

## III.2.17.2 Synthesis of Conjugated Polymers for Materials Science

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### A. INTRODUCTION

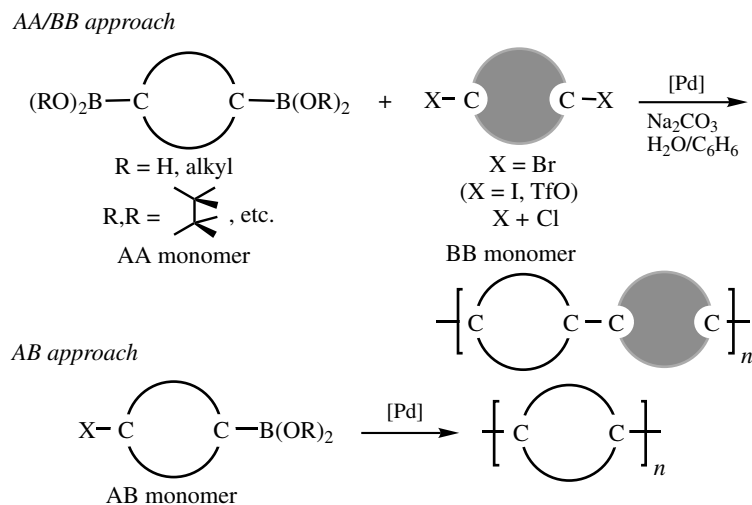
The present volume shows the impressive wealth of bond formation processes made possible by Pd-mediated reactions. In a very important class of these reactions C—C bonds are formed. Suzuki-,<sup>[1],[2]</sup> Heck-,<sup>[3]</sup> Stille-,<sup>[4]</sup> and Sonogashira/Hagihara-type<sup>[5],[6]</sup> and related reactions have revolutionized organic synthesis all the way from hydrocarbon chemistry to natural product and bioorganic synthesis. There have also been numerous attempts to utilize the potential of these reactions for polymer chemistry. Since most Pd-mediated cross-coupling reactions connect  $\text{sp}^2$  with  $\text{sp}^2$  or  $\text{sp}^2$  with  $\text{sp}$  hybridized carbons, poly(arylene)s (structure **A**), poly(arylene vinylene)s (structure **B**), and poly(arylene ethynylene)s (structure **C**) were the natural target polymers. The new opportunity to synthesize these kinds of polymers, which, except for some poly(arylenevinylene)s,<sup>[7]–[10]</sup> could never be synthesized before in a structurally controlled way, came just at a time when the young area of materials science with organic compounds and polymers for opto-electronic applications (i.e., optical indicators and displays) began to rise, triggered by the discovery of what normally is referred to as organic metals.<sup>[11]</sup> It is not surprising, therefore, that this started an avalanche-like effort by synthetic chemists to make the conjugated polymers of type A–C with different backbones, substituents, and functional groups, as well as a broad variety of bandgaps, redox-potentials, fluorescence properties, and so on, in order to generate optimal materials for a future market, the display technology. This section covers some of the important developments focusing on synthetic and structural issues but also provides some insight into why certain polymers were made and which properties were expected or realized. Conjugated oligomers<sup>[12],[13]</sup> will not be covered here as is the case for Pd-mediated polymerizations leading to C—N bond formations<sup>[14],[15]</sup> and polymerizations using catalyst systems based on metals other than Pd.<sup>[16],[17]</sup>

### B. SUZUKI POLYCONDENSATION

#### B.i. Some General Comments

Suzuki polycondensation (SPC) uses Suzuki cross-coupling (SCC), which has been described in detail including all mechanistic aspects in Part **III.2.2**. It is a step-growth

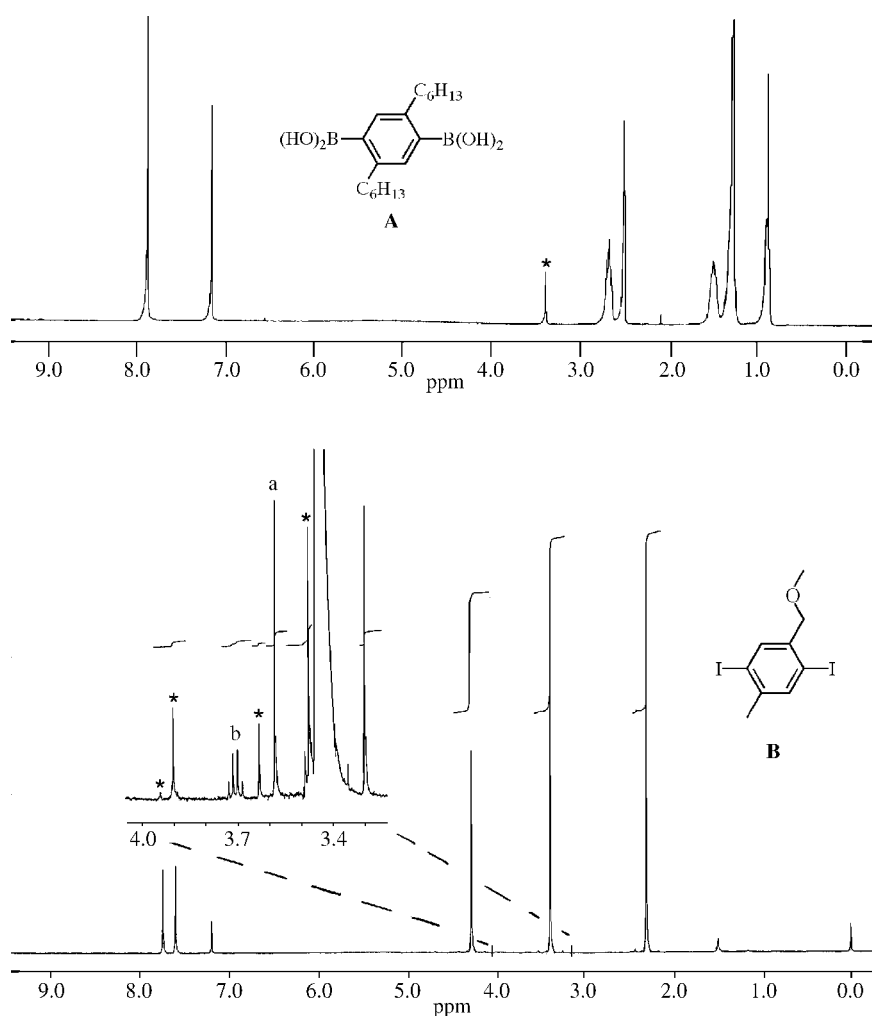
polymerization of bifunctional aromatic monomers to poly(arylene)s and related polymers according to the general outline in **Scheme 1**.<sup>[16],[18]</sup> The required functional groups, boronic acid or esters on the one side and bromide, iodide, and so on the other, may be present in different monomers (AA/BB approach) or combined in the same monomer (AB approach). Both approaches have been applied successfully. The majority of publicized work uses the former despite the advantages of the latter for achieving high molar mass material. AB-type monomers intrinsically have the stoichiometric balance between the two different functional groups, which, according to Carother's equation,<sup>[19]</sup> is a strict must in step-growth polymerizations when high molar mass polymer is concerned. There is a simple synthetic reason why the AA/BB approach is nevertheless favored. Normally it is easier to synthesize aromatic monomers with two identical substituents in opposite positions (for benzene: 1,4) than those with different ones. An additional factor is that once an aromatic dibromide is obtained, its conversion into the corresponding diboronic acid or ester can often be achieved in one simple step and at a large scale. The price, which has to be paid for this, however, is the necessity to apply the AA and BB monomers in strictly equal molar amounts. This requirement sounds almost trivial on paper. In reality, however, it may turn into a real experimental challenge. Purities, methods of how to completely transfer monomers into the polymerization vessel, and losses of a part of the functional groups during polymerization become important and all of a sudden even critical aspects, when the molar mass difference between two monomers is very large.<sup>[20]</sup>



Scheme 1

The matter of purity is of real importance for SPC and should therefore be addressed. As boron-based functional groups, free boronic acid or one of the many cyclic boronic esters are used. The latter esters may hydrolyze to the acids during polymerization, which then enter the normal cross-coupling or follow an independent mechanism.<sup>[21]</sup> Boronic acids always contain some water. Otherwise they are partially or completely condensed to cyclic boroxines. This water content has to be precisely

determined for the reasons mentioned above.<sup>[22]</sup> Boronic esters, which do not have the problem with additional water, tend to partially hydrolyze on the column upon attempted purification. This renders weighing and, thus, stoichiometry control also somewhat problematical. Nowadays, easy-to-apply solutions are available for both problems. They comprise procedures to prevent self-condensation,<sup>[22]</sup> use of pinacole esters to reduce ester hydrolysis,<sup>[23]</sup> rigorous application of high-field NMR, and, most importantly, series of test polymerizations. High molar mass polymer can be obtained only if the impurities are correctly quantified. **Figure 1** shows a 500 MHz proton NMR spectrum of diboronic acid **A**, which is one of SPC's *Drosophilas*. The small signal at  $\delta = 3.4$  ppm stems from water, whose content was determined as 2.7% (w/w) by NMR integration. Monomer **A** of this purity can be obtained on the several 10 g scale. The



**Figure 1.** The 500 MHz NMR spectra of monomers **A** (top) and **B** (bottom) for the determination of the achieved purities by NMR integration. Signals of impurities (\*), a spinning side band (a), and traces of diethyl ether as solvent (b) are marked.

boronic monomer counterparts in SPC are aromatic bromides, iodides, or triflates. The bromo group is by far the most often encountered coupling partner in SPC. Iodides<sup>[24]</sup> and triflates<sup>[25]</sup> were only seldomly used, although iodo compounds are increasingly attractive because they were recently found to furnish higher molar mass products than their bromo analogs (*vide infra*). Chloroaromatics, although successfully used in organic chemistry SCC,<sup>[26]</sup> have not been transferred to polymer chemistry yet. The purity of the dibromo monomers also has to be addressed with great care. Recrystallization for simple compounds and column chromatography for the more complex ones has to be repeatedly applied until a purity above 99% is achieved. **Figure 1** shows an enlarged part of a proton NMR spectrum of a “pure” sample of diiodo monomer B. The main signal at  $\delta = 3.9$  ppm stems from the methoxy group. The enlargement makes its <sup>13</sup>C-satellites visible (marked), which can be used as an internal NMR integration standard. Besides the spinning side bands, small signals also appear, which obviously stem from impurities. Since the intensity of the satellites is 0.5% of the main signal, the degree of impurities seems to be rather small. A quantification would, however, require knowledge of the impurities’ structures.

The circles in **Scheme 1** represent aromatic units, which are in practically all cases substituted benzenes but also include naphthalenes, thiophenes, pyridines, and pyrroles (with an acceptor on nitrogen). When substituted with boronic acids, electron-rich aromatics tend to undergo deboronification reactions,<sup>[27]</sup> which leads to stoichiometric misbalance with its detrimental impact on the achievable molar mass. This is why, for example, thiophenes in SPC are always used as dibromides and not as diboronic acids. These aromatic units are connected to one another to linear poly(arylene)s [for benzenes: poly(*para*-phenylene)s (PPP)] in more than 95% of all publicized cases. In a few examples, regularly kinked poly(arylene)s or related conjugated polymers containing additional olefinic or acetylenic units or other functional groups as part of the main chain are generated. Linear poly(arylene)s, namely, poly(arylene)s whose chemical constitution in principle allows the attainment of a totally straight conformation, are considered rigid-rod type polymers.<sup>[28]</sup> Though they certainly will have bent backbones and attain coiled conformations in solution, they have less conformational degrees of freedom available at low energetic cost than saturated polymers like polystyrene. As a consequence, these poly(arylene)s and the related poly(arylene-vinylene)s and poly(arylene-ethynylene)s pack easily, have little driving force to dissolve (molecularly disperse), and, thus, show poor solubility. The solubility of all *para*-linked nonaphenylene, for example, which is just a very short model for poly(*para*-phenylene) (PPP), is less than  $10^{-8}$  g/L in toluene at room temperature.<sup>[29]</sup> Any synthetic protocol for SPC that does not account for this problem is prone to fail. This is why in most cases when SPC comes into play, it is applied to monomers that carry flexible chains of some sort. These chains help for enthalpic and entropic reasons to keep the growing (and final) polymer in solution and accessible to further growth, until growth reaches its system intrinsic limits.<sup>[28]</sup> These limits are comprised of termination through reduction of the bromo group, or phosphorus incorporation through ligand scrambling channels (*vide infra*), or removal of catalytically active Pd complexes through precipitation of Pd(0) intermediates as Pd-black, and so on.

The substituents on the poly(arylene)s are not only important for solubility (and processibility) reasons. They can also be used to incorporate function, a feature that has been increasingly and astoundingly successfully utilized in recent years. As far as the electronic properties of the backbones are concerned, substituents may, however, be disadvantageous, too. They normally lead to an increase of the dihedral angle of consecutive

aromatic units, which reduces electronic conjugation and thus further increases the polymers' already quite large HOMO/LUMO gap.

