alkoxy radical. It can, for instance, react with another molecule by abstracting hydrogen.

At higher frequencies (shorter wavelength) of light, if the light energy is sufficiently high, $\pi \rightarrow \pi^*$ transitions can also take place. All aromatic compounds and all conjugated diene structures possess delocalized π systems. Because there are no n electrons, all transitions in these systems are $\pi \rightarrow \pi^*$. In general, the excited states of molecule are more polar than the ground states. Polar solvents, therefore, tend to stabilize the excited state more than the ground state. As shown in Fig. 10.4, the triplet state is lower in energy than the corresponding singlet state. This is due to the fact that the electron–electron repulsion is minimized, because they do not share each other's orbitals according to the Pauli exclusion principle. Thus, less energy is required for the triplet state.

The chemical reactivity of organic molecules is determined principally by the electron distribution in that molecule. When the electron distribution changes, due to absorption of light and subsequent transitions, photochemical reactions take place while the molecule is in an electronically excited state. The phenomenon of light absorption, formation of the excited states, and subsequent reactions obey four laws of organic photochemistry, as was outlined by Turro [87]:

1. Photochemical changes take place only as a result of light being absorbed by the molecules.
2. Only one molecule is activated by one photon or by one quantum of light.
3. Each quantum or photon which is absorbed by a molecule has a given probability of populating either the singlet state or the lowest triplet state.
4. In solution, the lowest excited singlet and triplet states are the starting points for the photochemical process.

The relationship between the amount of light or the number of photons absorbed and the number of molecules, that, as a result, undergo a reaction, is defined as the quantum yield. It is defined as the number of molecules involved in a particular reaction divided by the number of quanta absorbed in the process [1, 3].

Another fundamental law of photochemistry was formulated by Grotthus and Draaper [82, 83]. It states that only the light that is absorbed by a molecule can be effective in producing photochemical changes in that molecule. There is also a fundamental law of photochemistry that states that the absorption of light by a molecule is a one-quantum process, so that the sum of the primary processes, the quantum yield, must be unity [82, 83]. Also, the law of conservation of energy requires that the sum of the primary quantum yields of all processes be equal to unity. Mathematically this can be expressed as:

$$\Phi_{\text{total}} = \sum_i \Phi_i = 1$$

where Φ is the quantum yield. The quantum yield of photochemical reactions is important because it sheds light on the mechanisms of the reactions. The number of molecules involved in a particular photoreaction can be established by an analytical kinetic process and the number of quanta absorbed can be measured with the aid of an actinometer. The quantum yield can also be expressed in general kinetic terms [1]:

$$\Phi_i = \varphi_{\text{ES}}\varphi_R P_i \quad \text{or} \quad \Phi_i = \sum_i \varphi^i_{\text{ES}}\varphi^j_R P^j_i$$

The above equations signify that a quantum yield of a particular photo process is the product of two or three distinct probabilities. These are: φ_{ES} is the probability that the excited state will undergo the primary photoreaction necessary for the process. The probability that any metastable ground state intermediate will proceed to stable products is P_i and the probability that the excited state will undergo the primary photoreaction necessary of the process is φ_R.

The concept that matter can only acquire energy in discrete units (quanta) was introduced in 1900 by Max Planck [83]. The corollary of the quantization of energy is that matter itself must be quantized, i.e., constructed of discrete levels having different potential energies. Occupying these particular levels are electrons that obviously possess the energy of the level which they occupy. In a molecule, the intramolecular motions of the electrons and the associated molecular electronic levels must be taken into account. There are, in addition to electronic levels, modes of vibration and rotation that are also quantized. In other words, the absorption of a photon of light by any molecule is a reaction that must promote transitions between quantum states. This requires two conditions. These are: (1) for a molecular state m with energy E_m, there must be a state n of higher energy, E_n, so that $h\upsilon = E_n - E_m$; (2) there must be specific interaction between the radiation and the light-absorbing portion of the molecule that results in a change in the dipole moment of the molecule during the transition. If we designate the wave functions of the states m and n as ψ_m and ψ_n respectively, then the transition moment integral that may not equal to zero is:

$$R_{mn} = (\Psi_m / P\Psi_n)$$

where P is the electric dipole operator. It has the form of $P = e\sum r_i$, where e is the electronic charge and r_i is the vector that corresponds to the dipole moment operator of an electron i.

The increase in the energy of a molecule as a result of absorbing a quantum of radiation can be expressed in the relationship [85]:

$$\Delta E = hC/\lambda$$

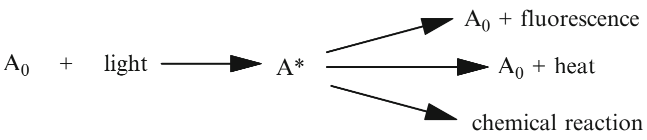
where λ is the wavelength of the interacting radiation. All reactions that are photochemical in nature involve electronically excited states at one time or other. Each one of these states has a definite energy, lifetime, and structure. The property of each state may differ from one to another and the excited states are different chemical entities from the ground state and behave differently. The return to the ground state from the excited state, shown in Fig. 10.4, can take place by one of three processes [85]:

1. The molecule returns directly to the ground state. This process is accompanied by emission of light of a different wavelength in the form of fluorescence.
2. An intersystem conversion process takes place to the T_1 state, where the electron reverses its spin. The slower decay of excitation from the triplet state to the ground state is accompanied by emission of phosphorescence.
3. The molecule uses the energy of excitation to undergo a chemical reaction

As explained above, in the triplet state the spin of the excited electron becomes reversed. This results in both electrons having the same spin. From purely theoretical approach, such an electronic configuration is not allowed. Due to the fact that the excited electron cannot take up its original position in the ground state until it assumes the original spin, the triplet state is relative long-lived. For instance, in benzophenone at 77°C the lifetime can be 4.7×10^{-3} s. Orchin and Jaffe wrote [88] that the triplet state has a lifetime of 10^{-3} s. By comparison, the lifetime of a singlet state is about 10^{-8} to 10^{-7} s. Also, in the triplet state the molecule behaves as a free-radical and is very reactive. The carbon atom has a higher electron density in the excited state than in the ground state. This results in a higher localized site for photochemical activity at the n orbital of the oxygen. Because the carbonyl oxygen in the excited state is electron-deficient, it reacts similarly to an electrophilic alkoxy radical. It can, for instance, react with another molecule by abstracting a hydrogen.

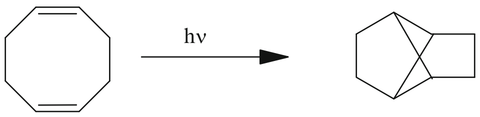
At higher frequencies (shorter wavelength) of light, if the light energy is sufficiently high, $\pi \rightarrow \pi^*$ transitions can also take place. All aromatic compounds and all conjugated diene structures possess delocalized π systems. Because there are no n electrons, all transitions in these systems are $\pi \rightarrow \pi^*$. In general, the excited states of molecule are more polar than the ground states. Polar solvents, therefore, tend to stabilize the excited state more than the ground state. As shown in Fig. 10.4, the triplet state is lower in energy that the corresponding singlet state. This is due to the fact that the electron–electron repulsion is minimized, because they do not share each other's orbitals as stated by the Pauli exclusion principle Thus, less energy is required for the triplet state.

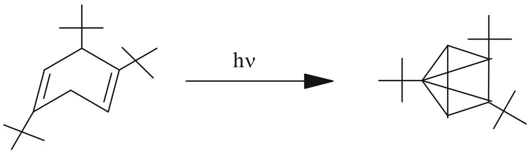
This dissipation of the excitation energy can also be illustrated as follows:

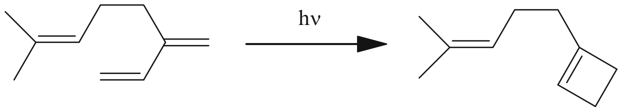


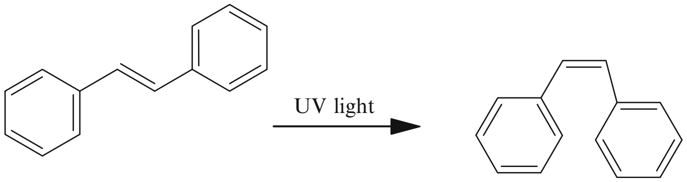
where A_o represents any organic molecule and A* represents the same molecule in an excited state.

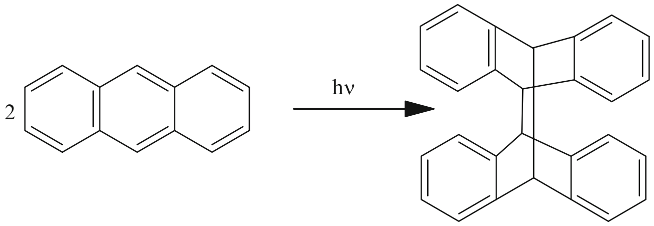
In the process of energy dissipation from the singlet and return to the ground states, the light emission by fluorescence is at a different wavelength than that of the light that was absorbed in the excitation. This is because some energy is lost in this process of the electron returning from its lowest excited state to the ground state. The energy, however, may also, depending upon the structure of the molecule, be dissipated in the form of heat, as shown above. And, also, a third form of energy dissipation can occur when the molecule undergoes a chemical reaction. Depending, again on the molecular structure, the chemical reactions can be rearrangement, isomerization, dimerization (or coupling), fragmentation, or attack on another [90–92] molecule. Some examples of such reactions are:

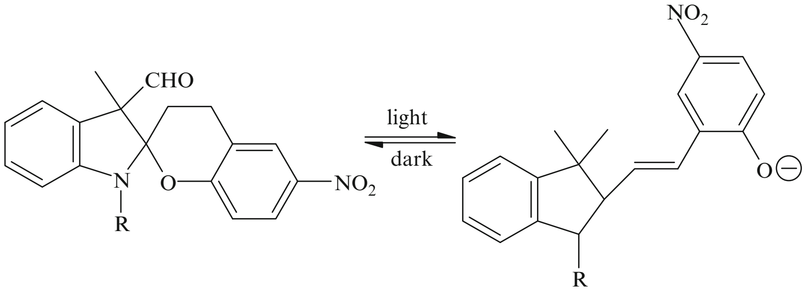




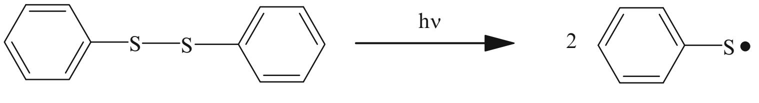








Many other examples can be found in the literature. Most familiar isomerization reaction is that of *trans*-stilbene to *cis*-stilbene, shown above. It was observed that the quantum yield of stilbene *cis*-*trans* isomerization decreased with an increase in viscosity of the medium [89]. In addition, it was also found that in a polymeric matrix, the photo-isomerization is not inhibited, provided that it occurs above the glass transition temperature of the polymer. An example of a fragmentation of a molecule is the decomposition of disulfides upon irradiation with ultraviolet light of the appropriate wavelength:



The same reaction takes place in peroxides. Ketones and aldehydes cleave by the mechanism of the Norrish reaction.

10.3.4 Energy Transfer Process

Photosensitizers are used in many photonic applications. To understand how they function, it is necessary to understand the energy transfer process. The term ***energy transfer*** [92, 93] refers specifically to **one-step *radiationless transfer*** of electronic excitation from a ***donor*** molecule to another, qualified, ***acceptor*** molecule, from one chromophore to another one. This excludes what is referred to as ***trivial energy transfers*** that result from the donor emitting light that is subsequently absorbed by an acceptor. Based on the energy and spin conservation laws, there are two a priori requirements for efficient energy transfer: (1) the process must be thermoneutral or exothermic to occur with highest efficiency, because the activation energies have to be low due to short lifetimes of electronically excited state, and (2) no net spin changes should occur. If a donor molecule was in the triplet state at the time of the energy transfer process, the acceptor molecule is then also promoted to the triplet state. Transfer of singlet to singlet energy should be possible, but it occurs less frequently, because of the shorter lifetimes of the singlet states [92, 93].

Energy transfer is thus a process by which excitation energy passes from one photo-excited molecule, often referred to as a ***sensitizer*** and in this case designated as S*, to another adjacent molecule in its ground state, often referred to as a ***quencher***, in this case designated as Q. The quencher must have a thermodynamically accessible excited state, one whose energy is lower than that of S*. A donor molecule must possess sufficiently long lifetime to be an efficient sensitizer. The reaction of energy transfer can be illustrated as follows:

$$S^* + Q \rightarrow S + Q^*$$

$$S^* \rightarrow S_0 + hv$$

where * designates an excited state. In the process of energy transfer, S* returns (or relaxes) to the ground state S. Energy transfer is further categorized as involving singlet (paired electron spins) or triplet (unpaired electron spins) states. Symmetry rules, as explained above, require a singlet S* to produce a singlet Q* and a triplet S^{3+} to produce a triplet Q^{3+}.

The quenching reaction of the excited state was expressed in a equation by Stern–Volmer. The reaction shown below is based on a quenching reaction that is accompanied by a release of heat:

$$S^* + Q \rightarrow Q^* + S_0 \quad (k_2)$$

$$S^* \rightarrow S_0 + \text{heat} \quad (k_3)$$

The equation is written as follows:

$$\Phi_0/\Phi_Q = \{k_1 + k_2[Q] + k_3\}/(k_1 + k_3)$$

In experimental studies of energy transfer, it is convenient to express the experimental results in another form of the Stern–Volmer equation, as follows,

$$\Phi_0/\Phi_Q = 1 + k_q\tau[Q]$$

where

Φ_0 is the quantum yield for a particular process in the absence of a quenching molecule
Φ_Q is the quantum yield of the quenched process
k_q is the bimolecular rate constant for the quenching process
τ is the lifetime of the state in the absence of a quenching molecules. It is equal to $1/(k_1 + k_3)$, and
[Q] is the concentration of the quenching molecules

Two processes were proposed to explain the mechanism of energy transfer. In the first one, energy transfers result from the interactions of the dipole fields of the excited donors and ground state acceptor molecules (long-range: Forster (dipole–dipole)) [86, 90]. This is referred to as the ***resonance transfer mechanism***. Such transfer is rapid when the extinction coefficients for absorption to the donor and acceptor-excited states involved in the process are large (10^4–10^5 at the maximum). When the dipolar interactions are large, resonance transfers are possible over distances of 50–100 Å. Close proximities of donors and acceptors, however, are required for weakly absorbing molecules. In the second mechanism [90] (short-range: Dexter (exchange)), the excited donor and acceptor are in very close proximity to each other, (up to ≈15 Å) such that their electronic clouds overlap slightly. In the region of the overlap, the location of the excited electron is indistinguishable. It may be at any one instant on either the donor or on the acceptor molecule. Should the pair separate when the excited electron is on the acceptor molecule, energy transfer has been achieved by the mechanism of electron transfer, discussed in the next section.

Both absorption and emission processes may be intramolecular, localized in a single molecule. On the other hand, they can also involve whole crystals that may act as absorbers and emitters. Such energy transfers can manifest themselves in different ways that include sensitized fluorescence or phosphorescence, concentration depolarization of fluorescence, photo-conduction, and formation of triplet acceptor molecules.

Intermolecular energy transfer can be electronic and vibrational and can take place in solid, liquid, and gaseous phases. In addition, the sensitized excitation of Q by S* has to take place within the time that the molecule S remains in the excited state. In summary, theoretical and empirical considerations suggest two modes of transfer, described above:

1. Only when the two molecules are in very close proximity to each other and their centers are separated by the sum of their molecular radii will transfer take place.
2. When the two molecules are at distances that exceed their collision diameters, resonance transfer or long range electronic excitation takes place though Coulombic interactions.

The transfers that take place by mechanism 1 are limited by diffusion of molecules in solution and should be affected by the viscosity of the medium. Transfers by mechanism 2, on the other hand, should be much less sensitive to the viscosity of the medium. It was shown by Foster [86] that the rate constant of resonance-energy transfer (mechanism 1), as a function of distance, is:

$$\text{Rate constant }(\mathrm{S}^* \rightarrow \mathrm{Q}^*) = 1(R_\mathrm{o}/R)^6/\tau S$$

where τS is the actual mean lifetime of S*, R is the separation between the centers of S* and Q, and R is the critical separation of donor molecules and the acceptor molecule. The efficiency of energy transfer was expressed by Turro et al. [94] as follows:

$$\Phi_\mathrm{et} = k_\mathrm{et}[\mathrm{S}^*][\mathrm{Q}]/\{k_\mathrm{et}[\mathrm{S}^*][\mathrm{Q}] + k_\mathrm{d}[\mathrm{S}^*]\}$$

The transfer by long-range excitation or mechanism 2 can be in the form a ***singlet–singlet*** transfer, a ***triplet–singlet transfer***, and a ***triplet–triplet transfer***. Due to the fact that the lifetime of triplet state of molecule is longer than the singlet one, it is more probable to be the one to participate in energy transfer. Molecules that undergo intersystem crossing with high efficiency, like benzophenone, are efficient triplet sensitizers. Such molecules must possess high energy in the triplet state and a lifetime of at least 10^{-4} s.

The two types of intermolecular energy transfers can be expressed as follows:

$$\text{Forster(dipole-dipole) long - range: } k_\mathrm{SQ}(R) = k_\mathrm{S}^0(R_0^\mathrm{SQ}R)^6$$

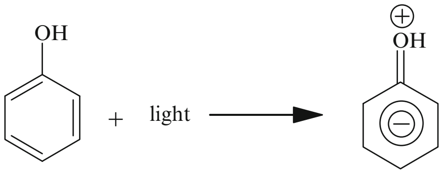
$$\text{Dexter(exchange) short - range: } k_{SQ}(R) = k^0_{SQ}\exp(-\alpha R)$$

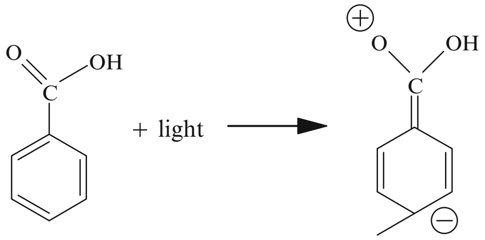
The nomenclature that was developed in connection with energy and charge transfer processes is as follows, an ***eximer*** is a transient dimer formed by the combination of an excited (usually aromatic) molecule and a second similar (usually unexcited) molecule. Such a dimer bonds only in the excited state and promptly dissociates in losing its excitation energy. The term ***exiplex***, explained by Birks [92], describes a complex between two molecules, one a donor and the other one, an acceptor, which subsequently dissociate in a deactivation process. One of the components of the ***exiplex***, either the donor or the acceptor, is in excited state while the counterpart, acceptor or donor, is in the ground state. An ***eximer*** is then just a special case in which the two constituent molecules are identical. While numerous charge-transfer complexes can form between certain molecules in the ground state, a number of compounds can form only charge–transfer complexes when either the donor or the acceptor is in an excited state. Formation of eximers was observed in a number of aromatic polymers, such as polystyrene, poly(vinyl naphthalenes), poly(vinyl toluene), and others [93].

An ***exterplex*** is composed of three molecules and often takes an important role in photophysical and photochemical processes. Polymers with pendant aromatic chromophores and dimeric compounds often show efficient ***exterplex*** formation due to high local chromophore concentration in their structure. It was observed that ***exiplex*** emission spectra from a chromophore is usually broad, structureless, and red-shifted to the corresponding monomer fluorescence. The extend of such a shift is a function of the distance between the two components of the complex. It is also strongly affected by the polarity of the media. Martic et al. [95] obtained emission spectra of the exiplexes of anthracene and *N*,*N*, dimethyl-*p*-toluidine in toluene and in polystyrene. While the maximum band of the emission spectra in toluene at 30°C is at 616 nm, in polystyrene it is shifted to 400 nm. The exiplex emission spectra in a copolymer of styrene with 4-*N*,*N*-diaminostyrene is at 480 nm. The maxima of the emission spectra are temperature-dependent. The maxima shifts in toluene solution to shorter wavelength and in polystyrene it is the opposite, and it shifts to longer wavelength with an increase in temperature. The maxima approaches common value at the glass transition temperature of polystyrene. Similar results were reported by Farid et al. [96] who studied formation of ***exiplexes*** of 4-(1-pyrenyl)butyrate in different solvents and in polymers.

Chemical and physical changes take place in molecules when they absorb energy and reach an excited state. This is particularly true of carbonyl compounds. There is a change, as already stated, in the dipole moments of the molecules. This is due to the fact that dipole moments depend upon the distribution of the electrons. In carbonyl compounds, this change is particularly large. Also the geometry of the molecule changes from the ground to the excited states. In addition, the chemical properties of the molecules change. Thus, phenol, for instance, is a weak acid, but in the excited state it is a strong acid. This can be attributed to the $\pi \rightarrow \pi^*$ transition where one of the pair of π electrons is promoted to an antibonding orbital.

By the same reason, the acid strength of benzoic acid is less than in the excited state because the charge in this case is transferred to carbonyl group. The excited states of both phenol and benzoic acid can be illustrated follows [93]:





10.3.5 The Electron Transfer Process

This process is particularly important in such photonic applications as solar cells. Simple migration of energy is a thermodynamically neutral process. It allows the excitation energy deposited at a site in a solid or in a concentrated solution to move to another position by transferring the excitation energy in the absence of an intermediate quencher. Electron transfer, however, is a process by which an electron is passed from an electron-rich donor to an electron-deficient acceptor [95]. This reaction is substantially accelerated when the donor or acceptor is excited. Electron transfer from an excited state donor molecule D* to a ground state acceptor A generates a radical cation $D^{+\bullet}$ and a radical anion $A^{-\bullet}$. The resulting radical ion pair exists as a charge-separated pair of ions:

$$D^* + A \rightarrow D^{+\bullet} + A^{-\bullet}$$

The oxidized and reduced species are usually highly energetic, storing a substantial fraction of the energy absorbed from the photon. The charge separation that occurs in such a photo-induced electron transfer provides a way to convert the excitation energy of the excited molecule to a chemical potential in the form of a radical ion pair.

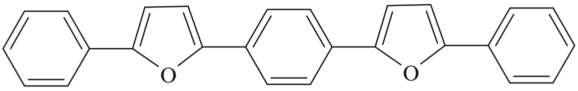
Electron migration can also be a movement of an electron either to a neutral electron donor from an oxidized one $(D + D^\bullet \rightarrow D^\bullet + D)$ or from a reduced acceptor to a neutral one $(A^\bullet + A \rightarrow A + A^\bullet)$ [93]. These thermoneutral processes that are called ***hole*** and ***electron migrations***, respectively, permit further spatial charge separation between an excited donor, D*, and a reduced acceptor, $A^\bullet$. This separation is beyond one that is initially produced in an ion pair by photo-induced electron transfer. After the absorption of light by a to a sensitizer, the energy migrations or the energy transfer move the excited state site where the excitation energy is converted to a radical ion pair by photo-induced electron transfer. A kinetic competition then takes place between the rates of several possible next steps. These steps can be chemical reaction of the radical ions, or they can be further charge migrations by ***sequential electron or hole transfers***, or actually nonproductive charge recombination, called ***back-electron transfer***. The back-electron transfer regenerates the ground states of both the donor and the acceptor.

10.3.6 The Charge Transfer Processes in Polymers

Charge transfer in polymers is either electronic (transfer of electrons or of positive charges alone) or it is ionic (transfer of protons or larger charged species). Electronic conduction can be also of two types. One type is conduction due to diffusion of electrons that are not localized on any particular molecule (this is usually found in liquids or in gases). The other type can be by conduction due to positive or negative charges that are localized on any particular part of the molecules. Such charges can be exchanges between like polymeric molecules (or between segments of single polymeric molecules).

This can occur without any net energy loss (***resonant charge transfer***). It was shown experimentally that the electrical conductivity in many polymeric materials, subjected to short irradiation pulses, consists initially of a "prompt" component. That means that very rapid transfer of a considerable amount of charge takes place over a comparatively short distance (≈100 Å). The movement of the charge is then terminated as a result of trapping in "shallow" traps [90, 93, 97]. This is followed by a "delayed" component that is very temperature-dependent and probably indicates a thermally activated charge-hopping process between the shallow traps. This continues until terminated (after ≈1 μm) by trapping in deep traps or by recombination [90, 93, 97].

