Functional Polymers

6

The overwhelming number of known polymers can be basically sub-divided into those for structural applications and those, which come over with specific functions. The former ones as well as the later ones, called *Functional Polymers*, play important roles since the early days of polymer science and technology. The latter ones, however, usually are not so much characterized by their thermo-mechanical properties, but rather by their inherent functionalities instead, which they develop due to special constitutional features. For example, some of their atoms or groups of atoms may undergo specific interactions with solvents, ions, cells, surfaces, fillers or other polymers. Alternatively, specific optical or electronic properties may result from the molecular and supramolecular architecture of these macromolecules. Polyelectrolytes like poly(acrylic acid) or poly(diallyldimethylammonium chloride), and polymeric stabilizers like polyvinylalcohol or polyethyleneglycol [poly(ethylene oxide), PEO], all of them characteristic examples of functional polymers, are large-scale technical products nowadays. They have found widespread application in e.g. hygiene and cosmetics products. Moreover, polymeric additives and compatibilizers simplify polymer processing and morphology design, and allow the preparation of transparent nanocomposites with improved or even novel property profiles. Photoresins and photoresists are key compounds of photolithography. As such, they are revolutionizing the printing technology, and paved the way for semiconductor and microelectronics industry. In the year 2000, moreover, the Nobel prize was awarded to A.J. Heeger, A.G. MacDiaramid and H. Shirakawa for the development of electrically (semi)conducting polymers, which are key players in our today's organic (opto)electronic.

The first synthetic functional polymers were developed in the early days of the twentieth century already. They were prepared using standard polymerization techniques like free radical or step-growth polymerization reactions. The increased material needs in modern technology and the increased complexity of polymeric materials, however, led to a strong expansion of this field especially in recent years. Today's synthetic techniques allow a much better control of the polymers' structure,

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architecture, functionality, molar mass and dispersity, and hence allow tailoring polymers according to the needs of a specific application. This accounts specially for the functional polymers, whose "function" is more in the focus than their mechanical properties – even though they have to fit the full range of application needs. For example, polymeric additives have to have a sufficient thermal stability to survive melt processing, and for the wide-spread thin-film applications the functional polymers require good mechanical film stability as well as sufficient thermal, chemical, and oxidative stability.

Representative classes of functional polymers include e.g.

- Polymers carrying ionically charged groups (polyelectrolytes), which undergo specific interactions and show specific solution and pH-responsive properties
- Amphiphilic block copolymers forming e.g. micelles and aggregates, and stabilizing additives and (nano)fillers
- Polymeric stabilizers (PVOH, PEG, various block and graft copolymers)
- Polymeric additives like rheology modifiers
- Polymeric carrier resins for catalytic or chromatographic applications (e.g. ion exchange resins)
- Intrinsically electron-conducting polymers
- Photoactive polymers
- Thermo-responsive polymers
- Bioactive polymers, bioconjugates and drug delivery systems

The scope of functional polymer systems has broadened tremendously in recent years. For example, various "hybrid" materials have been developed additionally, which combine synthetic and biological polymers as well as organic and inorganic/metallic components. Especially the field of biomaterials and polymers for biomedical applications cannot be addressed adequately in the context of this book, and only some selected examples of biodegradable polymers and biomaterials have been given earlier (see example 5.15: hydrolytic degradation of an aliphatic polyester and 5.16: hydrolytic degradation of cellulose). The synthesis of polylactide – as one of the most well-known and frequently used biodegradable polymers in medical application as e.g. wound dressing or degradable suture material – is covered by example 3.5. Many active components used in diagnostics, therapy as well as in biomedical studies are made biocompatible by "pegylation", the introduction of polyethylene glycol chains (PEG synthesis through ring-opening polymerization, see example 3.24 for poly(tetrahydrofuran)). Thus, many of the polymers described already in this book fit under the term "functional polymers", as prominent example polyelectrolytes are covered in Sects. 1.3.1.2 and 5.2.1, and some more references to already given examples will be referred to in the following chapters.

It cannot be the goal of this text book to address examples of all these and many further functional polymer structures and applications. Due to the very high – and continuously further increasing – importance of functional polymers in modern life and technology, this chapter will focus on some selected topics out of the broad

Fig. 6.1 Physically crosslinked gel

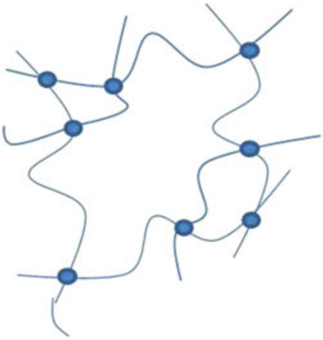


Fig. 6.2 Chemically crosslinked gel

scope of that polymer class instead, which have led to new applications in recent years. These are:

- Gels
- Responsive "smart" polymers
- Polymers with optoelectronic properties

6.1 Gels

Generally speaking, a gel consists of a crosslinked polymer and a liquid. The polymer or "gelling agent" absorbs large amounts of solvent without being dissolved. The term gel was established in 1861 by Graham and originated from gelatin. In food and coating industry, naturally occurring organic gelling agents like polysaccharides and proteins are frequently used. In food industry, hydrogels are used as additives in jelly, sauces, bakery products and in dairy products, in order to give them the desired texture and to prevent them from drying. Covalently cross-linked polyacrylates in superabsorbent polymers – used for hygiene articles such as baby diapers – have gained enormous economic importance.

Gels are classified by their source (natural or synthetic), chemical composition, the three-dimensional network structure and the liquid medium. Generally, one can differentiate between chemically (Fig. 6.1) and physically (Fig. 6.2) cross-linked gels. While chemical gels are characterized by covalent linkages between the structural units (see example 6.1), networks of physical gels are based on non-covalent interactions, such as dipole-dipole-interactions, hydrogen bonds, hydrophobic interactions, polyvalent metal ions, van der Waals forces, and host-guest interactions (see example 6.2). The outstanding feature of thermo-reversible organo- or hydrogels is their ability to form and cleave linkages depending on temperature (see example 6.3). These gels can be characterized by the type of their cross-linkage. Semi-crystalline polymers generate micro-crystallites in the low-molecular matrix, for example polyvinylchloride in dioctyl phthalate. Another reason for the formation of a thermo-reversible gel can be helix formation, as in bio-polymers like gelatin, agarose, carragennan and gellan gum. Additionally, phase-separation leads to formation of physical gels. In this case cross-linking points can be amorphous (e.g. atactic polystyrene) or crystalline. Recently, the development of hydrogels became increasingly important. Mainly smart gels are in the focus of research, due to their stimuli-responsive behavior towards temperature, electrical excitation, incident light, pH value and salt effects.

