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Chain-Growth Condensation Polymerization for the Synthesis of Well-Defined Condensation Polymers and π-Conjugated Polymers

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Contents

1. Introduction

Condensation polymerization is an important method of polymerization that yields not only engineering plastics such as polyamides, polyesters, and polyimides but also π-conjugated polymers, which have recently received considerable attention with the development of the information technology industry. The molecular weight of those polymers is generally difficult to control, and the polydispersity index theoretically approaches 2 at high conversion, which is unlike the behavior of living polymerization. An uncontrolled molecular weight and broad molecular weight distribution do not stem inherently from the reaction type of condensation polymerization, i.e. condensation steps with elimination of a small molecule species but from a polymerization mechanism for step-growth polymerization. Accordingly, if the mechanism of condensation polymerization could be converted from step-growth to chain-growth, living condensation polymerization would be possible. Nature already uses a chain-growth condensation polymerization process to synthesize perfectly monodisperse biopolymers such as polypeptides,[1] DNA,[2] and RNA.[3] For example, in the biosynthesis of polypeptides, the amino group of an aminoacyl-tRNA, monomer, selectively reacts with the terminal ester moiety of polypeptidyl-tRNA in a ribosome to elongate the peptide chain.

Even in artificial condensation polymerization of AB monomers, the chain-growth mechanism could be involved in the following two cases. (1) The change of the substituent effect induced by bond formation of the monomer drives the reactivity of the polymer end group to become higher than that of the monomer (Scheme 1A). (2) In condensation polymerization based on a coupling reaction with a transition metal catalyst, the catalyst is intramolecularly transferred to and activates the elongated polymer end group after the coupling reaction of the monomer with the polymer (Scheme

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1B). In this review, we describe chain-growth condensation polymerization by these two approaches and others.

2. *p*-Substituted Aromatic Condensation Polymers: Polymerization through the Resonance Effect

2.1. Early Work

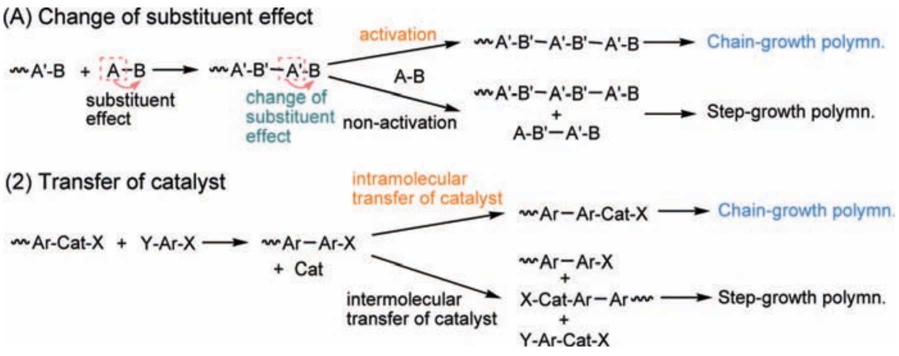
One way to achieve selective reaction of a monomer with the polymer end group would be the enhancement of reactivity of the polymer end group by the change of the substituent effect induced by bond formation of the monomer. Aromatic monomers having a nucleophilic site and an electrophilic site at the para position would be susceptible to the change of the substituent effect through the resonance effect. There are some reports of such selective, though not predominant, reactions of monomers with polymer end groups. For example, Lenz investigated the condensation polymerization of a series of metal *p*-halothiophenoxides and found the amount of unreacted monomer to be higher than predicted from reaction conversion based on Flory's statistical treatment, in which all functional groups of monomer and polymer are of equal reactivity (Scheme 2).[4] This indicates that the substitution of the halogen atoms on the polymer end groups occurs faster than the substitution of the halogen atoms on the monomers. The enhancement of the reactivity of the polymer end group was attributed to the weaker electron-donating ability of the sulfide linkage in the polymer, as compared to the strong electron-donating ability of the thiophenoxide anion in the monomer. Lenz termed this effect preferential polymer formation. However, the molecular weight and polydispersity of the polymers were not measured, probably because the poly(phenylene sulfide) obtained was insoluble in familiar organic solvents.