There is a major difference between *eximers* of polymers and those of small molecules. The difference is that at least in some polymers a large part of the excitation of the excimer site appears to be a result of singlet energy migration [93]. Also, in polymeric materials with a number of identical chromophores, either in the backbone or as pendant groups, when photons are absorbed, the excited states cannot be considered as localized. In simple cases of rigid lattices, the excitations are distributed over the entire volume of the material as a wave-like linear combination of local excitations [87, 90, 91, 93]. They are referred to as ***tight-binding excitations*** [90, 91, 93]. As one might expect, excimer formations in polymers depend upon the properties of the chromophores and upon their location on the polymeric chain [90]. In addition, polymer tacticity, conformation, and distance between chromophores can greatly affect the formation of eximers. Also, it is possible to distinguish between two different types of energy transfers in polymeric materials. The transfer of excitation can take place either from or to large molecules from small ones. Thus, for instance, a polymer transfer of the excitation energy can be localized from a chromophore on one polymeric chain to another. An example of a transfer to a small molecule is an energy transfer from a polymer, like polystyrene to a scintillator molecule, like 1,4-bis[2-(5-phenyloxazolyl)]benzene shown below [95]:



More than that, transfer can also take place from one group of atoms, or from a chromophore, located on a polymeric chain in one section of the molecule, intramolecularly, to another one located at another section of the same polymer. Thus, in copolymers from monomers with two different chromophores groups, the energy absorbed by one group of chromophores can be transferred to the chromophores from the other group. This can take place by either Foster or exchange mechanism. The possibility of energy transfer from one chromophore to an adjacent different chromophore in polymeric chains depends to a large extent upon the lifetime of the excitation and its alternative modes of deactivation. For this reason, the most readily observed form of energy migration is one that occurs through the mechanism of the triplet [88, 90, 93, 97].

Intermolecular energy transfer from one polymeric material to another while the molecules are in solution or in the melt can also take place [17]. This was demonstrated on an ***intramolecular excimer*** and ***exiplex*** formation in solutions of polyesters containing naphthalene or carbazole moieties in their chemical structures [98].

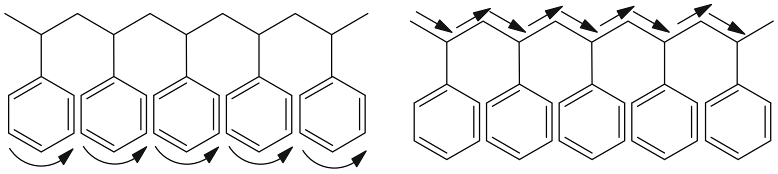
In general, the migrations of energy in polymers are somewhat more complex, because chain folding and conformations are additional factors that enter into the picture. The separation between interacting units can be affected by the composition of the polymer, the geometry of the polymeric chains, and the flexibility of the backbones [99].

There are two limiting cases for the effects of polymer folding on energy transfer efficiency. Folding of a polymer before excitation into a conformation in which the sensitizers are held within a hydrophobic pocket improves the efficiency of energy migration. This takes place with a large number of intramolecular hops or when bond interactions intervene between the sensitizer and the ultimate trap [93]. If the polymers are flexible, however, they can also bend after photo-excitation to bring otherwise distant chromophores close enough so that energy can hop from one to the other, skipping intervening units and thereby considerably shortening the effective migration distance along an individual polymer chain [93]. For flexible polymers in solvents that promote folding, this motion can take place even faster than excited state decay [99].

Intramolecular singlet energy migration can also proceed via electronic coupling through the bonds that form the polymer backbone. In a random walk, the excitation energy migrates without directional control, moving back and forth along a chain or across space. Through-space interactions between pendant chromophores are also common in polymers with large numbers of absorbing units [18]. One should also include movement of excitation across folds or loops that can form in polymeric chains. Such folds can be the result of packing into crystalline domains or simply from temporary collisions.

In principle, the excitation can be localized for some finite time (however small) on a particular chromophore before it is transferred to another one in the chain. Guellet [94] defines *intramolecular energy migration* as any process that involves more than one exchange of excitation energy between spectroscopically identical chromophores attached by covalent bonds to a polymeric chain [12]. He further terms "energy transfer" as a single step migration between two chromophores, while one that involves several or more chromophores as "energy migration" [93].

The polymers with multiple sensitizers offer several routes for energy migration. This can be illustrated as follows [99]:



Route A Route B

A very common arrangement is for the photosensitive groups to be aligned outside of a spiral arrangement of the polymeric chain in close enough proximity to each other for energy transfer. Also, as mentioned earlier, folding of a polymer before excitation into such a conformation that the sensitizers are held within a hydrophobic pocket improves the efficiency of energy migration when a large number of intramolecular hops. Efficiency of energy migration is also helped through-bond interactions that intervene between the sensitizer and the ultimate trap [99]. Also, as mentioned before, flexible polymer frameworks can bend the polymeric chains in such a manner as to bring otherwise distant chromophores close enough together so that after excitation the energy can hop from one to another. In such a case, the energy migration can skip intervening units and thereby considerably shorten the effective migration distance along a single polymer chain. As stated above, for flexible polymers in solvents that promote folding, this motion can be even faster than excited-state decay [99].

Intermolecular energy migration can also occur between two different polymeric molecules. Thus, for instance, Turro et al. [95] investigated inter- and intramolecular energy transfer in poly(styrene sulfonate). They found that excimer formation between adjacent phenyl groups is a dominant reaction both along a single chain and between two different chains [95]. At low densities of excited states, singlet energy transfer between a sensitizer and its nearest quencher (perhaps on another chain) dominates, whereas at high excited state densities, energy migration takes place through the series of donors [99].

Guellet quotes Webber, who reported that he used the following equation (that he called crude but useful) to obtain rough estimates of the energy migration diffusion rate along the polymer backbone [94]:

$$k_{\mathrm{q}} = 4\pi N_0 (D_{\mathrm{Q}} + k_{\mathrm{g}}) PR/1,000$$

where D_Q is the normal diffusion constant of the quencher and k_g is the energy migration diffusion rate along the polymer.

In some aromatic vinyl polymers, excimer emission can occur after an initial excitation of an aromatic chromophore. This is followed by intramolecular singlet energy migration, either along the polymer chain, or intermolecularly along the chromophores. Here too, it can be through different chains in a polymer that is in bulk form and the chains are in close proximity to each other. The process generally continues until the excitation is trapped at some chain conformation that is suitable for excimer formation. Such a chain conformation is referred to as ***eximer-forming site***. If the polymer is in solution and viscosity is low, interconversion of chain conformations proceeds fairly rapidly. In such cases, the lifetimes of any particular conformation are limited by the collision processes as well as by the magnitude of the rotational barriers with respect to thermal energy [93]. In the solid state, however, the rotational freedom of the polymeric chain is considerably reduced. Large-scale conformational changes are unlikely. There still is the possibility, however, that adjacent chromophores will be in a marginal eximer-forming site [94].

10.3.7 The Antenna Effect in Polymers

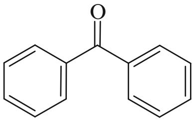
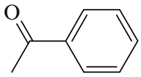
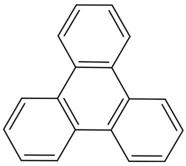
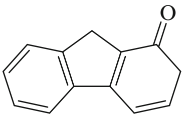
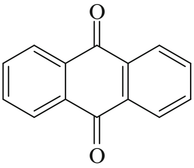
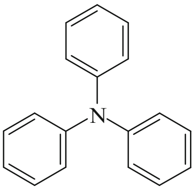
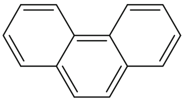
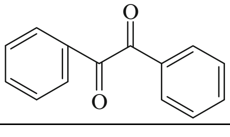
It was originally observed by Schneider and Springer [101] that efficient fluorescence occurs from small amounts of acenaphthalene that is copolymerized with styrene. Fox et al. [100] observed the same effect in a copolymer of styrene with small amount of vinyl naphthalene. The emission of naphthalene fluorescence is much higher than from solution of a mixture of the two homopolymers. It was suggested by both groups that this phenomenon is due to energy migration between styrene sequences to the naphthalene moieties. Guellet and coworkers carried out quantitative studies of this phenomenon with various polymers that contained naphthalene or phenanthrene as the donors and anthracene as the trap [94]. This effect is similar to one observed in ordered chlorophyll regions of green plant chloroplasts (antenna chlorophyll pigments). It was, therefore, named the ***antenna effect***.

Guellet [94] demonstrated that the effect is not entirely due to energy migration among the chromophores that form the antenna, but rather a combination of migration and direct Forster energy transfer to the trap [94]. It was concluded that energy migration and transfer in such systems are primarily due to long-range Forster transfer by dipole-dipole mechanism (discussed earlier). In the absence of any trap in the polymer, the energy will migrate along the backbone of the polymer chain until it is deactivated by some other processes. In the presence of a singlet energy trap, the lifetime of the excitation will be reduced and the length of energy migration will be reduced. The difference between this form of energy transfer and one observed in solid aromatic polymers is that the photon energy is collected within a single polymer molecule and all energy transfer is intramolecular. The antenna effect permits collection of the photon energy from the entire region of space (the hydrodynamic volume of the polymer) and transmitting it to the traps located on the polymer chain. The efficiency is relatively independent of concentration and can be very efficient even in dilute solutions [93].

10.4 Photosensitizers

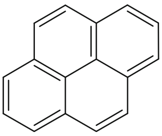
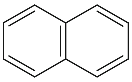
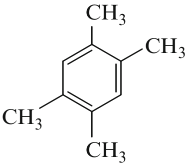
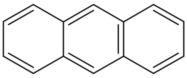
As explained in Sect. 10.3, photosensitizers are molecules that absorb the energy of light and act as donors by transferring this energy to acceptor molecules. The molecules that receive the energy may in turn undergo various reactions, such as polymerizations, isomerizations, couplings, and others. Many different molecules can act as photosensitizers, but the most useful ones are various aromatic compounds. In Table 10.1 are listed some common photosensitizes that appeared in various publications

Table 10.1 Some often used photosensitizers

Photosensitizer	Chemical structure	Φ
Benzophenone		1.0
Acetophenone		0.99
Triphenylene		0.95
Fluorenone		0.93
Anthraquinone		0.88
Triphenylamine		0.88
Phenanthrene		0.76
Benzil		0.87; 0.92

(continued)

Table 10.1 (continued)

Photosensitizer	Chemical structure	Φ
Pyrene		0.40
Naphthalene		0.40
Durene		
Anthracene		

From various literature sources. Φ represents the quantum yield of triplets

in the literature. The process of photosensitization and energy transfer involves formation of charge transfer complexes. A good photosensitizer, therefore, is not only a molecule that readily absorbs light energy, but also one that readily transfers it to another molecule. Some compounds are capable of forming such transfer complexes in the ground state, but many more form *exiplexes* in the excited state. Others can form complexes between a compound in the ground state and another one in the excited state and are called ***excimers*** or ***excited dimers***. The difference between the excited state of a dimer and an exiplex is that the dimers possess binding energy in the ground state, while exiplexes lack any binding energy in the ground state. This is described in Sect. 10.3.1. The emission spectra from two molecules that are capable of forming ***exciplexes*** depend upon the distances between the two molecules. An equation for the excited state wave function of a one-to-one exciplex that forms from a donor molecule D and an acceptor molecule A was written by Guellet as follows [94]:

$$\Psi_E = \alpha\Psi_1(D^+A^-) + \beta\Psi_2(D^-A^+) + \gamma\Psi_3(D^*A) + \delta\Psi_4(DA^*)$$

The first two terms on the right side of the above equation correspond to charge resonance states and the last two to the excitation resonance states. Thus, a photosensitizer, as explained in Sect. 10.3, can act in two ways, by energy transfer and by electron transfer. To be exact, one may feel that a true photosensitizer is one that acts by energy transfer alone. This, however, is not always the case. Also, in the event of electron transfer, the process can lead to photo-induced decomposition via electron transfer [102].

The rate of absorption of light by a sensitizer that corresponds to excitation from the ground state to the excited singlet can be expressed as [94]:

$$I_{abs} = d[S_0]/dt - d[S_1]/dt$$

The measurement of fluorescence and phosphorescence spectra of photosensitizers is very important in providing information about the energy of the excited states. It also allows identification of the phenomena.

The process of energy transfer requires that the excited donor diffuse to the proximity of an acceptor within the time period of its excited lifetime. This is subject to the viscosity of the medium and the efficiently of the collision process and the range r in which the collisions can occur. The observed rate constant for energy transfer k_{ET} is governed by the molecular rate constant k_{diff} for diffusion-controlled reaction. This is defined by the Debye equation:

$$k_{\mathrm{diff}} = 8RT/3{,}000\eta$$

$$k_{\mathrm{ET}} = \alpha k_{\mathrm{diff}}$$

where α is the probability of energy transfer. R is the universal gas constant, T is the temperature in Kelvin, η is the viscosity of the medium in poise. The Schmoluchowski [94] equation defines the diffusion constant in terms of the diffusion coefficient of the sensitizer and the acceptor:

$$k_{\mathrm{diff}} = 4\pi/1{,}000(R_{\mathrm{s}} + R_{\mathrm{a}})(D_{\mathrm{s}} + D_{\mathrm{a}})N_{\mathrm{a}}/2)\{1 + [R_{\mathrm{s}} + R_{\mathrm{a}}/(\tau_0(D_{\mathrm{s}} + D_{\mathrm{a}})/2)^{0.5}]\}$$

where D_{s} and D_{a} are the diffusion coefficients of the sensitizer and the acceptor R_{s} and R_{a} are the molecular radii of the sensitizer and the acceptor, N_{a} is the Avogadro number, and τ_0 is the lifetime of the excited state of the sensitizer.

10.5 Photocross-linkable Polymers

Some photocross-linking of polymers can be traced back to ancient days, when pitch was photocross-linked for decorative purposes [102]. In modern times, wide varieties of photocross-linkable polymers were developed. The early practice of photo imaging relied mainly upon the photo-dimerization reactions. These reactions are common, photo-induced, reactions of organic chemistry, namely intermolecular cyclization. This reaction of cyclization that takes place between two reactive species, with one of them electronically excited, is actually predicted by the Woodward–Hoffmann rule [104]. In contrast, the reactions of thermally excited ground states of molecules proceed by different pathways. Many polymers were synthesized that possess pendant groups capable of photo-cyclization intermolecularly to be used in the photo-imaging technology. Photocross-linking technology today, however, also uses coupling reactions of radicals, chain growth polymerizations that result in photocross-linking, and some ionic reactions. The light-induced polymerizations of multi-functional monomers that transform liquid resins into solid polymers almost instantly and selectively in the illuminated areas are now versatile processes. They can, however, be achieved in a variety of ways. Thus, for instance, Decker discussed work in the less explored areas of photo-curing, namely laser-induced ultra-fast polymerization and UV curing of binary polymer systems [105]. By using highly sensitive acrylate photoresists, relief images of micronic size can be obtained by fast scanning with a focused laser beam. Also, polymer networks of different architectures can be obtained by UV irradiation of various monomer blends, e.g., acrylate-epoxide, acrylate-vinyl ethers, acrylate-polyene, vinyl ether-maleate, and thiol-polyene [104]. This does not mean, however, that photocross-linking of polymers is now unimportant technologically or scientifically. The fact that considerable research still continues in the field is a direct indication of that.

The light cross-linkable reaction, like all cross-linking reactions, results in ***gelation*** and the extent of gelation is important in this process. This extent is tied to the quantity of the functional groups in the reaction mixture. Carothers equations relate the critical extent of the gelation, p_{c}, at the gel point to the functionality of the reactants:

$$p_{\mathrm{c}} = 2/f_{\mathrm{ave}}$$

where f_{ave} is the functionality. This equation, however, was written for reaction mixtures that contain two different functional groups in stoichiometric proportions to each other. All the functional groups, however, for various reasons, might not participate in photocross-linking reactions. Even though these reactions may involve identical groups, this equation probably would not apply.

A statistical approach was developed by Flory [107, 108] and by Stockmayer [109] to derive an expression for predicting the extent of reaction at the gel point. It is expressed as

$$p_{\mathrm{c}} = 1/[r(f_{\mathrm{wA}} - 1)(f_{\mathrm{wB}} - 1)]^{0.5}$$

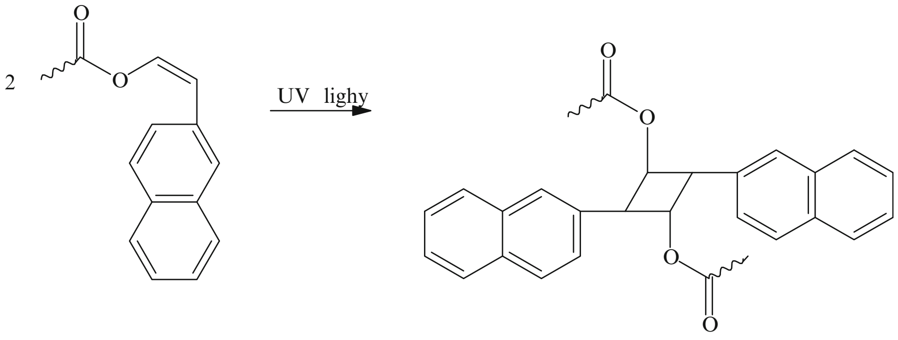
where f_{wA} and f_{wB} are weight average functionalities of A and B functional groups. Here the functionalities are defined as,

$$f_{\mathrm{wA}} = \sum f_{\mathrm{A}i}^2 N_{\mathrm{A}i} \Big/ \sum f_{\mathrm{A}i} N_{\mathrm{A}i} \quad \text{and} \quad f_{\mathrm{wB}} = \sum f_{\mathrm{B}i}^2 N_{\mathrm{B}i} \Big/ \sum f_{\mathrm{B}i} N_{\mathrm{B}i}$$

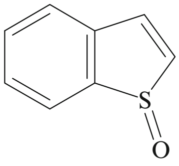
When the cross-linking, however, takes place by cyclization through dimerization of pendant groups, it appears that the gelation should probably be treated instead as a case of multiple dimerizations.

10.5.1 Polymers That Photocross-link by Formation of Cyclobutane Rings

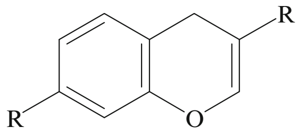
Many of the photocross-linkable polymers for photo-imaging in use today react by a 2π + 2π type dimerization with the accompanying formation of the cyclobutane rings [108, 109]. The formation of the cyclobutane ring can be simply shown on the photocross-linking reaction of poly(naphthyl vinyl acrylate), a polymer that also undergoes this type of dimerization [110]:



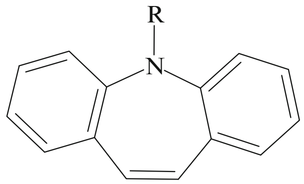
The naphthalenes become bonded to cyclobutane ring in 1,2 and 1,3 positions. Many polymers with other functional groups can also photocross-link by 2π + 2π addition. Following is an illustration of some of these groups [111, 112]:



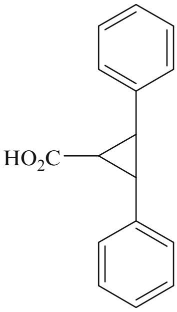
banzothiophene oxide

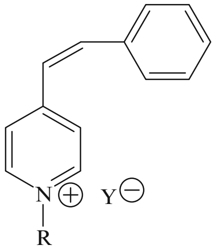


coumarin

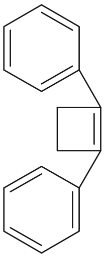


dibenzazepene

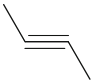




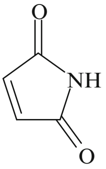
stilbazole



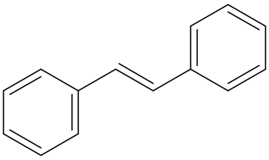
diphenylcyclobatane



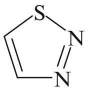
alkyne



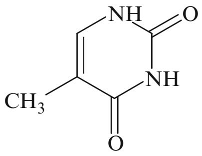
maleimide



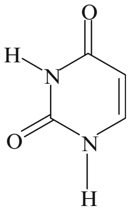
stilbene



1,2,3-thiadiazole

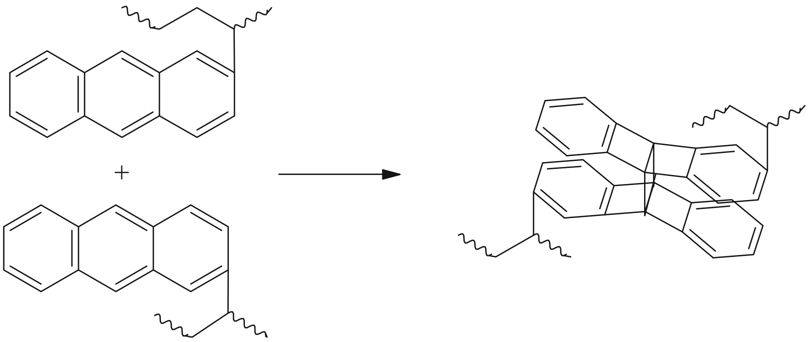


thiamine



uracil

Pendant groups with anthracene moieties, however, are believed to cross-link by a 4π + 4π type cycloaddition [114]:



Many photo-dimerizations of functional groups, like the ones shown above, require the presence of photosensitizers. These compounds may be selectively excited to their triplet state by sensitizers with the right type of energy levels. For efficient energy transfer to occur, the triplet energy of the donor should be approximately 3 kcal/mole greater than that of the acceptor [113, 114]. This type of sensitization is believed to be diffusion controlled [115].

Trecker [116] lists the steps of the sensitized dimerization reaction as follows:

Excitation: S (sensitizer) $+ h\nu \rightarrow S^*$
Energy loss: $S_3^* \rightarrow S$
Sensitization: $S_3^* + D \rightarrow {}^\bullet S - D^\bullet$
Dimerization: ${}^\bullet S - -D^\bullet + D \rightarrow S + {}^\bullet D - D^\bullet$
Dimer: ${}^\bullet D - D^\bullet \rightarrow$ dimer(s)

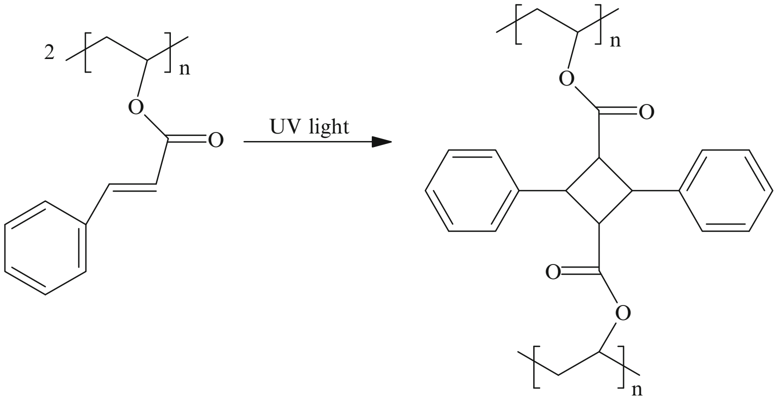
The quantum yield expression for this scheme of dimerization is shown as follows [115]:

$$1/\Phi = 1/\phi\alpha + k_3/\phi\alpha k_4(D)$$

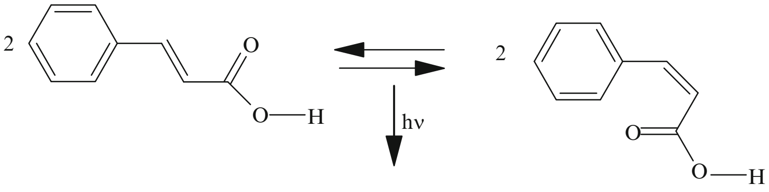
where Φ represents the quantum yield of dimer formation, ϕ is the efficiency of sensitizer intersystem crossing, D is the initial concentration of the reactive groups, and k's are the specific rate constants for the reactions shown in the above scheme.