Example 6.1 Synthesis of Hydrophilic Physically Crosslinked Gel-Building Polymer

Safety precautions: Before this experiment is carried out, Sect. 2.2.5 must be read as well as the material safety data sheets (MSDS) for all chemicals and products used.

0.5 g of dried poly(acrylic acid) (1,800 g/mol) is mixed with 5 mol-% [with regard to the repeating units of poly(acrylic acid)] of dodecyl amine (64 mg). The mixture is grinded, filled into an 8 ml vial with a stir bar and flushed with argon. The vial is then closed with a septum and put into the MW cavity. The reaction takes place at 75 W for 5 min (preheating time = 2 min). The temperature is measured using a fiber optic temperature gage and controlled by permanent adjustment of the air cooling (T = 140°C). A gel-forming polymer is obtained after neutralization with NaOH. $\eta_{0\ [\mathrm{PAA}\ 1{,}800,\ 1\ \mathrm{g/ml}]} = 0.58$; $\eta_{0\ [\mathrm{Gel},\ 1\ \mathrm{g/ml}]} = 1{,}168$

Example 6.2 Synthesis of Hydrophilic Chemically Crosslinked Gel-Building Polymer

Safety precautions: Before this experiment is carried out, Sect. 2.2.5 must be read as well as the material safety data sheets (MSDS) for all chemicals and products used.

7.2 g of acrylic acid and 20 ml of distilled water are placed in a 100 ml flask and stirred for 15 min under nitrogen. 200 mg of butanediol diacrylate (BDDA) is added to the mixture. 0.5 mol% of sodium disulfite and 0.5 mol% of potassium peroxodisulfate is dissolved in 1 ml water and added to the solution. The reaction mixture is stirred 1 h under nitrogen. Within 1 h the gel effect occurs and the polymerization ends. Yield: quantitative. The amount auf water sorption is quantified by the degree of swelling: the ratio of the swollen polymer mass to that of dry polymer. The dry polymer shows a degree of swelling in water of about a factor of 5 (after 1 h) and a factor of 130 (after 24 h), respectively.

Example 6.3 Synthesis of a Thermo-Sensitive Gel

Safety precautions: Before this experiment is carried out, Sect. 2.2.5 must be read as well as the material safety data sheets (MSDS) for all chemicals and products used.

5 g of n-isopropylacrylamide and 20 ml of distilled water are placed in a 100 ml flask and stirred for 15 min under nitrogen. 640 mg of butanediol diacrylate (BDDA) is added to the mixture. 0.5 mol% of sodium disulfite and 0.5 mol% of potassium peroxodisulfate are dissolved in 1 ml water and added to the solution. The reaction mixture is stirred 1 h under nitrogen. After 1 h a white solid precipitates. The solid is filtered out and dried at 70°C. Yield: quantitative. The polymer is soluble in water below 32°C and precipitates from aqueous solution above that temperature.

6.2 Responsive "Smart Polymers"

"Smart polymers" are macromolecular materials that change their properties and/or shape depending on their environment and their surroundings. Some examples of environmental changes that can affect polymers are temperature, the presence of water, chemicals or analytes, pH changes, the presence/intensity of light, electrical fields, mechanical forces etc.

Whereas in the beginning many standard polymers have been considered as "smart" due to their specific design needed in an application, the term is today used only for those polymers that respond in a *dramatic* way to very *slight* changes in their environment. In addition, the responses achieved today have been greatly enlarged due to the increasing preparation of various functional composites. Thus, the introduction of magnetic particles induces magnetic responses in polymeric materials and gels, and e.g. new sensoric properties can be introduced into polymers by incorporation of various quantum dots. Whereas specific responses have been known and studied for a long time in biological macromolecules, smart polymers are becoming increasingly prevalent as polymer chemists learn about the chemistry and triggers that induce conformational changes in polymer structures and devise ways to take advantage of, and control them. New polymeric materials are being chemically formulated that sense specific environmental changes e.g. in biological systems, and adjust in a *predictable* manner, making them useful tools for diagnostics, sensors, microsystems, drug delivery or other metabolic control mechanisms. But uses of smart polymers cover also well-known hydrogels, classical degradable polymers or photoresins.

Certainly, a highly important and well-known class of polymers are those which undergo major changes in solubility by a light-induced process, like photopolymerization, photodegradation (ablation) and photocrosslinking (see also Sect. 3.1.4 and example 3.13). These polymers, known as photoresins or photoresists, are the base of modern computer and communication technology: they allow the photolithographic creation of patterns which are then reproduced in mass production (printing technologies) or into the semiconductors (integrated circuits). A waste variety of materials have been developed adapted to the light used for patterning. The major challenge today is the increased miniaturization in the information technology which requires smaller and smaller features with high requirements on the responsiveness of the polymers used. Thus, polymeric resists are today available for UV-, deep-UV- or even electron-beam lithography. One distinguishes between positive and negative working photoresins. In the first case, solubility of the resin is enhanced upon irradiation (e.g. degradation process or activation of a dissolution enhancer). In the second case, the solubility is reduced by e.g. polymerization processes or crosslinking. Early examples for UV-resists are polyvinylalcohol/cinnamoyl acid (negative) and novolac/naphthochinone diazide (positive) resins. Today often chemically amplified resins are used, which are based on photocatalytic processes. The photopolymerization (see example 3.13) is mainly used in the printing technology e.g. for the preparation of large-scale printing plates according to letter press technique (so-called *flexoprint* process) used to print on packaging materials like plastic foils. Other photoactive polymers as well as polymers having specific electrical properties or those responding to electric fields (piezoelectric polymers) are covered in Sect. 6.3.

Another important class of responsive polymers is that which responds on chemical changes. The most important trigger is pH. It allows changes in the charged status of the polymers (see Sect. 1.3.1.2 and 5.2.1 on polyelectrolytes) leading to major changes in solubility upon pH changes. Especially, hydrogels – polar, slightly crosslinked materials (see Sect. 5.2.1.2, example 5.11) – are addressed here due to the possibility to adapt the degree of swelling significantly by the applied pH. Changes in the swelling allows for controlled uptake and release of water and included components like drugs or others. In addition, pH-responsive gels – mostly based on poly(acrylic acid) gels – are increasingly used in microsystems as actuators. They can open or close valves and channels e.g. in a lab-on-a-chip device upon changes in pH due to the changes in the degree of swelling. In addition to hydrogels, various polymers have been developed for sensors, diagnostic or separation techniques. They usually show a specific interaction with various analytes from water vapour and volatile organic compounds (VOC) to salts, metal ions, various analytes and chemicals to drugs and biomolecules. In the simplest way, thin polymer layers made up e.g. from polyimides are used in humidity sensors: they take up and release water vapour in a controlled fashion. The corresponding changes in the thin film (thickness, refractive index or conductivity) are measured in the sensor to quantify the uptake. In more complex systems, specific interacting groups are introduced (e.g. in ion exchange resins, see example 5.9 and 5.10 or in cyclodextrin-containing polymers, see example 3.14a) which allow a selective uptake of specific analytes. A further expansion of chemically responsive polymers is demonstrated by the concept of *Molecular Imprinting*. Here analytes are not only included in the functional polymer due to specific interactions but also by adaption the analytes’ shape in three-dimensional cavities.