As for SCC, SPC involves only the carbon atoms, which carry the functional groups. Polymerizations proceed regiospecifically. This is important because some of the properties of poly(arylene)s depend on their backbone's ability to attain straight conformations without kinks. Also, the functional group compatibility of SPC is the same as for SCC. Aldehydes, nitro and cyano groups, sulfonic esters, ethers, various protected alcohols and amines, amides, and so on., can be present. Even free hydroxy and free amines have been reported, though they do not seem to work too well. The reaction conditions are like the ones Suzuki and co-workers reported in the original paper of 1981 (See **Sect. III.2.2**).<sup>[30]</sup> Other solvent systems were also applied whenever required by the solubility of the polymer. For example, SPC has even been done in water using both water-soluble monomers and catalyst precursors.<sup>[31]</sup> The mechanism of SPC is supposed to involve the same steps of oxidative addition, transmetallation, and reductive elimination as for SCC. The standard catalyst precursor is  $\text{Pd}(\text{PPh}_3)_4$ . Though SPC has not yet been developed to a reaction that is catalytical in an industrial sense, 0.5 mol % of Pd complex is sufficient in many cases. Pd complexes with other phosphine ligands have also been employed. For example, *ortho*- and *para*-tolyl ligands proved successful.<sup>[22],[24]</sup> Though the choice of the best catalyst precursor is still a matter of intuition, it is accepted that the complex used should be as pure as possible. Thus, the commercially available  $\text{Pd}(\text{PPh}_3)_4$  should not be used as obtained but rather should be recrystallized and used directly thereafter (under nitrogen). Best results are normally obtained when the Pd complexes are self-prepared and used fresh. Even if kept in a Teflon-sealed tube in a high-quality glove box (<1 ppm oxygen), aging cannot be prevented, which inevitably leads to a reduction of molar mass after a few days of storage.

#### B.ii. Types of Polymers Prepared and Some of Their Application Aspects

Since the discovery of SPC in 1988 (first published in 1989)<sup>[32]</sup> approximately 70 structurally different polymers with conjugated, fully or partially aromatic backbones were prepared. From an inspection of the overview provided in **Chart I** one can see that the vast majority of these polymers are PPPs, which just differ in their substitution pattern. Whenever possible, the structures were drawn so that the mode of synthesis can be extracted: only one aromatic in the repeat unit (r.u.) indicates an AB-type approach, whereas two indicate an AA/BB-type one. In the latter case the left aromatic of the r.u. stems from a diboronic acid or ester monomer, respectively, and the right one from a dibromide [or diiodide (**14**), di(trifluoromethylsulfonate) (**23**)]. For some of the more complex systems, like **37** or **56–58**, this rule cannot be applied and the literature needs to be consulted. Not all of the polymers shown were prepared in one step from monomers that already carry the final substitution pattern. Polymers **43–46**, for example, were obtained by chemical modification of PPP **13** and the double-stranded polymers **48–50**, **52**, **54**, and **55** from single-stranded SPC precursor polymers (*vide infra*). The polymers in **Chart I** are divided into the eight groups a–h according to their structural features, which correlate with certain properties in many but not all cases: (a) polymers with alkyl or alkoxy chains, (b) amphiphilic PPPs, (c) polyelectrolytes, (d) PPP precursors for ladder polymers, (e) polymers with main chain chirality, (f) dendronized PPPs, (g) poly(arylene vinylene)s and poly(arylene ethynylene)s, and (h) others. These classes will be discussed in the following, focusing on typical or successful representatives.

*Group (a) Polymers.* This class comprises polymers **1**,<sup>[32],[33]</sup> **2**,<sup>[34]</sup> **3**,<sup>[35]</sup> **4**,<sup>[36]</sup> **5**,<sup>[37]</sup> **6**,<sup>[38]</sup> **7**,<sup>[39],[40]</sup> **8**,<sup>[41]</sup> **9**,<sup>[42]</sup> **10**,<sup>[42]</sup> **11**,<sup>[42]</sup> **12**,<sup>[43]</sup> **13**,<sup>[43]</sup> **14**,<sup>[44]</sup> **15**,<sup>[44]</sup> **16**,<sup>[45]</sup> **17**,<sup>[45]</sup> **18**,<sup>[45]</sup> **19**,<sup>[46]</sup> **20**,<sup>[47]</sup> **21**,<sup>[48],[49]</sup> **22**,<sup>[50]</sup> **23**,<sup>[25]</sup> **24**,<sup>[25]</sup> and **25**.<sup>[25]</sup> Polymer **1** is an important representative of this class, although it did not gain much importance in materials science. Its successful synthesis in 1988 marks the birth of SPC. For the first time, a structurally defined, all-para linked, and processable PPP derivative of reasonable molar mass was available. This achievement initiated an enormous, worldwide effort into otherwise inaccessible, structurally defined representatives of this class of conjugated polymers. The result of this effort after a little more than ten years can be seen in **Chart I**. This amazing development was not only driven by synthetic chemists, for whom poly(arylene)s had been an embarrassing blank space on the list of “wanted” polymers, but also by physicists and material scientists. They stressed the point that the use of SPC polymers with their unprecedented structural integrity would enable one to more reliably correlate the measured properties of a polymer-based device with the polymer’s structure. The opportunity for a systematic and rational tailoring of suitable polymers for certain applications also came within reach for this kind of conjugated polymers.

Light-emitting polymers have received considerable attention in the last decade following the discovery of electroluminescence (EL) in conjugated polymers and the development of polymer-based light-emitting diodes (LEDs) for large area and flat display technologies.<sup>[51],[52]</sup> From the three primary colors, only red and green LEDs showed sufficient efficiencies and lifetimes for commercial use. Thus, there was a strong need for blue-emitting polymers with high photoluminescence (PL) efficiency to achieve full color polymer emissive displays. This is the point where PPPs come into play. They have a relatively large HOMO/LUMO gap, which should give rise to a blue emission. Leising and co-workers were able to show this for the parent material.<sup>[53]</sup> The development of a commercializable polymer-based LED is a complex enterprise and many variables have to be considered and adjusted. A couple of **Chart I** PPPs have been investigated under this aspect. Polymer **21**( $x = 0$ )<sup>[49]</sup> seems to have won the race. Dow Chemical Corp. has announced the development of a blue-emitting LED based on this polymer and stated its imminent commercialization. Polymer **21** has just the right emission in the deep blue at  $\lambda = 465\text{--}470$  nm, which cannot easily be reached by PPPs without partially planarized benzene rings. It has the additional advantage that it can easily be modified by copolymerization to give, for example, **21** ( $x = 1$ )<sup>[48]</sup> for which, besides the right color, relatively high PL and EL efficiencies were demonstrated. The optoelectronic properties of polymers **24** and **25** for their use in multilayer LEDs were also investigated.<sup>[25]</sup> The interested reader is referred to the literature for details.<sup>[51],[52]</sup>

A long-standing problem of surface sciences, the interaction of organic compounds with metal surfaces, was addressed with polymers **12** and **13**.<sup>[43]</sup> As observed earlier for a rigid-rod poly(imide)s with terphenylene units (polymer **70**)<sup>[54],[55]</sup>, these polymers adsorb onto gold surfaces in ultrathin layers (15–25 Å) from solution. On copper, the thickness of these layers depends on the presence or absence of oxidizing agents. Thicknesses on copper of up to 900 Å were found. The metal surfaces can be completely hydrophobized by these layers, as is indicated by contact angles of approximately 90°. Upon addition of alkylthiols, the adsorbed polymers on gold are pushed aside and a nonhomogeneous mixture of domains of ordered, chemisorbed alkylthiols and thicker polymer layers are formed. Finally, polymers **14** and **15**<sup>[44]</sup> gained some importance as one-dimensional matrices with (protected) hydroxy anchor groups (one-dimensional matrices) to which other large substituents like dendrons can be attached.

(a)

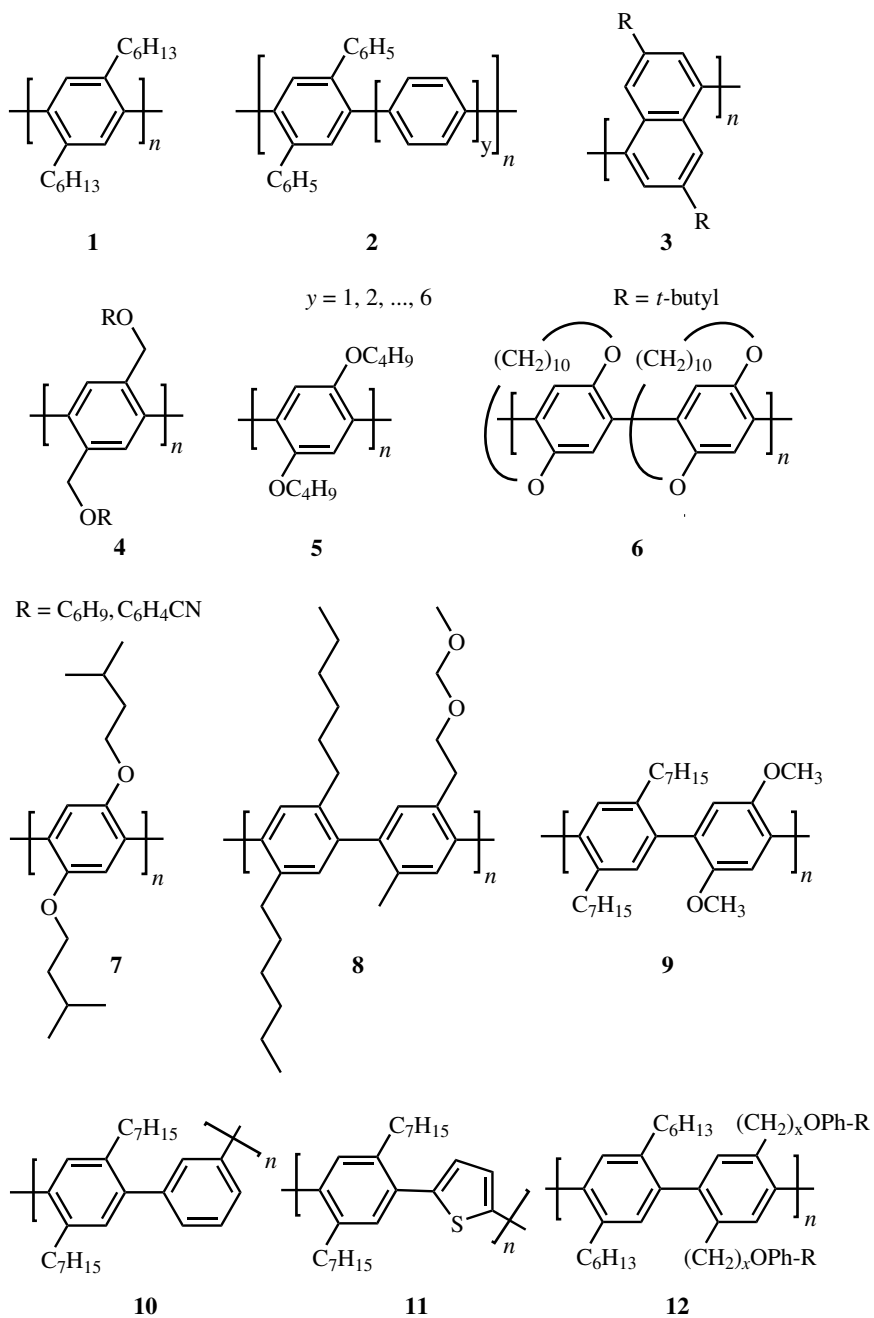


Chart Ia (Continued)

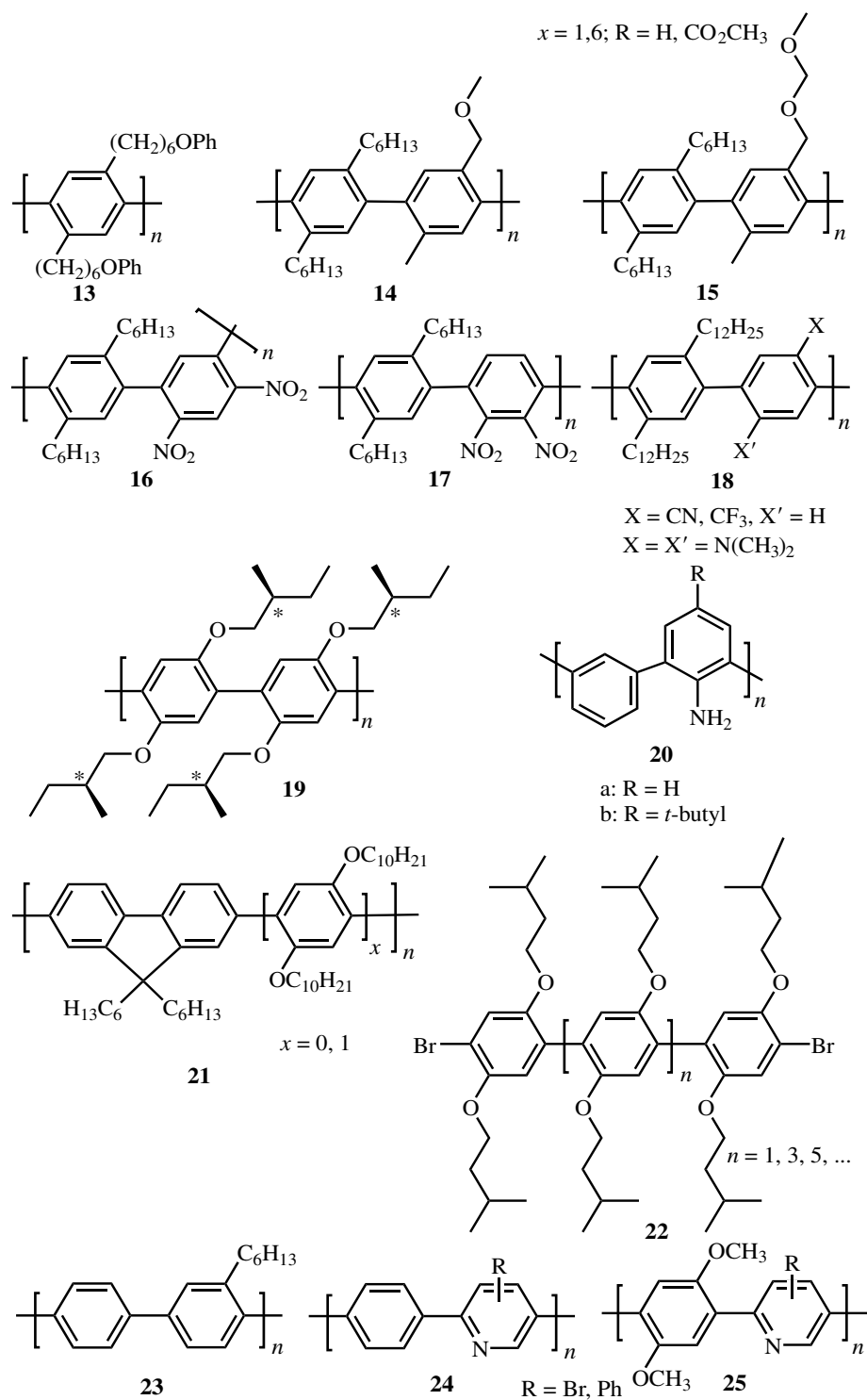


Chart Ia



*Group (b) Polymers.* All polymers of this section, **26**,<sup>[56],[57]</sup> **27–33**,<sup>[58]</sup> **34**,<sup>[59]</sup> **35**,<sup>[59]</sup> and **36**,<sup>[60]</sup> carry oligoethyleneoxide (OEO) chains, which were incorporated to mediate some compatibility of the unpolar PPP backbone and polar media like salts or water. Research is directed toward either the potential application of PPPs as separators in rechargeable solid-state lithium cells (**26**)<sup>[56],[57]</sup> or the study of the aggregation behavior of these structurally novel rigid-rod amphiphiles in colloidal solutions or on surfaces (**27–36**).<sup>[58]–[60]</sup> For **26** a structural model was also developed according to which the rods are ordered in layered structures separated by a matrix of the side chains. This matrix can be systematically swollen by blending with Li salts, which are preferentially incorporated into this matrix. Initial investigations into the aggregation behavior of polymers **27–33** show that they form reversible aggregates in tetrahydrofuran solution.