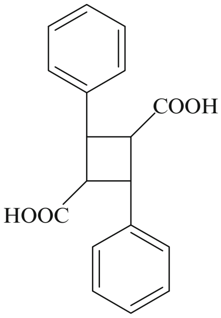
10.5.1.1 Polymers with Pendant Cinnamoyl Functional Groups

Minsk et al. [117] may have been the first to synthesize a photocross-linkable polymer, namely poly (vinyl cinnamate). The photochemistry of this compound is similar to the photo-cyclization of cinnamic acid that is discussed bellow in this section. It is interesting that the reaction of cyclization of cinnamic acid can take place even in the solid crystalline stage. This illustrates that the reaction requires very little molecular motion. Similar reactions occur in polymeric materials that are functionalized with cinnamate groups. The photocross-linking of poly(vinyl cinnamate) is illustrated below:



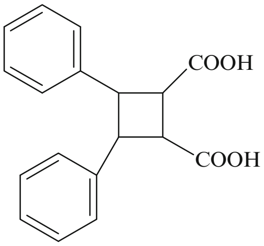
Much earlier, well before Minsk, in 1895, Bertram and Kursten [118] recognized that solid cinnamic acid undergoes a chemical change when exposed to light. Following this, Ruber [119] established that the change is a dimerization of the acid to form a cyclobutane derivative. This dimerization results in formation of truxillic and truxinic acids:





truxillic acid

+



truxinic acid

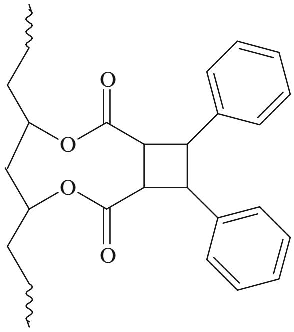
Schmidt and coworkers [120, 121] studied the reaction mechanism and came to the following conclusions:

1. Photo-dimerization of cinnamic acid and its esters is controlled by the crystal lattice.
2. Dimerizations are possible when olefinic double bonds of the two neighboring molecules in the crystals are 4.1 Å or less apart.
3. Dimerizations are not possible when the double bonds are 4.7 Å or more apart.

The dimerization reaction takes place upon irradiation with light of a wavelength longer than 300 nm. It was demonstrated subsequently [122], however, on poly(vinyl cinnamate) that the adducts dissociate again upon irradiation with light of 254 nm. Photo-dimerization and formation of cyclobutane groups were demonstrated to be enhanced as a result of sensitized irradiation [123].

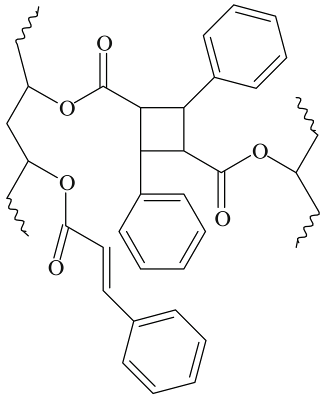
When dealing with poly(vinyl cinnamate), it is reasonable to assume that the degree of order in the relationship of one cinnamic group to another is much lower than is found in a crystal lattice of cinnamic acid. On the other hand, it should be higher than in solutions of cinnamic acid, where the groups are far enough apart so that very little photo-dimerization takes place. Photocross-linking of poly(vinyl cinnamate) can include the following reactions [124]:

1. Truxinic acid type dimerization in irradiated poly(vinyl cinnamate) that can occur intramolecularly. It can be shown as follows:



This is accompanied by formation of both folded and parallel chains

2. Truxillic acid type intermolecular dimerization in irradiated poly(vinyl cinnamate), on the other hand, can be illustrated as follows:



dimerization of this type would be accompanied by formation of folded chains.

Reactions of formations of folded and parallel chains are similar with the exception that the reacting cinnamic groups are further apart in folded chains and come together only by virtue of chain folding. Chains located parallel to each other but at the right distance can also conceivably yield truxinic acid type dimerization. This would be similar to the arrangements in crystal lattices. Formation of a truxillic dimer, like in reaction 2, shown above, requires favorable folding or two different chains. Also, there is accompanying possibility that the double bonds may simply polymerize by a chain propagating reaction [125]. This was observed with some cinnamate esters [125]. Attempts were made to determine the reaction products of photocross-linked poly(vinyl cinnamate) by first hydrolyzing it, and then by isolating and identifying the acids. The results showed that α-truxillic acid does form. Formation of β-truxillic acid, however, was not demonstrated. In addition, among the reaction products there is also a large quantity of unreacted cinnamic acid. This indicates that only a small portion of the double bonds participate in the reaction. Also, it should not be forgotten that only small changes in unsaturation in polymer molecules, as a result of cross-linking, can have a profound effect on solubility.

Studies [126] of electronic structures in photo-isomerization and photo-dimerization of cinnamic acid showed that phosphorescence of cinnamic groups occurs at about 20,000/cm. Also, it was demonstrated when photosensitizers are present, the critical distance between donor, sensitizer, and acceptor molecules (cinnamic acid) is about 10 Å [126]. Although all the details of incipient photocross-linking of poly(vinyl cinnamate) have to date still not been fully worked out, most accept that all three mechanisms take place. These are: dimerizations to truxillic and truxinic acid type structures and polymerizations through the double bonds. The excited states of the molecules can be produced by direct irradiation and also through intersystem crossing from an appropriate photosensitizer [126].

Several criterions were derived from proper selection of sensitizers [127, 128]. These are:

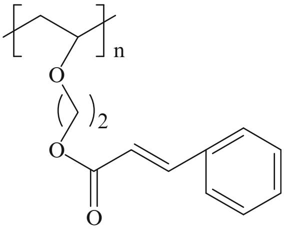
1. The triplet state must be at the energy level close to 50–55 kcal/mole for the cinnamate moiety.
2. The quantum yield of the ratio of phosphorescence to fluorescence should be higher than unity.
3. The mean lifetime of a triplet state must be greater than 0.01 s. The photosensitizing activity (characterized by the triplet state) of derivatives of cinnamic acid is beyond the phosphorescence of the cinnamate group (at about 20,000/cm, as stated above). An energy transfer diagram for poly (vinyl cinnamate) photosensitization with a sensitizer like 2-nitrofluorene was published [128]. The rate of dimerization obeys first-order kinetics. In addition, polymers consisting of flexible segments exhibit higher rates of photo-dimerization than do those composed of rigid segments.

Table 10.2 Effectiveness of sensitizers on relative speed of cross-linking of poly(vinyl cinnamate)

Sensitizer	Relative speed	Sensitizer	Relative speed
(None)	1	4-Nitroaniline	100
Naphthalene	3	3-Nitrofluorene	113
Benzanthrone	7	4-Nitromethylaniline	137
Phenanthrene	14	4-Nitrobiphenyl	200
Crysene	18	Picramide	400
Benzophenone	20	4-Nitro-2,6-dichlorodimethylaniline	561
Anthrone	31	Michler's ketone	640
5-Nitroacenaphthene	84	*N*-Acyl-4-nitro-1-nathylamine	1,100

From ref. [131] and other sources

It was also demonstrated that greater photosensitivity can be obtained by separating the cinnamic group from the polymer backbone by introducing –CH_2–CH_2–O– spacers as follows [129, 130]:

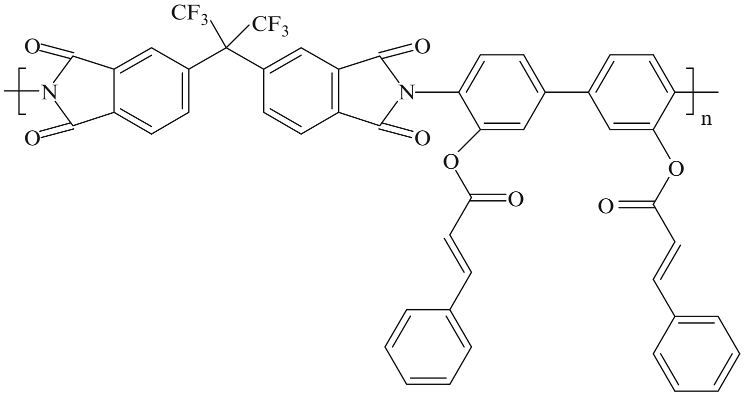


In addition, Tsuda and Oikawa carried out molecular orbital calculations of the electronic structures in the excited states of poly(vinyl cinnamate) [131, 132]. They based their calculations on the reaction of intermolecular concerted cycloaddition that take place according to the Woodward–Hoffmann's rule. This means that the cyclobutane ring formation takes place if a nodal plane exists at the central double bond in the lowest unoccupied MO(LLUMO) and not in the highest occupied MO (HOMO) of the ground state cinnamoyloxy group. This is within the picture of Huckel MO or Extended Huckel MO theory. The conclusion is that the concerted cycloadditions occur favorably in the lowest triplet state T_1 and in the second excited singlet state S_2 [132].

The effectiveness of photosensitizers in accelerating the cross-linking reaction of poly(vinyl cinnamate) is illustrated in Table 10.2.

Some 4 decades after the original development of poly(vinyl cinnamate) into a useful photocross-linkable polymer, a novel optical property of the polymer was observed. When the material is irradiated with linearly polarized light, it exhibits polarization holography [133, 134]. The exposure of thin films of poly(vinyl cinnamate) to linearly polarized ultraviolet light causes uniaxial reorientation into liquid crystal layers [135–142]. Poly(vinyl cinnamate) and its derivatives have the ability to align in thin films the liquid crystal moieties in the direction that is perpendicular to the polarization axis of the linearly polarized ultraviolet light [143–145]. Schadt et al. [136] suggested that the surface-settled homogeneous alignment of nematic liquid crystals results from photo-dimerizations of the cinnamate moieties and formation of cyclobutane rings (as shown earlier) with an azimuthally oriented order. This, he feels, determines the direction of the liquid crystal alignment [140]. Ichimura et al. [141] suggested a different photo-alignment process. They claimed that the photo-induced homogeneous liquid crystalline alignment is caused by polarization of photo-chromophores at the uppermost surfaces of the substrates due to repeated A/Z photo-isomerizations, similarly to azobenzenes [140–149]. This was also shown to take place with stilbenes [140]. In addition, it was demonstrated by them [149] that both photo-isomerization and photo-dimerization contribute to liquid crystalline alignment. Photo-regulation in a polymethacrylate with *o*-cinnamate side chains displays preferential formation of *Z*-isomer. Dimerization, on the other hand, takes place more favorably in other polymers, including poly(vinyl cinnamate) [150].

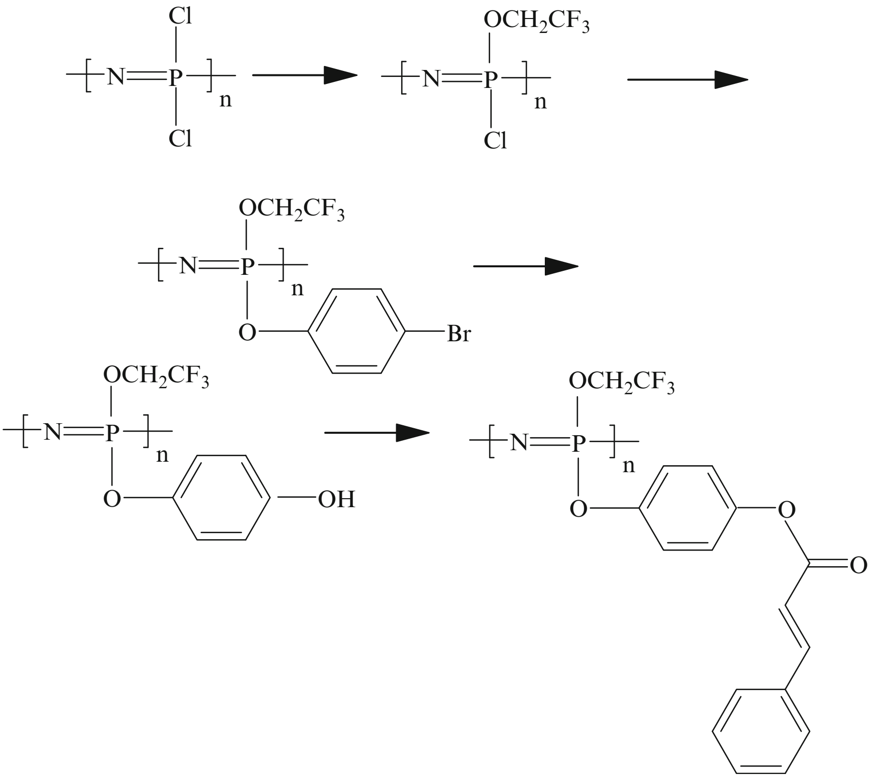
The liquid crystals alignment in films prepared from materials with cinnamate group after irradiating the films with linearly polarized UV light is quite uniform. All the aggregate structures, lamellar crystals, produced by the photocross-linking reaction were found to be square in shape [151]. This has application in flat panel liquid crystal displays. It led others to synthesize polymeric materials that could be useful in photo-alignment. Lee et al. [152] synthesized a soluble photo-reactive polyimide with cinnamate chromophore side groups. The polymer, poly(3,3′-bis(cinnamoyloxy)-4,4′-biphenylene hexafluoroisopropylidene diphthalimide), has a reasonably high molecular weight and forms good quality films through conventional solution spin-casting and drying.



The polymer is thermally stable up to 340°C and positively birefringent. The photochemical reactions of the polymer in solution and in films, as well as its molecular orientations, are induced by exposure to linearly polarized ultraviolet light. As one might expect, the cinnamate chromophores undergo both photo-isomerization and photo-dimerization. Also, exposure to UV light induces anisotropic orientations of the polymer main chains and of the cinnamate side groups in the films. The irradiated films homogeneously align nematic liquid crystal molecules along a direction at an angle of 107° with respect to the polarization of the linearly polarized ultraviolet light. This coincides with the orientation direction of the polyimide chains. Thus, the liquid crystal alignment process is principally governed in irradiated polyimide films by the polymer main chains and the unreacted cinnamate side groups [151].

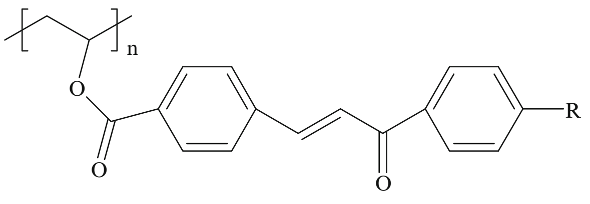
Nagata and Hizakae [153] reported preparation of a series of photocross-linkable biodegradable polymers by condensation of dichlorides of 4,4′-(adipoyldioxy)dicinnamic acid and alkane diols of various methylene lengths. They also used various poly(ethylene glycols) with molecular weights ranging from 200 to 8,300.

Among other interesting polymers with cinnamate functional groups are high polymeric phosphazenes that bear cinnamate groups [154]. A typical polymer synthesis is a follows:

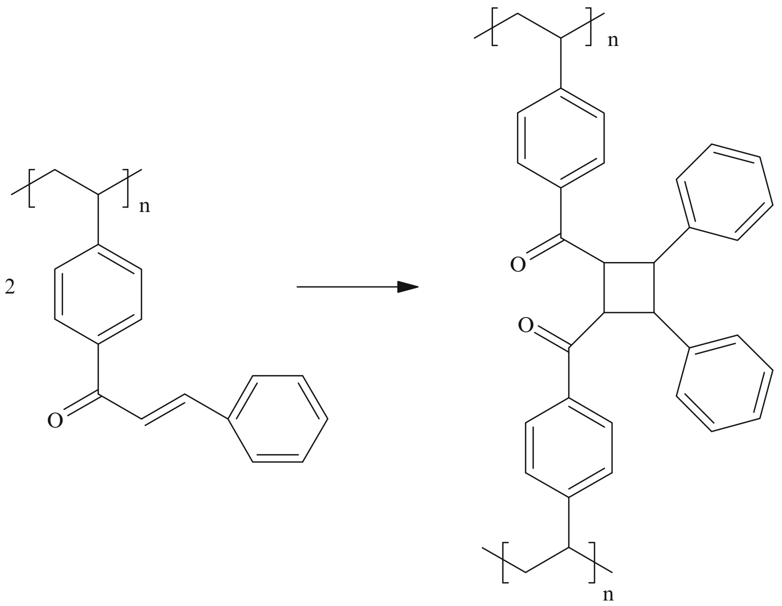


10.5.2 Polymers with Functional Chalcone Groups

Pendant chalcone groups on polymers behave similarly to pendant cinnamate groups. Thus, photocross-linkable polymer can be formed, for instance, from poly(vinyl alcohol) by a reaction with 4′-substituted-4-caboxychalcone in homogeneous dimethyl formamide solution, using 2,4,6-trinitrochlorobenzene as the condensing agent [155].



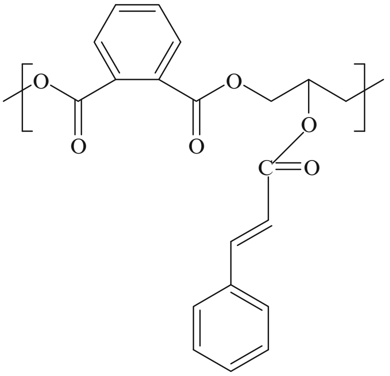
The photosensitivity of this polymer is in the range of 1–5 mJ/cm^2, according to Watanabe et al. [155]. When the R group shown above is *p*-Br, *m*-NO$_2$, or (CH$_3$)$_2$N, the cross-linking is via formation of biradicals derived from the double bonds of the cinnamoyl groups and an abstraction of protons from the neighboring methyne or methylene groups. This reaction of dimerization can be illustrated as follows [156]:



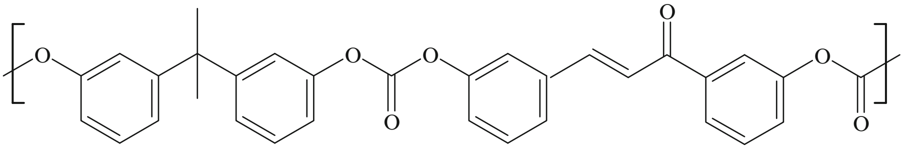
Formation of polymers by reaction of free-radical polymerizable methacryloyl groups and a photocross-linkable pendant chalcone units was also reported [157]. The photocross-linking reaction takes place in thin films and in solutions upon irradiation with high pressure mercury lamps. The reaction can be monitored through changes in the UV absorption spectrum. The rates of photocross-linking in solutions were reported to be faster than in films. Photocross-linking in the presence of a triplet photosensitizer shows no significant changes in the rate of disappearance of the double bonds. This particular polymer with a pendant chalcone unit was found to photocross-link at a high rate even in the absence of a photosensitizer and is of interest as negative photoresist [158].

10.5.3 Polymers with Functional Groups Similar to Cinnamates

As stated earlier, the photocross-linking reactions of poly(vinyl cinnamate) and the reversibility of cross-linking depends upon irradiation with light of the proper wavelength. In addition, some intramolecular cyclizations also take place. Because the reactions found extensive commercial applications, a number of other polymers that resemble poly(vinyl cinnamate) were developed. Following are two examples of such functional groups [159]:



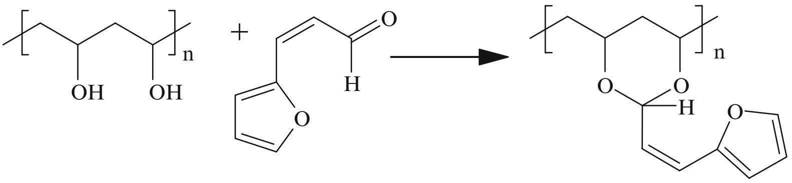
polyester



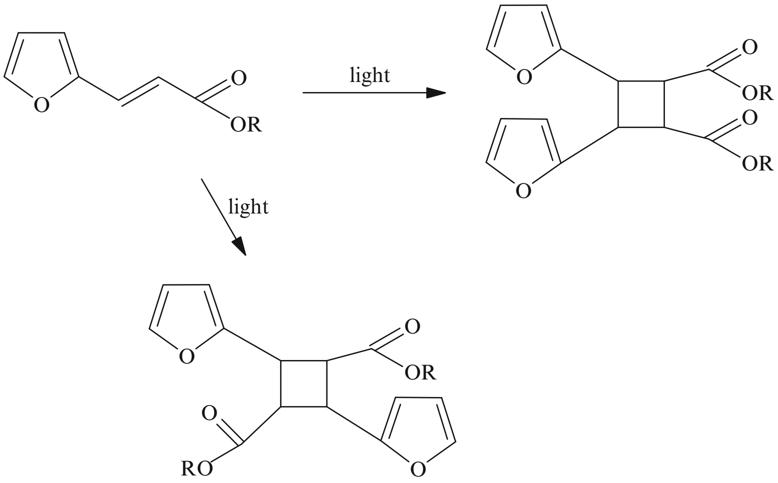
polycarbonate

10.5.4 Polymers with Pendant Furan Groups

Tsuda [160] attached 2-furylacrolein to a polymeric backbone by the following reaction:



In the presence of photosensitizers, this polymer was found by Tsuda to cross-link at a considerably faster rate than does poly(vinyl cinnamate) [160]. He showed that the cross-linking reaction also results in formation of cyclobutane derivatives. The cross-linking is illustrated on 3-furfurylacrylic ester:



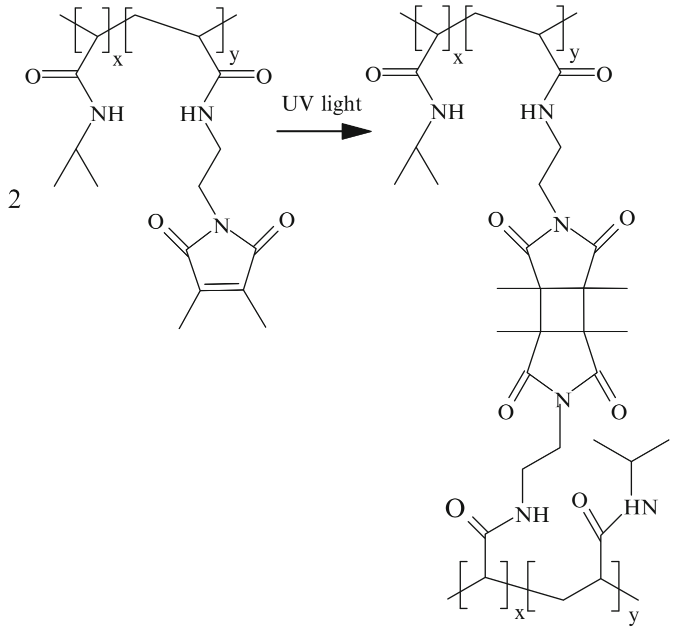
Tajima, Arai, and Takeuchi [161–163] studied the effects of singlet oxygen on photocross-linking of poly(furfuryl methacrylate). The singlet oxygen was generated by fullerene C_{60}. The reactions were carried out in 1,1,2,2-tetra-chloroethane solutions that contained the polymer and fullerene C_{60}. Gelation occurs when exposed to visible light in the presence of photosensitizers. These solutions gel after several hours and subsequently solidify completely [163].

It is interesting to note that fullerines are also effective in causing sensitization of poly(furfuryl methacrylate) and are effective in causing cross-linking upon with UV irradiation [164]. This is attributed to their long-lasting ability to sensitize oxygen even when they themselves undergo oxidation The sensitivity of poly(furfuryl methacrylate) increases linearly when the concentration of C_{60} is increased from 5×10^{-5} to $\mathrm{I} \times 10^{-3}$ mol/L. Saturation of sensitivity in the high C_{60} concentration regions was observed to be due to deficiency of oxygen molecules in the resist films. It was concluded that the dissolution rate of oxygen from the atmosphere into the resist film is lower than its consumption rate [164].

Preparation of photocross-linkable furan-containing polyimides was also reported [165]. It was also found that the polymer cross-links with the aid of singlet oxygen. Formations of fine pattern images can be formed. This was taken as clear evidence of the successful photolithography in this photo-curable system that uses C_{60} as the photosensitizer [165].