One of the more recently developed material classes is that of thermo-responsive polymers. This accounts mainly for those polymers showing a so-called lower critical solution temperature (LCST) or – to a much less extent – an upper critical solution temperature (UCST), meaning polymers that change their solution status significantly upon temperature changes. In general, this behaviour is the result of a delicate balance of hydrophilic and hydrophobic groups in the polymer. The major aspect in this response is thermodynamic, and is based on the dissociation of hydrogen-bonds upon heating. Below LCST, water-polymer hydrogen bonds dominate, whereas above LCST polymer-polymer interactions start to dominate leading to precipitation. One of the most well-known example in this regard is poly(*N*-isopropylacrylamide) (PNiPAAm) and others poly(*N*-alkylacrylamide)s that exhibit a lower critical solution temperature (LCST) and remarkable hydration-dehydration changes in aqueous solution in response to relatively small changes in temperature. Below LCST, PNiPAAm chains hydrate to form an expanded structure; above LCST, i.e. above the cloud point at a given concentration, T_c, PNiPAAm chains dehydrate and collapse. PNiPAAm-based hydrogels have attracted much attention since their LCST in water is in the physiologically interesting range. Thus, these polymers may be applied in the biomedical field as stimulus-sensitive materials. Other examples for polymers showing LCSTs are cellulose derivatives, poly(ethylene oxide) (PEO), polyethyloxazoline (see example 3.27), polyvinylmethylether, or poly(*N*-vinylcaprolactam). Similar as for pH-sensitive gels, thermoresponsive polymers are often prepared as gels which change the degree of swelling upon temperature changes, allowing for significant changes in volume as well as for changes in release and up-take properties. Applications again are seen in the biomedical field or in actuators. An example for a thermoresponsive hydrogel is given in Sect. 6.1 (example 6.3).

6.2.1 Polymer Networks with Shape Memory Effect

Further examples of thermo-responsive polymers are shape-memory polymers. Shape memory behavior is known for some time for metals and alloys with use in medical application, aerospace, and micro-machinery/actuators. However, it can also be observed in polymers of specific bulk structure. These smart materials have the ability to return from a deformed state (temporary shape) to their original (permanent) shape induced by an external stimulus (trigger). Most shape-memory polymers (SPM) can retain two shapes, and the transition between them is induced by temperature. In some recent SMPs, heating to certain transition temperatures allows to fix three different shapes. In addition to temperature change, the shape change of SMPs can also be triggered by an electric or magnetic field, light or solution. Shape memory polymers cover a wide property-range from stable to biodegradable, from soft to hard, and from elastic to rigid, depending on the structural units that constitute the SMP and include thermoplastic and thermoset (covalently cross-linked) polymeric materials. Representative shape-memory polymers are segmented polyurethanes with ionic or mesogenic components made by prepolymer methods. Other block copolymers also show the shape-memory effect, such as block copolymers of polyethylene terephthalate (PET) and poly(ethylene oxide) (PEO), block copolymers containing polystyrene and poly(1,4-butadiene), and ABA triblock copolymers made from poly (2-methyl-2-oxazoline) and poly(tetrahydrofuran), but also partially dehydrochlorinated poly(vinyl chloride) and nylon/polyethylene graft copolymers are reported to perform as SMPs.

Fig. 6.3 Photo series demonstrating the shape memory effect of a polymer network from a temporary shape to a permanent shape at 25°C after twisting and freezing at −20°C (from *left* to *right*)

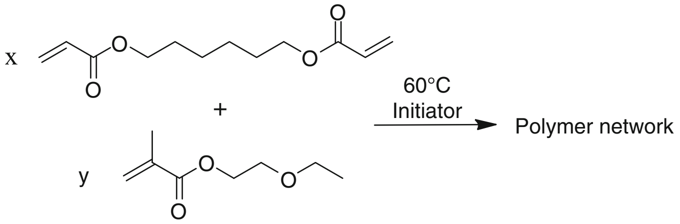
Polymers exhibiting shape-memory effects have both a visible, current (temporary) form and a stored (permanent) form. Once the latter has been manufactured by conventional methods, the material is changed into another, temporary form by processing through heating, deformation, and finally, cooling. The polymer maintains this temporary shape until the shape change into the permanent form is activated by a predetermined external stimulus. The structural reasons of this effect lie in the molecular network structure of the polymers, which contains at least two separate phases e.g. as in segmented block copolymers. The phase showing the highest thermal transition, T_{perm}, is the temperature that must be exceeded to establish the physical cross-links responsible for the permanent shape. The switching segments, on the other hand, are the segments with the ability to soften above a certain transition temperature (T_{trans}) and are responsible for the temporary shape. Exceeding T_{trans} (while remaining below T_{perm}) activates the switching by softening these switching segments and thereby allowing the material to resume its original (permanent) form.

Industrial applications of shape memory polymers are e.g. as foams in the building industry and in sportswear. Further potential applications include self-repairing structural components. More recently, especially potential biomedical applications are discussed as, e.g., intravenous cannula, self-adjusting orthodontic wires and selectively pliable tools for small scale surgical procedures.

Shape memory polymers (SMPs) are generally applied as polymer networks. The existence of permanent cross-links is the reason for their performance. SMPs can be either chemically or physically cross-linked polymer networks. Molecular chains with a thermal transition at $\mathrm{T}_{\mathrm{trans}}$ serve as molecular switch triggering the shape memory effect. Due to the flexibility of the network chains, the polymer can show extensive deformation at temperature above $\mathrm{T}_{\mathrm{trans}}$. In contrast, by freezing the SMP below $\mathrm{T}_{\mathrm{trans}}$, the network chains lose their mobility, and the polymer can be frozen in a temporary shape. The cross-links stabilize the permanent shape of the networks in the course of shape memorizing. The photo series demonstrates the shape memory effect of a polymer network (Fig. 6.3) showing the transition from a temporary shape to a permanent shape at room temperature after twisting and freezing at −20°C depending on time.

Example 6.4 Synthesis of a Bicomponent Polymer Network Through a Radical Polymerization of Methacrylic Acid 2-Ethoxyethyl Ester and bis*(Acrylate)*

Safety precautions: Before this experiment is carried out, Sect. 2.2.5 must be read as well as the material safety data sheets (MSDS) for all chemicals and products used.