In the condensation polymerization of chlorophenylsulphonyl phenoxide, increased reactivity of the polymer end group was demonstrated by the relation between conversion and reaction time (Scheme 3). Furthermore, comparison of the rate constants for the displacement of chlorine atoms with hydroxide showed that a model of the polymer end group reacted 20 times faster than the monomer. Thus, the electronic effects of a substituent in one ring were transmitted to the other via the sulfone linkage.[5]

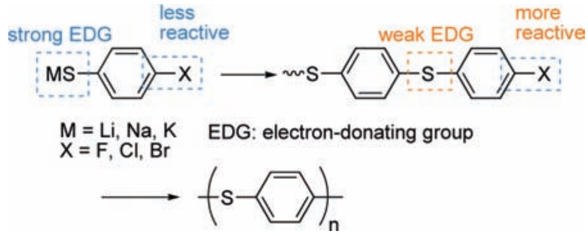
The rate constant of the polymerization of a potassium salt of 4-fluoro-4′-hydroxybenzophenone was calculated by using linear free energy relationships based on the rate constants of the reaction of substituted 4-halogenobenzophenones with the potassium salts of substituted 4-hydroxybenzophenones (Scheme 4).[6] According to this calculation, the rate constant of the reaction of the monomer with the polymer was estimated to be 10-fold greater than that of the reaction of the monomers with each other. The difference was thought to arise from the deactivating effect of the phenoxide anion in the monomer on nucleophilic substitution in the adjacent ring. In the computer simulation of the variation of the concentration of each molecular species with reaction time, the concentration of the dimer and higher oligomers was always very low in comparison with the slowly decaying monomer concentration. The characteristic aspect of this polymerization is that the first stage of the reaction is very much slower than all later stages. Hence, as soon as the dimer is formed, the other polymeric species are formed rapidly from it. This means that the *n*-mer is formed mainly by the reaction of the (*n*-1)-mer with the monomer, that is, by chain-growth polymerization. However, the actual polymerization of this monomer was not reported.

Robello clearly showed that sodium 4-halobenzenesulfinate (**1**) can undergo chain-growth condensation polymerization and polymerized it in the presence of 4-fluorophenyl sulfone (**2**) as an initiator for a chain-type polymerization (Scheme 5).[7] A small amount of **2** served to greatly increase the yield of polymer; in its absence, lower and inconsistent yields of polymer were obtained. This observation showed that the reaction of two molecules of **1** was very slow, and the reaction of **1** with **2** or with the polymer end group was much faster. However, the polymer that precipitated during the

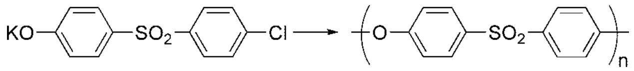
Scheme 1



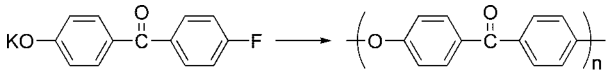
Scheme 2



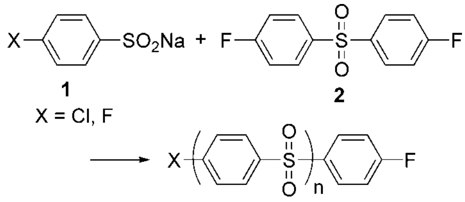
Scheme 3



Scheme 4



Scheme 5

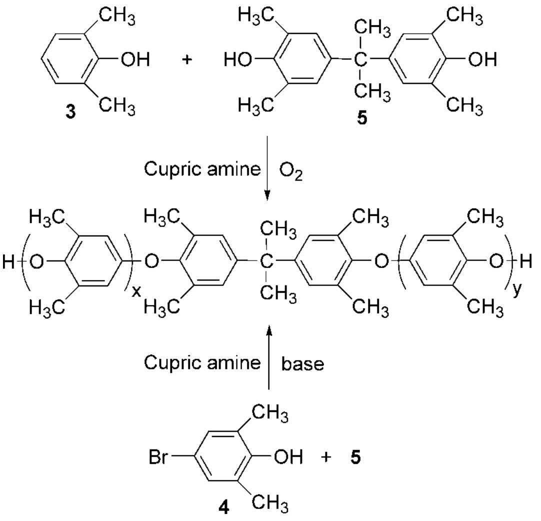


course of the reaction was not soluble; and its molecular weight, estimated by elemental analysis, was rather low, contrary to the supposition that the polymerization proceeded by chain polymerization from **2**. The actual polymerization mechanism appeared to be more complicated: step-growth polymerization could occur together with chain-growth polymerization, and chain transfer to the polymer backbone could also occur, both effects resulting in a decreased molecular weight.