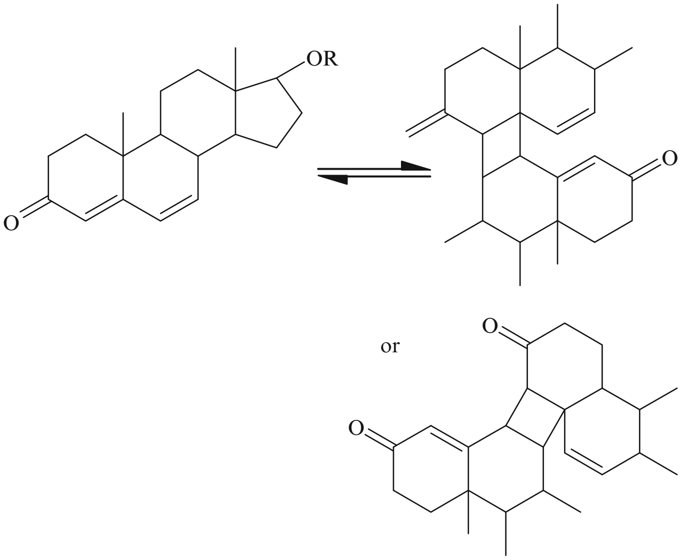
10.5.5 Polymers with Pendant Maleimide Groups

Preparation of photocross-linkable *co-* and terpolymers of *N*-isopropylacrylamide, 2-(dimethylmaleimido) *N*-ethylacrylamide as the photosensitive component, and 3-acryloylaminopropionic acid or *N*-(2-(dimethylamino)ethyl)-acrylamide as ionizable comonomers was reported [166]. Here too, cross-linking takes place through formation of cyclobutane moieties:

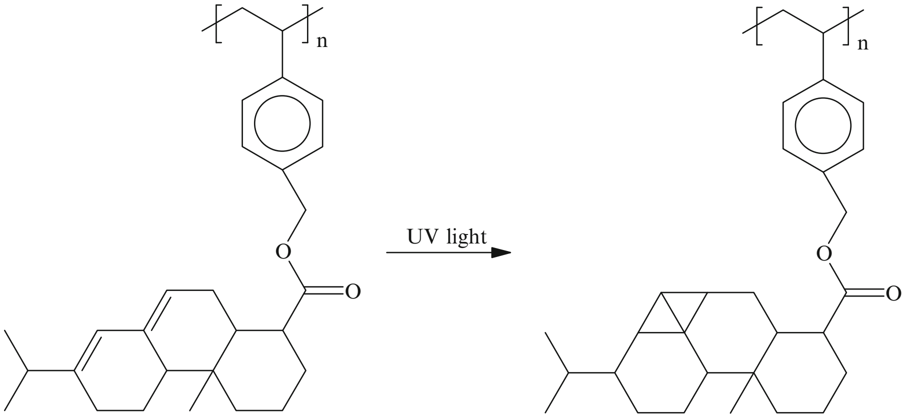


10.5.6 Polymers with Pendant Abietate and Dibenzazepine Groups

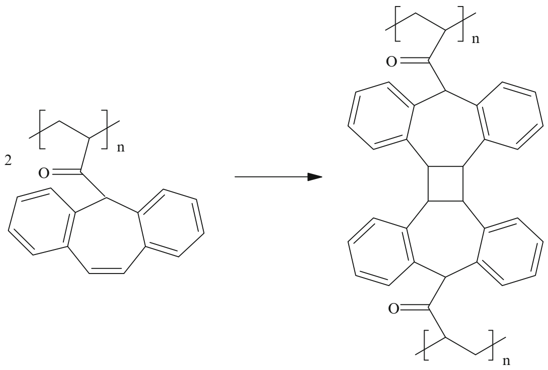
Poly(vinylbenzyl abietate) in the film state is cross-linkable via photo-dimerization of the conjugated carbon-carbon double bonds of the abietic acid moieties [166]. What the photo-dimerization product looks like is not clear. Formation of a cyclobutane rings in photo-dimerization of steroids was represented as follows [166]:



Also, judging from the photoreaction of cholestra-3,5-diene [166], one might expect some internal cyclization:

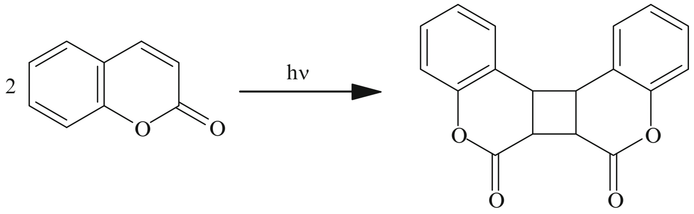


The cyclodimerization reaction of dibenzazepine was reported by Hyde et al. [167]. When attached to a polymer, the cross-linking reaction can be visualized as follows:



The cross-linking can result from either direct absorption of the light or in the presence of triple sensitizers like Michler's ketone [168]. The 2π + 2π addition leads to a formation of a cyclobutane cross-link.

Coumarin photo-dimerization is a known reaction [169]:

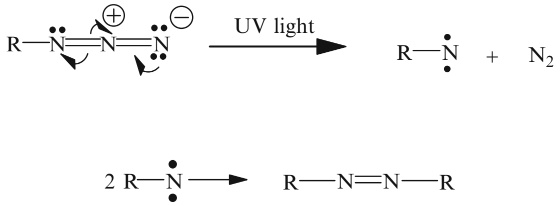


This was utilized by Tian et al. [168] to prepare a new class of liquid crystal homopolymers of poly{ll-[4-(3-ethoxycarbonyl-coumarin-7-oxy)-carbonyl-phenyloxy]-undecyl methacrylate} containing a coumarin moiety as a photocross-linkable unit. The preparations included polymers of various chain lengths. Also, liquid crystalline-coil diblock and liquid crystalline-coil-liquid crystalline triblock copolymers with polystyrene as the coil segment were formed. The polymers were reported to have been synthesized with the aid of atom transfer radical polymerization. The dimerization of the coumarin moieties takes place upon irradiation with light of $\lambda > 300$ nm to yield cross-linked network structures.

Lee et al. [169] reported the preparation of new soluble and intrinsically photosensitive poly(amide-*co*-imide)s containing *p*-phenylenediacryloyl moiety. The copolymers were formed from *p*-phenylenediacryloyl chloride, aromatic dianhydrides, and two equivalents of aromatic diamines. The products were subsequently imidized by reactions with the poly(amide-*co*-amic acid), acetic anhydride, and pyridine. The polymers were stable up to 350°C, showed good solubility in polar aprotic solvents, and became insoluble after the irradiation due to the photo-dimerization of phenylenediacryloyl moiety. The photo-reactivity increases with the irradiation temperature [169].

10.5.7 Polymers That Cross-link by Dimerization of Nitrenes and by Other Combinations of Free-Radicals to Form Covalent Bonds

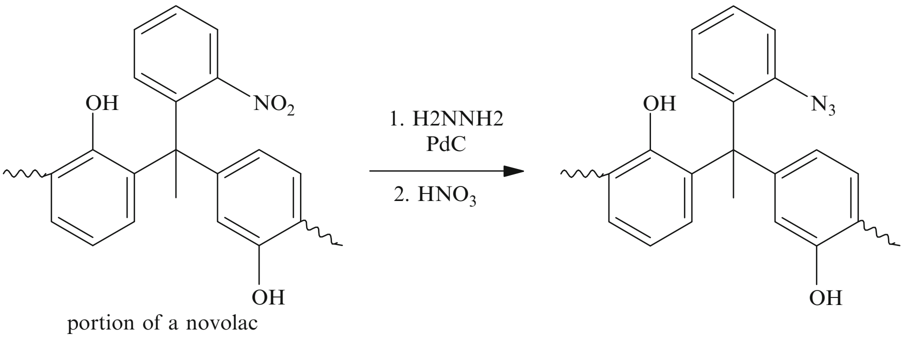
The aromatic azide groups photo-decompose into nitrenes when irradiated with UV light: The nitrenes, that form, possess two unpaired electrons, similarly to carbenes, and dimerize readily into *azo* groups



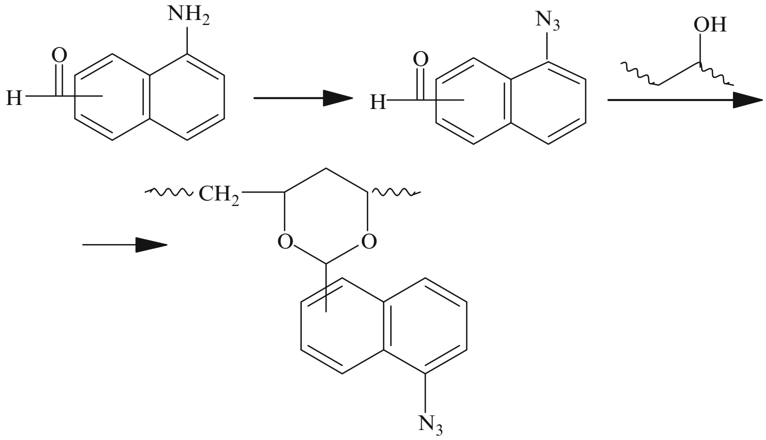
This reaction is utilized in photocross-linking.

10.5.8 Polymers with Pendant Azide Groups

Both azide and sulfonyl azide groups are photo-reactive and decompose into active nitrene groups and nitrogen upon irradiation. The dissociation of the azide moiety follows almost every transition from an excited n → π* state to a high vibrational level of the ground state [170, 171]. Introductions of pendant azide and sufonyl azide groups into polymeric structures are possible in a variety of ways and many publications describe different approaches. Thus, Tsuda and Yamaoka [81] introduced azide groups into a phenolic novolac resin by the following scheme:



Tsunoda and Yamaoka [173, 174] also condensed formyl-1-naphthyl azide with poly(vinyl alcohol). All steps in the synthesis were not disclosed. The preparation was illustrated as follows:



Preparations of azide derivatives from styrene-maleic anhydride copolymers, cellulose, and gelatin by attaching aromatic azide compounds are described in the literature [175]. Most of the resultant polymers cross-link rapidly when exposed to light of 260 μm wavelength. Also, as much as 90% of the hydroxy groups of poly(vinyl alcohol) can be esterified with *p*-azido-benzoyl chloride. These reactions must be carried out in mixtures of chloroform and aqueous sodium hydroxide [175]. Earlier, Merrill and Unruh [175] described formation of derivatives from poly(vinyl alcohol) and attachment of aromatic azide groups.

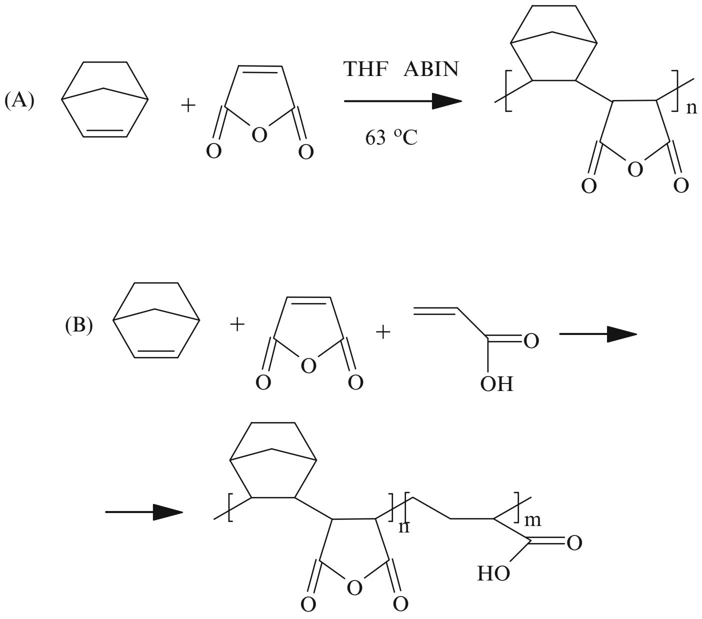
Most of these azide polymers photocross-link at a faster rate than does poly(vinyl cinnamate), when exposed to light of 260 μm. In addition, they responded well to photosensitization. Also, it was observed [50] that the 4-isomer of azidophthalate shows greater speed increase than does the 3-isomer. In general, the poly(vinyl alcohol) derivatives were reported to exhibit higher cross-linking speeds than do other azide functionalized polymers [176].

The reaction product of *p*-azidobenzoyl chloride with polyvinyl alcohol was investigated by Tsuda and coworkers [179]. In the polymer studied by them, over 90% of the hydroxy groups were esterified. The photocross-linking reaction was followed by observing changes in the ultraviolet and infra-red absorption spectra. It was shown that the simple photochemical reaction occurs stochiometrically upon irradiation. Also an absorption band was observed at 1,500/cm in the infra-red region of the irradiated and cross-linked polymer. This band is due to N=N stretching vibration of the *azo* group. Based on that, Tsuda concluded the cross-linking reaction takes place by dimerization, as expected [179].

There are reports in the literature that photosensitive azide polymers formed from polymers substituted with isocianate groups [176, 177]. The preparation and properties of many other polymers containing pendant aryl azide groups were described by Delzenne and Laridon [178]. The polymers were prepared by interfacial polycondensation of azido-substituted acid chlorides with diols and diamines. Also, in one experiment, a cinnamate moiety was combined with an azide group, together in one pendant functional structure [178]. It was found, however, that addition of the azide groups to the cinnamate side chain does not increase reactivity. A marked wavelength dependence was observed on π → π* and n → π* transitions that occurs in both functional groups [179].

10.5.9 Polymers Designed to Cross-link Upon Irradiation with Laser Beams

To accommodate the needs of photolithography, some polymers were developed that cross-link upon irradiation with an Ar-F excimer laser source at 193 nm [180]. To this end were synthesized cycloolefin-maleic anhydride-alternating copolymers. This material was formed by free-radical copolymerization of norbornene and maleic anhydride:



To render the polymers soluble in aqueous base, acrylic acid terpolymerization was also carried out as shown in (B) above.

10.6 Photo-Responsive Polymers

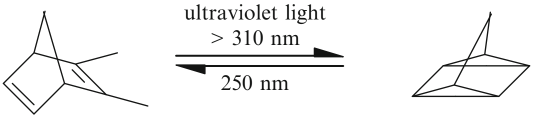
Photo-responsive polymers are materials that are able to respond to light irradiation by undergoing reversible changes in their chemical structures and/or their physical properties. Also, photochromism refers to the photo-induced reversible transformations in chemical compounds between two electronic states characterized by different absorption spectra [181]. There are many ways in which the photo-responsiveness of polymers can manifest itself. One might observe changes in viscosity of polymeric solutions, in contraction of polymeric chains, in sol–gel transitions, in electrical conductivity, or even in color changes as a result of irradiation with light of an appropriate wavelength. Another interesting manifestation of photo-responsiveness in some special polymers is a change in the permeability to gases in films. These changes can and are utilized in many ways. Thus, for instance, structural changes due to isomerization are employed to align liquid crystals and photoconductivity is utilized in xerography. Over the last 2 or 3 decades, the photo-responsive materials have grown in practical and scientific importance, because such materials are useful in many applications.

10.6.1 Polymers for Harvesting the Sun's Energy

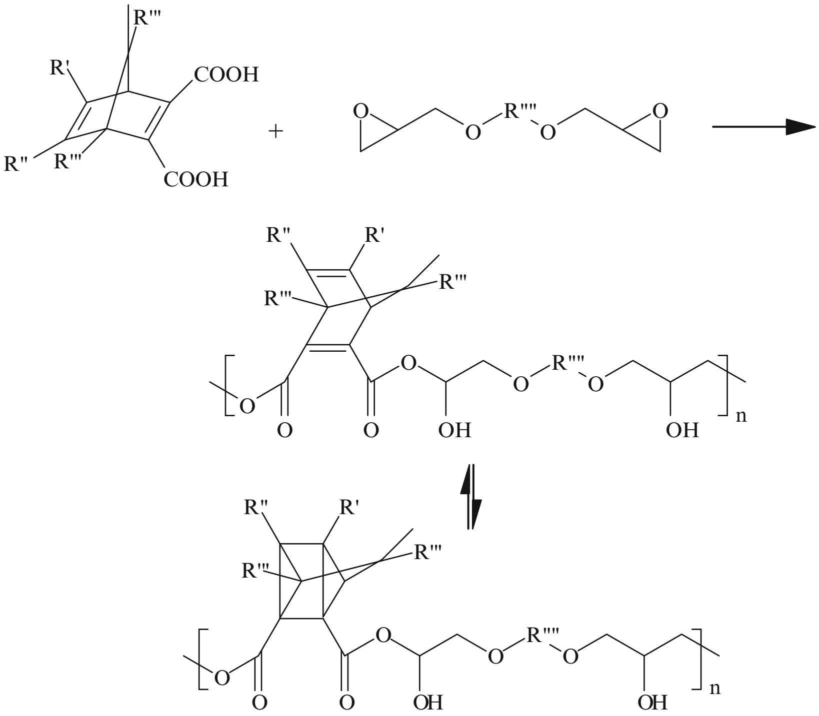
The goal of harvesting light energy has led to research in polymeric materials that could potentially mimic photosynthesis or harvest the sun's heat. In such materials, the choice of chromophores is the most critical variable. The location of the chromophores on the polymeric chains and the tacticity of the polymers are also very important. Weber pointed out, for instance, that among a number of chromophores attached to polymeric chains, naphthalene and carbazole form very stable *eximers*, while phenanthrene and diphenyl anthracene do not [182]. At present, many polymeric materials are utilized in the vast areas of nonsilver-based imaging, information storage, remote sensing, electroresponsive materials for displays, and others. Fox and Cozzens had to conclude, however, that none compare in efficiency to naturally occurring photon-harvesting polymers for photosynthesis [183].

10.6.1.1 Polymers with Norbornadiene Moieties

One approach to harvesting light energy is to utilize pendant groups that reversibly absorb light energy, rearrange, and then release this absorbed energy as heat in a rearrangement back to the original structure. To that end, research is going on in various laboratories to develop systematically derivatized polymer arrays than can collect and convert light energy. Among these, photo-rearrangements from norbornadiene to quadricyclane and back are of considerable interest, because photo-energy can be stored as strain energy (about 96 kJ/mol) in a quadricyclane molecule and later recovered [184]

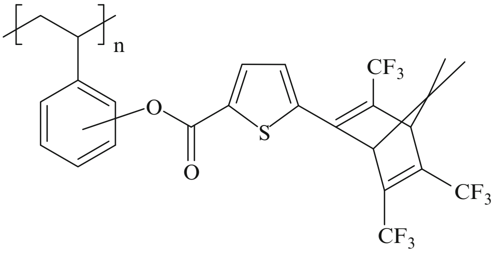


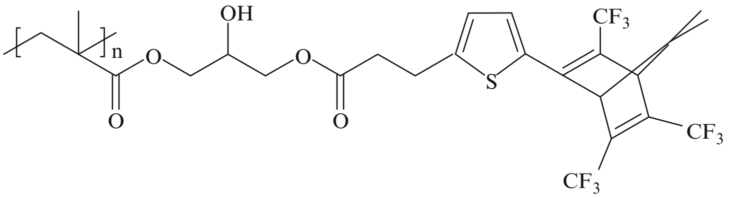
This photo-isomerization reaction is referred to as a ***valence isomerization***. It is a reaction in which electron reshuffling occurs and the nuclei move to make or break new π and σ bonds. A number of polymers were, therefore, prepared with the norbornandiene moieties either in the backbone or as pendant groups. Among them are polyesters that were synthesized with donor-acceptor norbornadiene residues in the main chain [184] by polyaddition of 5-(4-methoxyphenyl)-l,4,6,7,7-pentamethyl-2,5-norbornadiene-2,3-dicarboxylic acid or 5,6-bis(4-methoxyphenyl)-7,7- dimethyl-2,5-norbornadiene-2, 3-dicarboxylic acid, with bis(epoxide)s. This preparation of and the accompanying photo-rearrangements can be illustrated as follows:

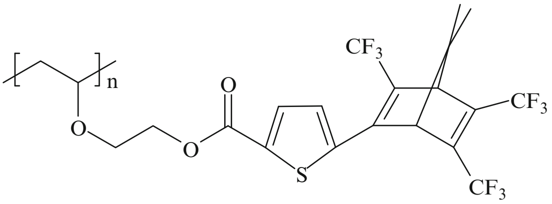


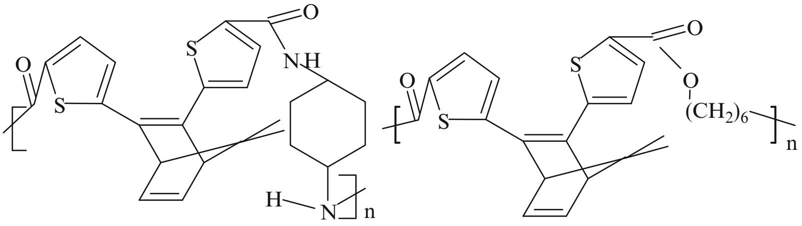
The photo-rearrangements of the norbornadiene residues in the resulting polyesters were observed to proceed smoothly to the quadricyclane groups. Also, it was found that the norbornadiene residues in these polyesters show resistance to fatigue in repeated cycles of the interconversions [184].

The goal to utilize photochemical valence isomerization between norbornadiene and quadricyclane for solar energy collection and storage was reported by others [185]. Nagai et al. synthesized five different polymers with trifluoromethyl-substituted norbornadiene moieties in the side chains and in the main chain [185]:



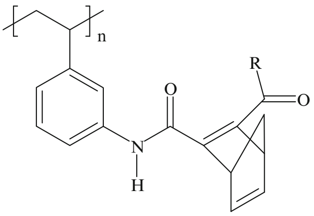






All of the above polymers exhibit large absorption bands in the visible region of the spectra and the norbornadiene moieties in these polymers isomerize very rapidly. In addition, the norbornadiene moieties also exhibit efficient fatigue resistance [185].

Kawatsuki et al. [186] synthesized styrene polymers with pendant norbornadiene groups attached via amide linkages:



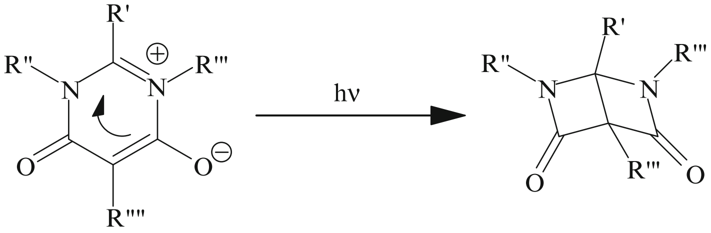
where R is a methoxy or a ring-substituted aniline group attached through the nitrogen or at another position. These pendant groups also undergo reversible conversions into quadricycline units in polymer films when irradiated by ultraviolet light of two different wavelengths. The materials exhibit high photosensitivity as well as a large red-shift in the absorption spectrum upon irradiation.

Sampei et al. [187] reported that polyaddition of 2,5-norbornadiene-2,3-dicarboxylic acid diglycidyl ester to adipoyl chloride gave a polyester containing norbornadiene residues in the polymer backbone and in the pendant groups. When a photochemical rearrangement of norbornadiene residues took place in polymer films, the rate of the photochemical reactions in the polymer backbones was higher than that in the side chains [187].

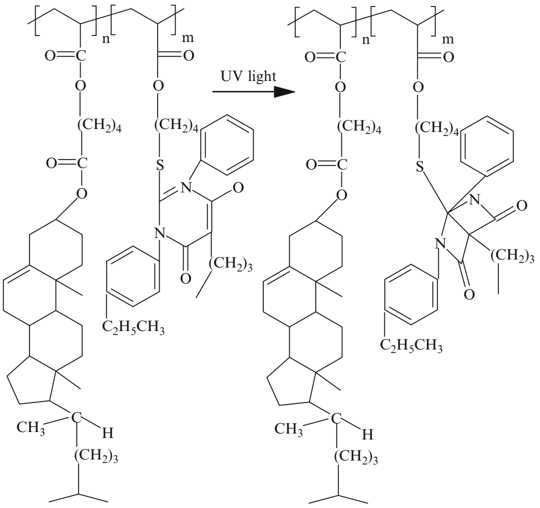
Kawashima et al. [188] reported preparation of donor-acceptor type norbornadiene carboxylic acids compounds with carbamoyl groups, such as dipropylcarbamoyl, methylphenylcarbamoyl, propylcarbamoyl, and phenyl-carbamoyl. Benzyl esters were also prepared. Addition of these groups to polystyrenes formed polymers with pendant donor-acceptor type norbornadiene. Some were formed with 100% substitution. It was found that the polymers containing phenylcarbamoyl groups exhibit especially high photo-reactivity. In addition, the rate of the photochemical reaction in films of these norbornadiene polymers increases efficiently by an addition of 4,4′-bis(diethyl-amino)benzophenone photosensitizer. As a result, all the norbornadiene groups of the polymers isomerize to the quadricycline groups in as little as 20 s. The stored thermal energy of the irradiated polymers was found to be 32–52 kJ/mol.