(b)

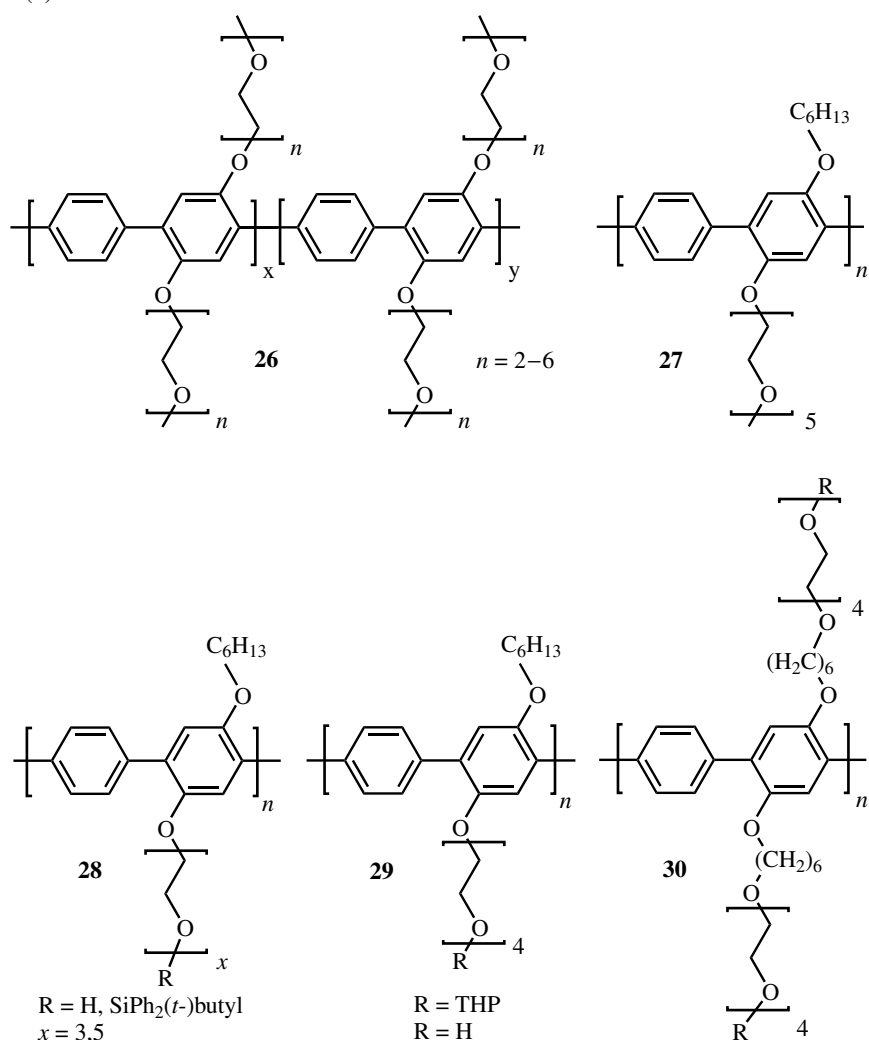


Chart I b (Continued)

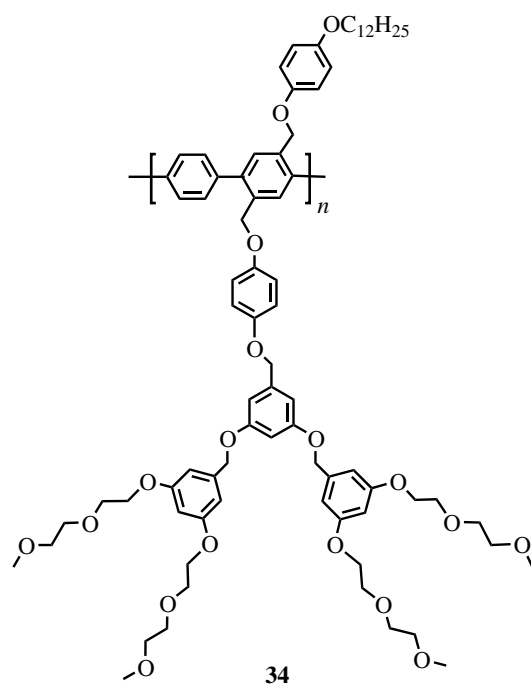
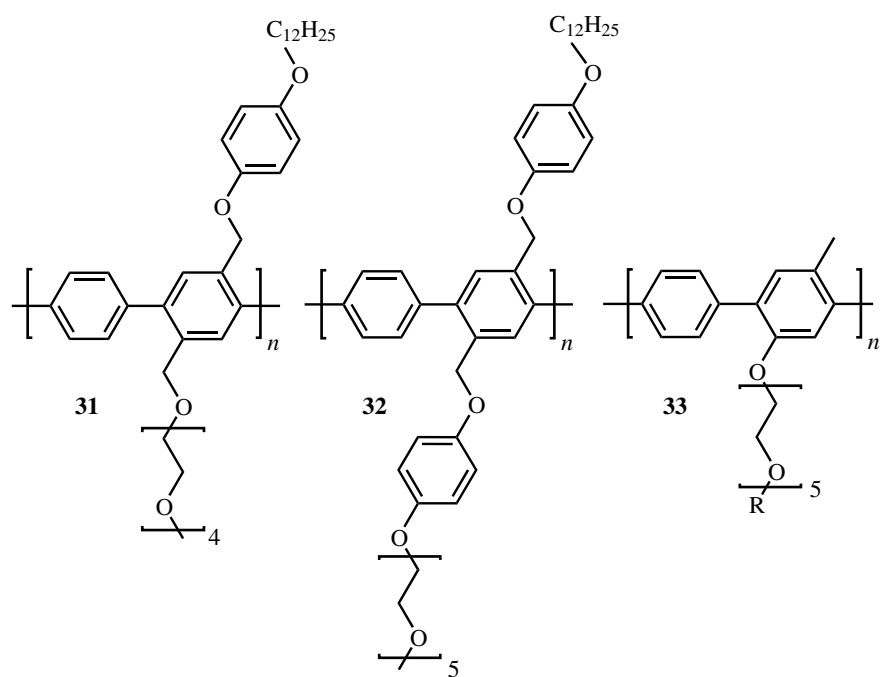


Chart 1b

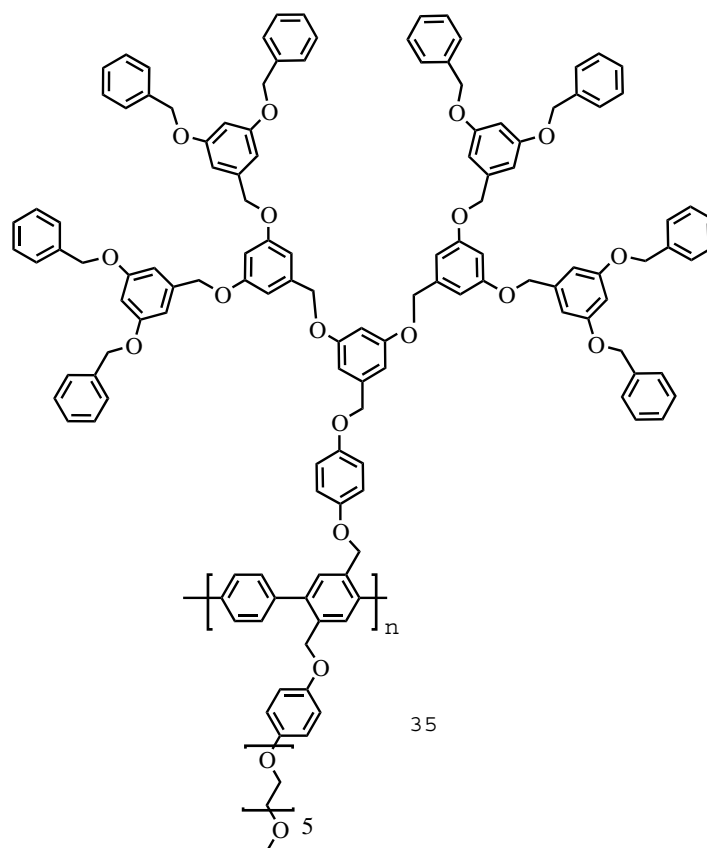
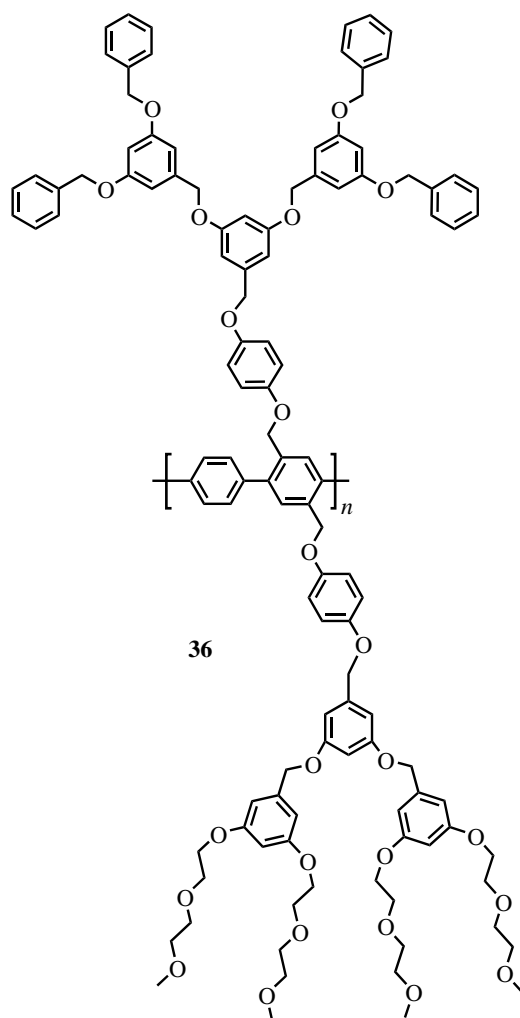


Chart 1b (Continued)

Amphiphile **36** forms transferrable Langmuir monolayers at the air/water interface with the backbones arranged parallel to the surface and the EOE chains dipping into the water phase. This finding was interpreted as evidence for the unusual ability of amphiphilically equipped PPPs to segregate lengthwise (referring to the backbone) in polar and unpolar domains.<sup>[60]</sup>

*Group (c) Polymers.* PPP polyelectrolytes **37**,<sup>[31]</sup> **38**,<sup>[61]–[63]</sup> **39**,<sup>[64]–[66]</sup> **40**,<sup>[67]</sup> **41**,<sup>[68]</sup> **42**,<sup>[69],[70]</sup> **43**,<sup>[71]</sup> **44**,<sup>[71]</sup> **45**,<sup>[71]</sup> and **46**,<sup>[71],[72]</sup> were prepared mainly for three reasons. First to show that SPC can be run in water, which broadens the applicability of this method considerably; second to construct blue-emitting EL devices utilizing the supramolecular ordering effects of charged macromolecules; and third, to investigate the formation of hierarchical structures in both solution and solid state. Wallow and Novak did the decisive experiment to prove the compatibility of SPC with an entirely aqueous medium.<sup>[31]</sup> The usage of dibromobiphenyl monomer bearing two carboxylic acid functions and a water-soluble Pd catalyst precursor with monosulfonated triphenylphosphine ligands together with a biphenyl bisboronic acid ester gave indeed polymer **37**,<sup>[31]</sup> which, because of its decoration with the two acid functions, turned out to be soluble in dilute aqueous base. Similar to some of the group 1 polymers, PPPs **38**,<sup>[60]–[63]</sup> **41**,<sup>[68]</sup> and **42**,<sup>[69],[70]</sup> were

**Chart 1b**

investigated for their EL behavior. EL devices were prepared by spin-coating a solution of saponificated **38** onto an indium–tin oxide (ITO)-covered glass substrate. ITO and aluminum were used as hole-injecting and electron-injecting electrodes, respectively. Intensive blue EL emission could be observed already at about 4 V if sodium counterions were used. Unfortunately, the lifetimes of the devices under operation were between 12 and 24 h, which is significantly too short for any commercial application. Blue emissions were also observed for polymers **41**<sup>[68]</sup> and **42**.<sup>[69],[70]</sup> LEDs constructed with them by both layer-by-layer electrostatic deposition and hybrid ink jet printing methods also showed some decline of initial properties.