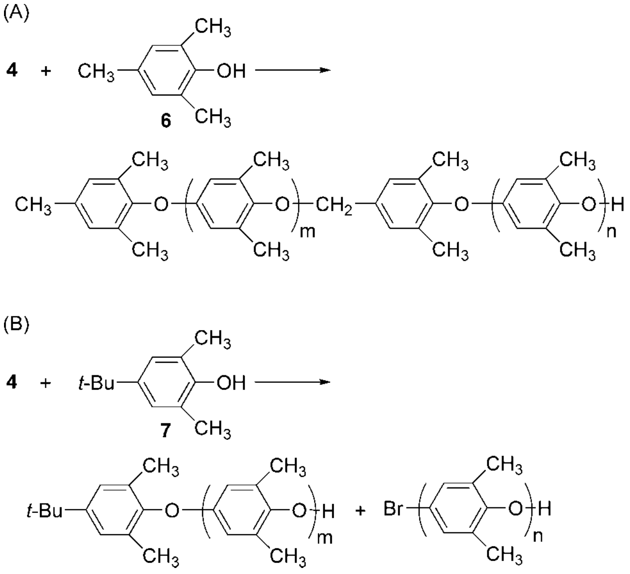
Oxidative polymerization of 2,6-dimethylphenol (**3**) or 4-bromo-2,6-dimethylphenol (**4**) has the character of chain-growth polymerization. In the oxidative polymerization of **3** catalyzed by cupric amine complexes, Heitz found that the degree of polymerization (DP) of poly(2,6-dimethyl-1,4-phenylene oxide) obtained at low conversion was much higher than expected from the conversion according to Flory's theory.[8] The mole fraction of the oligomers was much lower than that of monomer **3**, indicating that the reactivity of dimer, trimer, and the higher homologues was greater than that of the monomer. This polymerization behavior was attributed to a lower redox potential of the oligomers, compared to that of **3**. This kind of polymerization has been called "reactive intermediate polycondensation". The polymerization of **3** in the presence of diphenol **5**, a bifunctional initiator, was also carried out (Scheme 6). The bifunctional polymer containing the **5** unit and the monofunctional polymer derived from self-polycondensation of **3** were produced in short reaction times. With increasing reaction time, the monofunctional polymer was converted to the bifunctional one.

When **4** was used as a monomer, the polymerization proceeded with a base such as potassium *tert*-butoxide to yield a high molecular weight polymer (Scheme 6). Contrary to the oxidative polymerization of **3**, no oxygen was needed for polymer formation, but the bivalent state of copper was necessary. Polymerizations of **4** were also carried out by varying the mole ratio of **5** to yield polymers, the molecular weights of which were in good agreement with the values calculated on the basis of the mole ratio of **4** to **5** (M_n = 880−3900). The polydispersities were not noted. The low molecular weight fraction characterized by gas chromatography contained monofunctional dimer and trimer formed by **4** itself without the **5** unit.

Scheme 6

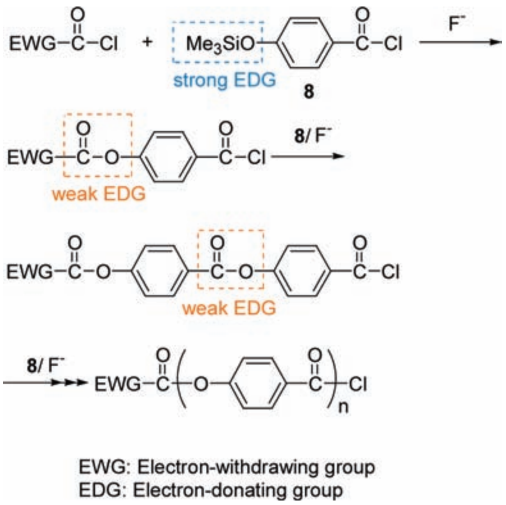


Scheme 7



Percec also synthesized poly(2,6-dimethyl-1,4-phenylene oxide) by phase-transfer catalyzed polymerization of **4** in the presence of 2,4,6-trimethylphenol **6** as a chain initiator.[9a] The polymerization was followed as a function of reaction time. The yields of polymer increased with increasing reaction time, and in contrast to classical step polymerization, the molecular weight of polymer increased rapidly at the beginning of polymerization. The molecular weight and polydispersity of the resulting polymer increased with increasing **4**:**6** mole ratio. With **4**:**6** ratios of 1−5, the M_w/M_n values were 1.14−1.26 for polymer precipitated in methanol. About 18−45% of the structural units derived from **6** were incorporated into the polymer chain as benzyl ether units (Scheme 7A). These units were formed by α-hydrogen abstraction at the 4-methyl group of 2,4,6-trimethylphenolate.