10.6.1.2 Copolymers of Methacrylates with Cholesteric Monomers

Groups, like 6-oxo-1,6-dihydropyrimidin-3-ium-4-oleates, are light-sensitive and undergo intramolecular photo-cyclization to bis-β-lactams when irradiated with UV light between 320 and 490 nm [189].



This was utilized to form copolymers of methacrylates with colesteric monomers [190]. An example of such copolymers and the rearrangement is shown below [190]:

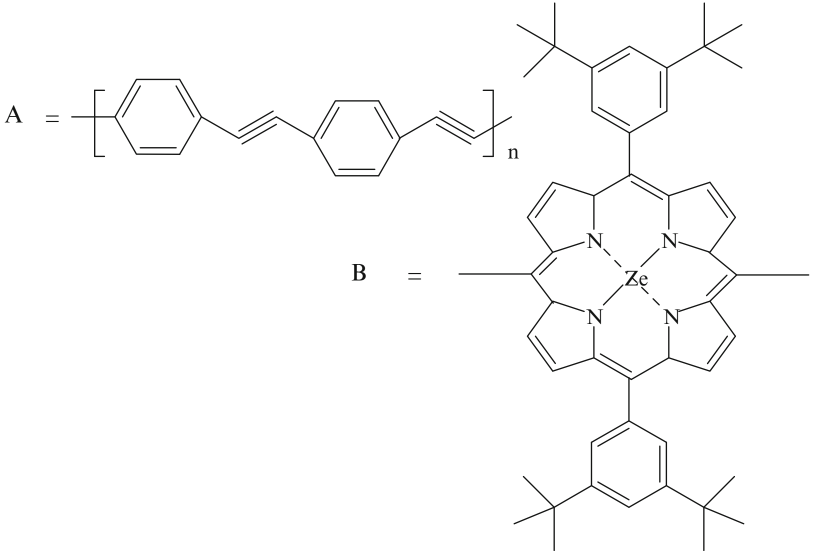


It was found that the rate of photo-rearrangement is affected by the length of the alkyl side group in the 5 position of the pyrimidinium oleate and by the embedding of a chromophore, as shown above [190].

In photosynthesis, antenna pigments harvest energy and transfer it into a reaction center for redox reactions [191]. Different antenna chromophores that surround the reaction center are arranged morphologically in an order of energy gradient [192–194]. Such an arrangement allows the energy to be sequentially transferred and efficiently funneled into reaction centers over small distances in the direction of decreasing band gaps. Considerable research has been carried out on means to develop the sequential multistep energy transfer systems. This was done not just to mimic the natural light-harvesting process [192–194], but also for possible applications and use in optoelectronic and biological systems [195]. It is speculated that a conjugated polymeric backbone, with well-designed interruptions of conjugation by insulating spacers, might allow tuning the emission properties and by providing an alternate model [196].

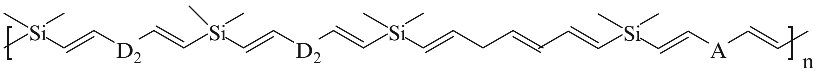
Based on this concept, Krebs and coworkers [197] reported a synthesis of a light-harvesting material that consists of three structural domains. Two of them are conjugated homopolymers that are linked with a zinc porphyrin:

$$-\!\left[A\right]_n\!-B-\!\left[A\right]_m\!-$$



Sections A and B of the above block copolymer are illustrated above. The polymer has a constant ratio of the zinc porphyrin to the incorporated monomer units, regardless of the molecular weight. The ratio of zinc porphyrin to the polymer blocks can be varied in the material by varying the size of the blocks A. Studies of energy transfer from the polymer to the zinc porphyrin showed that there is actually very little energy transfer when the material is in solution. On the other hand, there is quantitative energy transfer in the solid state. Also, it was observed that the light-harvesting properties of the three-domain structures depend on the chain lengths of the conjugated polymers.

Cheng and Luh reported that they are also trying to develop polymers that would mimic natural photosynthesis with synthetic polymers [198]. They point out that silylene moieties have been used extensively as insulating spacers [198]. In general, when the silylene spacer contains only one silicon atom, no conjugative interactions between the π systems and the silicon moiety are observed [199]. They believe, therefore, that introduction of an energy gradient with three well-designed chromophores into a silylene-spaced polymeric chain may lead to sequential energy transfer. To achieve this goal, they carried out preparations of regioregular silylene-spaced copolymers composed of energy gradients with three different chromophores. One of the polymers prepared in this way can be illustrated as follows:



Their synthesis utilized rhodium-catalyzed hydrosilylation of bis-vinylsilanes and bis-alkynes. The ratio of the three chromophores in the above polymer is 1:2:1, corresponding to D1, D2, and A chromophores, respectively. Cheng and Luh found that upon excitation of the donor chromophore D1, only emission from the acceptor A was observed [199].

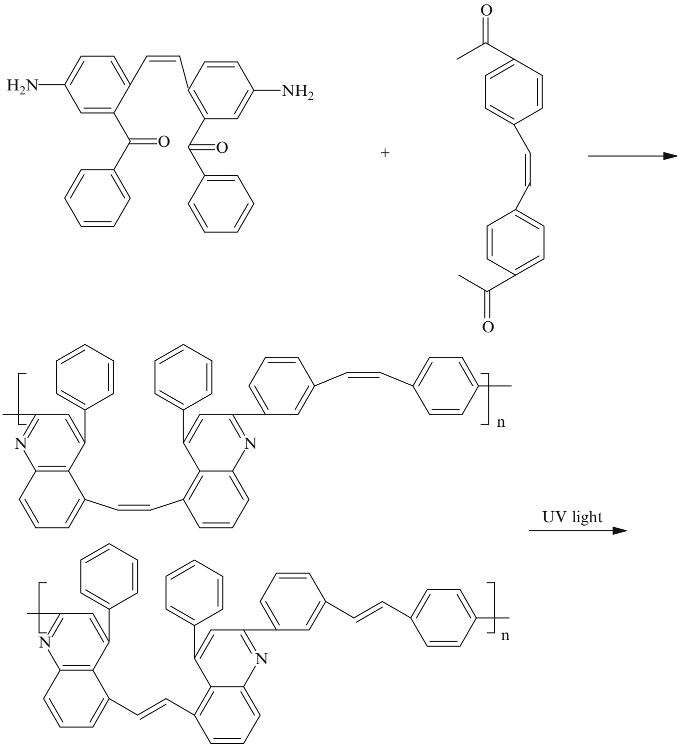
10.6.2 Photo-Isomerization of Polymeric Materials

Among all the photo-rearrangements, a *cis-trans* isomerization reaction is the most useful one. A well-known example is that of *cis*-stilbene to the *trans* isomer. This reaction has been described in many books [200]. The isomerization reaction takes place because many olefins in the excited singlet and triplet states have a perpendicular instead of a planar geometry. This means that in the excited state the *cis-trans* isomerism disappears. Upon return to the ground state, S_0, it is possible for either isomer to form. The return, however, usually takes place to the more stable form. Generally, photo-isomerization of chromophores in dilute solutions is a first-order reaction.

10.6.2.1 Photo-Isomerization of the Olefinic Group

An example of olefinic groups rearrangement is work by Onciu et al. [201] who formed three bis (trimellitimide)s by condensing three aromatic diamines with trimellitic anhydride. This was followed by preparation of two series of photo-reactive copoly(amide-imide)s by direct polycondensation of the bis(trimellitimide)s and 1,4-phenylenediacrilic acid with either 4,4′-diphenylmethanediisocyanate in one case or with 1,6-diisocyanatohexane in another case, respectfully. All of the copoly(amide-imide)s were found to be soluble in polar aprotic solvents and to yield transparent, flexible, and tough films [201]. When the polymers are irradiated in solution, the *p*-phenylenediacryloyl units undergo *trans–cis* photo-isomerization and (2 + 2) photo-cycloadditions [201]. The fully aromatic polyamides also undergo a photo-Fries rearrangement. The photo-Fries reaction, however, is completely suppressed in polymers that contain an aliphatic amide moiety [22]. The same processes are also observed in the polymer films [201].

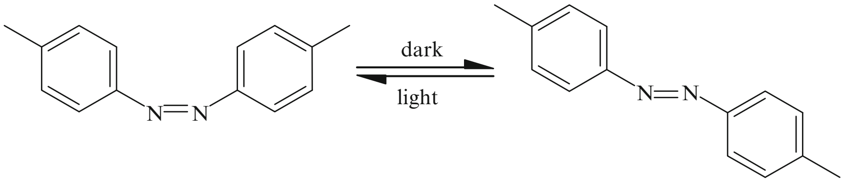
Polymers prepared by condensation of 4,4′-diacetylstiblene as the bis(ketomethylene)monomer with 4,4′-diamino-3,3′-dibenzoylstilbene, a bi(amino ketone), exhibit photo-viscosity effects in dilute solutions due to *cis-trans* isomerization [202]. The preparation of the polymers and the photo-rearrangements can be illustrated as follows:



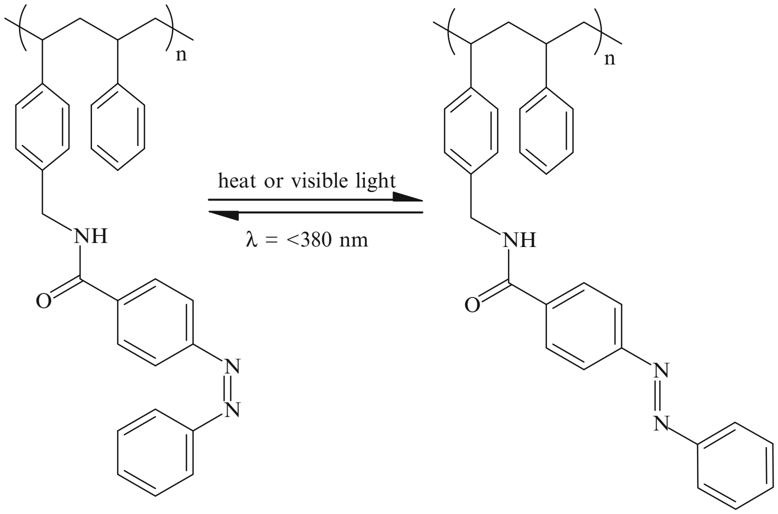
The changes in viscosity can vary from 2 to 23% as a result of irradiation.

10.6.2.2 Photo-Isomerization of the *Azo* Group

Azobenzene is a well-known photo-responsive chromophore, and its photo-induced and thermal geometric isomerizations have been extensively explored [200]. Azobenzene and its derivatives assume both *trans* and *cis* conformations with respect to the *azo* linkage. *Azo* π → π* excitation and *azo* n → π* excitation trigger *trans*-to-*cis* and *cis*-to-*trans* isomerizations [203–205]. The *azo* linkage normally exists in the more stable *trans* form. Also, the *trans* isomer of azobenzene exhibits an intense absorption around 320 nm due to the π → π* transition, while the *cis* isomer shows a weak absorption of the n → π* transition, around 430 nm [206]. Reversible isomerizations between *cis* and *trans* structures are due to these transitions. Photo-isomerization can proceed almost quantitatively [207]. By comparison, the thermal isomerizations from *cis* to *trans* configurations take place due to low activation energy of the *cis*-to-*trans* process. Isomerizations of the *azo* chromophore in compounds are often accompanied by drastic changes in a number of properties such as, for instance, changes in the dipole moments [208]. The isomerization back to the *trans* configuration can be readily carried out either thermally, or by visible light irradiation. Changes in the molecular structure, such as *cis-trans* isomerization in polymers, can induce contraction and expansion of the polymeric chains on both microscopic and macroscopic scale. This was demonstrated on a polymers with *azo* linkages. Exposure from dark to light can result in a contraction of as much as 0.5% [209]:

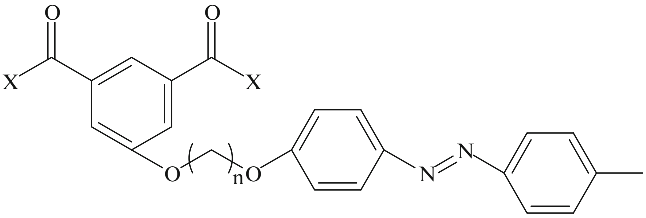


One example is a copolymer of styrene, where azobenzene structures are attached in the comonomer to the benzene portion through amide linkages [210]:



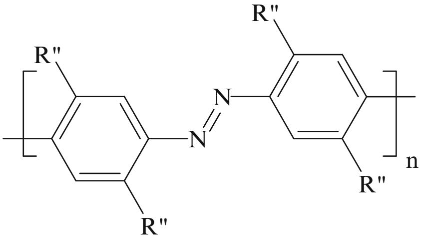
After 10 min of irradiation with ultraviolet light, the photo-stationary state is reached, consisting of 79% of the *cis* isomer. Back isomerization to *trans* of the sample is slow in the dark(less than 10% in 60 min), but is much faster when exposed to visible light [210].

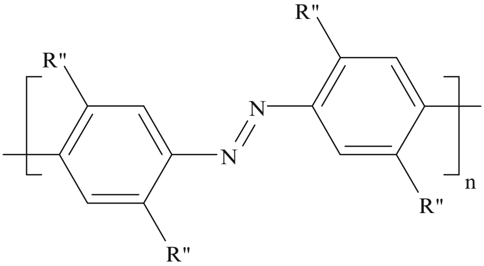
A Japanese patent [211] describes preparation of isophthalic type polyesters that include monomers with pendant *azo* groups:

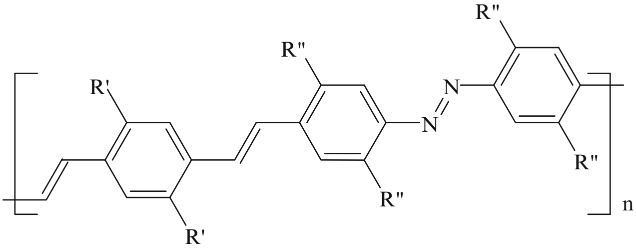


where Y is a hydrogen or a lower alkyl group; $m = 1–3$; $n = 2–18$. Polyesters based on this monomers are claimed to be useful for optical recording media such as holograms recording with low light absorption or without loss and wide range of working wavelengths.

Izumi and coworkers carried out similar preparations of conjugated polymers with azobenzenes in the main chain [212, 213]. Application of various palladium-catalyzed coupling methods such as the Suzuki coupling and the Heck reactions allowed formation of poly(*p*-phenylene)- and poly(phenyl vinylene)-based polymers:







where R′, R″ = H or n-C_6H_{13}.

These isomerization processes are also accompanied by changes in the three-dimensional hydrodynamic volumes of the polymers [213].

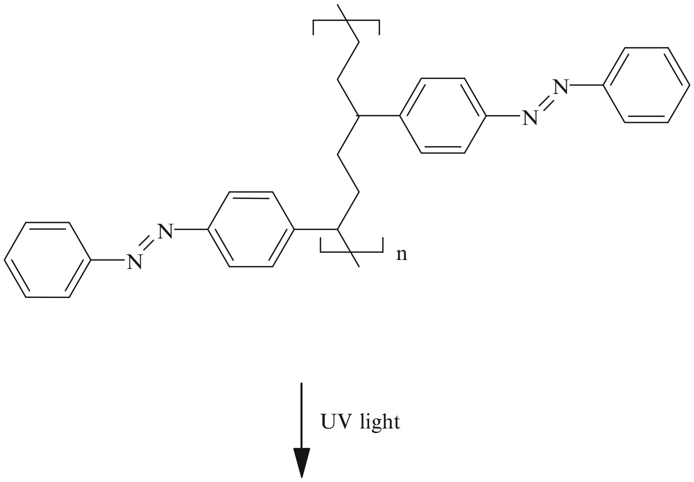
10.6.3 Changes in Viscosity and Solubility of Polymeric Solutions

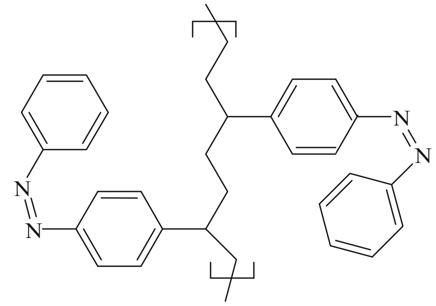
Changes of viscosity in polymeric solutions that are associated with photo-induced conformational changes of the macromolecules were observed by Lovrien [214]. He reported that solutions of a copolymer of methacrylic acid and *N*-(2,2′-dimethoxyazobenzene)acrylamide exhibit an increase in specific viscosity when irradiated with UV light. He also observed a decrease in the viscosity of a poly (methacrylic acid) and chrysophenine solution in water under the influence of UV light [214]. This was followed by various reports of photo-viscosity effects in solutions of azobenzene-based polymers. Matejka and Dusek [215] studied a copolymer of styrene and maleic anhydride with azobenzene in the side chains. UV light irradiation of a solution of this polymer in 1,4-dioxane causes a decrease in specific viscosity between 24 and 30% and in tetrahydrofuran between 1 and 8%. They also observed that this decrease in viscosity is reversible. The magnitude of the effect was found to be related to the quantity of azobenzene linkages present in the polymer.

Hallensleben and Menzel [218] found that irradiation of poly(5-(4-phenylazobenzyl)-L-glutamate) in 1,4-dioxane solution with UV light ($\lambda > 470$ nm) decreases the viscosity by 9%. Here too this change in viscosity is accompanied by a *trans* to *cis* isomerization that was estimated to be 23%. With additional irradiation by 360 nm UV light, the viscosity decreases an additional 9% and the isomerization to *cis* reaches 89%.

Irie et al. [217] synthesized a number of polyamides with azobenzene groups in the backbone. All the polymers exhibit photo-viscosity effects. In solutions in *N*,*N*′-dimethylacetamide, a 60% reduction in specific viscosity can be achieved by UV light irradiation ($410 > \lambda > 350$ nm). The initial viscosity is regained by storage in the dark at room temperature for 30 h.

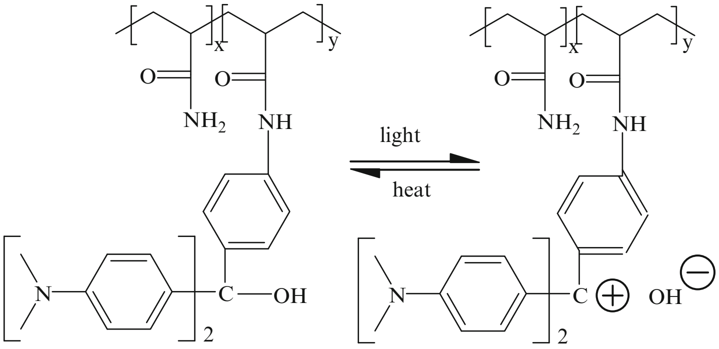
Changes in viscosity of solutions in dimethylsulfoxide of a range of polyureas with azobenzene groups in the polymer backbone were reported [216]. The irradiations were carried out at 35°C with UV light between 410 and 350 nm. It was observed that the intrinsic viscosity is about 40% lower during UV irradiation than in the dark. Also, toluene solutions of polydimethylsiloxane with azobenzene residues were shown to exhibit 20% lower viscosity under UV light irradiation than in the dark [219]. This effect was attributed by them to conformational contraction of the polymer chains due to dipole–dipole interaction between neighboring chromophores [220]. This conformational change might possibly be illustrated as follows:





Also, when copolymers of polystyrene and 4-(methacryloyl-amino)azobenzene containing 2.2–6.5% of the latter are irradiated in a cyclohexane solution with 15 flashes of 347 nm of light. The polymeric chains contract [221]. This occurs at a high rate per second as a consequence of isomerization. At a later stage, several hundred seconds after the flash, there is evidence of polymer aggregation and precipitation [221]. In addition, when azobenzene residues are introduced into the main chain of poly(dimethylsiloxane), reversible solution viscosity changes can be obtained by irradiation with ultraviolet light [221].

Isomerization from *cis* to *trans* and back of *azo* groups, however, is not the only mechanism that can affect photo-viscosity change in polymeric solutions. Thus, reversible solution viscosity changes were also observed [222] in solutions of poly(dimethylacrylamide) with pendant triphenylmethane leucohydroxide in methanol. This can be illustrated as follows:

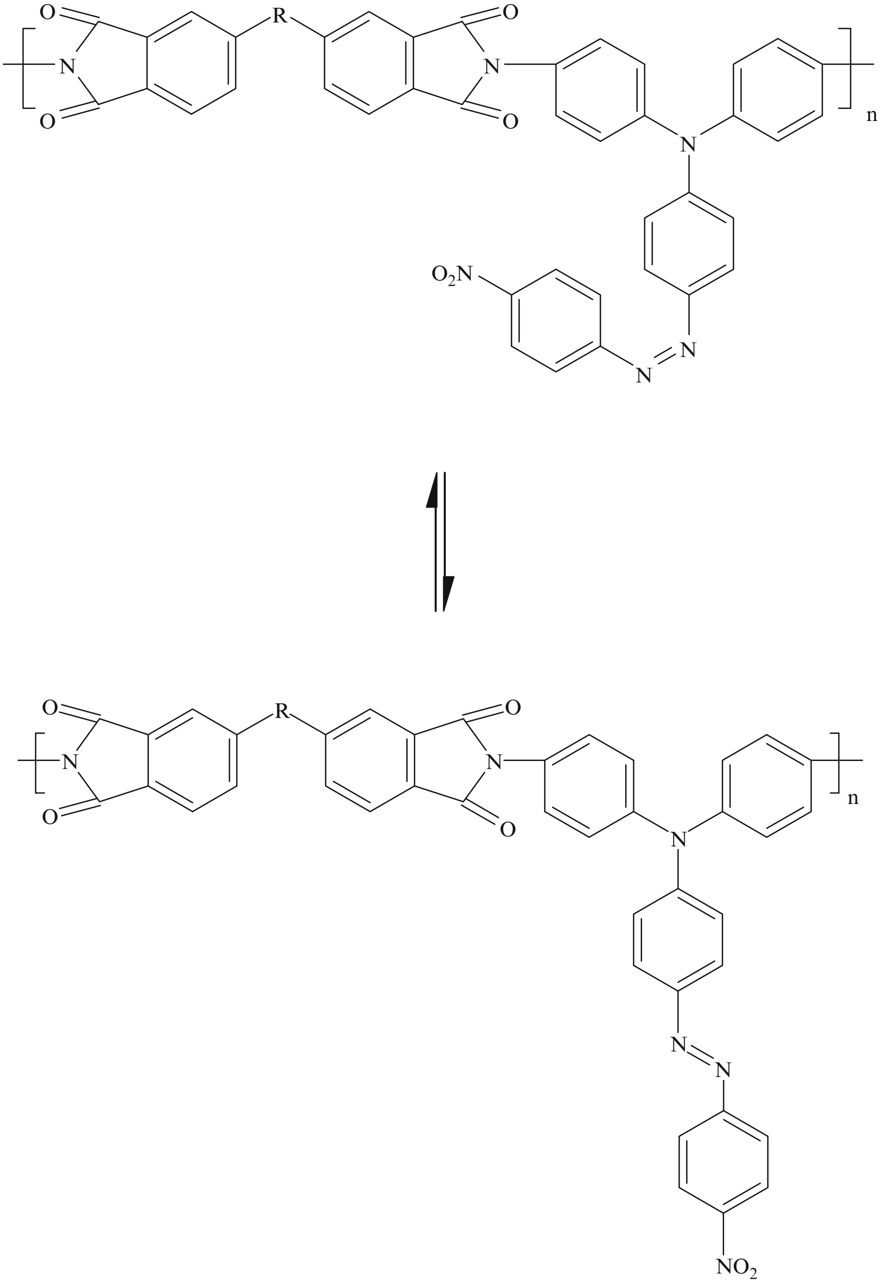


So, as shown, the viscosity changes are due to positive charges that form on the pendant groups.