For saponificated polymer **39**<sup>[66]</sup> a model was developed to describe how rigid-rod polyelectrolytes aggregate in water. An analysis of the small-angle X-ray patterns of aqueous solutions of the fully anionic **39** reveals the formation of cylindrical micelles with a diameter of  $d = 3.1$  nm and a radial aggregation number of 11 independent of

(c)

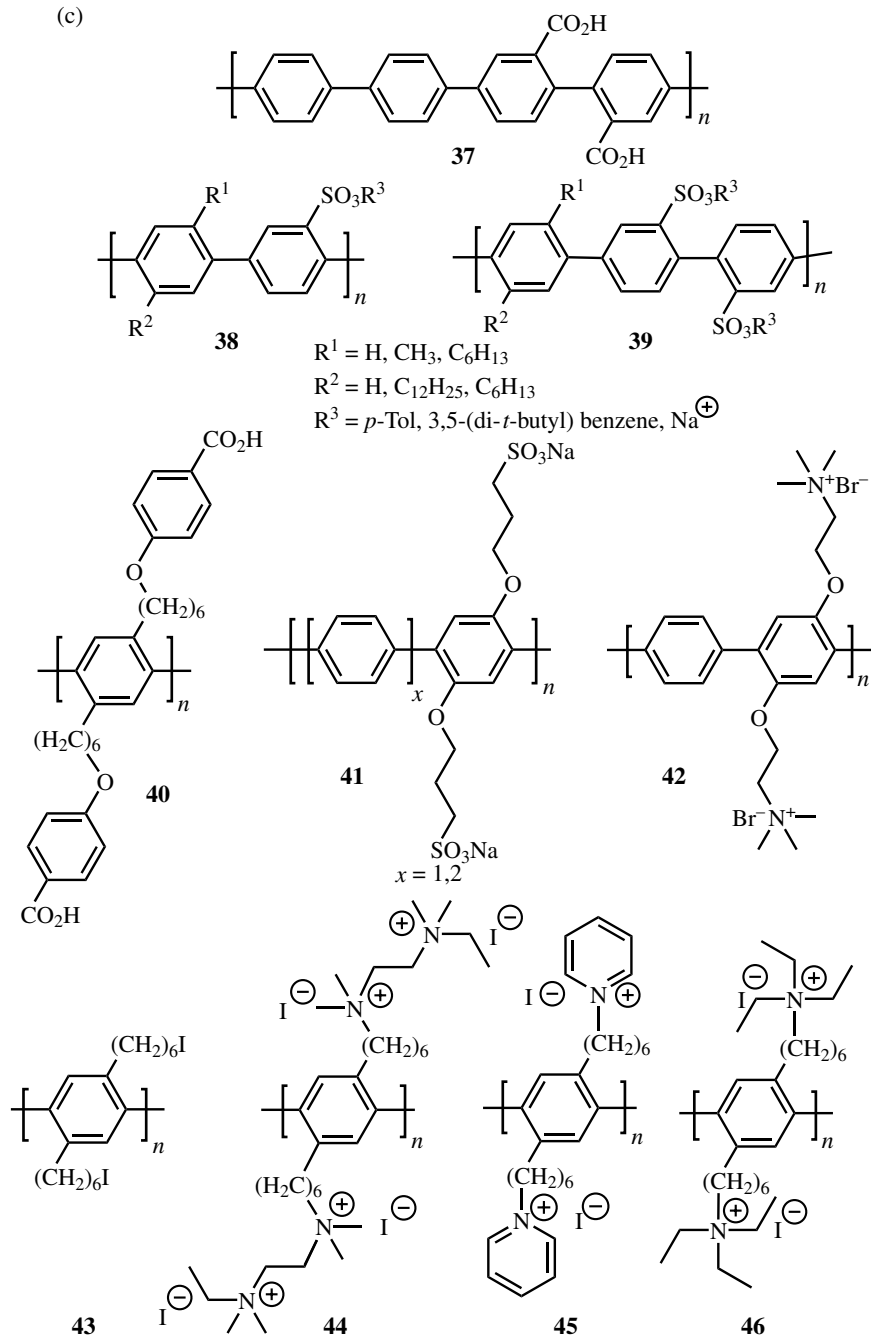


Chart I c (Continued)

concentration. In these micelles, all PPP backbones lie parallel to one another on the surface of a cylinder with the sulfonate groups pointing outward and the unpolar dodecyl chains inward. In salt-free solutions these micelles do not deaggregate into single polymer molecules even at concentrations as low as  $c = 0.001$  g/L. From static and dynamic light scattering it was concluded that above a critical concentration the micelles form lyotropic objects, which consist of approximately 130 micelles and are oblate spheroids with dimensions of 400 and 600 nm. Cylindrical aggregates in solution were also found for polymer **46**, which in the solid-state aggregates in columnar mesomorphous structures. Polymer **43**,<sup>[71]</sup> though not a polyelectrolyte, is mentioned here, because it is an important intermediate on the way from **13** to PPPs **44–46**.<sup>[69]</sup> Polymer **44** is exceptional as it carries four charges at every r.u.

*Group (d) Polymers.* Ladder polymers have been of long-standing interest for their thermal, electrical, and optical properties.<sup>[73],[74]</sup> One of two basically possible routes into this class of polymers starts from a single-stranded polymer, which is designed to allow a second independent strand to be made by some subsequent chemical modification. Polymers **47**,<sup>[75]–[82]</sup> **51**,<sup>[83],[84]</sup> and **53**<sup>[85],[86]</sup> are examples for this. They carry functional groups with which ring closures between two consecutive benzene rings were achieved to give ladders **48**, **52**, and **54**, respectively. The conversions of these reactions can be driven to approximately 90–95%. Polymers **49**, **50**, and **55**<sup>[87]</sup> were obtained accordingly. Polymers **48** and **49**<sup>[88]</sup> have excellent EL characteristics but have not yet reached the level adequate for technical production.

*Group (e) and (f) Polymers.* Development of enantioselective polymer-based catalysts is important in the efficient production of optically pure, chiral organic compounds including drug molecules. The major advantage of polymer-based catalysts is the ease of recovery and their reuseability. Applications in flow reactors may also be feasible. Polymers **56–58**<sup>[89]–[96]</sup> are good examples here. Complexed with  $\text{AlMe}_3$  or  $\text{Me}_2\text{AlCl}$ , they were used to catalyze hetero-Diels–Alder reactions in a highly enantioselective manner. Dendronized polymers, which are polymers with dendritic side chains, have gained some importance in research directed toward molecular objects on the nanometer scale. For polymers like **59**<sup>[97],[98]</sup> and **60**<sup>[20],[99]</sup> it was proved that, because of the enormous steric congestion at each repeat unit, they are exceptionally rigid and attain a cylindrical shape in solution and when adsorbed on surfaces. This matter has been treated comprehensively in the literature.<sup>[100]</sup> From a synthetic point of view, polymer **60** is rather amazing. It was obtained in high yield and very high molar mass, which proves that SPC proceeds with conversions above 98% even in cases where monomers are sterically enormously loaded. The complex mechanistic cycle of SPC does not seem to be influenced by this detrimentally.

*Group (g) Polymers.* Though poly(arylene vinylene)s and poly(arylene ethynylene)s are normally prepared by other reactions (see below), SPC has also been applied to a few representatives of these classes of polymers. Besides polymers **61–63**,<sup>[39],[101]</sup> the already mentioned polymer **57** also formally belongs to this group. Polymer **62** was used to compare some of its EL and PL characteristics with those of the formally identical polymer prepared by Heck polycondensation (Sect. C). Differences were actually observed and attributed to some defective connections occurring during the Heck procedure.

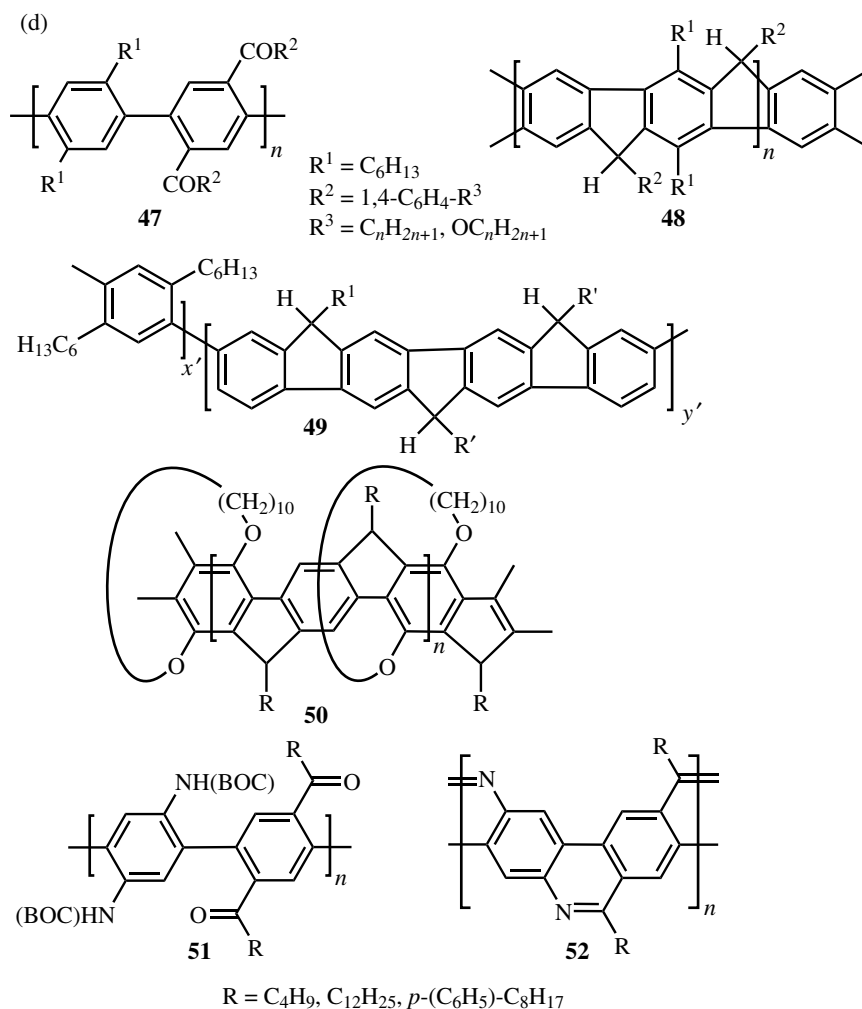


Chart I d (Continued)

*Group (h) Polymers.* Most polymers of this group did not gain importance as materials for an application but should be noted for synthetic considerations. Polymers **64–66**<sup>[102]</sup> show that SPC can be applied to monomers containing functional groups between two aromatic units. The dendritic macromolecule **67**<sup>[103],[104]</sup> proves that besides the conventional bifunctional SPC monomers the trifunctional 3,5-dibromo benzenboronic acid can also be employed. Whereas unprotected pyrrole cannot be subjected to SPC, the *tert*-butoxycarbonyl-protected pyrrole can. The corresponding 2,5-dibromopyrrole derivative together with 2,5-didodecylbenzene bisboronic acid furnishes polymer **68**<sup>[105]</sup> whose thermal treatment gives the polyarylene copolymer **69** with one or three pyrrolic units per r.u., which otherwise is not accessible. Polymer **70**<sup>[54],[55]</sup> is a novel rigid-rod type poly-imid, polymer **71**<sup>[106]</sup> can be used for retro-Diels–Alder chemistry to access unusual poly(arylene ethynylene)s, and, finally, the reduction of polymer **72**<sup>[107]</sup> yields the radical anion **73**, which was investigated as a model for one-dimensional polaronic ferromagnetism.