Scheme 8

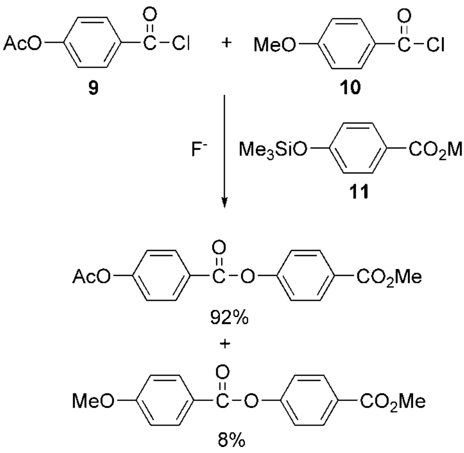


The polymers synthesized with **4**:**6** ratios of 30 and 40 displayed bimodal molecular weight distributions. To suppress the side reaction involving **6**, 4-*tert*-butyl-2,6-dimethylphenol (**7**) was used instead of **6** (Scheme 7B). The molecular weights of the polymers were controlled from 4600 to 9200 by the **4**:**7** ratio, and M_w/M_n was almost constant (1.30−1.42) irrespective of the **4**:**7** ratio. The polymers obtained by using **7** contained structural units derived from **7** only at the chain ends and displayed a monomodal molecular weight distribution, but polymer containing no **7** unit was also produced in a low amount. Other chain initiators were studied for this polymerization, but the molecular weights of the resulting polymers were much higher than calculated values based on a mole ratio of **4**:**6** or **4**:**7** in the feed.[9b−d]

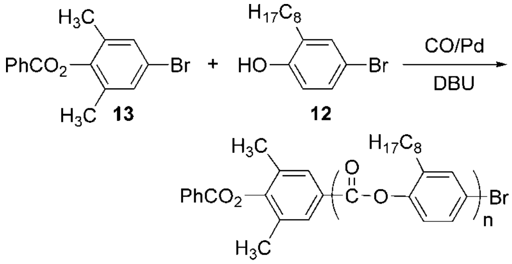
We realized that monomer **8**, the polymerization of which had been reported by Kricheldorf,[10] could undergo an interesting change in the substituent effect during polymerization. Thus, the acyl chloride moiety of **8** would be deactivated by the trimethylsiloxy group of **8** as a strong-electron donating group, whereas the acyl chloride moiety of the polymer might become more reactive than that of **8** because the ester linkage of the polymer is a weaker electron-donating group than that of the trimethylsiloxy group (Scheme 8). This means that the polymer end group would always be more reactive than the monomer and, thus, would satisfy the requirement for chain-growth condensation polymerization.

Before attempting polymerization, we performed a model reaction to confirm the difference in the above substituent effects between a monomer and a polymer.[11] We chose **9** as a model of the propagating end, **10** as a model of the acyl group of monomer **8**, and **11** as a model of the nucleophilic site of **8**. When the reaction of **11** with equimolar amounts of **9** and **10** was performed in the presence of fluoride ion at room temperature, **11** reacted selectively with **9** (Scheme 9). The observed selectivity indicated that monomer **8** could undergo chain-growth condensation polymerization. However, the polymerization of **8** proceeded with concomitant precipitation of polymer, and it was not determined whether chain-growth condensation polymerization had actually occurred.

Scheme 9



Scheme 10

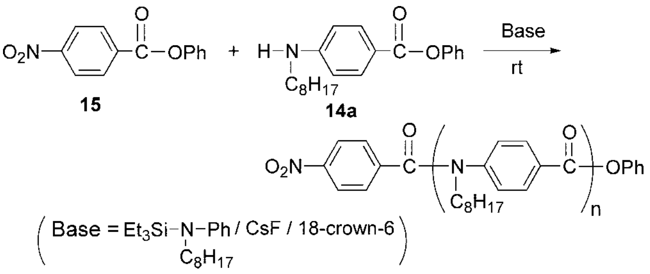


A modified monomer in which an octyl group was introduced was prepared to increase the solubility of the polymer, but it was difficult to purify the monomer. Then the Pd-catalyzed polymerization of 4-bromo-2-octylphenol (**12**) and carbon monoxide was investigated because this polymerization would afford the same soluble polyester and because insertion of Pd(0) into 4-substituted bromobenzenes had been reported to have similar substituent effects: electron-withdrawing groups enhancing the insertion, and electron-donating groups making the reaction sluggish.[12] The polymerization of **12** and carbon monoxide was carried out in the presence of a Pd catalyst, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base, and 4-bromo-2,6-dimethylphenyl benzoate (**13**) as a chain initiator at 115 °C (Scheme 10).[13] The molecular weight of the polymer obtained increased in proportion to time in the initial stage, and the polymer contained the initiator unit **13**, indicating that chain-growth condensation polymerization proceeded from **13**. However, the molecular weight gradually decreased in the middle and later stages because the phenoxide of **12** reacted not only with the polymer end group but also with the ester linkage of the polymer backbone (transesterification).