The solubility of a copolymer of styrene in cyclohexane was found to change reversibly upon ultraviolet light irradiation when the copolymer contains small amounts (~2 mol%) of spirobenzopyran among the pendant groups [223]. This is believed to be due to photo-isomerization of the pendant spirobenzopyran groups to the polar merocyanine form with the resultant decrease in polymer–solvent interaction and subsequent precipitation of the higher molecular weight fractions of the polymer. A copolymer with a high content of spirobenzopyran groups (12.3 mol%) performs as a negative photo-resist with high contrast [223].

10.6.4 Application to Optical Data Storage

Due to possible utilization of photo-induced orientation in polymeric films in optical data storage, this phenomenon and the quadratic nonlinear optical effects were extensively investigated in the last few years. It was reported, for instance, that to study photo-isomerization in a polymeric environment, a series of polymers containing *azo* dyes with large differences in the second order transition temperature were compared [225]. Particular emphasis was placed on the relationship between photo-isomerization, T_g of the polymers, and their molecular structure. As a result, it was shown that light-induced nonpolar orientation in very high T_g polyimides (T_g up to 350°C) can take place even at room temperature. The polymers used in one of these studies can be illustrated as follows [225]:



where R = $(CF_3)_2$–C< in one polymer and –COO–$(CH_2)_2$–COO– in another.

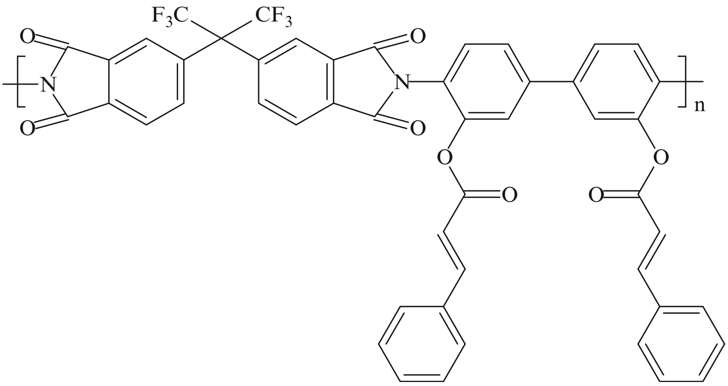
From the behavior of the mean absorbance, it was concluded that all the *azo* chromophores revert to the *trans* form on completion of a thermal back reaction. The observed increase in the dichroic ratio over the first 25 h is believed to be due to the thermal back isomerization and not due to the relaxation of the induced orientation [225]. Heating polymers at 170°C for 1 h fails to erase the green light-induced dichroism in the samples. This dichroism is, however, completely erased on heating the samples above their T_g for 10 min. Irradiation of the films with incident light gives holograms [226].

10.6.5 Liquid Crystalline Alignment

The relationship of glass transitions to mobility and isomerization in confined polymer systems aroused much interest. It was influenced by need for alignment in liquid crystalline flat panel displays, because in these displays films of polyimides are widely used. The surfaces are usually treated to produce uniform alignment of the liquid crystals into suitable "pretilt" angles. The treatments consisted of rubbing process with velvet fabrics. Search for new methods, however, led to development of molecular structures that undergo alignment upon irradiation with linearly polarized UV light [222, 223]. Polymer-stabilized liquid crystals are low-molar-mass liquid crystal. Their bulk alignment or their texture is stabilized by a polymer network. Such polymer network is usually in low concentration [222, 223]. Several types of polarized-light-induced liquid crystalline aligning of molecules were reported in the literature [223].

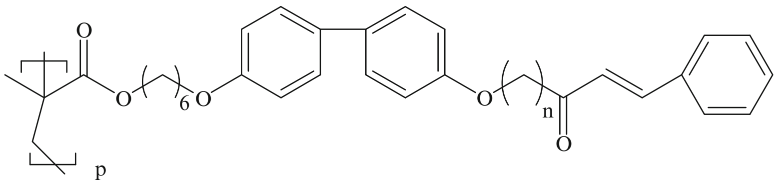
One photo-alignment material is poly(vinyl cinnamate). The polymer and its copolymers were reported to have the ability to align in thin films in the direction perpendicular to the axis of the linearly polarized ultraviolet light. This photo-alignment mechanism has not been fully elucidated at present. A drawback to using poly(vinyl cinnamate) and its copolymers is a low glass transition temperature. As a result, they remain mobile after treatment and chain orientation. Other materials with higher T_g are, therefore, needed. Among the most promising ones are polyimides. They form liquid crystal alignment layers in flat panel displays and possess good optical transparencies, adhesion, heat resistance, and dimensional stability, and are good insulators.

There are various reports in the literature about preparations of soluble photo-reactive polyimides with cinnamate chromophore side groups. Thus, it was reported by Lee et al. [224] that they prepared a photo-reactive polyimide with cinnamate chromophores side groups:



This polyimide is claimed to be thermally stable up to 340°C and has a glass transition temperature of 181°C. Also, it was demonstrated that the cinnamate chromophores, upon irradiation with linearly polarized ultraviolet light, undergo both photo-isomerization and dimerization. In addition, the light exposure induces anisotropic orientation of the polymer main chains and of the cinnamate side groups in the film. The irradiated films align homogeneously the nematic liquid crystal molecules along one direction at an angle of 107° with respect to the polarization. The liquid crystalline alignment was found to be thermally stable up to 200°C.

It was also reported [225] that photo-reactivity of side-chain liquid crystalline polymers can align liquid crystals both in a parallel mode or perpendicularly, depending on the degree of the photoreaction of the polymers. Presumably, this particular polymer can multiphoto-align the liquid crystal pattern without a change of the direction of the linearly polarized UV light. The chemical structure of such an aligning polymer is depicted as follows:

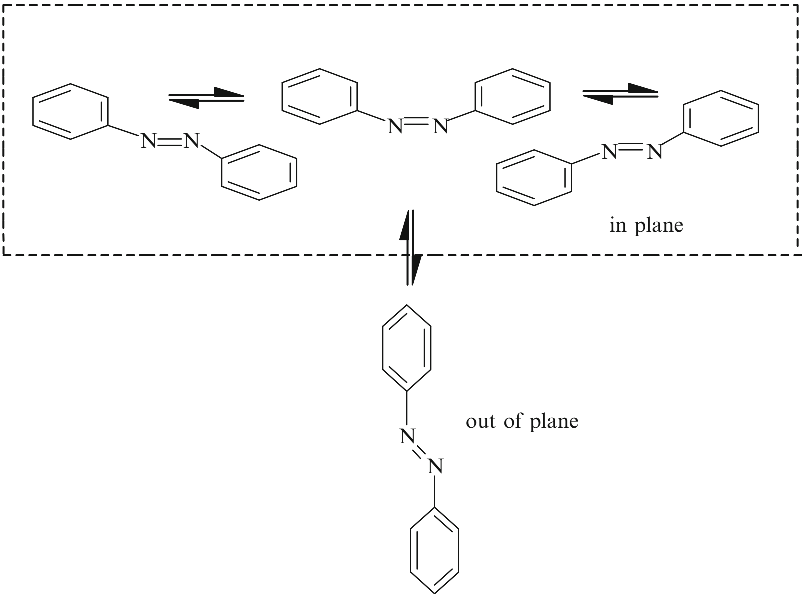


where $n = 2$ or 6.

It was concluded [226], therefore, that the liquid crystals align both parallel and perpendicular to the incident E direction on the photocross-linked polymer film by changing the degree of the reacted cinnamoyl group. That can be controlled by irradiation time. A bias-tilt angle between the liquid crystals director and the substrate is also realized by controlling the irradiation angle of the light [226].

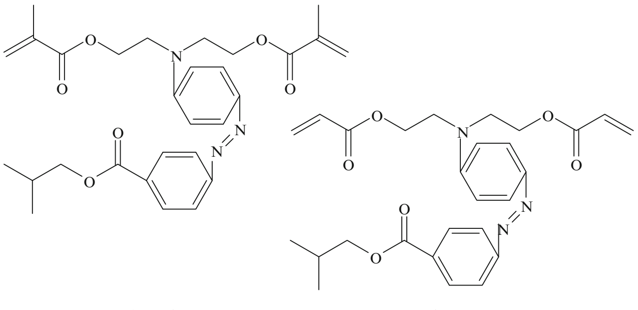
Another approach to liquid crystalline alignment is based on photo-isomerization of *azo* compounds in polymeric materials or as part of the polymer structure [227]. In recent years, investigation of the use of azobenzene-containing polymers for liquid crystalline alignment became quite thorough because of the potential application in holographic storage as well as optical and photonic use [228–230]. The photo-alignment of liquid crystalline polymers containing azobenzene groups has an advantage of local variation of the orientation order due to pixel-wise irradiation. This is a process that is reported to take place via angular-dependent excitation, a series of *cis-trans* photo-isomerization cycles, and rotational diffusion within the steady state of the photoreaction. This results in the photochromic side group becoming oriented perpendicularly to the electric field vector of the incident light and establishing an oblate order in the films.

Thus, studies of exposure of films of liquid crystalline polymers with azobenzene side chains to linearly polarized light of 436 nm [231] show successive occurrences of uniaxial in-plane orientations, followed by out-of-plane orientations of azobenzenes [231]. Two kinds of orientation modes were observed. These are possibly extreme cases, when linearly polarized light with the electric vector parallel to the xz-plane comes along the z-direction. One is the uniaxial in-plane orientation of the azobenzene with a dipole moment parallel to the x axis from the x- to y-direction and the other is out-of-plane (homeotropic) one toward the z-direction. Marked dependence of photo-orientation processes on film temperatures was observed. In-plane orientation was generated in the glassy state. Photo-orientation at higher temperatures, slightly below the transition temperature between smectic and nematic phases, gives rise to distinct transformations from in-plane orientation at the early state to successive out-of-plane reorientations [232]. These orientations can be illustrated as follows:

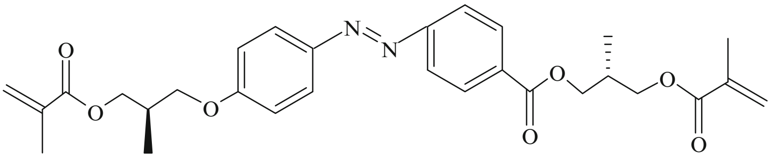


Also, it was reported [233], that irradiation of a liquid crystalline polyester with azobenzene side chains with light of an argon laser (514, 488, or 351 nm) results in orientation of 4-cyano-4′-alkoxyazobenzene side groups. The polyester is characterized by smectic and nematic phases and shows a strong tendency to form J-aggregates. The orientation process is cooperative, whereas the light-induced orientation of the photochromic moiety causes an ordering of the alkylene spacers and even of the main-chain segments into the same direction. It was concluded [226] that the most probable mechanism of this two-step process is the angular-selective transformation of the bulky *trans*-isomers to the rod-like *cis*-isomeric formed by the red light. The aligned *cis*-azobenzene side groups become strongly J-aggregated. Very high values of dichroism of about 0.8 and birefringence of about 0.3 were generated as a result of this combination of the photo-induced orientation process and the thermotropic self-organization, which takes place simultaneously under the irradiation conditions. The process results in a uniaxial prolate order of the film, whereas conventional photo-orientation leads to a biaxial oblate order [93]. Thus, the direction of photo-induced orientation and the type of the three-dimensional orientation order can be controlled by the wavelength of the irradiating linearly polarized light. This can also be done in the same film of a smetic polyester with 4-cyano-4′-alkoxyazobenzene side group [233].

Zhao and coworkers [234, 235] reported that an azobenzene polymer network can also optically align ferroelectric liquid crystals. This was done by dissolving two chiral dimethacrylate and one chiral diacrylate monomers containing azobenzene groups in a commercial ferroelectric liquid crystal host. The monomers were illustrated as follows:

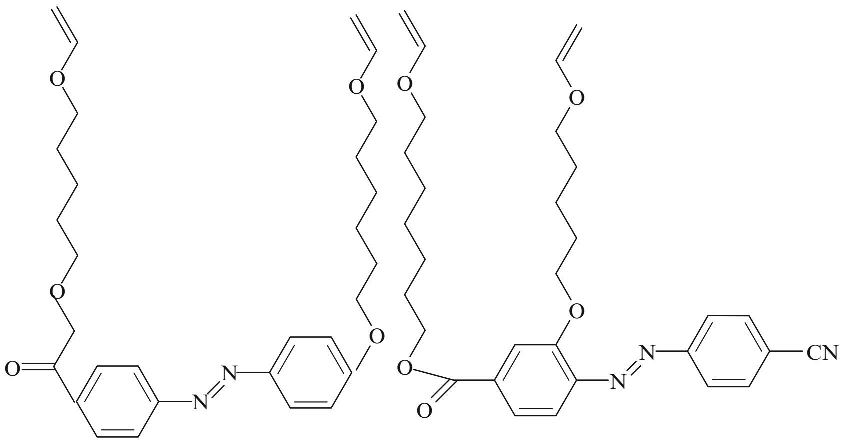


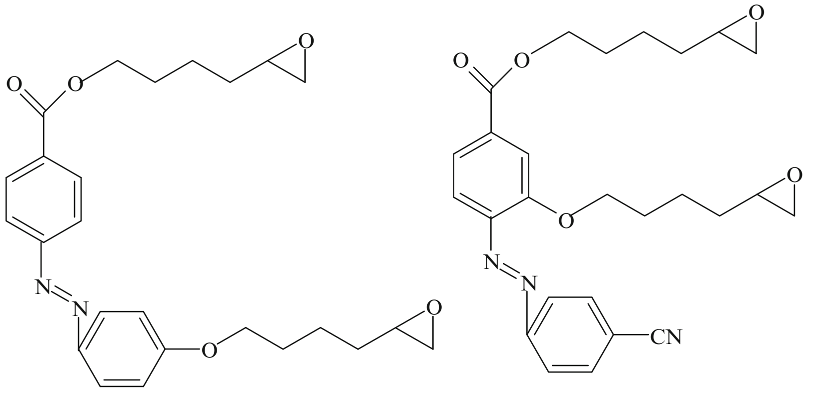
methacrylate acrylate



The monomers were then thermally polymerized and simultaneously irradiated with linearly polarized light. Two of the monomers were able to induce bulk alignment of the liquid crystals in direction perpendicular to the polarized light. Monomer #1 was effective in concentrations as low as 1%. It was also concluded from the experimental evidence that the photo-induced bulk alignment of the ferroelectric liquid crystals may take place by a mechanism that is different from one that takes place in achiral azopolymers.

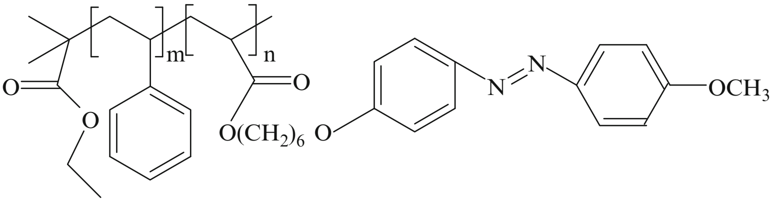
In addition, Zhao and coworkers [236] reported photo-induced alignment of ferroelectric liquid crystals using azobenzene polymer networks of polyethers and polyepoxides. Bulk alignment was achieved by polymerizing several divinyl ethers and diepoxide monomers bearing an azobenzene moiety. Here too, thermal polymerizations were conducted in solution within the ferroelectric liquid crystals, while exposing the reaction mixture to linearly polarized irradiation. The monomers can be shown as follows:





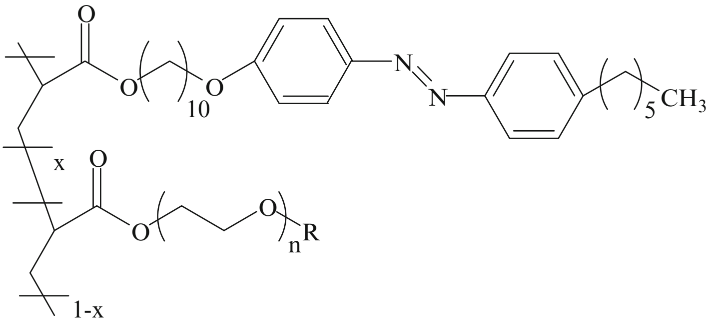
Polymerization of these monomers was achieved by cationic mechanism. The monomers were also found capable of inducing and stabilizing bulk alignment of the liquid crystals. Zhao and coworkers [234–237] concluded, however, that the mechanism of action might be different from the one obtained with chiral azobenzene polymethacrylates. Instead, the results suggest to them that the mechanism might be based on formation of an anisotropic azobenzene polyether or polyepoxide network.

In still another subsequent work, Zhao and coworkers [237] used block copolymers composed of polystyrene and liquid crystalline azobenzene-containing polymethacrylate copolymers as a model system



to investigate the confinement effects on the photo-alignment, photochemical phase transition, and thermochromic behavior of the azobenzene polymer. The study showed [237] that when confined in the microphase-separated domains in the diblock copolymers, the azobenzene polymer behaves differently than it does as a homopolymer free from confinement. The confinement effects are manifested by (1) decreased photo-induced and thermally enhanced orientation of azobenzene mesogenic groups in different aggregation states, (2) slower transformation from a liquid crystalline phase to the isotropic state triggered by the *trans–cis* photo-isomerization and slower recovery of the liquid crystalline phase after the thermally induced *cis-trans* back isomerization, and (3) severely reduced and even suppressed changes in the aggregation states of azobenzene groups on heating, which is at the origin of the thermochromic property. The common cause of these confinement effects is the restriction imposed by the confining geometry on either an order-disorder or a disorder-order reorganization process involving the motion and rearrangement of azobenzene groups [237].

Zettsu and Seki reported [238] preparation of a group of azobenzene-containing polymers that can be used in photo-induced surface relief formations. These are soft liquid crystalline azobenzene-containing copolymers of acrylate with methacrylate monomers bearing oligo(ethylene oxide) chains. The copolymers display a smectic liquid crystal phase at room temperature. After preexposure to ultraviolet light, thin films of the liquid crystalline polymers show highly sensitive photo-induced material transfer to generate the surface relief structures. The typical exposure dose required for full polymer migration is as low as 50 mJ/cm^2.



The inscribed surface relief structures can be rapidly and fully erased either by irradiation with incoherent nonpolarized ultraviolet light or by heating close to the clear point of the soft liquid crystalline polymers. It is also possible to chemically cross-link the polymers with mixed vapors of hydrogen chloride and formaldehyde after surface relief inscription. This results in a drastic improvement of the shape stability, maintaining the structure at high temperatures up to 250°C. After cross-linking, the *trans*-to-*cis* photo-isomerization readily proceeds without any modification of the surface morphology and can, therefore, be applied to the photo-switchable alignment of nematic liquid crystals [238].

10.7 Photo-Conducting Polymers

Unless polymers contain long sequences of double bonds, they are fairly good insulators, particularly in the dark. Nevertheless, a number of common polymers show measurable increase in conductivity, when irradiated with light. When polymeric materials, like poly(vinyl fluoride), poly(vinyl acetate), poly(vinyl alcohol), or poly(*N*-vinyl carbazole), are exposed to light, they develop charged species. The species can migrate under an electric field and thus conduct electricity. When poly(*N*-vinyl carbazole) is doped with photosensitizers or compounds that form charge-transfer complexes, the photosensitivity can be increased and even extended into the visible region of the spectrum. Since discovery in 1957 that poly(*N*-vinyl carbazole) has photoconductive properties, there has been increasing interest in the synthesis and study of this and other polymeric materials with similar properties that allow various photonic applications. Related polymers are presently utilized in photocopiers, laser printers, and electro-photographic printing plates.

Photoconductive polymers can be p-type (hole-transporting), n-type (electron-transporting), or bipolar (capable of transporting both holes and electrons). To date, most photoconductive charge-transporting polymers used commercially are p-type.

Poly(vinyl carbazole) and other vinyl derivatives of polynuclear aromatic polymers, such as poly (2-vinyl carbazole) or poly(vinyl pyrene), have high photoconductive efficiencies. These materials may take up a helical conformation with successive aromatic side chains arranged parallel to each other in a stack. In such an arrangement, the transfer of electrons is facilitated. Also, it is believed that the primary mechanism for poly(vinylcarbazole) charge carrier generation is due to excitation of the carbazole rings to the first excited singlet state. This polymer absorbs ultraviolet light in the 360-nm region and forms an exciton that ionizes in the electric field. The excited state by itself is not a conductive species. The addition of an equivalent amount of an electron acceptor, like 2,4,7-trinitrofluorenone, shifts the absorption of this polymer into the visible region by virtue of formation of charge transfer states. The material becomes conductive at 550 nm. This associated electron-positive hole pair can migrate through the solid polymeric material. Upon dissociation of this pair into charged species, an electron and a positively charged hole, the electron becomes a conductive state. To achieve this, additional energy is required and can be a result of singlet–singlet interaction [239], singlet–triplet interaction [240], singlet–photon interaction [239], triplet–photon interaction [239], and two–photon interaction [240]. Kepler carried out fluorescence quenching studies and concluded that the migration of the exciton is the most probable energy transfer mechanism of poly(vinyl carbazole) [241]. He, furthermore, suggested that the exiton can visit 1,000 monomer units during its lifetime [241]. This is a distance of about 200 Å.

Kang and coworkers [242] also explored steady state and pulsed photo-conductivities in 4–8 μm thick films of *trans*-polyphenylacetylene and also *trans*-polyphenylacetylene films doped with inorganic and organic electron acceptors, particularly iodine and 2,3-dichloro-5,6-dicyano-*p*-modulated by shallow electron traps in the undoped polymer and by trapping the charge-transfer complex in the doped polymer [242]. Guellet [94] states that photo-conductivity σ is equal to the current density J divided by the applied field strength ε, where J is aperture/unit electrode area. This is related to the number of negative-charge carriers (usually electrons) per unit volume, and p is the number or positive charge carriers (or positive holes) per unit [94]

$$\sigma = J/\varepsilon = ne\mu_{\mathrm{n}} + pe\mu_{\mathrm{p}}$$

where e is the charge on the electron, and μ_n and μ_p are the mobilities of the negative and positive carriers, respectively. Photo-conductivity and mobility of the charge carrying species can be determined from a relationship [94]:

$$\mu = d^2/Vt$$

where d is the thickness of the film, V is the applied voltage, and t is the carrier drift time. The photo-effect is evaluated in terms of the effective gain, G. It represents the number of generated carriers reaching the external circuit per unit time, compared with the number of photons absorbed at the same time [94]:

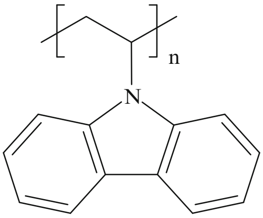
$$G = J_p/eI_0(1 - T)A$$

where J_p is the photocurrent, e is the electric charge, I_0 is the number of incident photons per cm^2/s, T is the optical transmittance of the film, and A is the area of the sample that is being illuminated.

10.7.1 Photoconductive Polymers Based on Carbazole

As stated above, the primary mechanism for charge-carrier generation in poly(vinyl carbazole) appears to be due to the excitation of the carbazole rings to their excited singlet states [112]. While the singlet excited state is not a conductive species, the conductivity is believed to be the result of an associated electron-positive hole pair migrating through the solid polymeric material. Dissociation of the electron pair produces a separate electron and a positive hole in such a way that the electron ends up in the conducting state [94]. This requires acquisition of more energy. One way that can be accomplished is by exciton–surface interaction [243]. Regensburger published an absorption spectrum, fluorescence spectrum, and photocurrent spectrum for a 7.6 µm films of poly(*N*-vinyl carbazole) [244]. The shape of the response of the photoconductor to the wavelength of the light flash is very close to the shape of the absorption spectra. Bauser and Klopffer explain this as a result of interaction of singlet excitons with trapped holes [245].