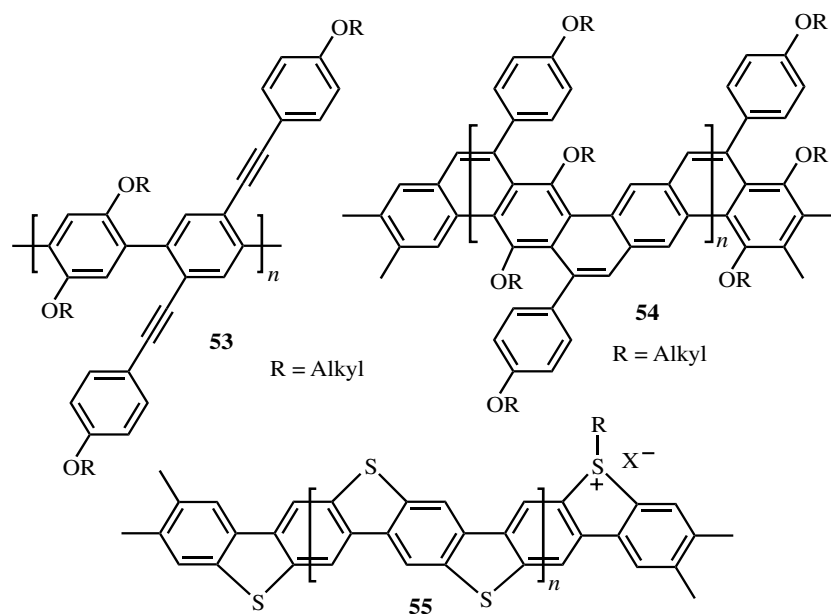


Chart I d

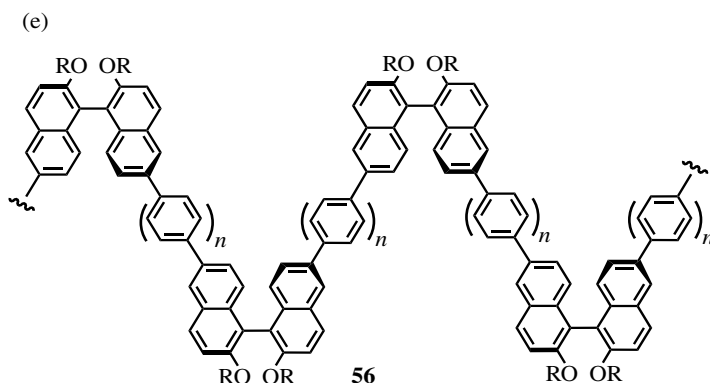
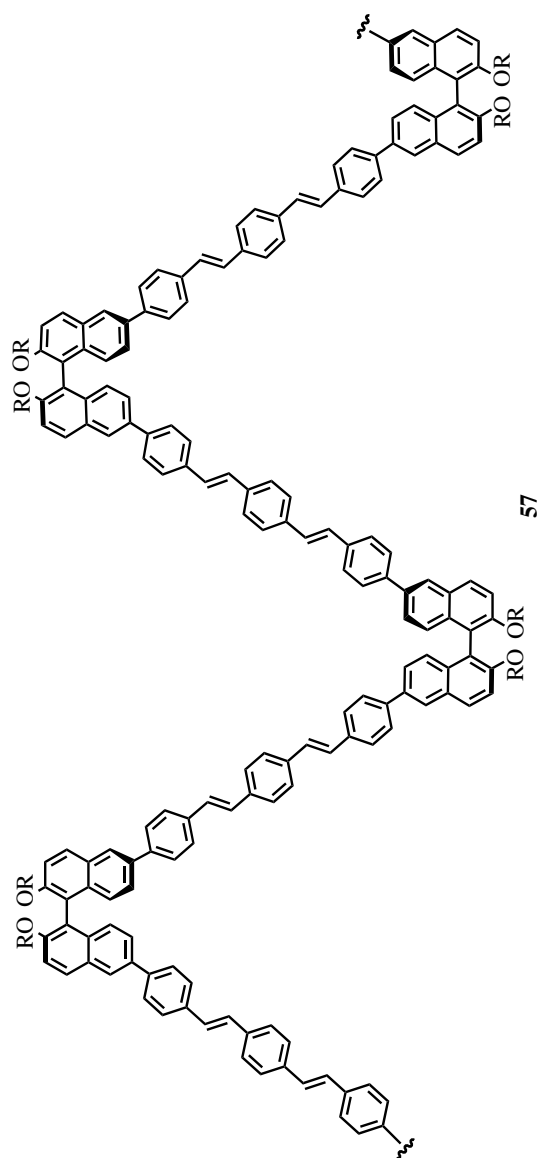


Chart I e

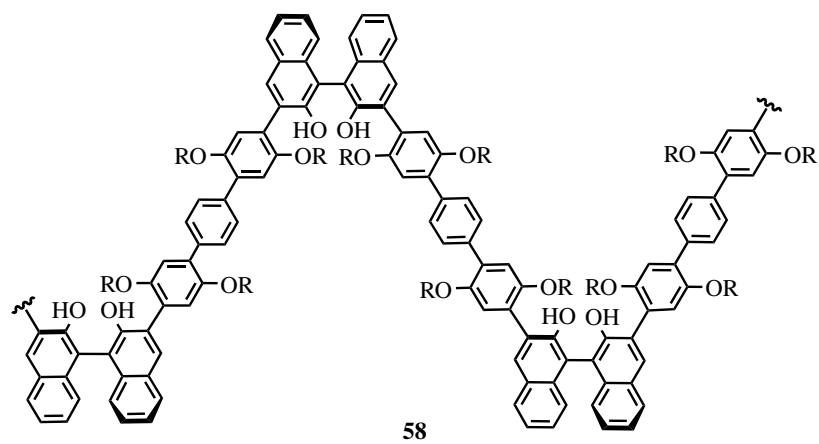
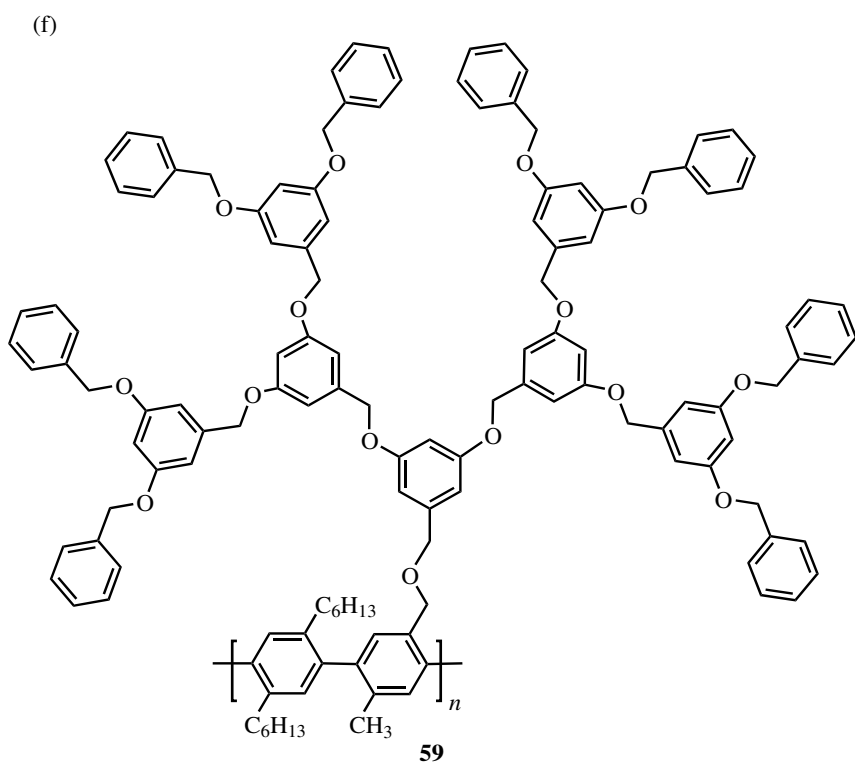
### B.iii. Molecular Weight Determinations, Degrees of Polymerization, Mechanistic Considerations, and Diiodo Versus Dibromo Monomers

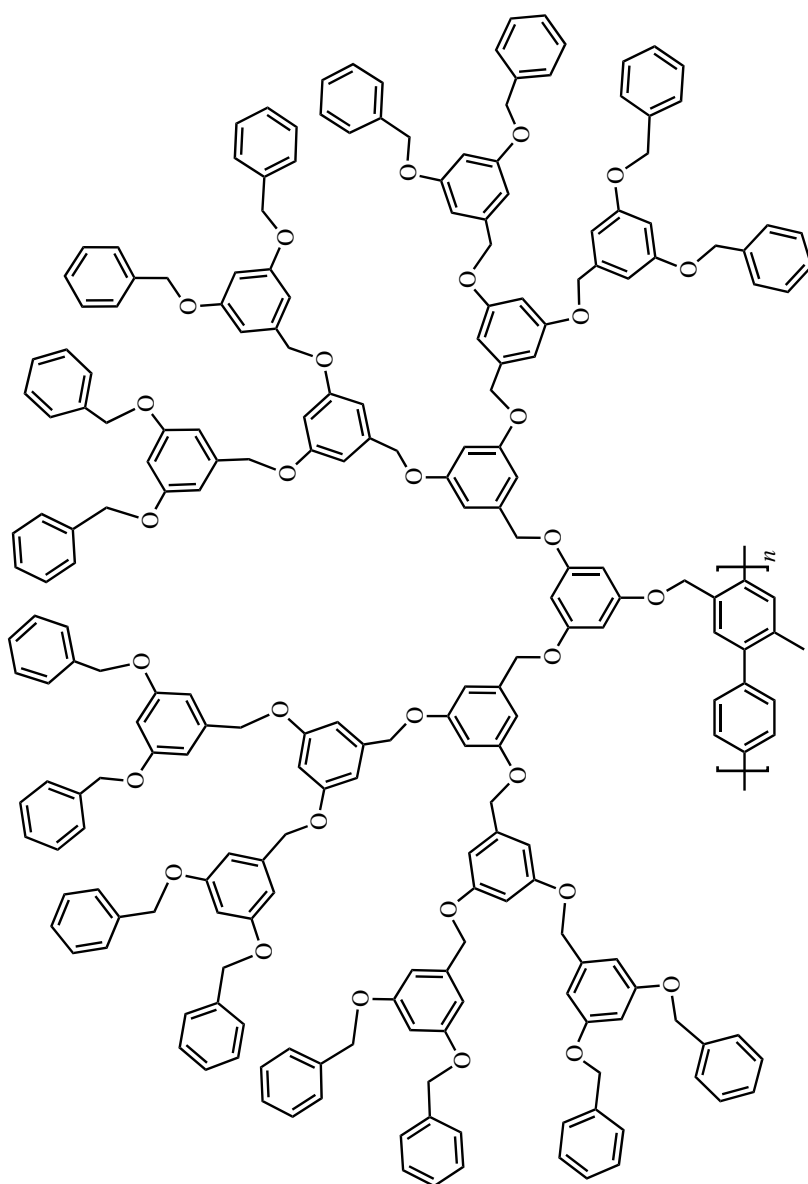
PPPs, polyarylenes in general, and other fully conjugated polymers like poly(arylene vinylene)s and poly(arylene ethynylene)s are considered as rigidrods. Rod-type macromolecules have, for a given molar mass, a larger hydrodynamic volume than flexible ones. In practically all cases the molar masses and distributions of rigid-rod polymers are determined by gel permeation chromatography (GPC), a method that separates according to hydrodynamic volume. Narrow samples of different molar mass PS are used for the calibration. A GPC molar mass of a PPP derivative of 20,000 means nothing more than that this sample has the same hydrodynamic volume as a sample of PS with the actual molar mass of 20,000. With the above argument, the actual molar mass of the PPP will be





**Chart 1e (Continued)**

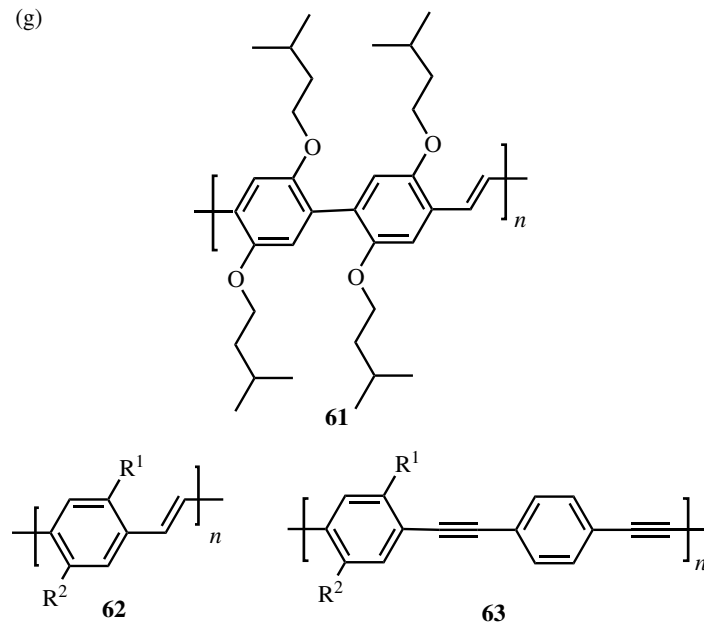
**Chart I e** (Continued)**Chart I f**



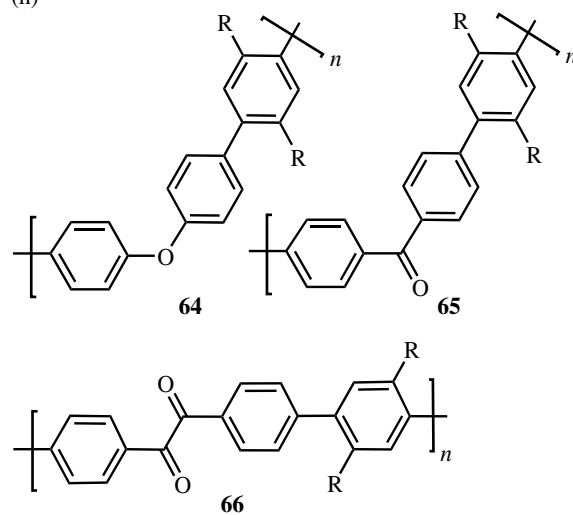
60

Chart If (Continued)

(g)

 $R^1 = R^2 = 2\text{-ethylhexyloxy}$  $R^1 = R^2 = \text{methoxy}$  $R^1 = \text{phenyl}, R^2 = \text{H}$ **Chart I g**

(h)