20.0 g (126 mmol) of methacrylic acid 2-ethoxyethyl ester and 2.0 g (10 wt%) of 1,6-hexanediol diacrylate are added to a 25 mL two-neck round-bottom flask equipped with a septum. While stirring, the reaction mixture is purged with nitrogen. After 30 min. 15.4 mg (0.07 wt%) of a radical initiator 2,2′-azobis(2,4-dimethyl)valeronitrile are added to the reaction mixture. The liquid is injected into a mold and heated to 60°C for 24 h. The cross-linked polymer is removed from the mold. In a vacuum drying cabinet the rest monomer is extracted from the polymer network (125°C and 1.2 mbar, 2 days).

6.3 Polymers with Specific (Opto)Electronic Properties

Functional polymers are of increasing importance even in the field of (opto) electronics and related areas. Polymeric materials show plenty of desirable features when compared with traditional inorganic materials. For example, they are rather cheap, easily processable from the melt or solution (coating, printing, etc.), film-forming and flexible (unlike fragile inorganic materials). Also, well-established and convenient reactions of organic and organo-metallic chemistry can be used to tailor these materials to a specific purpose.

Optoelectronics in general deals with the conversion of electrical power into electromagnetic radiation (i.e., visible light), and vice versa with the conversion of (sun)light into electrical power (photovoltaics, PV). The devices commonly used for these two conversion processes are known as *light-emitting diodes* (LEDs) and *solar cells* (SCs), respectively. If organic polymers play the major role in these devices, they are named "organic" or "polymer-based". Abbreviations are used such as OLEDs, POLEDs, OSC, PSC, OPV, and so on. The principal architectures of OLEDs and OSCs are shown in Fig. 6.4, and additionally the most relevant elementary processes occurring in those devices are sketched.

In an operating OLED device, electrons are withdrawn from the functional polymer at its interface to the anode as soon as a sufficiently high voltage is applied. Chemically spoken, the polymer is oxidized, a so-called "hole" (electron-deficient site) is injected, which formally is characterized by a positive charge. Accordingly, this oxidation process is called "hole injection". From the cathode side, on the other hand, electrons are injected into the functional material, the polymer is reduced, and a negative charge carrier – called "electron" – appears at the interface.

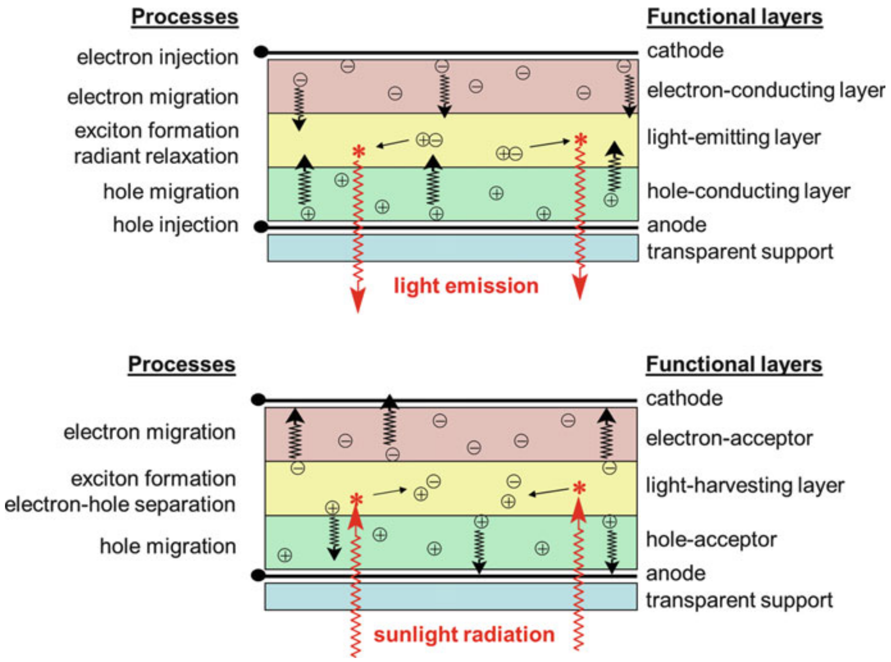


Fig. 6.4 Fundamental architectures and elementary processes occurring in operating OLEDs (*top*) and OSC (*bottom*) devices

Driven by the electric field, the injected charge carriers migrate into the polymer bulk, and hence move toward each other from the opposite interfaces. When inside the organic layer an electron meets a hole, they recombine: an electron–hole pair is formed, which represents an electronically excited state (exciton). The exciton finally can relax into the electronic ground state by emission of light (radiant relaxation, often termed as “electro-luminescence”). Such electro-luminescence is possible without restrictions if a singlet exciton is formed: in this case, radiant relaxation is spin-allowed fluorescence. Unfortunately, most of the excitons formed in OLEDs are triplet excitons. In this case, radiant relaxation is spin-forbidden. If conventional organic polymers are used as electro-luminescent materials, therefore, this (major) fraction of excitons gets lost, and heats up the device due to non-radiant relaxation processes. However, it is possible to offer alternative pathways to the radiant triplet relaxation: introduction of so-called triplet emitters, which open pathways for radiant relaxation with spin-inversion, help increasing power efficiency of such devices: they open the complementary electro-phosphorescence option for light generation. Therefore, development of tailored phosphorescence emitters (e.g., transition-metal complexes) is a hot-topic in current functional-polymer research.

In an operating solar cell, the fundamental processes are inversed to those in OLEDs: upon absorption of light, a chromophoric unit of the functional polymer, or of a dye embedded into the polymer matrix, changes from its electronic ground state into an excited state. In other words, one electron moves from the *highest occupied molecular orbital* (HOMO) of the absorbing entity into its *lowest unoccupied molecular orbital* (LUMO). The formed excited state (exciton) may relax back following radiant or non-radiant pathways – which either results in the emission of a fluorescence quantum (photo-luminescence) or in heating (excitation of vibration modes). Alternatively, the exciton will make use of its nature as an electron–hole pair, and separate into an "isolated" hole and an "isolated" electron located at different sites. After successful charge-carrier separation, electron and hole move in opposite directions to their respective electrodes. In order to minimize downstream recombination and deactivation processes, this latter migration process should proceed via different pathways for holes and electrons.