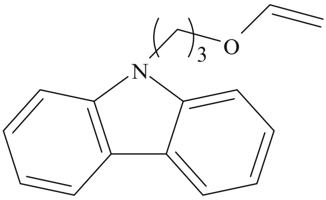
Lyoo used a low-temperature initiator, 2,2′-azobis(2,4-dimethyl-valeronitrile), to polymerize *N*-vinyl carbazole in a heterogeneous solution in a mixture of methyl and *t*-butyl alcohols [247]. The polymer that formed has the M_n molecular weights $>3 \times 10^6$. The author emphasized that this method provides ultrahigh-molecular-weight polymer and conversions greater than 80%.



The optical transparency of poly(vinyl carbazole) films produced by this room temperature process appears to be quite high, although transparency decreases at high conversions. In film form, this material is useful for photoconductors, charge-transfer complexes, and electroluminescent devices. The higher polymer molecular weight typically enhances film mechanical properties [247].

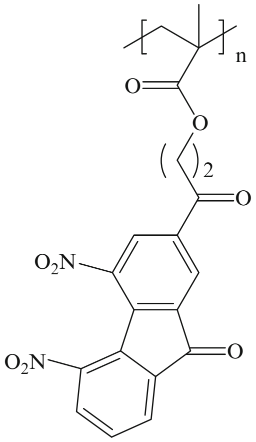
Horhold and Rathe [248] reported that they have prepared poly(9-methylcarbazole-3,6-diyl-1,2dipenylvinylene). The polymer ($M_n = 10{,}000$) was formed by dehalogenating polycondensation of 3,6-bis(α,α-dichlorobenzyl)-10,9-methylcarbazole with chromiun(II) acetate. This polymer was found to be also highly photoconductive. Its dark conductivity increases by doping it with arsenic pentafluoride [248].

Photoconductive polymers and copolymers were also synthesized by Haque et al. [249] from 2-(9-carbazolyl)-1-propenyl vinyl ether:



The polymers and copolymers form by a cationic polymerization mechanism, using boron trifluoride or ethylalumionum dichloride as the catalysts [249].

Charge transfer complexes also form from poly(vinyl carbazole) that acts as the donor, with poly [2-(methacroyloxy)ethyl-4,5,7-trinitro-9-oxo-2-fluorene-carboxylate] that acts as the acceptor [250]:

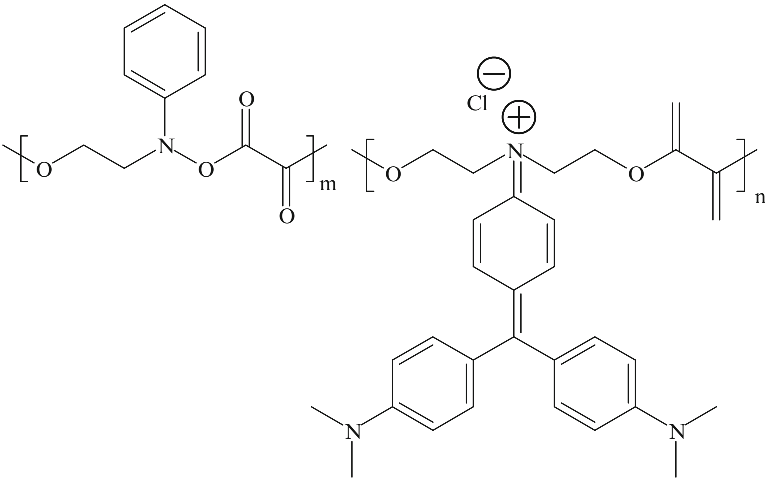


The required mole ratio of components in the complex is 1:1 [250].

Charge transfer complexation occurs in a similar manner in poly(2-carbazolylethyl acrylate) molecularly doped with 2,4,7-trinitrofluorene. Quantum efficiency of the hole propagation of the copolymer with the 0.05–1.0 molar ratio of trinitrofluorene to carbazole chromophores is higher than in the corresponding trinitrofluorene and ethyltrinitrofluorene doped homopolymer of poly(2-carbazolylethyl acrylate) [251].

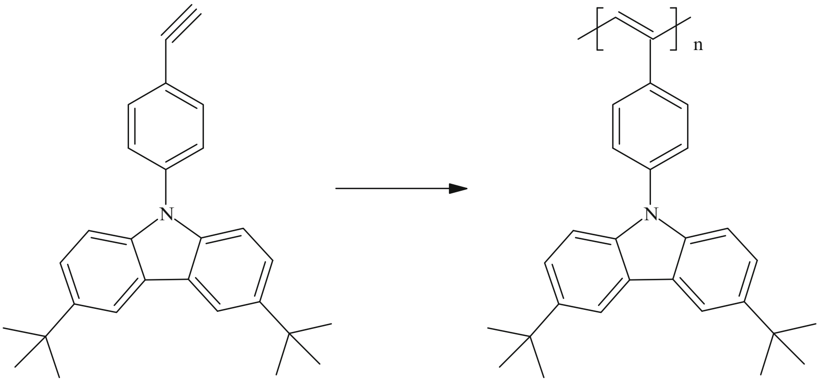
Kim and Webber studied delayed emission spectra of poly(vinyl carbazole) that was doped with dimethylterephthalate and pyrene [252]. On the basis of their results, they concluded that at room temperature dimethylterephthalate does not completely quench the triplet excitation state of poly (vinyl carbazole). They also concluded that phosphorescent states of poly(vinyl carbazole)-dimethylterephthalate are similar, implying a significant charge-transfer character in the former.

In 1985, polymeric triphenylmethane dyes based on condensation polymers such as polyesters and polyurethanes were prepared [252]:



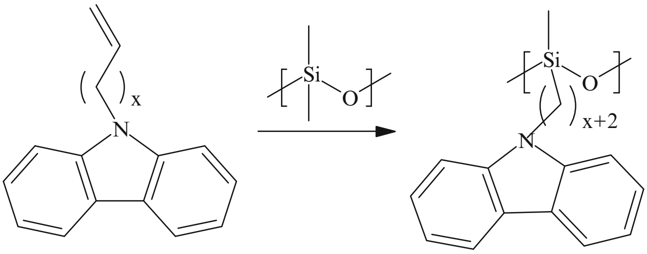
These dyes were then shown to sensitize photo-conductivity of poly(*N*-vinyl carbazole).

Polyacetylene derivatives exhibit unique characteristics such as semiconductivity, high gas permeability, helix inversion, and nonlinear optical properties [253]. Attempts were made, therefore, to incorporate carbazole into polyacetylene in hope of attaining enhance properties [253].

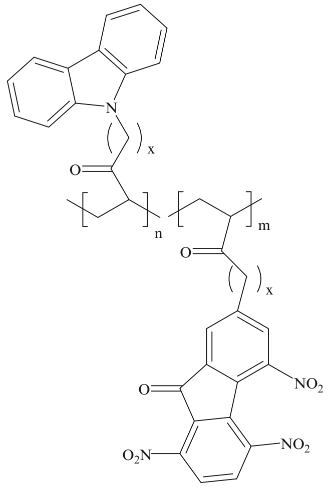


It was found [122] that the current conducted by this polymer during irradiation is 40–50 times higher than it is in the dark. On the other hand, the electron mobility of the di-*t*-butylcarbazolepolyacetylene (shown above) is lower than in poly(vinyl carbazole). This was attributed to the bulkiness of the butyl groups [254].

Siloxanes with pendant carbazole groups were synthesized by Strohriegl [254] by the following technique:

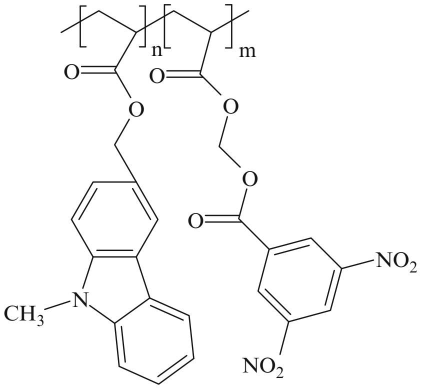


The material, however, did not turn out to be photoconductive. The photo-conductivity of copolymers was also investigated. Copolyacrylates with pendant donor and acceptor chromophores, such as 2-*N*-4,5,7-trinitrofluorenone-2-ethyl acrylate, do exhibit photo-generation properties [254]. These copolymers



can be prepared by free-radical copolymerization of the appropriate monomers. Photo-conductivity in the visible is obtained by charge transfer complexation.

Similar work was done earlier by Natansohn [255], who copolymerized *N*-methyl, 1,3-hydroxymethyl carbazolyl acrylate with acryloyl-3′-hyroxypropyl-3,5-dinitrobenzoate:

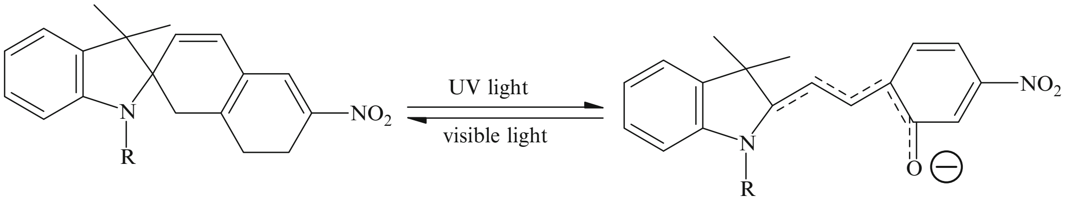


Illumination of the copolymer samples induces a certain degree of ionization accompanied by proton transfer. There is a permanent increase in the quantity of radicals generated by light. Another number of radicals apparently forms during illumination, but disappears in the dark [254].

It was reported [256] that a polymer formed by condensation of *N*-(3-isopentyl)-3,6-diformylcarbazole and 4-14-bis[(-aminoethyl)aminophenyl-*azo*]nitrobenzene yields a new polyazomethine, carbazole-*azo* polymer. The product is soluble in organic solvents. The polymer possesses carbazole moieties and *azo* type nonlinear optical chromophores in the backbone. It shows high photo-conductivity and nonlinear optical properties.

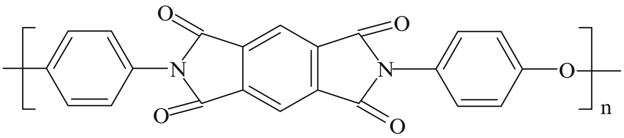
10.7.2 Photo-Conducting Polymers That Are Not Based on Carbazole

When spiropyran is incorporated into plasticized poly(vinyl chloride) membranes and placed between two identical NaCl solutions and irradiated with ultraviolet light for long periods, the potential decreases [257]. This was shown by Ryba and Petranek to be a result of the spiran ring opening up [257]:



When the irradiation is interrupted and the membrane is irradiated with visible light, the potential returns to its original value, because the ring closes back to the spiran structure [125].

The addition of electron donors, like dialkyl aniline, to Kapton polyimide film

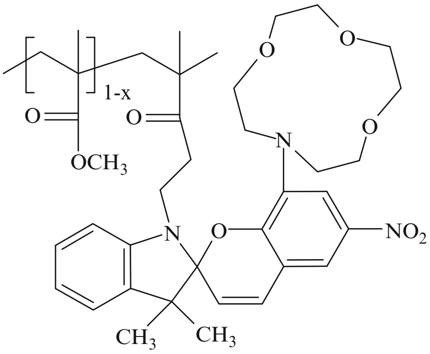


results in an enhancement of photocurrent by as much as five orders of magnitude, compared with the virgin material [258]. Freulich explains the mechanism of enhancement as a result of radiation absorption by the charge-transfer complex formed between the added electron donor and the imide portion of the polymer backbone. Excitations are followed by rapid and complete electron transfer from the donor to pyromelitimide to yield the radical anion of the polymer and the radical cation of the donor [258]. These species undergo rapid back-electron transfer. In other words, the dialkyl aniline donates one of the unpaired electrons in a typical photo-reduction reaction to the carbonyl group. The reaction is reversible and the photo-conduction is by a mechanism of the ion radical returning to the ground state.

Studies of the thermochromic, solvatochromic, and photoconductive properties of 3-, 4-, 6-, and 9-poly[(butoxycarbonylinethyl urethane)-diacetylenes] result from changes from rod (red or blue) to coil (yellow) conformations of the polymer backbone [259]. Photo-excitations of the solutions of these polymers in the rod state result in a large transient photo-conductivity, while only very small conductivity signals are observed in the coil state. The thermochromic shift that occurs in going from the rod state at room temperature to the coil state at 65°C is accompanied by a decrease in the photo-conductivity. The large conductivity signal in the rod state is attributed to the formation of mobile charge carriers possibly via interchain charge transfer within aggregates. The decay of the photo-conductivity is nonexponential and extends to microseconds.

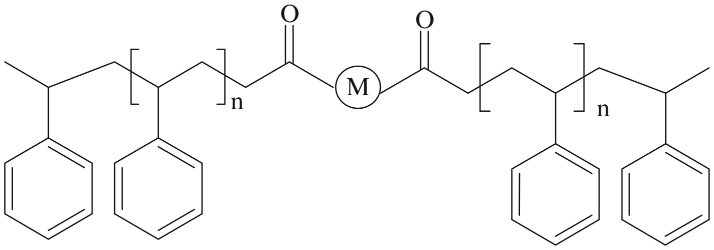
Wong et al. [260] reported that they prepared a soluble rigid-rod organometallic polymer containing electron-donating and electron-withdrawing *trans*-[-Pt-(tibutylphosphine)$_2$-acetylene-R-acetylene-]$_n$ (where R = bithiazol-ediyl) groups. The polymer was formed by cuprous iodide-catalyzed dehydrohalogenation reaction. The electron-donating and electron-withdrawing properties of the thiazole ring confer solubility to the polymer. This polyacetylene is luminescent with a singlet emission peak at 539 nm and photo-conducting. The glass transition temperature of the polymer is 215° and it shows relatively good thermal stability. The π-conjugation of the ligands extends into and through the metal core and the absorption peaks show a significant red-shift of 17–26 nm compared to the bithienyl counterparts due to the presence of the electron-withdrawing imine nitrogen atoms [260].

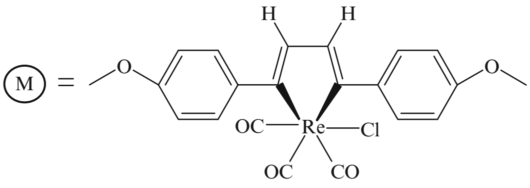
Kimura et al. [259] reported applying organic photochromic compounds to photochemical switching of metal-ion complexation and ionic conduction by combining photochromism with metal-ion binding property of crown ether derivatives. They synthesized vinyl polymers, incorporating a crowned spirobenzopyran moiety at the side chain:

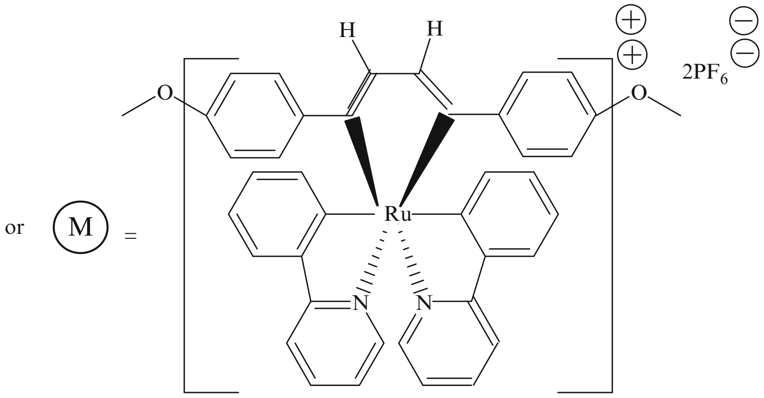


The crowned spiropyran in the electrically neutral form can bind an alkali metal ion with the crown ether moiety. At the same time, the spirobenzopyran portion isomerizes to the corresponding merocyanine form photo-chemically. The zwitterionic merocyanine form of crowned spirobenzopyran moiety brings about a significant change in the metal-ion binding ability. This prompted the authors to apply the compound to photo-responsive ion-conductive materials. They observed that the ion-conductivity was increased by ultraviolet light and decreased by visible light [259].

Chan and coworkers [269] prepared polystyrenes and poly(methyl methacrylate)s that contain metal complex cores:







When the polymers are doped with a hole-transporting triphenylamine, an enhancement in photoconductivity in the visible region is observed. This suggests that the metal complexes serve as photosensitizers instead of charge carriers [260]. Chan et al. [260] observed an electric field-dependent charge separation process in these polymers. It is described well by the Onsager's theory of charge germinate recombination. This theory assumes that some fraction of absorbed photons produce bound thermalized electron-hole pairs that either recombine or dissociate under the combined effects of the Coulombic attraction and the electric field. The photo-generation efficiency is given as the product of the quantum yield of thermalized pair formation and the pair dissociation probability:

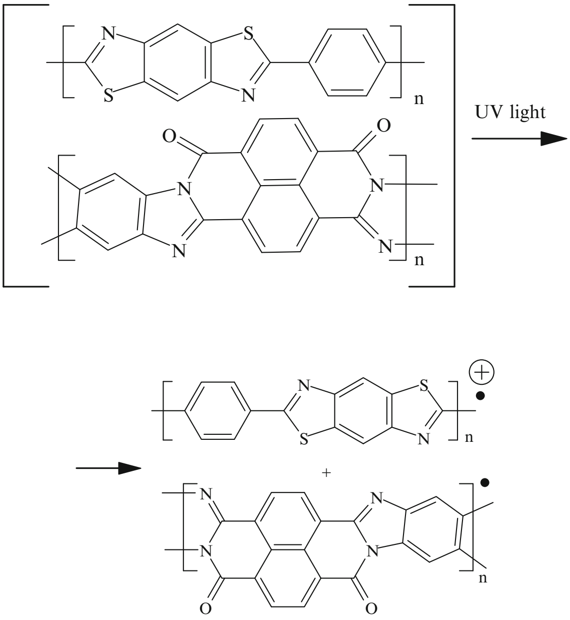
$$\Phi(r_0, E) = \Phi_0\left[1 - \left(\frac{eEr_0}{kT}\right)^{-1}\sum_{g=0}^{\infty} I_g\left(\frac{e^2}{4\pi\varepsilon_0\varepsilon_r kTr_0}\right) I_g\left(\frac{eEr_0}{kT}\right)\right]$$

where I_g is a recursive formula given by

$$I_{g+1}(x) = I_g(x) - x^{g+1}\exp(-x)/(g+1)$$

where $I_0(x) = 1 - \exp(-x)$, Φ is the primary yield of thermalized bound pairs, r_0 is the initial thermalization separation between the bound charges, ε_r is the relative permeability, and E is the applied electric field strength.

Jenekhe and de Paor [261] reported exciplex formation and photoelectron transfer between several **n-*type*** (***electron accepting***) π-conjugated rigid-rod polymers and donor triarylamine molecules. In particular, they reported an investigation of an **n-*type*** conjugated polymer poly(benzimido azobenzophenanthroline ladder) [132]. No evidence was observed by them of a ground state charge transfer or any strong interactions between the conjugated polymer pairs. Transient absorption spectra of a blend of thin films in the 420–730 nm region were obtained at various time delays following photoexcitation at 532 nm. Dramatically enhanced photo-induced bleaching in the 430–480 nm region was observed. Jenekhe and de Paor propose that they observed enhanced photo-bleaching in the blends and that it is a consequence of photo-induced electron transfer [261]. The electron transfer was illustrated as follows:

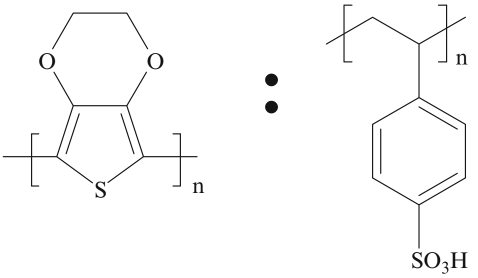


Molecular materials, such as 2-(2-hydroxyphenyl)benzoxazole and 2-(2-hydroxyphenyl)-benzothiazole, which contain intramolecular hydrogen bonds are known to undergo excited state (charge transfer) intramolecular proton transfer upon photo-excitation.

10.8 Polymer-Based Solar Cells

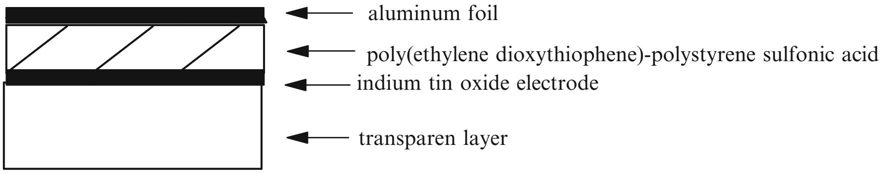
Polymer-based solar cells, also known as organic photovoltaic cells, have been around since the 1990s. But their performance, and their efficiency by end of 2010, to convert light to electricity, after much research, has reached only approximately 8%. This is not good enough to compete with inorganic solar cells, like those based on cadmium teluride, that convert 10–15% of light to electricity. This single digit value of organic solar cells pales even further when compared with some highly specialized, high-priced state-of-the-art inorganic devices with conversion efficiencies topping 40%. The promise of low-cost organic solar cells, however, has encouraged intense research in many laboratories in efforts to improve the efficiency. Such research usually focuses on solution-processable organic polymers that can be converted to semiconductors [262]. The polymers used are regarded as intrinsic wide band gap semiconductors, where the band gaps are above 1.4 eV. This can be compared to insulators, where the band gaps are below 3 eV. Doping of the film forming materials is done to introduce extrinsic charge carriers and convert them into organic semiconductors. Such charge carriers, as explained in Sect. 10.2, can be positive, p-type, or negative, n-type.

Originally, a donor-acceptor bilayer device of two films was used as an n–p junction in solar cells. Thus, they were fabricated as sandwich structures. An example would be one where a transparent substrate is first coated with a conductor, like indium-tin oxide. A conducting polymer like, poly (ethylene dioxythiphene), doped with polystyrene-sulfonic acid, would then be applied from and aqueous solution. The indium-tin oxide acts as an electrode for hole injection or extraction. The polymer is then covered with a conductor, an aluminum foil. The doped polymer can be illustrated as follows:



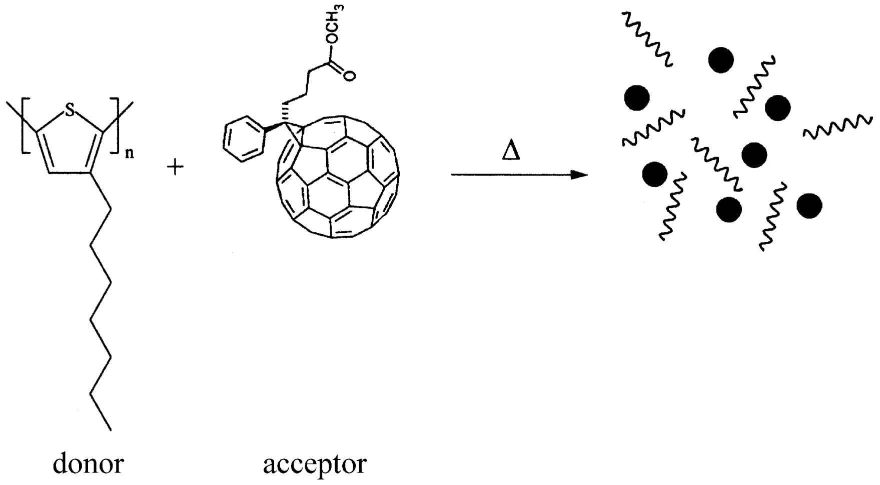
semi conducting polymer doping material

The construction of the above-described solar cell can be illustrated as follows:



The donor material, containing a chromophore, absorbs the light energy and generates excitons. Excitons are high-energy couples where the energetic electrons are bound to positively charged electron vacancies or holes. To produce electric current, the electron-hole pairs must migrate to the interface between the electron donor and electron acceptor materials. Upon reaching the interface, the electron-hole pairs splits into separate mobile charges. The charges then diffuse to their respective electrodes. The electrons are transported by the electron-accepting material to the cathode and the holes by the hole-accepting material (electron donor) to the anode. To put it in other words, the Coulomb-correlated electron-hole pair, the excitons, diffuse to the donor-acceptor interface where exciton dissociation occurs via an electron-transfer process to the n-type layer. With the aid of an internal electric field, the n-type layer then carriers the electrons in the opposite direction. The electric field in turn generates the photocurrent and the photo voltage. Such devices are known as **planar heterojunction** cells. Such an arrangement, however, is not very efficient, because the excitons can decay back to the ground level before they diffuse into to the n-type layer. To overcome the difficulty, the concept of a **bulk heterojunction** was introduced [263]. By blending donor and acceptor materials together an interpenetrating bicontinuous network of junctions, large donor-acceptor interfacial areas can be achieved. This results in an enhanced quantum efficiency of charge separation and in efficient charge collection. Gaudiana [264] likened the morphology of a bulk heterojunction active layer to a sponge. The solid part represents the nano-sized interconnected bits of acceptors. The polymer is represented by the holes that are intimately connected to other holes throughout the sponge and never far from a solid region. Blending the phases on that scale, in effect, distributes small regions of interface throughout the photoactive layer. As a result, excitons need only to diffuse only a short distance before quickly reaching a donor–acceptor interface where they can dissociate into separate charges.