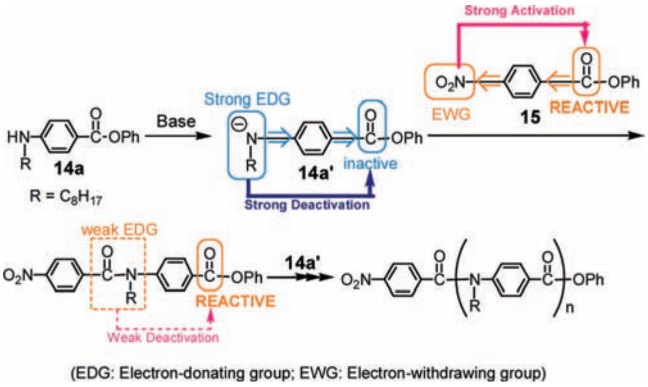
2.2. Polyamides

We changed the target of chain-growth condensation polymerization from polyesters to polyamides because transamidation is much slower than transesterification. Then we found that condensation polymerization of phenyl 4-(octylamino)benzoate (**14a**) proceeded homogeneously in the presence of a base (a combination of *N*-octyl-*N*-triethylsilylaniline, CsF and 18-crown-6) and phenyl 4-nitrobenzoate (**15**) as an initiator in tetrahydrofuran (THF) at ambient temperature to yield well-defined aromatic polyamides with very low polydispersities ($M_w/M_n \leq 1.1$) (Scheme 11).[14] The M_n of the polymer was controlled by the feed ratio of monomer **14a** to initiator **15** up to 22 000, and the polydispersity was quite narrow (Figure 1A). Furthermore, the M_n values also increased in proportion to monomer conversion,

Scheme 11



Scheme 12



indicating that this polycondensation proceeded as a chain-growth polymerization (Figure 1B).

This result is explained by different substituent effects between the monomer and polymer (Scheme 12). The base abstracts the proton of the amino group of monomer **14a** to generate the aminyl anion **14a′**. This anion deactivates the phenyl ester moiety of **14a′** by its strong electron-donating ability through the resonance effect, thus preventing a monomer from reacting with another one. The anion monomer **14a′** would react with initiator **15** having an electron-withdrawing group, because the phenyl ester moiety of **15** is more reactive than that of **14a′**. The amide obtained has a weak electron-donating amide linkage, and the phenyl ester moiety of the amide is more reactive than that of **14a′**. Thus, the next monomer would selectively react with the phenyl ester moiety of the amide. Growth would continue in a chain polymerization by the selective reaction of **14a′** with the polymer terminal phenyl ester moiety. This monomer **14a** underwent chain-growth polymerization to yield the polyamide with low polydispersity even under normal conditions for step-growth polycondensation, where the initiator **15** was not added. The polymerization probably involves the formation of the dimer of **14a**, which initiates chain-growth polymerization faster than step-growth polymerization.[15]

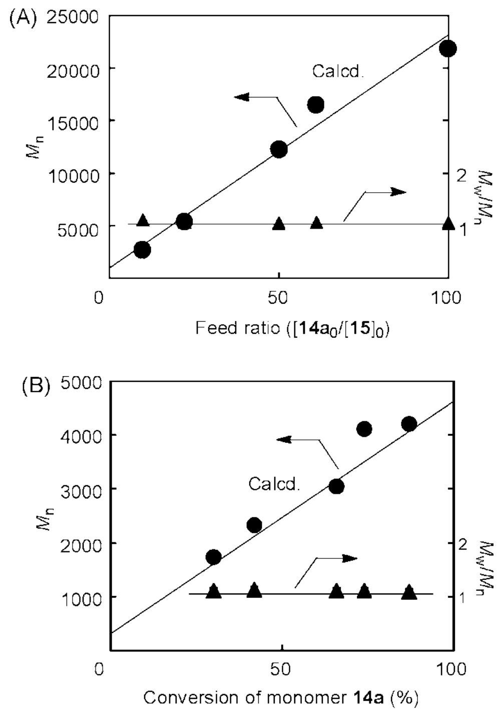
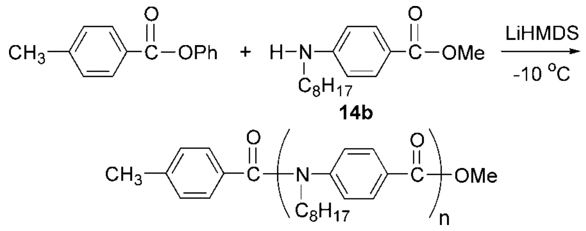


Figure 1. Chain-growth condensation polymerization of **14a** for aromatic polyamides: (A) M_n and M_w/M_n for poly**14a**, obtained with base in THF at 25 °C, as a function of the molar feed ratio of **14a** to **15**: [**14a**]$_0$ = 0.67 M; [**15**]$_0$ = 6.7−67 mM; conversion = 100%. The line indicates the calculated M_n values assuming one polymer chain per unit **15**. (B) M_n and M_w/M_n for poly**14a**, obtained with base in the presence of **15** in THF at 25 °C, as a function of monomer conversion: [**14a**]$_0$ = 0.33 M; [**15**]$_0$ = 0.31 M. The line indicates the calculated M_n values assuming one polymer chain per unit **15**.