As one can see, functional polymers for (opto)electronic devices must feature many other abilities in addition to light absorption or light emission. First of all, they must be able to transport charge carriers, i.e. the electrons and holes, from the electrodes to the recombination and emission zone (in OLEDs), or vice versa from the absorbing dyes to the respective electrodes (in OSCs). Thus, they must be electrically conducting. More precisely, they should rank among the electrical *semi*-conductors: in the ground state, they act as insulators to prevent short circuits. After appropriate activation, however, which might be achieved due to injection or (light-induced) formation of charge carriers, they convert into a conductive state. Now, charge-carrier transport proceeds through the polymeric material predominantly via redox cascades enabled by hopping and tunnelling processes, and its principal direction is given by the applied electrical field. Depending on the molecular constitution of the polymer, either it can provide high mobility for electrons only, for holes only, or for both types of charge carriers simultaneously.

Most semi-conducting polymers that are used in optoelectronics have a backbone, which contains alternating carbon-carbon single and multiple bonds. Therefore, they are called "π-conjugated polymers". Nevertheless, one should keep in mind that in those macromolecules π-electron conjugation by far is not spread over the whole backbone, but is limited to rather short segments: the so-called "effective conjugation length" has been shown to include some few repeating units only, even if perturbations of chain geometry are minimized. As a consequence, the absorption and emission properties do not change with increasing chain length if a minimum contour length of the system is exceeded. On the other hand, changes of the local environment and the degree of ordering of the chain segments within the functional film may cause severe effects due to associated changes of the effective conjugation. Attachment of lateral substituents to the "conjugated" polymers therefore not only is a measure to improve solubility and to adjust electronic properties, but also to stabilize the material in the functional film in the morphology requested to develop the targeted properties. Important examples of semi-conducting organic polymers are shown in Fig. 6.5.

Moreover, semi-conducting polymers for OLEDs must ensure well-balanced hole- and electron-injection from the electrodes as well as comparable (but not too

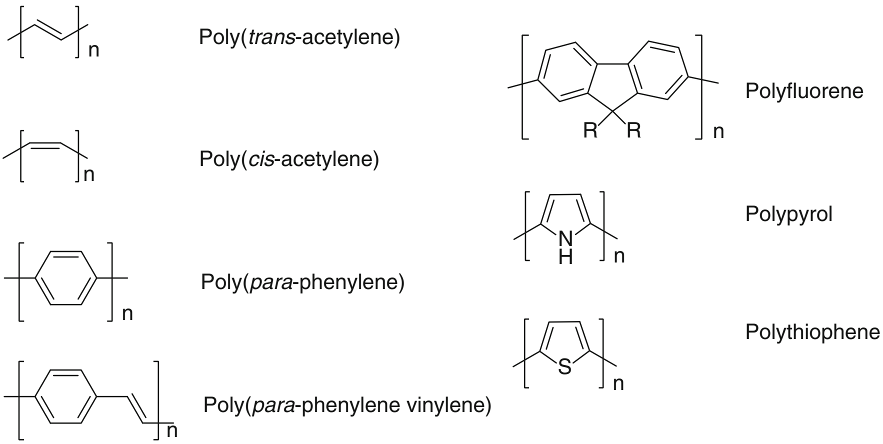


Fig. 6.5 Some important examples of the basic structures of intrinsically (semi)conducting polymers

high) charge-carrier mobility for electrons and for holes. In solar cells, on the other hand, the semi-conducting polymeric material should offer separated pathways for electrons and holes in order to minimize loss of energy by downstream electron-hole recombination processes.

Another hot topic in modern functional polymer research deals with the development of materials that can be used as electrode materials: these polymers must offer high charge-carrier mobility, well-adapted energy levels of their frontier orbitals, and light should be able to pass without scattering and absorption, i.e., the electrode material should be transparent for visible light even in the conducting state. Today, inorganic oxides such as indium tin oxide (ITO) are used as transparent anode materials. However, intense research has born first examples of organic polymers, mainly based on polythiophenes (such as PEDOT:PSS, also known as Baytron® P, from H.C. Starck Co.; see Fig. 6.6), that might be used as alternatives.

In addition to applications as functional materials in OLEDs and OSCs, semi-conducting polymers are needed for other (opto)electronic devices as well. With regard to displays, sensors, and radio-frequency identification tags (RFIDs) for example, it is a challenge to create polymer-based organic transistors (thin-film transistors, OTFT; field-effect transistors, OFETs). Figure 6.7 sketches an optional OFET design, and additionally shows schematically its principle of operation.

An OFET is composed of three electrodes, a source electrode, a drain electrode, and a gate electrode. The gate electrode is separated from the source and drain electrodes by an insulator layer (silicon dioxide, or insulating polymers like polyhydroxystyrene). Between source and drain electrode, moreover, an organic semi-conductor is placed. If no electric field is applied, the semi-conductor performs as an insulator: charge carriers cannot cross over from the source to the gate electrode. The transistor is in the "off state". If a sufficiently high electric field V_G is applied between source and gate electrode, on the other hand, charge carriers

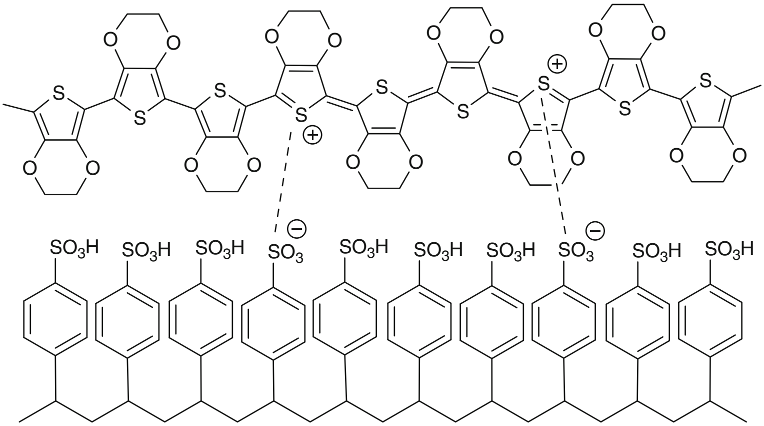


Fig. 6.6 Idealized chemical constitution of PEDOT:PSS

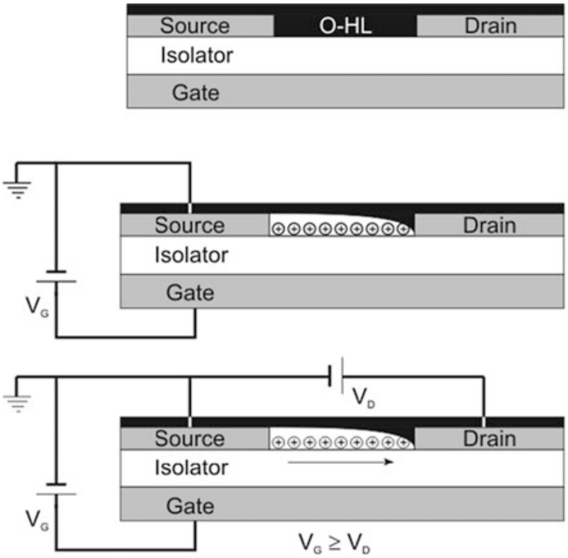


Fig. 6.7 Example architecture of a field-effect transistor and its basic function principle

appear at the interface between semi-conducting polymer and insulator. Due to the presence of these charge carriers, the organic material changes from its insulating state into the semi-conductor state. Consequently, charge transport is possible from the source to the drain electrode if there is an appropriate drain voltage V_D applied. Now, the transistor is in the “on state”.