An advancement in efficiency of polymeric solar cells, from 3 to 5%, came in 2009 when it was observed that promising efficient charge transfer materials can be prepared from combinations of poly (alkyl-thiophenes) donors with 1-(3-methoxycarbonyl)propyl-1phenyl-[6,6]-methanofullere acceptors [265]. Mild heating disperses the acceptor molecules among the donor molecules:



This led to exploration of many other combinations of various other polymers with different derivatives of fullerine and with various chromophores. In an attempt to lower highest occupied molecular orbitals (HMO) of the polymer with stronger electron-withdrawing groups, new polymers were developed. The results were summarized in a review [265].

As a result of the research, several research groups reported attaining 5% efficiencies with the combinations of poly(3-hexyl thiophene) with 1-(3-methoxycarbonyl)propyl-1phenyl-[6,6]-methanofullere. Numerous other conducting polymers including copolymers containing fluorene, carbazole, cyclopentadithiophene were investigated.

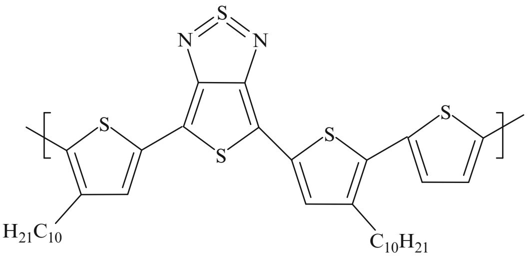
The efficiency of organic solar cells is usually defined as:

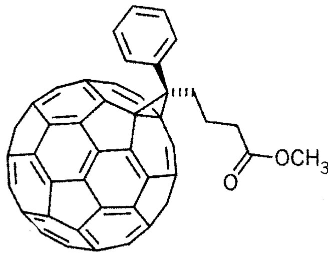
$$\eta = (J_{\mathrm{sc}} V_{\mathrm{oc}} \mathrm{FF}) / P_{\mathrm{in}}$$

where P_{in} is the input energy of solar radiation. The output short circuit current density is J_{sc} and V_{oc} is the open circuit voltage. FF is the fill factor. Much of the research effort to date has been based on attempts to increase V_{oc}. This is based on empirical correlation between the magnitude of the open circuit voltage and the difference in energies between HMO of the donor and LUMO of the acceptor. It is expected that by lowering the HMO of the donor, V_{oc} can be increased [266].

To achieve this goal, two research teams headed by Yu and by Yang tested a series of copolymers prepared by reacting a benzodithiophene derivative with various thienothiophenes. The aim was to lower the polymers' HMO by attaching successively stronger electron-withdrawing groups to the polymer backbone. The result was that by replacing an alkoxy group that was adjacent to a carbonyl group with an alkyl chain at the same position, the group lowered the HOMO level by roughly 0.1 eV. They lowered the level by another 0.1 eV by adding a fluorine atom. Solar cells prepared with this polymer were found to be 6.8% efficient [267]. Subsequently, Yu et al. reported slightly improved conversion efficiency of over 7% [268].

It is interesting that at the time of the publication of the review, it was reported in *Chem. and Eng News* [269] that Heeger and Gong developed a broad spectrum donor acceptor combination that can detect photons throughout the whole light spectrum, from the ultra-violet to the infra-red. The combination of the two materials can be illustrated as follows:



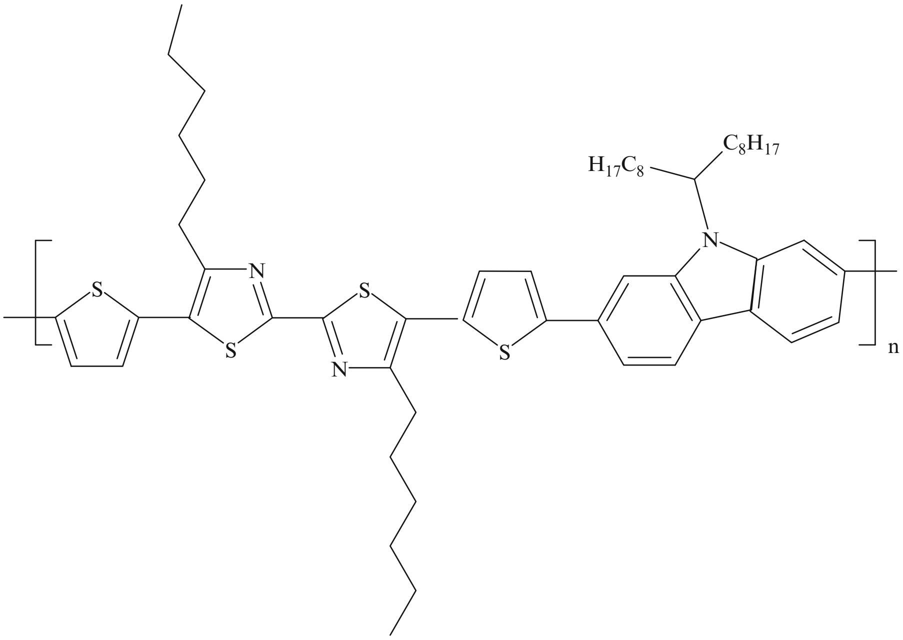


According to a subsequent write up in *Chem. and Eng. News* [270], a private laboratory called "Solamer" claimed, without disclosing details, to have achieved efficiency of 8.13%. They also stated that they hope to achieve efficiency of 10% by end of 2011.

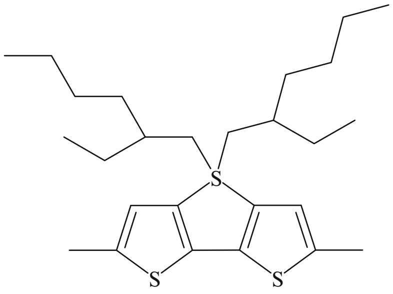
Syntheses of various polymers for solar cells were also reviewed by Cheng et al. [271] where they point out that there is a need to develop better p-type materials that have good film properties and act as very efficient chromophores, with good hole mobility and suitable molecular orbitals levels. They also point out that magnitude of the band gap and the energy positions of the HOMO and LUMO energy levels are the most important characteristics for determining the optical and electrical properties of a given conjugated polymer. These, of course, will in turn greatly influence the ultimate photovoltaic performance and conversion of light energy to electrical energy. The wavelength of the maximum photon flux density of the solar spectrum is located at approximately 700 nm, which corresponds to a low energy of 1.77 eV. The absorption spectrum of a conjugated polymer should cover both the red and near-infra-red ranges to match the greater part of the terrestrial solar spectrum and absorb the maximum photon flux. Thus, it is highly desirable to develop conjugated polymers with broader absorptions through narrowing their optical band gap. At the same time, these materials must efficiently absorb light. The overall high extinction coefficients of the polymers are also of critical importance.

Following are presented some of the published results from recent and current research, to illustrate the bulk of the effort in the field. The examples are chosen at random and there is no implication that these are the best ones published to date.

Li and coworkers [272] reported synthesis and photovoltaic properties of three donor-acceptor copolymers containing bithiazole acceptor. One of them was illustrated as follows:

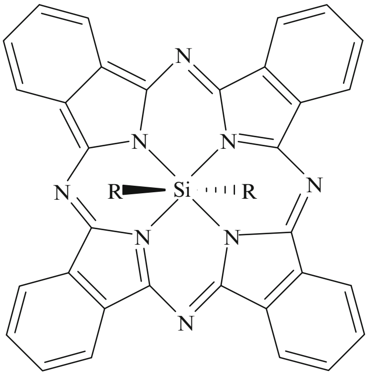


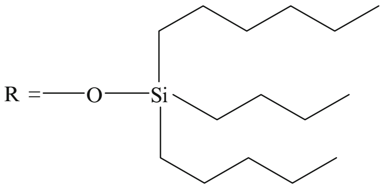
The other two copolymers were similar. The copolymer that yielded the best results had the carbazole replaced with the following molecule:



The results indicate that donor units of carbazole influence the band gaps, electronic energy levels, and photovoltaic levels. The hole mobility was measured at 3.07×10^{-4} cm^2/V s.

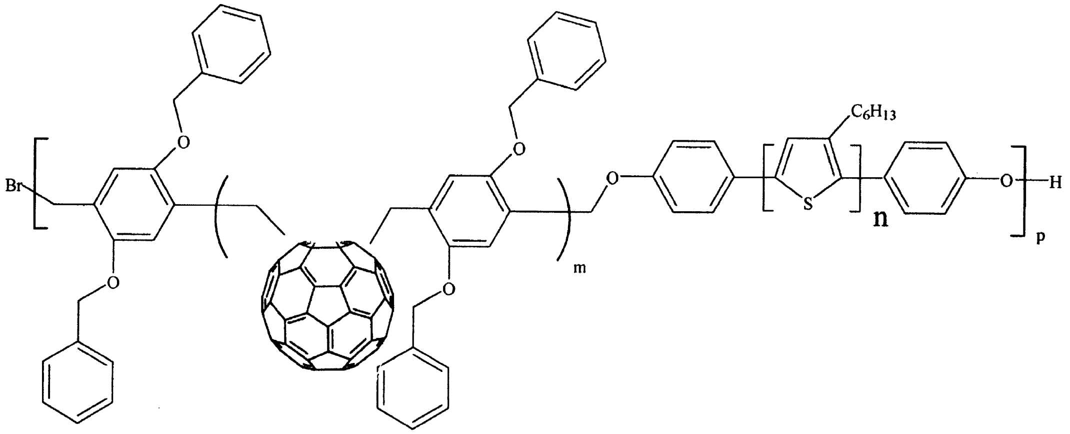
Honda et al. [273] reported injecting a photosensitizer dye into a bulk heterojunction solar cell, based on regioregular poly(3-hexylthiophene) and 1-(3-methoxycarbonyl)propyl-1phenyl-[6,6]-methanofullere. The dye photosensitizer was illustrated as follows:



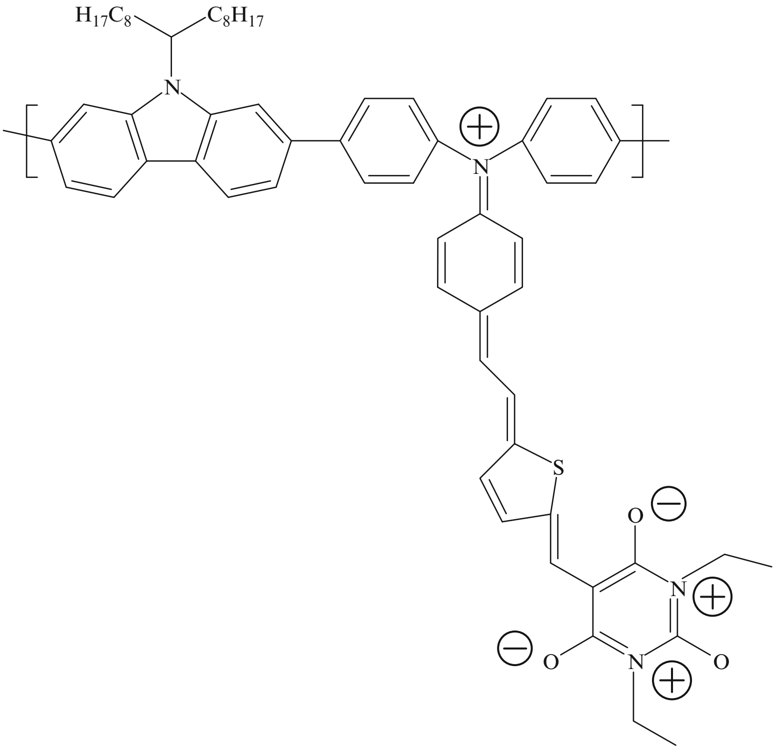


They reported that injection of the dye resulted in an increase in the photocurrent.

Hiorns et al. [274] reported preparation of a block copolymer that incorporated fullerene molecules into the backbone of the polymer. They observed a band gap of 2.3 and 2.2 eV for the block copolymer:

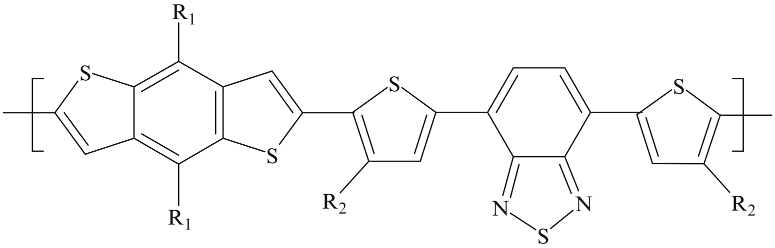


Li and coworkers [275] reported syntheses of four alternating copolymers of carbazole and triphenylamine with conjugated side chain acceptor groups:



The four copolymers that were synthesized contained different acceptor end groups, aldehyde, monocyano, dicyano, and 1,3-diethyl-2-thiobarbituric acid. Through changing the acceptor groups, the electronic properties and energy levels of the copolymers were effectively tuned. Their results indicate that it is an effective approach to tuning the bandgaps in conjugated polymers. The polymers were used as donors in polymer solar cells. They reported, however, conversion efficiency of only 2.76%.

You and coworkers [276] reported syntheses of two low-band gap polymers based on benzo(1,2-*b*:4,5-*b*)dithiophene:

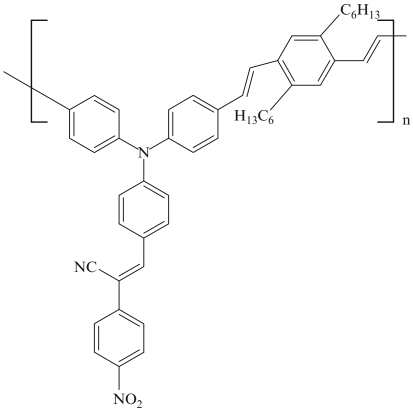


where R_1 = 3-butylnonyl and R_2 = nonyl and in the send polymer, R_1 = 3-hexylundecyl and R_2 = hydrogen.

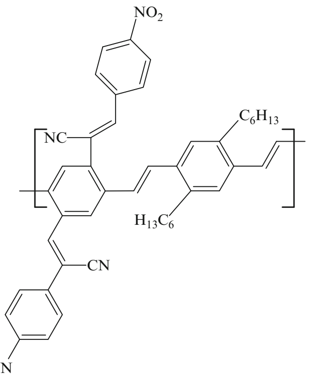
Both polymers were reported to have performed well in preliminary bulk heterojunction solar cells, reaching power conversion efficiency greater than 4%.

Jenekhe, Watson, and coworkers [277] reported synthesizing three new donor-acceptor conjugated polymers incorporating thieno[3,4-*c*]pyrrole-4,6-dione acceptor and dialkoxybithiophene or cyclopentadithiophene donor units. The thieno[3,4-*c*]pyrrole-4,6-dione acceptor containing materials were studied in bulk heterojunction solar cells and organic field-effect transistors. The polymers had optical band gaps of 1.50–1.70 eV. The highly electron-rich character of dialkoxybithiophene in these polymers, however, destabilizes their HMO and significantly affects the photovoltaic efficiency with power conversion efficiencies below 1.5%. On the other hand, cyclopentadithiophene copolymers achieved a better power conversation efficiency greater than 3%.

Sharma and coworkers [278] reported synthesis of two low-band gap copolymers. One consists of alternating dihexyloxyphenylene and α-[4-(diphenylamino)phenyl methylene]-4-nitrobenzene acetonitrile. The other one consists of alternating dihexyloxyphenylene and α,α′-[(1,4-phenylene) dimethylidyne]bis(-4-nitrobenzene acetonitrile):



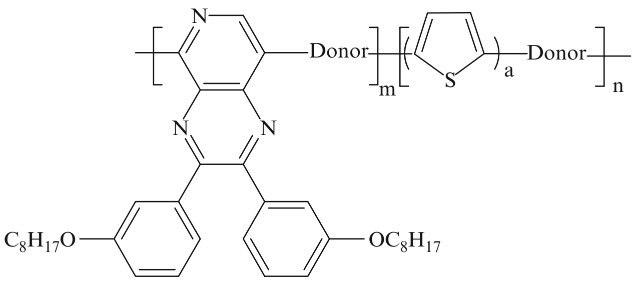
polymer 1

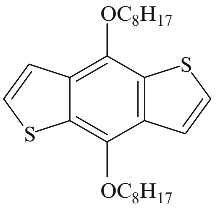


polymer 2

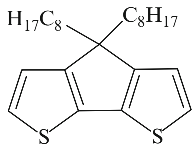
They reported that these copolymers showed broad absorption curves with long-wavelength absorption maximum around 620 nm and optical band of 1.68 and 1.64 eV for both polymers. Both polymers were studied for photovoltaic response in bulk heterojunction solar cells. They observed an overall power conversion efficiency of 3.15 and 2.60% for the cast polymers. Further improvement led up to 4.06 and 3.35% for the devices based on thermally annealed materials.

Wei and coworkers [279] used Stille polycondensation to prepare a series of low-band gap copolymers, by conjugating the electron-accepting pyrido[3,4-*b*]pyrazine moieties with electron rich benzo[1,2-*b*:3,4-*b*]di thiophene or cyclopentadithiophene units. All resulting polymers exhibited excellent thermal stability and sufficient energy offsets for efficient charge transfer and dissociation. The band gaps of the polymers could be tuned in the range 1.46–1.60 eV by using the two different donors, which have different electron-donating abilities. The three-component copolymers, incorporating the thiophene and bithiophene segments, respectively, absorbed broadly, covering the solar spectrum from 350 to 800 nm. The best device performance resulted in power conversion efficiency of 3.15%.The polymeric materials were illustrated as follows:



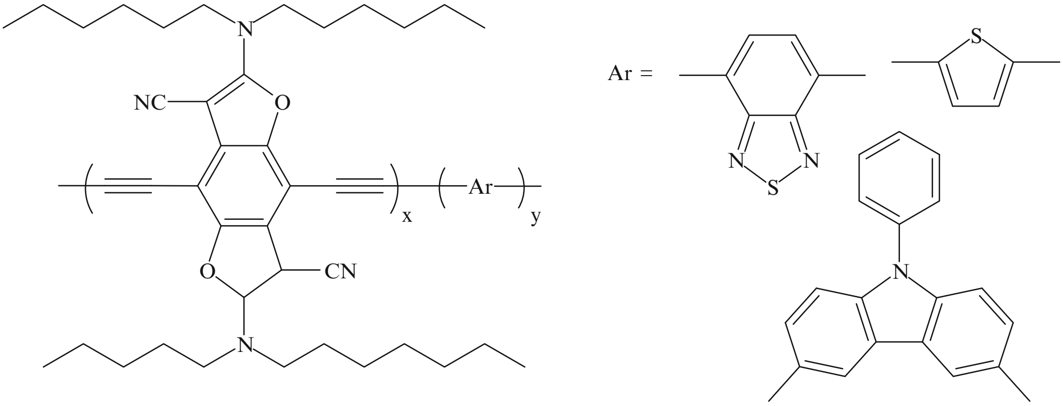


donor



donor

Liu et al. [280] synthesis and evaluation of n-conjugated copolymers were based on a soluble electro active benzo[1,2-*b*:4,5-*b*]difuran chromophore. The comonomer units consisted of thiophene/benzo [*c*][1,2,5] thiadiazole/9-phenylcarbazole. These copolymers cover broad absorption ranges from 250 to 700 nm with narrow optical band gaps of 1.71–2.01 eV. The band gaps and the molecular electronic energy levels can be tuned by copolymerizing the benzo[1,2-*b*:4,5-*b*]difuran core with different n-conjugated electron-donating or withdrawing units in different ratios.



Bulk heterojunction solar cell devices were fabricated by Liu and coworkers, using the copolymers as the electron donor and ([6,6′]-phenyl-C_{61}-butyric acid methyl ester) as the electron acceptor. The preliminary research has revealed power conversion efficiencies of 0.17–0.59% under AM 1.5 illumination (100 mW/cm^2).

Thompson and coworkers [281] point out that despite the correlation between the absorption and J_{SC}, most polymers used in currently high-performing solar cells have limited absorption breadths and rely largely on band gaps. As a result, there is a heavy reliance on fullerenes (especially on $PC_{61}BM$, 1-(3-methoxycarbonyl)propyl-1phenyl-[6,6]-methanofullere) to absorb photons in the short wavelength range and considerable absorption losses in the longer wavelengths. Although fullerenes absorb in the short wavelength region and are thus complementary to many polymers, they point to the evidence that 60% of excitons formed in the $PC_{61}BM$ phase decay before being harvested and do not contribute to J_{SC} [282]. This research group mixed graphene oxide that acts as a surfactant with fullerenes C_{60} and single-walled carbon nanotubes in water, coated a glass slide with the solution, and heated it to reduce the graphene oxide to graphene. They claimed that chips using this photovoltaic layer were much more efficient at converting light into electricity that the organic devices developed with covalent chemistry.

Simultaneous to doing research on polymeric materials, research is also being carried out on improving the construction of solar cells. One strategy is to stack two light-absorbing materials in a tandem cell to harvest greater fraction of the solar spectrum. By inserting gold nanoparticles between the two layers, Yang Yang and coworkers coupled the two tandem cells and demonstrated a considerable boost inefficiency of light conversion to electricity [283].

Review Questions

Section 10.1

1. How are the support materials utilized? Discuss

Section 10.1.1.1

1. Describe the Merrifield resin.
2. What are the two types of cross-linked polystyrenes that are used for support?

3. What is Tentagel? Describe and illustrate?
4. What is Jenda Gel? Explain and illustrate.
5. Describe the general use of cross-linked styrene derivatives for support.

Sections 10.1.1.2–10.1.4

1. Illustrate an isobutylene-based support material.
2. Describe an acrylic material used for support.
3. Describe a polyether-based support resin.
4. Describe a gel for drug release.

Section 10.1.3

1. Describe immobilized enzymes.
2. Describe nonenzyme immobilized catalysts.
3. Describe immobilized reagents.

Section 10.2

1. Discuss polyacetylene.
2. Discuss polypyrrole.
3. Discuss polythiophene and its derivatives.
4. Discuss polyaniline.
5. Discuss poly(phenyl vinylene).

Sections 10.3–10.6

1. Explain what is meant by a photonic polymer.
2. Discuss the nature of light.
3. Discuss interaction of light with organic molecules.
4. What is the energy transfer process?
5. What is an electron transfer process?
6. Describe the charge transfer process in polymers.
7. Describe the antenna effect in polymers.
8. What is a photosensitizer? Give some examples.
9. Discuss photocross-linking of polymers and give some examples.
10. Describe polymers that are designed to harvest sun's energy.
11. Discuss photo-isomerization of polymeric materials.
12. How is photo-isomerization utilized in liquid crystalline alignment?

Section 10.7

1. Explain photo-conductivity in polymers. Give examples, those that are based on carbazole and those that are not based on carbazole.

Section 10.8

1. Describe a planar heterojunction solar cell.
2. Describe a bulk heterojunction solar cell.
3. What is the equation that defines the efficiency of organic solar cells.

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