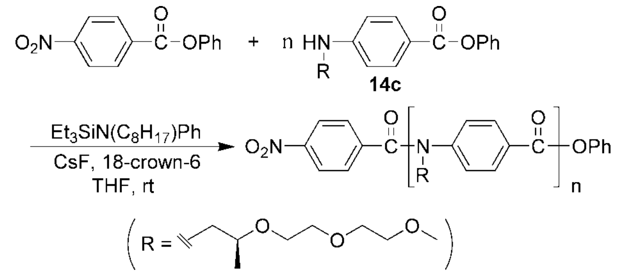
Scheme 13



The above synthetic method for well-defined aromatic polyamides, however, requires an unusual base, *N*-octyl-*N*-triethylsilylaniline, along with CsF and 18-crown-6; and the monomer has a phenyl ester moiety as an electrophilic site, which is not common as compared with a methyl or an ethyl ester. Furthermore, it is necessary to separate the obtained polyamide from byproducts such as *N*-octylaniline and phenol by HPLC. For a more convenient synthesis, the polycondensation of the corresponding methyl ester monomer **14b** with a commercially available base has been developed.[16] The methyl ester **14b** is polymerized with lithium hexamethyldisilazide (LiHMDS) in the presence of an initiator in THF at −10 °C (Scheme 13). The highly pure polyamide with a defined molecular weight and low polydispersity was obtained after simple treatment of the reaction mixture with aqueous NaOH solution followed by evaporation, because the byproducts in this polycondensation after treatment with water are low-boiling methanol, ammonia, and hexamethyldisiloxane. The condensation polymerization of a similar monomer containing a 3-acyl-2-benzothiazolthione as the electrophilic site instead of the methyl ester moiety of **14b** with Grignard reagent as a base has also been reported.[17]

When the polymerization was carried out with a monomer **14c** bearing a chiral tri(ethylene glycol) unit as the *N*-substituted group, solutions of the obtained polyamide showed dispersion-type CD signals characteristic of a coupled oscillator and much larger than those of the corresponding monomer (Scheme 14, Figure 2). Because the chain-growth condensation polymerization gives *N*-substituted poly(*p*-benzamide)s with controlled molecular weight and low polydispersity, it is easy to investigate the effect of the chain length of the polyamides on the CD spectra, and we found that the intensity of the CD

Scheme 14



spectra depended on the molecular weight of the polyamide, as well as temperature. Detailed analysis of the CD spectra, as well as X-ray crystallographic analysis of model oligomers, revealed that the polyamide adopts a helical conformation with three monomer units per turn.[18]

Block copolymers of aromatic polyamides have been synthesized by chain-growth condensation polymerization of 4-(alkylamino)benzoic acid esters **14**. An example is the block copolymer of *N*-alkyl and *N*-H polyamides shown in Scheme 15.[19a] First, *N*-octyl monomer **14a** was polymerized, and then monomer **14d**, with a protecting group on the amino group, and a base were added to the reaction mixture. The added **14d** polymerized smoothly from the ends of the poly**14a** chains to yield the block copolymer of poly**14a** and poly**14d**. The protecting group was quantitatively removed with trifluoroacetic acid to afford the desired block copolymer of *N*-alkyl and *N*-H polyamides with narrow polydispersity. The reason **14d** was used for this block copolymerization was that a monomer with a primary amino group did not polymerize under the polymerization conditions.[19b] The block copolymer self-assembled in THF by virtue of intermolecular hydrogen bonding of the *N*-H polyamide unit. Scanning electron microscopy (SEM) images showed micrometer-sized bundles and aggregates of flake-like structures.[19a] Recently, block copolymers of *N*-octyl- and *N*-fluoroalkyl polyamides with narrow polydispersity were also synthesized and their self-assembly was studied.[20]