Such transistors can be used e.g. as switches in display applications, which manage the individual pixels. In this respect, it is an issue to develop functional polymers which can be processed from solution and nevertheless result in thin

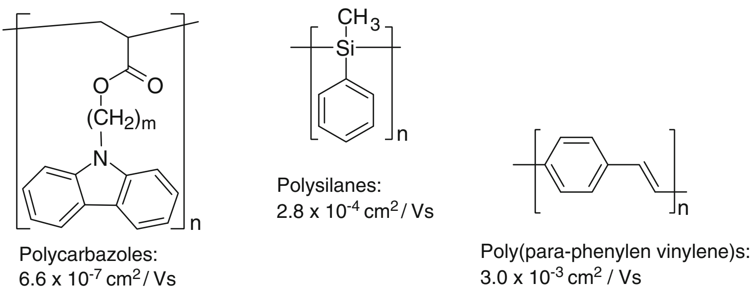


Fig. 6.8 Polymeric photoconductors, including the charge-carrier mobility achieved so far

layers showing very high degrees of ordering: perfect ordering is essential to get high charge-carrier mobility in the "on state". Accordingly, it is a major issue to design tailored polymers that self-organize in such a perfect fashion even when processed from solution. Otherwise, polymer-based transistors will not compete successfully with small-molecule systems. For sensor-applications, on the other hand, advantage can be taken of the high sensitivity of the thin-film transistor performance toward perturbations in the semi-conducting layer. In this context, it is an important field of research to increase the selectivity of those transistors with respect to specific analytes.

Photoconductors represent another class of functional polymers showing modulated electrical conductivity depending on external parameters: the material is electrically insulating in the absence of light since no free charge carriers are available (Fig. 6.8). Upon exposure to light, excitons are formed due to light-absorption and convert the material into its semi-conducting state. Advantage is taken of this effect in e.g. xerography and laser printing technologies.

In essentially all cases mentioned above the constitution of the polymers itself is responsible for the fact that the material is able to convert into an electrically semi-conducting (and sometimes conducting) state. Therefore, they are called *intrinsically conducting polymers*. This specification is applied to differentiate them from e.g. polymer-based *composite materials*, which develop electrical (and maybe thermal) conductivity just because of the presence of conducting fillers, which are dispersed appropriately in the otherwise non-conducting polymer matrix. One promising strategy in this respect is to add carbon-based (preferentially nano-scalic) fillers such as carbon black, carbon nano-tubes or graphenes into the insulating bulk polymer, and to process the composite subsequently in a fashion that allows the filler particles to develop a so-called *percolation network* through the whole material (Fig. 6.9). These percolation paths represent the highways for the charge carriers. If very high degrees of filling are realized and the processing is perfectly adapted, even heat transport can be observed through these composites. The latter option is expected to be of benefit for electro-mobility, heat management of batteries, bipolar plates of fuel cells, and cooler units of computer processors.

On the other hand, reliable prevention of nano-particle aggregation and agglomeration in the matrix of an insulating polymer as well is a key issue in the field of

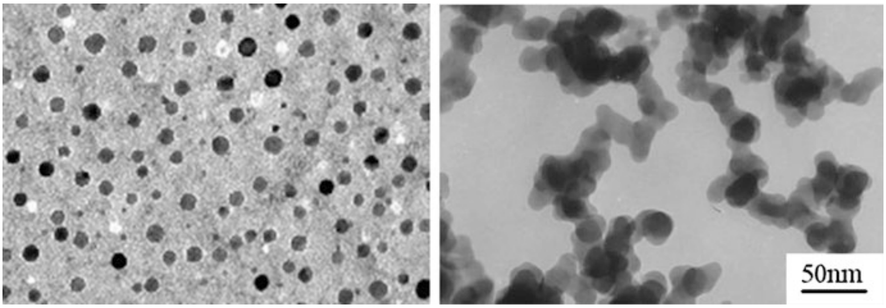


Fig. 6.9 Functional polymer nano-composites; *left*: well-dispersed TiO_2 nano-particles in a polystyrene matrix for increasing the composite's refractive index, *right*: percolating carbon-black nano-particles in a carbonate matrix to realize an electrically conducting material

functional polymers. For example, if conducting nano-particles are embedded in a polymer matrix without mutual contact, macroscopic conductivity is prevented, but the material may show very high dielectric constants, which again are desired for applications in e.g. miniaturized electronic devices. Based on closely related concepts, it is also possible to increase the refractive index of a transparent polymer: when mixed with nano-scale particles of high refractive indices such as titanium dioxide or zirconium dioxide, a composite material may result, which shows higher refractive indices than the pure polymer. Application of the materials as optical lenses is one option – if aggregation of the filler nano-particles can be prevented reliably (Fig. 6.9).

Finally, it should be mentioned that, in addition to the above examples, many further aspects may be encountered why and where functional polymers can be applied in combination with light and/or electrical power. For example, shape-anisotropy of polymers can cause the formation of lyotropic and/or thermotropic mesophases (liquid-crystalline polymers, LCPs). Alike, small-molecule mesogens, LCPs undergo specific interactions with light depending on the type and extent of mesoscalic order in the liquid-crystalline state. Since many semi-conducting polymers are rod like in shape (and thus anisotropic), not only modulated conductivity and emission can be observed depending on the respective structure, but even special effects such as emission of polarized light when applied in OLEDs.

Another topic related with π-electron conjugation in functional polymers is their nonlinear optical (NLO) behavior: such materials can be used to convert red light into light of shorter wavelength by frequency doubling or tripling. One advantage offered by shorter wavelengths is the higher capacity for processing and storage of information and optical computing. Moreover, these materials are of interest for photonic devices like optical switches, modulators and waveguides. High transparency and low light scattering are requested too. Polymeric materials showing excitingly high second-order and third-order nonlinear susceptibilities have been developed. One of the so far unsolved challenges, however, is ensuring sufficient long-term stabilities of material and effects.