**Chart I h**

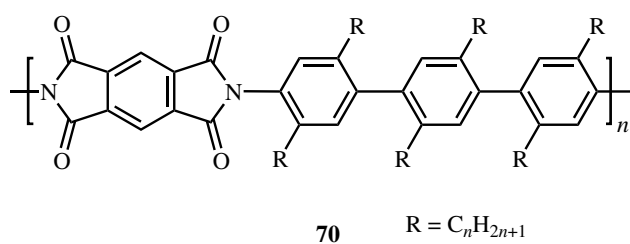
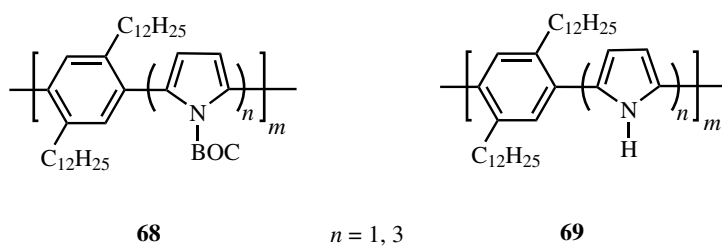
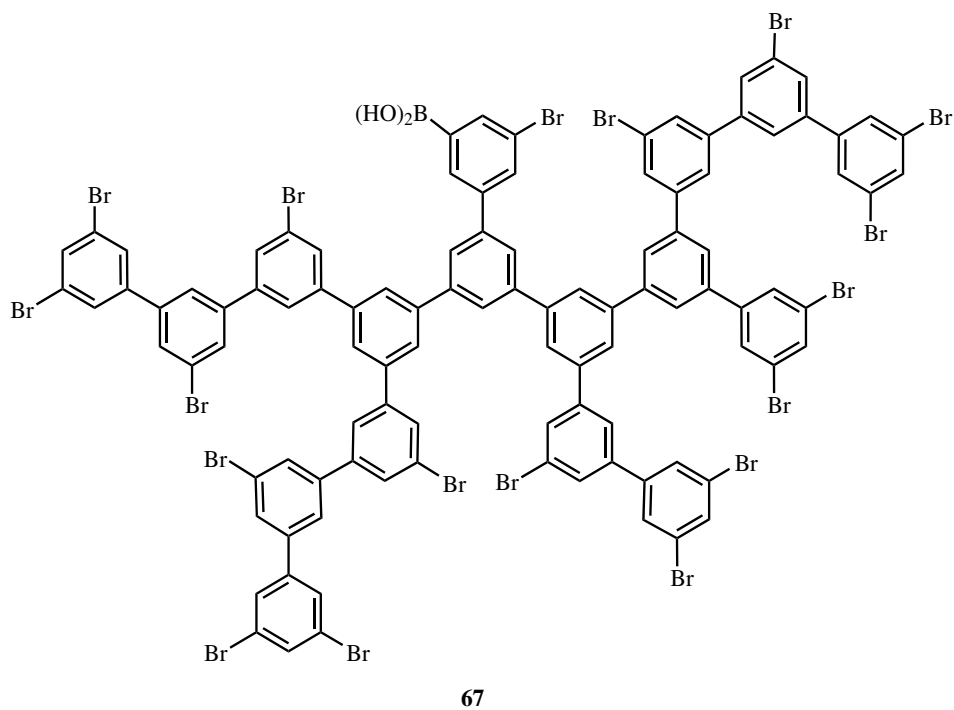


Chart I h (Continued)

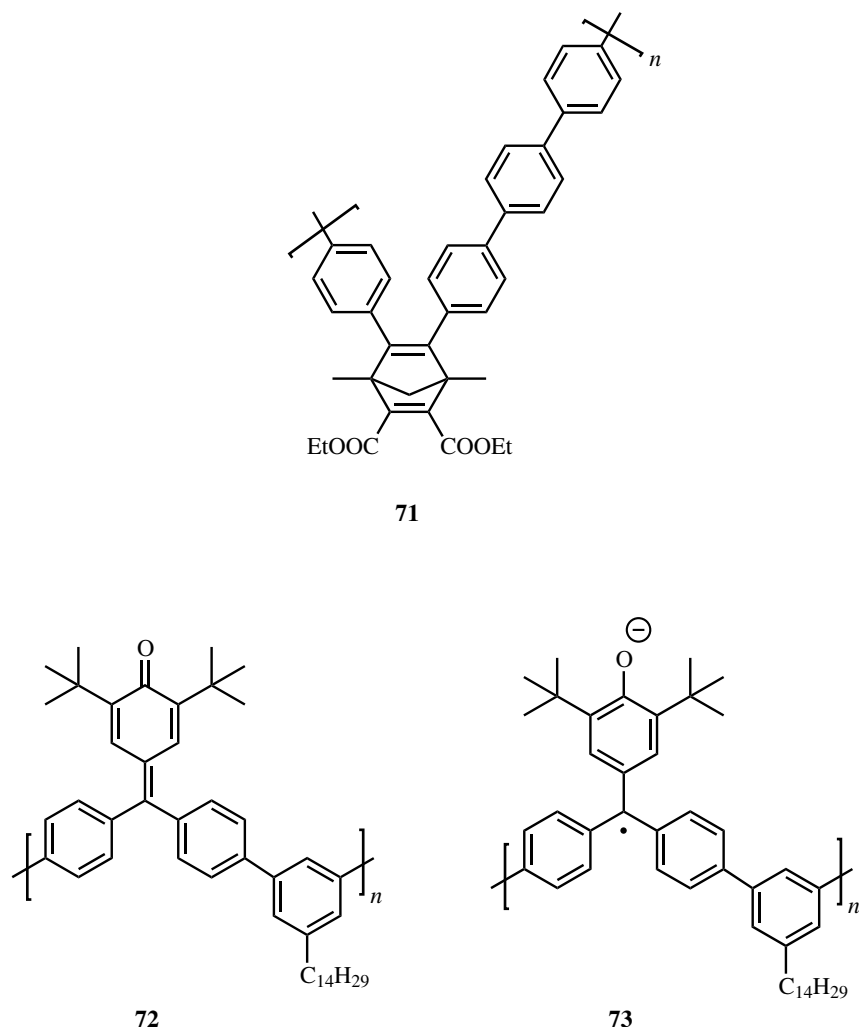
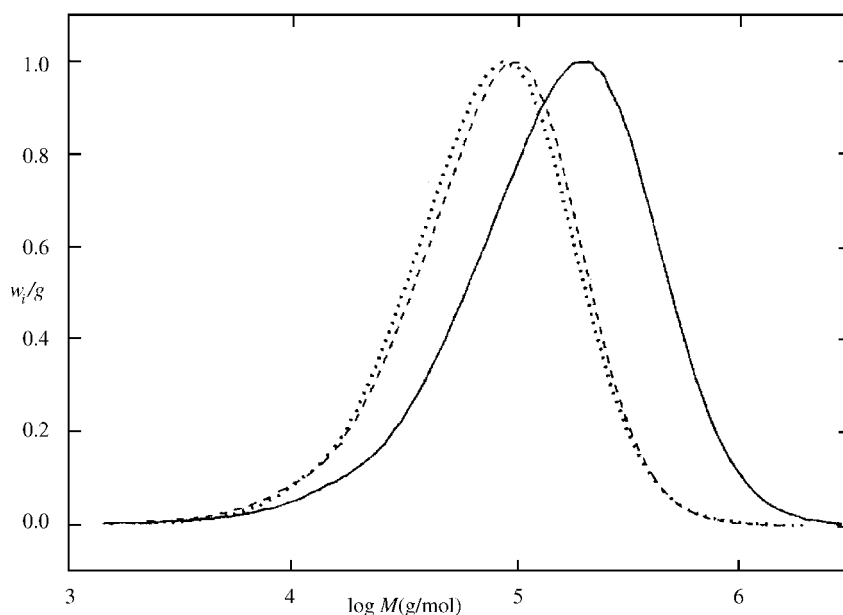


Chart 1h

lower. The number 20,000 is just an upper limit. With this in mind, all publicized GPC molecular weights of the PPP derivatives presented here should be considered with care.

Fortunately, there is a thorough study available in which the actual molar mass of PPP **39** ( $R^1 = \text{methyl}$ ,  $R^2 = \text{dodecyl}$ , and  $R^3 = 3,5\text{-di-}i\text{-tert-butylphenyl}$ ) was determined by light scattering, osmometry, and size exclusion chromatography using universal calibration and compared with the masses obtained from PS calibration.<sup>[64]</sup> The universal calibration was done on the basis of the Mark–Houwink–Sakurada equation using nine fractions of **39** with molar masses ranging between  $27 < M_w < 189 \text{ kg/mol}$ . A calibration based on the worm-like chain model gave very similar results. As can be seen from **Figure 2**, both these calibrations lead to almost superimposable elution curves at much lower molar mass than PS. A quantification of this difference reveals that PS overestimates the real molar mass of PPP **39** by a factor of almost 2. Although substituents certainly have an effect on the stiffness and thus the hydrodynamic volume of a polymer

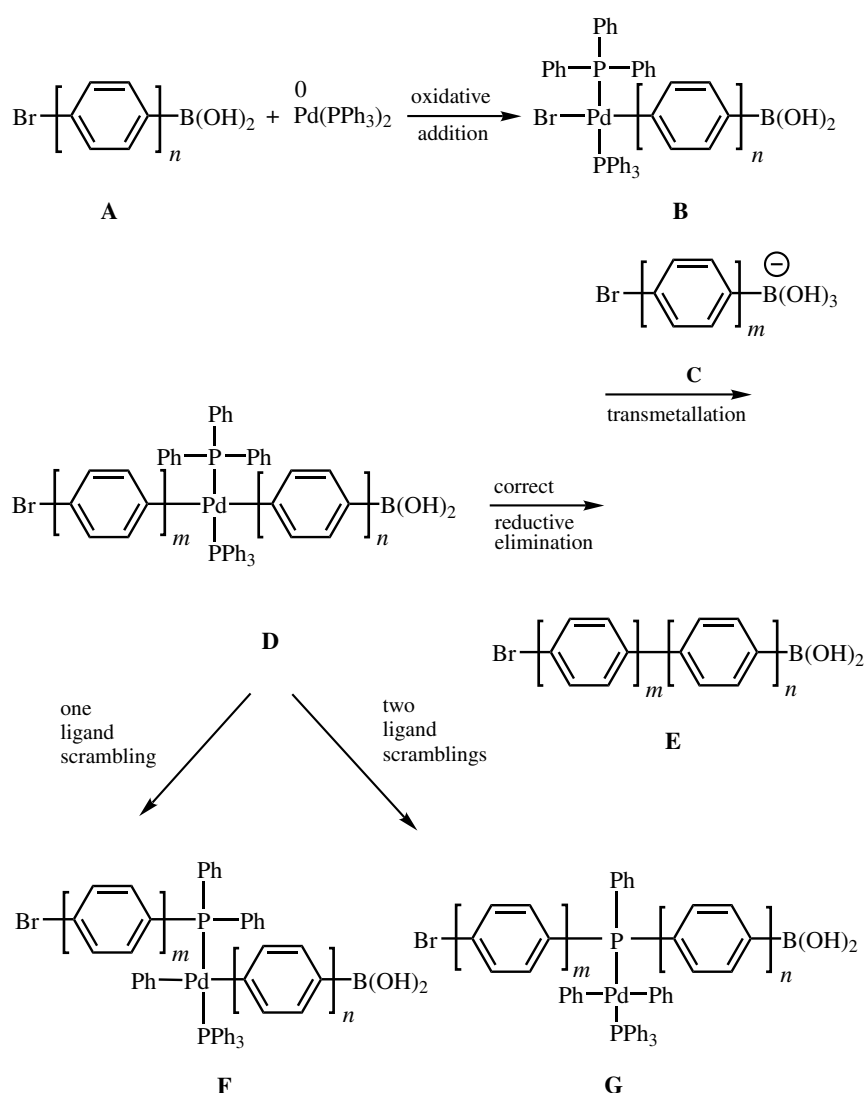


**Figure 2.** GPC elugram of polymer 39 ( $H M_w = 113$  kg/mol) in THF: PS calibration (solid line); universal calibration based on the Mark–Houwink–Sakurada equation (dashed line) and on the work-like chain model (dotted line).

chain, it is reasonable to assume that this effect will normally be small. As a rule of thumb, GPC molar masses of PPP derivatives should, therefore, generally be corrected by this factor of 2 to lower values in order to have a more realistic estimate of the actual molar mass. For very large substituents like in the dendronized polymers **59** and **60**, an additional aspect comes into play. If a given polymer's mass per unit length is much larger than a PS's mass it can happen that GPC calibrated with PS underestimates the real molar mass. In the case of polymers like **59** and **60**, the factors of underestimation can reach 1.5–4 as was proved by light and small angle neutron scattering investigations.<sup>[108]</sup> It should be noted that this underestimation by GPC is the clear exception to the rule.

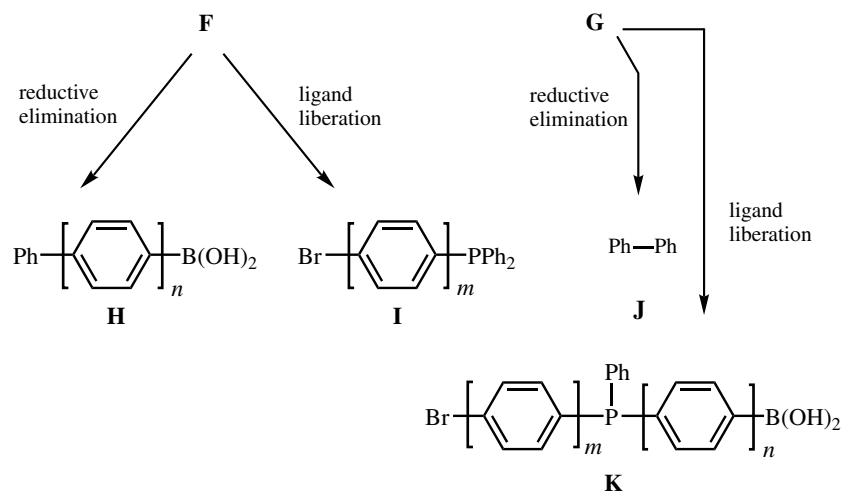
The reported degrees of polymerization (DP) for polymers **1–73** mostly rest on GPC data referenced to PS. They vary greatly. Applying the above-mentioned rule of thumb (factor 2), an average DP for SPC polymers lies in the range 30–60. Unfortunately, in many cases not even qualitative information is given on the monomer's purity and how the catalyst precursors were treated. This range represents, therefore, a lower threshold for the intrinsically achievable DP. Two of a few available, quite different examples may suffice to prove the much greater potential of SPC for high molar mass polymers. The molar masses of polymers **39**<sup>[64]</sup> and **59**<sup>[98]</sup> were determined by state-of-the-art methods and their DP values were found to be 107 and 110, respectively. According to Carother's equation, such numbers translate into conversions per C—C bond-formation step of over 99%. Thus, if properly applied, SPC can in fact compete with the best step-growth polymerizations known. It should be mentioned at this point that since such very high molar masses were not needed for many of the reported SPC polymers, a special synthetic effort was not required. As far as optoelectronic properties are concerned, for example, typical polymer characteristics have already been obtained for quite short chains.