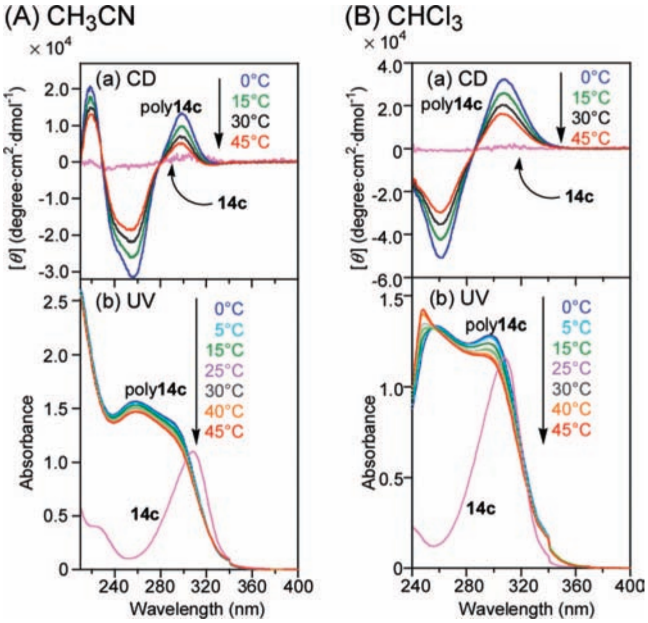
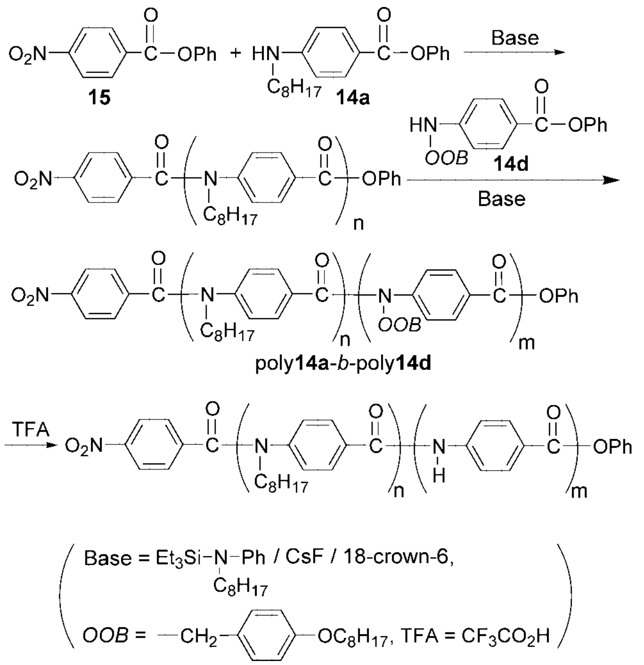
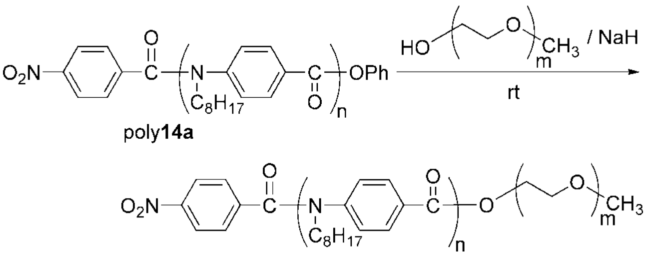


Figure 2. (a) CD and (b) UV spectra of polyamide poly**14c** in (A) CH_3CN and (B) $CHCl_3$ at 0 °C (blue line), 15 °C (green line), 30 °C (gray line), and 45 °C (red line), and monomer **14c** at 15 °C (pink line).