Finally, it should be mentioned that conventional (electrically) isolating bulk polymers as well can develop highly attractive functional characteristics in combination with e.g. electrical voltage. This is if they are arranged in an appropriate layered or porous micro-morphology and charge carriers are introduced and immobilized at the internal interfaces or surfaces of these “piezoelectric” systems. Under these conditions, the materials expand or contract in an electrical field depending on the applied voltage. On the other hand, these materials can generate electrical voltage – and hence produce electrical power – if deformed mechanically. These effects can be used for microphones, loudspeakers, sensors, actuators, and many other devices.

Example 6.5 Synthesis of Poly{[2-(β-Ethylhexyloxy)-5-Methoxy]-Para-Phenylene Vinylene} (“MEH-PPV”) Via Gilch Reaction

Safety precautions: Before this experiment is carried out, Sect. 2.2.5 must be read as well as the material safety data sheets (MSDS) for all chemicals and products used.

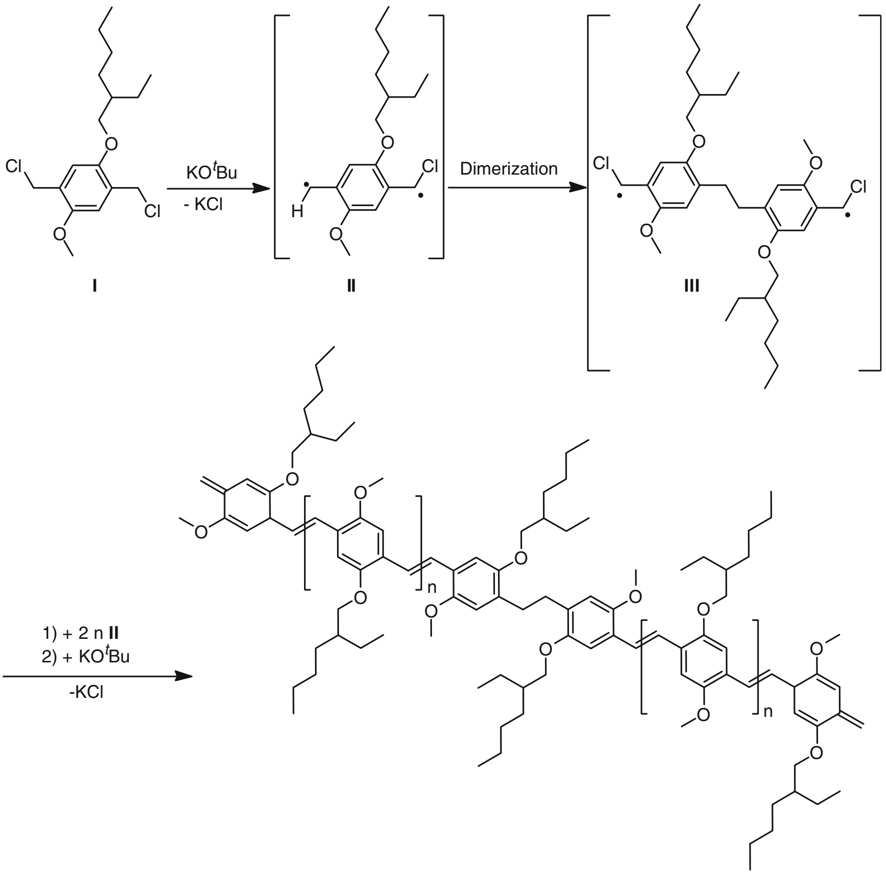
Preparation of 1-(β-Ethylhexoxy)-4-Methoxybenzene

Under an atmosphere of nitrogen, sodium methanolate (13.6 g, 251.0 mmol) is dissolved in methanol (50 ml). 4-Methoxyphenol (30.12 g, 251.0 mmol) dissolved in methanol (50 ml) is added dropwise over a period of 30 min. Stirring at room temperature is continued overnight to complete deprotonation. 2-Ethylhexylbromide (48.42 g, 251.0 mmol) is dissolved in methanol (100 ml) and added slowly over 3 h to the above solution. The reaction mixture is stirred at room temperature for 60 h and heated to reflux for an additional 30 h. The mixture is concentrated under reduced pressure. The residue is dissolved in a 1:1 (v/v) mixture of diethyl ether and water (400 ml). The organic phase is extracted with aqueous 0.2 M NaOH (3 × 100 ml) followed by pure water (3 × 100 ml), dried ($MgSO_4$) and concentrated in vacuo. The remaining solution is purified via flash chromatography using silica gel as the stationary phase and toluene as the eluent (Rf: 0.69). Yield: 42 g (72%).

Preparation of 2,5-*bis*(Chloromethyl)-1-(β-Ethylhexoxy)-4-Methoxybenzene

Under an atmosphere of nitrogen and vigorous stirring, aqueous HCl (37%, 87.9 g, 892.30 mmol) is added to a mixture of 1-(β-ethylhexoxy)-4-methoxybenzene (36.67 g, 155.43 mmol) and para-formaldehyde (12.80 g, 426.20 mmol). Acetic anhydride (162.31 g, 1589.88 mmol) is added dropwise. When addition is complete, the solution is heated to 70°C for 3.5 h. The reaction mixture is allowed to cool down to room temperature overnight. Concentrated aqueous sodium acetate (150 ml) is added within 2 h. Then, aqueous NaOH (110 ml, 25%) is added slowly within 4 h while the temperature is not allowed to rise above approx. 50°C. The white precipitate is molten at 60°C and precipitated under vigorous stirring and cooling using an ice bath. The precipitate is filtered off, washed with water (1,000 ml) and dissolved in *n*-hexane (500 ml). The organic phase is washed with water (3 × 200 ml) and dried (Na_2SO_4). The solvent is removed under reduced pressure. The residue is crystallized twice from *n*-hexane. Yield: 34 g (65%).

Polymerization Via Gilch Reaction



Under an atmosphere of nitrogen, the above monomer (0.5 g, 1.5 mmol) is dissolved in dry THF (100 ml). Potassium *tert*.-butanolate (1.0 M in THF, 6 ml, 6 mmol) is added quickly, and the mixture is stirred at room temperature for 20 h. Conc. acetic acid (2 ml) is added, the solution is concentrated down to 50 ml, and the polymer is precipitated by pouring the whole reaction mixture into methanol (200 ml). The formed solid is filtered off and dried in vacuo (40°C).

Example 6.6 Synthesis of Poly[9,9-bis(2-Ethylhexyl)Fluorene] Via Yamamoto Coupling

Safety precautions: Before this experiment is carried out, Sect. 2.2.5 must be read as well as the material safety data sheets (MSDS) for all chemicals and products used.