The mechanism of SPC is believed to basically follow the one developed for SCC. There is, however, an additional aspect that only comes into play if bifunctional compounds are subjected to SCC, as it is in the case for SPC. A few years ago, reports appeared in the literature that shed light on potential side reactions of SCC, an aryl-aryl exchange between aryls at a Pd center and the phosphorus of the ligand.<sup>[109]</sup> Consequently, aryl boronic acids (and related compounds) were found to couple not only with the aryl halide provided but also with aryls of the phosphine ligand. In low molar mass chemistry this scrambling is disadvantageous but may be still acceptable as long as the yields of side products are not too high and they can be separated off. In SPC, however, aryl-aryl scrambling would be devastating. Novak pointed out that phosphorus-containing groups could be incorporated not only as terminators, but also as integral parts of the backbone. **Scheme 2**,



Scheme 2





Scheme 2 (Continued)

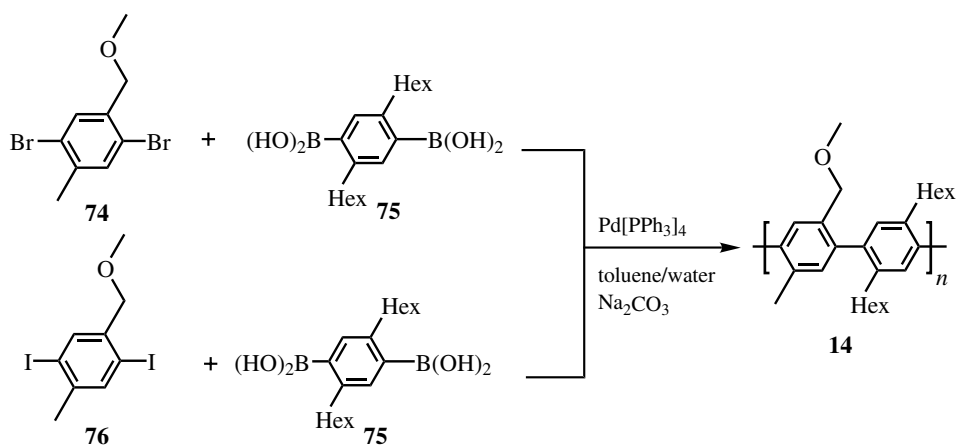
in which substituents are omitted for clarity, shows some of the possible pathways. Up to compound **D** everything is assumed to proceed the normal way. **D** now has the option to do what is required for SPC, which is to set **E** free by reductive elimination, or to undergo one or even two ligand scramblings to give **F** and **G**. These intermediates are now the source of side products, some of which contain phosphorus. Phosphorus acts in **I** as a terminus and in **K** as a kink and electronic insulator. In further steps networks may be formed with phosphorus as netpoints (not shown).<sup>[109]</sup>

Novak and co-workers, in fact, found NMR spectroscopical evidence for phosphorus in SPC polymers.<sup>[110]</sup> Since this would considerably decrease the value of this method for the synthesis of structurally perfect rod-like polymers, as was believed to be the case, this matter was thoroughly investigated using polymers **14** and **15**.<sup>[24]</sup> In several independent preparations using different catalyst precursors and reaction conditions, the extent of phosphorus incorporation was quantified. According to  $^{31}\text{P}$ NMR spectroscopical results using internal integration standards, one phosphorus atom is found on roughly every 400 r.u. It has, meanwhile, been accepted that this degree of incorporation of phosphorus in SPC polymers is negligible and need not be considered in all practical cases.

As mentioned earlier, chloroaromatics have not been employed in SPC so far, although the variety of dichloroaromatics is much broader than of dibromo or even diiodo ones. There are a few reports regarding SPC with diiodo monomers.<sup>[92],[94],[109],[111]</sup> Since SCC of iodoaromatics proceeds at a high rate under especially mild conditions, the potential for SPC for diiodo monomer **74** was investigated and directly compared with the otherwise identical dibromo monomer **76** (Scheme 3). The main focus was on the achievable molecular weight and the degree to which phosphorus is incorporated.<sup>[24]</sup> Scheme 3 shows the reactions performed and Table 1 the molar masses obtained (referenced to PS and a PPP standard<sup>[64]</sup>). The considerable increase in molar masses of polymer **14** prepared from **76** compared to **74** needs no further comment. Fortunately, this increase does not need to be paid for by an increased imperfection of the backbone by phosphorus incorporation. Roughly only every fourth chain contained one phosphorus atom, which is most likely located at the chain's terminus.

**Table 1. Molecular Weights of Polymer 14 Synthesized from Dibromo (74) and Diiodo Monomer (76)**

Entry	Monomer	$M_n$ ( $10^3$ g/mol)	$P_n$	$M_w$ ( $10^3$ g/mol)	$P_w$	PD <sup>a</sup>	Yield (%)
1	<b>74</b>	17.9 (13.2) <sup>c</sup>	47 (35)	53.0 (44.3)	140 (117)	3.0 (3.3)	99
2	<b>74</b>	18.3	49	56.8	150	3.1	96
3	<b>74<sup>b</sup></b>	28.0 (19.4)	74 (51)	91.5 (47.7)	242 (126)	3.3 (2.5)	99
4	<b>74<sup>b</sup></b>	31.3	83	100.0	264	3.2	96
5	<b>76</b>	49.7	131	152.0	402	3.1	99
6	<b>76</b>	53.9 (37.3)	143 (99)	167.7 (85.4)	444 (226)	3.1 (2.3)	99

<sup>a</sup>PD =  $M_w/M_n$ .<sup>b</sup>Pd[(*p*-tolyl)<sub>3</sub>]<sub>3</sub> was used as catalyst precursor.<sup>c</sup>Data in parentheses refer to a poly(*para*-phenylene) standard.**Scheme 3**

### C. POLYCONDENSATIONS USING HECK-, STILLE-, AND SONOGASHIRA/HAGIHARA-TYPE CROSS-COUPLING REACTIONS

#### C.i. Some General Remarks

The polycondensations described in this section use the Pd-mediated Heck, Stille, and Hagihara/Sonogashira cross-coupling reactions. Like SPC, they all involve C—C bond formation between unsaturated carbon atoms ( $sp^2$  or  $sp$  hybridized) and lead to conjugated polymers mostly of the poly(arylene vinylene) and poly(arylene ethynylene) type. In a few cases polyarylenes were also synthesized. Scheme 4 provides a general outline of these three reactions applied to polymer synthesis showing only AA- and BB-type monomers. AB-type monomers have also been used but less frequently. The circles represent aromatic units, which are mostly substituted benzenes but also pyridines and thiophenes, among others. The distannyl monomer's circle in (b) can also be a vinyl group. As mentioned for SPC, most monomers also carry flexible chains for solubility reasons. The mechanisms are proposed to be the same as for the cross-coupling of

$$\text{X}-\text{C} \begin{array}{c} \text{---} \end{array} \text{C}-\text{X} + \text{CH}_2=\text{CH}-\text{R} \longrightarrow \left[ \text{C} \begin{array}{c} \text{---} \end{array} \text{C}-\text{CH}=\text{CH}-\text{R} \right]_n$$

$$\text{X} = \text{I, Br, Cl, TfO}$$

$$\text{X}-\text{C} \begin{array}{c} \text{---} \end{array} \text{C}-\text{X} + \text{Me}_3\text{Sn}-\text{C} \begin{array}{c} \text{---} \end{array} \text{C}-\text{SnMe}_3$$

$\text{X} = \text{I, Br, OTf}$

$$\longrightarrow \left[ \text{C} \begin{array}{c} \text{---} \end{array} \text{C}-\text{C} \begin{array}{c} \text{---} \end{array} \text{C} \right]_n$$
$$\begin{array}{c} \text{X}-\text{C} \quad \text{C}-\text{X} \\ \text{X = I, Br} \end{array} + \text{HC}\equiv\text{C}-\text{[grey circle]}-\text{C}\equiv\text{CH}$$
  

$$\longrightarrow \left[ \text{C} \quad \text{C}-\text{C}\equiv\text{C}-\text{[grey circle]}-\text{C}\equiv\text{C} \right]_n$$

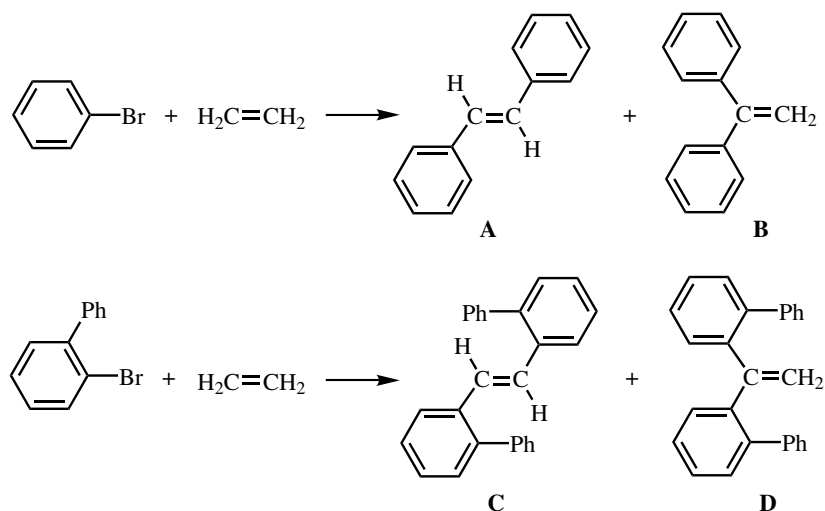
### Scheme 4

monofunctional compounds and the reader is therefore referred to the respective parts in this volume. One should, however, always keep in mind that side reactions in polymer synthesis either lead to termination or formation of structural defects in the backbone, which can neither be healed nor removed by purification as is the case in low molar mass organic chemistry. All three polymerizations are of the step-growth type and the comments made above for SPC in regard to achievable molar mass, required stoichiometric balance, monomer purity, and so on, therefore fully apply here as well.

There are side reactions occurring in Heck,<sup>[3]</sup> Stille,<sup>[4]</sup> and Hagihara/Sonogashira cross-coupling reactions.<sup>[5],[6]</sup> The most important ones for the present context are geminal instead of vicinal substitution (Heck), ligand scrambling and homocoupling (Stille), and oxidative acetylene coupling to diacetylenes (Hagihara/Sonogashira). Judged on the

wealth of available publicized material it is appropriate to say that side reactions, though also occurring in SPC, have a more detrimental effect on the polymerizations discussed here. Side reactions have been intensively investigated by Heitz and co-workers. In thorough and detailed studies mostly of Heck<sup>[112]</sup> but also of Hagihara/Sonogashira polycondensations,<sup>[113]</sup> they were traced and quantified using both model reactions and “real” polymerizations. Synthetic procedures on how to reduce as many of them as far as possible were also developed.

The problem with the geminal (leading to 1,1-disubstituted vinylidene groups) versus the vicinal substitution (leading to 1,2-disubstituted vinylidene groups), which is still an unsolved problem of Heck polycondensation, may be illustrated by the simple example in Scheme 5 in which bromobenzene and 2-phenyl bromobenzene are coupled with ethylene under otherwise identical conditions. For bromobenzene, products **A** (the vicinal one) and **B** (the geminal one) are obtained in the ratio **A/B** = 94:6. For 2-phenyl bromobenzene, the corresponding products are formed in the ratio **C/D** = 40:60. Thus, the substitution of bromobenzene with an *ortho*-phenyl group renders a 6% side reaction into a 60% main one. This example gives a taste of the delicacy of regiochemical structure control in Heck polycondensation and also shows that this side reaction cannot be totally suppressed.



Scheme 5

The poly(arylene vinylene)'s conjugated backbone makes these polymers interesting candidates for LED applications. For such applications it is essential that the conjugation along the backbone is not interrupted too often by electronically insulating defects, like geminally disubstituted vinylidene groups are. The degree to which these defects are generated during polymerization was investigated spectroscopically with NMR.<sup>[112]</sup>

The molar masses of the polymers prepared were only seldom investigated in detail. In a number of publications they are not given at all. From the scattered data available, termination during Heck and Stille polycondensations seems to be especially critical. Most degrees of polymerization (DP) reported range between 20 and 40. For Hagihara/Sonogashira polycondensations somewhat higher DP values can be expected. Most of the polymer

structures given in the following section should be considered idealized. Defects were normally neither identified nor quantified and their existence not even mentioned.