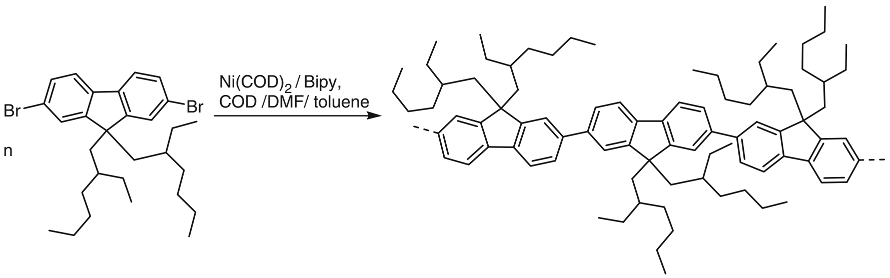
Preparation of 2,7-Dibromo-9H-Fluorene

In a 1 L round bottom flask wrapped in aluminum foil, a solution of fluorene (50.0 g, 300.8 mmol) in $CHCl_3$ (450 ml) is cooled to 0°C. Ferric chloride (0.716 g, 4.5 mmol) is added. At 0°C, bromine (32.6 ml, 632 mmol) is added slowly over 15 min. The ice bath is removed and the solution is allowed to warm slowly. The mixture is stirred overnight at room temperature, washed with aqueous $Na_2S_2O_3$ until the solution is clear and slightly yellowish only, and extracted with $CHCl_3$. The organic layer is washed with water, dried ($MgSO_4$), and the solvent is removed. The desired product is obtained in essentially quantitative yields (98 g) as colorless crystals.

Preparation of 2,7-Dibromo-9,9-bis(2-Ethylhexyl)Fluorene

2,7-Dibromofluorene 50 g (154 mmol) is dispersed in DMSO (200 ml). Benzyltrimethylammonium chloride (1.5 g, 8 mmol) is added as a phase-transfer catalyse. Nitrogen is passed through the suspension for 10 min, and subsequently aqueous NaOH (100 ml, 50%) is added at room temperature slowly. Stirring is continued at room temperature for a further 1 h. 2-Ethylhexyl bromide (65.4 g, 339 mmol) is added slowly, and the mixture is stirred overnight at room temperature. MTB ether (300 ml) and water (100 ml) is added, stirring is continued for further 15 min, the organic layer is separated, washed with saturated aqueous NaCl (3 × 100 ml) and water until the color of the solution changes from violet via green to reddish-orange. The organic layer is dried (Na_2SO_4), and the solvent is removed in vacuo. The oily residue is purified via column chromatography (eluent: pentane, $R_f = 0.85$). After removal of the solvent, slightly yellowish oil is obtained. In order to remove the monoalkylated product, the oil is dissolved in THF (250 ml) and a solution of KO^tBu (20 g) in THF (200 ml) is added. The mixture is stirred for 30 min, filtered under an atmosphere of nitrogen over basic aluminum oxide pad, the solvent is removed, the residue dissolved in hexane and filtered. The hexane is removed in vacuo. This procedure is repeated until no discoloring is observed any more upon addition of KO^tBu. The residue is dissolved in ethanol (200 ml, 60°C) and the solution stored in the fridge at –21°C for 1 week. 2,7-Dibromo-9,9-bis-(2-ethylhexyl)-fluorene (63.5 g, 75%) is obtained as colorless waxy solid.

Polymerisation Via Yamamoto Coupling



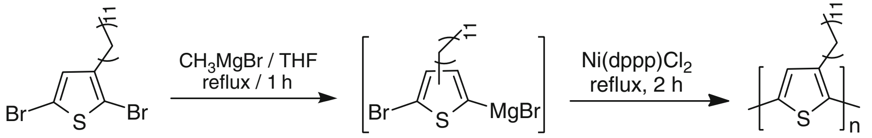
Under an atmosphere of nitrogen, Ni(COD)$_2$ (1 g, 3,65 mmol, 2 äq.), 2,2′-bipyridine (569 mg, 2,2 mmol, 2,3 äq.) and cycloocta-1,5-diene (COD) (324 μl, 2.6 mmol, 1.45 äq.) are dissolved in a mixture of DMF (3 ml) and toluene (8 ml) and then heated to 80°C for 30 min. Subsequently, the above monomer (1.00 g, 1.82 mmol), dissolved in dry toluene (5 ml), is added under an atmosphere of nitrogen, and the reaction mixture is stirred at 80°C for 6 d. The reaction mixture is allowed to cool down to room temperature, aqueous HCl (50 ml, 2 M) is added, and the mixture is stirred at room temperature for 15 min. Methylene chloride (200 ml) is added, the organic layer is separated, washed with 2 M aqueous HCl (2×200 ml). To the resulting solution a saturated aqueous solution (400 ml) of Na$_4$EDTA is added vigorously and then washed with aqueous NaHCO$_3$ solution and dried (Na$_2$SO$_4$). The solvent is removed in vacuo; the residue is dissolved in a small volume of methylene chloride, filtered over a short pad of silica gel, concentrated down to 30 ml, and then poured into acetone (300 ml). The precipitate is extracted with acetone in a Soxhlet apparatus to remove lower oligomers, the remaining polymer is dissolved in methylene chloride and precipitated in methanol excess. The yield is approx. 70–80%.

Example 6.7 Synthesis of Poly(3-Dodecylthiophene) Via Grignard Coupling

Safety precautions: Before this experiment is carried out, Sect. 2.2.5 must be read as well as the material safety data sheets (MSDS) for all chemicals and products used.

Preparation of 2,5-Dibromo-3-Dodecylthiophene (Adv. Mater. 1999, 11 (3), 250)
3-Dodecylthiophene (19.41 g, 77.06 mmol) is dissolved in 100 ml of THF. N-Bromosuccinimide (27.43 g, 154 mmol) is added to the solution over a period of 5 min. The solution is stirred at room temperature for 2 h. The solvent is removed in vacuo and 250 ml of hexane is added. The mixture is filtered through a silica plug and the solvent is removed in vacuo. A Kugelrohr distillation (120°C, 0.02 Torr) affords the title compound (26.26 g, 83.3%) as the highest boiling fraction, a clear, colorless oil.

Preparation of Head-to-Tail Polydodecylthiophene (HT-PDDT)



2,5-Dibromo-3-dodecylthiophene (1.28 g, 3.12 mmol) is dissolved in 18 ml of dry THF. Methylmagnesium bromide (3.15 ml, 1.0 M solution in butyl ether) is added and the mixture is heated to reflux for 1 h. Ni(dppp)Cl_2 (16.9 mg) is added and the solution is stirred at reflux for 2 h. The mixture is poured into 150 ml of methanol and filtered into a soxhlet thimble. Soxhlet extractions are performed with methanol (to remove monomer and salts), hexanes (to remove catalyst and oligomers), and chloroform. The chloroform fraction is reduced and dried in vacuo to afford 0.510 g (65% yield) of the title polymer as a violet film.

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