### C.iii. Selected Polymers

**Charts II, III, and IV** summarize some polymers prepared using Heck-, Stille-, and Hagihara/Sonogashira-type chemistry, respectively. Polymers **77**,<sup>[112]</sup> **78**,<sup>[112]</sup> **79**,<sup>[114]</sup> and **80**<sup>[115]</sup> are representative for Heck-type polymers. Polymer **77** is an interesting candidate because its degree of imperfection was determined and compared with that of the structurally identical polymer (**62**) prepared by SPC. The fraction of 1,1-disubstituted vinylidene units in **77** was found to be so high that its average conjugation length is lower than for the SPC analog **62**. Both the PL and EL spectra of the two polymers vary greatly. Polymer **78** is a beautiful example of how problems with insufficient structure control can be at least partially overcome. Though defects in **78** can still be seen by NMR spectroscopy, they have no detrimental effect on the conjugation length anymore. Polymer **79** is an example for a poly(arylene vinylene) with a defined head-tail sequence of the repeat units and polymer **80** represents a variety of

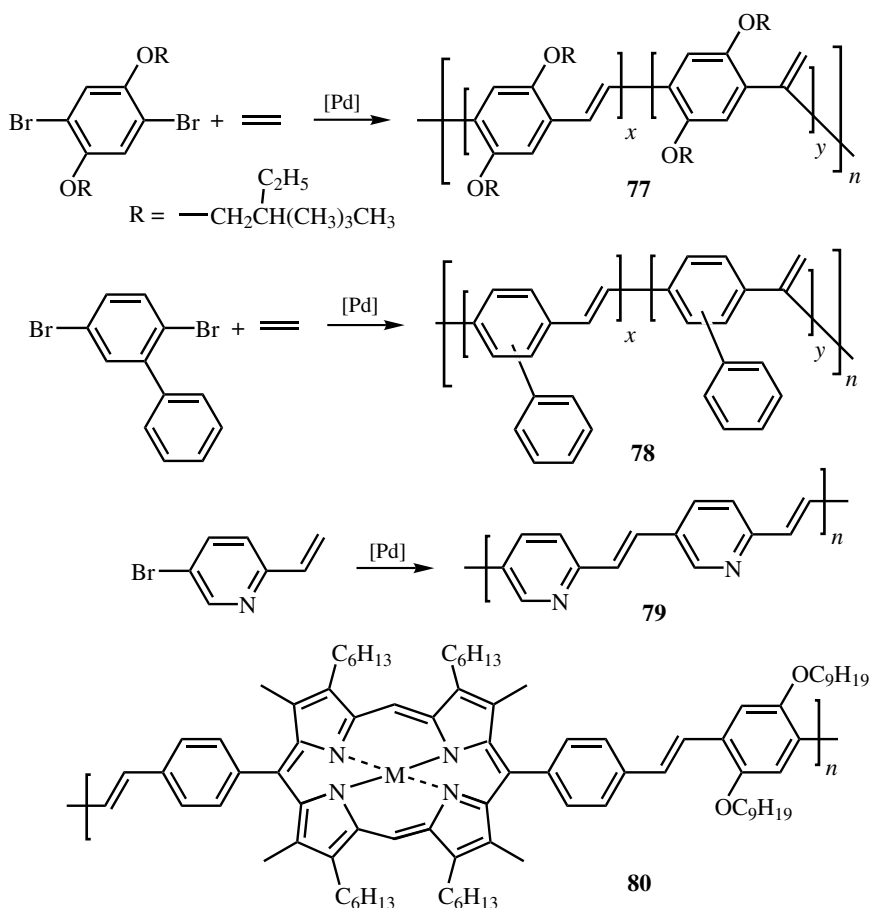


Chart II

rather complex polymer structures that were synthesized for their optical properties. For the use of this and related polymers as photorefractive materials the reader is referred to a pertinent review article.<sup>[116]</sup> For other Heck-PPVs the literature should be consulted.<sup>[117]–[125]</sup> A driving force for the development of PPVs by Heck polycondensation was the desire to use them as the active material in green luminescent LEDs. In retrospect one has to say, however, that this hope could not yet be realized. The PPVs normally used in commercial devices are prepared according to the Wessling procedure, which involves the thermal elimination of tetrahydrothiophene and hydrogen chloride from a methanol- and water-processible sulfonium precursor polymer.<sup>[7],[8]</sup>

Chart III contains the Stille polymers **81**,<sup>[126]</sup> **82**,<sup>[114]</sup> **83**,<sup>[114]</sup> **84**,<sup>[127]</sup> **85**,<sup>[128]</sup> **86**,<sup>[128]</sup> and **87**,<sup>[129]</sup> which have quite low molar masses and questionable structural integrity. Nevertheless, polymers **85** and **86**, for example, were tested for some sensor applications through host/guest effects. Thiophene oligomers were also prepared.<sup>[130]</sup> Chart IV, finally, contains the poly(phenylene ethynylene)s (PPE) **88**,<sup>[131]</sup> **89**,<sup>[132]</sup> and **90**.<sup>[133]</sup> Other PPEs have also been prepared<sup>[134]–[157]</sup> some of which were successfully employed for the fabrication of EL devices<sup>[157]</sup> and photoluminescent liquid crystal displays.<sup>[156]</sup> Polymer **88** is noteworthy as the first soluble and yet fully *para*-linked representative. The acetylenic monomers for polymers **89** and **90** carry protecting groups at the coupling sites.

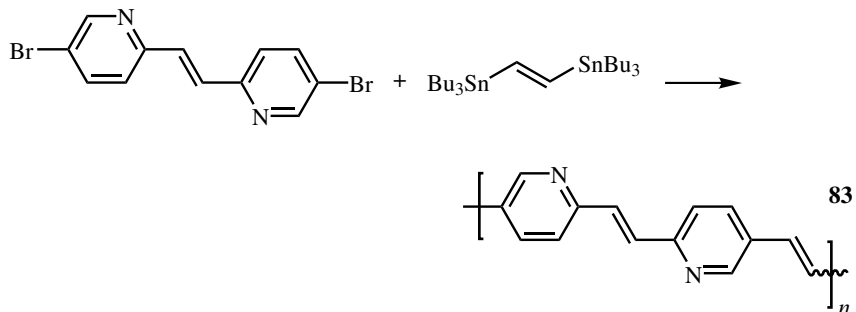
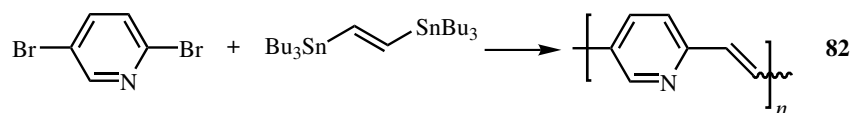
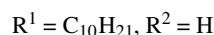
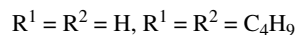
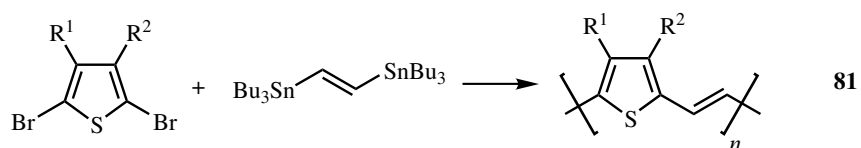


Chart III

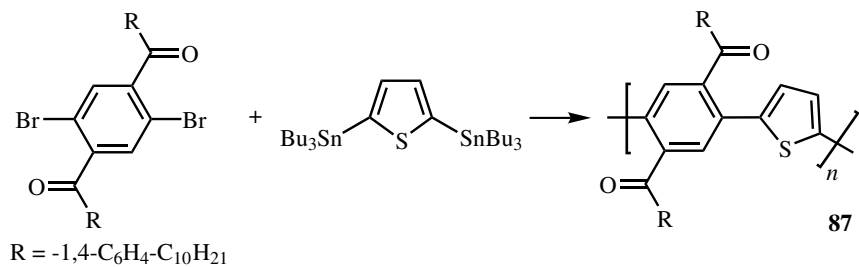
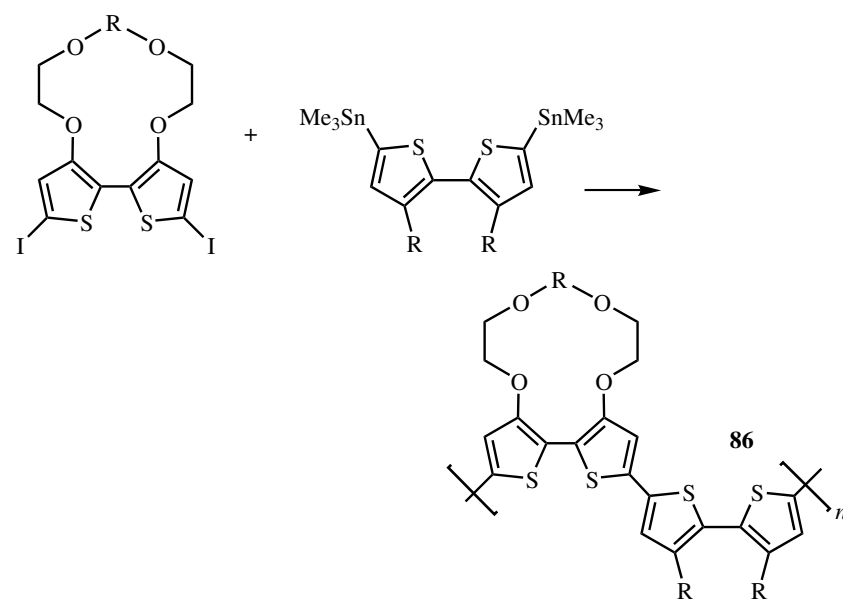
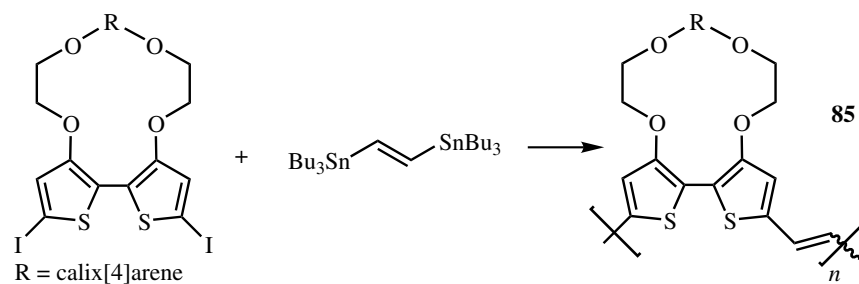
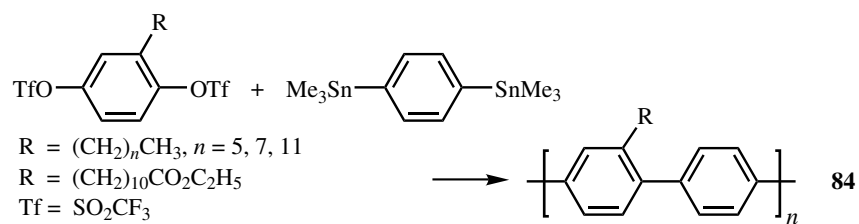
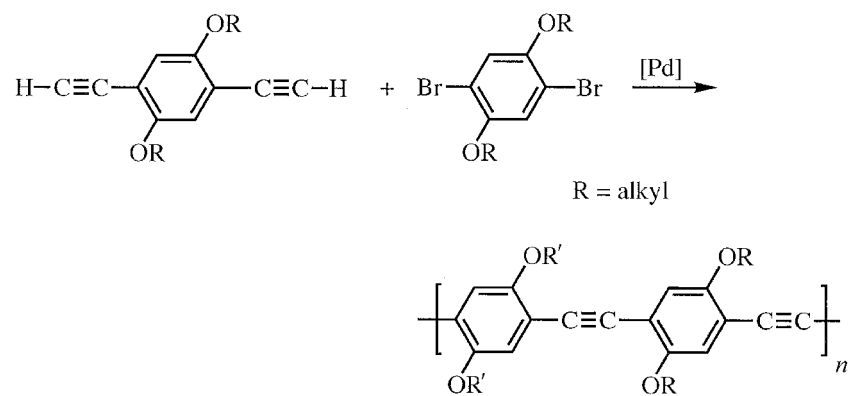
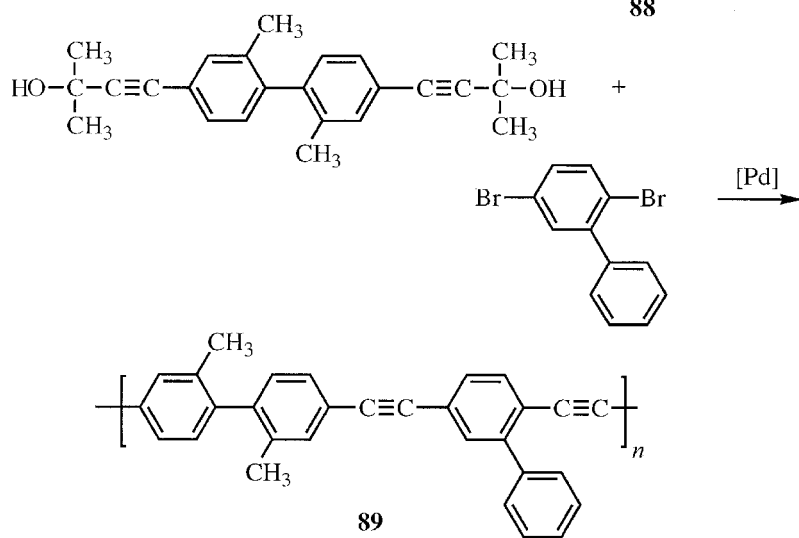


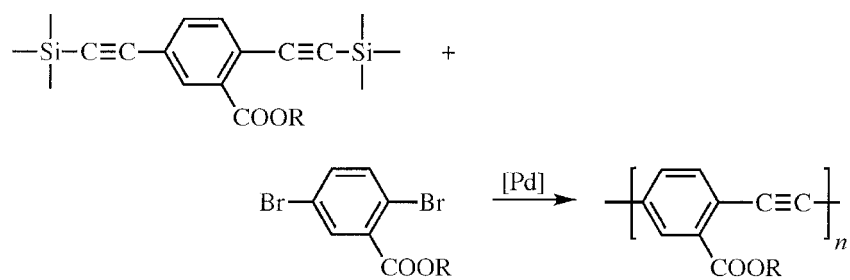
Chart III (Continued)



88



89



90

Chart IV



## D. OUTLOOK

In a little over ten years the area of conjugated polymers with all-hydrocarbon backbones has been revolutionized. Previously “nonexistent” polymers like poly(arylene)s, poly(arylene vinylene)s, and poly(arylene ethynylene)s were made available with a broad variety of substitution patterns. This decoration with substituents not only made them soluble and processible but also mediated function. Though there are still some synthetic hurdles to be overcome, the future of Pd-mediated syntheses of polymers looks bright. The ever increasing demand for conjugated polymers will nourish chemists’ creativity and involvement to overcome these hindrances and to design new polymer structures. The costs for the polymers synthesized via the Pd-mediated step-growth procedures reported here are high. Apart from commodity polymers, however, this does not discourage their application. Only very small amounts are needed and the price of a device does not really depend on the costs of its organic active component. A good example for this is polymer **21**, which is already commercially produced. One final comment from a chemist who sees the chemical world from the vantage point of synthesis: many, many step-known growth polymerizations found huge markets. All of them connect monomers via carbon hetero bonds, mostly CO or CN, none of them via C—C single bonds. This is what makes the polymerizations described here so special. Ten years from now a few more of them will have made it to technical production.

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