Scheme 15



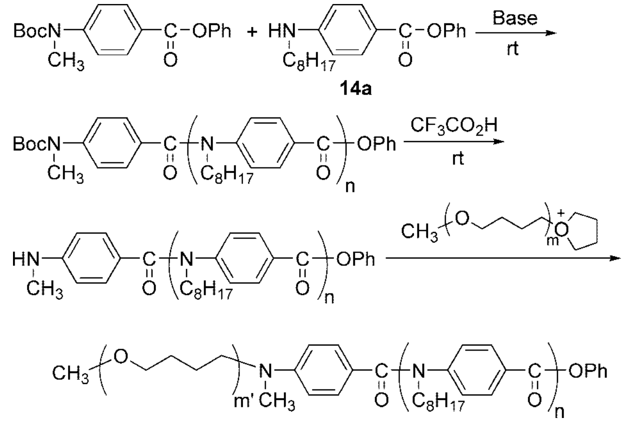
Scheme 16



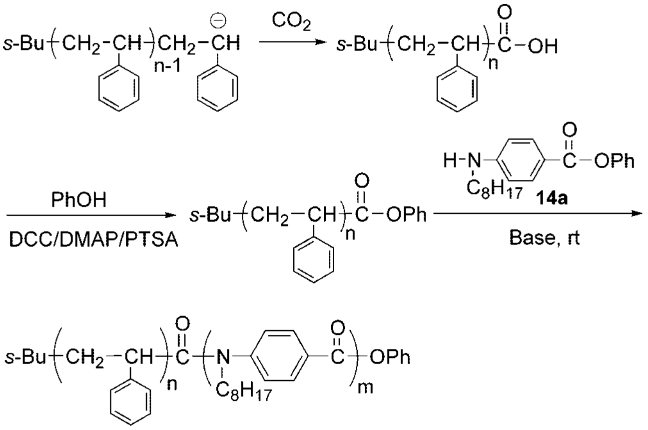
Block copolymers of aromatic polyamide and conventional coil polymer are prepared by the reaction of the polymer end group of the polyamide with the living propagating group of the coil polymer. Thus, the phenyl ester moiety of the polyamide reacts with the anionic living end of the coil polymer, whereas the amino group of the polyamide reacts with the cationic living end of the coil polymer. For example, poly(ethylene glycol) (PEG) monomethyl ether was reacted with the polyamide, prepared by the chain-growth condensation polymerization of **14a**, in the presence of NaH to yield a block copolymer of polyamide and PEG (Scheme 16). Excess PEG was used in this polymer reaction, but unreacted PEG was able to be washed out with water to isolate the block copolymer.[19b,21] Similar reaction of PEG with a polyamide obtained by the chain-growth condensation polymerization of **14a** with phenyl terephthalate as a bifunctional initiator gave a triblock copolymer of PEG−aromatic polyamide−PEG.[22]

Polyamide with a terminal amino group was prepared by the polymerization of **14a** with an initiator bearing the *tert*-butoxycarbonyl (Boc) group on the amino group, followed by treatment with trifluoroacetic acid to remove the Boc group. The terminal amino group of the polymer reacted with living poly(THF) to yield a block copolymer of polyamide and poly(THF) (Scheme 17). When difunctional living poly(THF) initiated by trifluoromethanesulfonic anhydride was reacted with the above polyamide, polyamide−poly(THF)−polyamide triblock copolymer was produced.[23]

Scheme 17

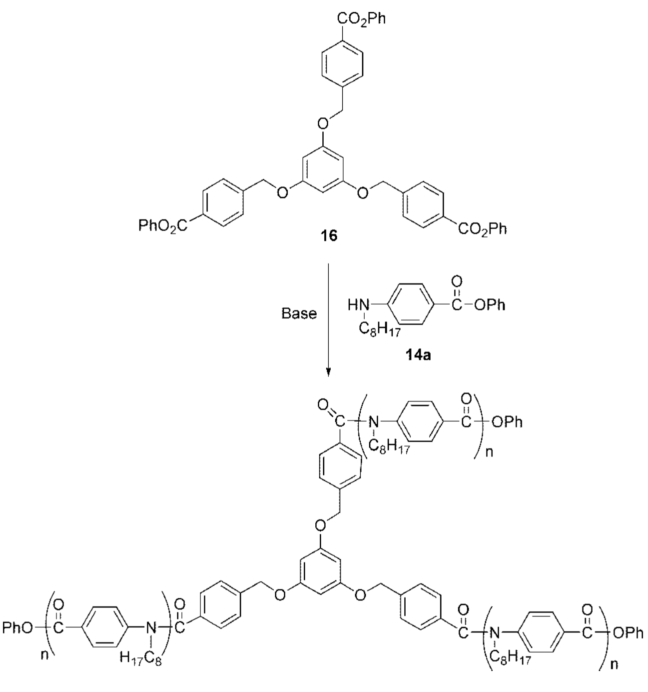


Scheme 18



Another approach to block copolymers of the aromatic polyamide and coil polymer is the macroinitiator method: the chain-growth condensation polymerization of **14a** from a macroinitiator derived from coil polymer. A diblock copolymer of polystyrene and the polyamide was synthesized with this approach (Scheme 18). First, polystyrene with a terminal carboxyl group was prepared by anionic living polymerization of styrene, followed by quenching with dry ice, and then the carboxyl group was converted to the phenyl ester by using phenol and a condensation agent. From this terminus, chain-growth condensation polymerization of **14a** was carried out to yield the desired block copolymer. When low-molecular-weight macroinitiators were used, the block copolymers with low polydispersity were obtained in good yields. When high-molecular-weight macroinitiators were used, the block copolymer was contaminated with the homopolymer of the polyamide. This is probably because the polymer effect of polystyrene decreased the efficiency of initiation from the macroinitiator to induce self-polycondensation of **14a**.[24] To overcome this problem, a macroinitiator of aromatic polyamide was used for the polymerization of styrene. Thus, the polymer end group of the polyamide was converted to the dithiobenzoate moiety, and reversible addition−fragmentation chain transfer (RAFT) polymerization of styrene was carried out in the presence of this polyamide as a macro chain transfer agent to yield well-defined diblock copolymer consisting of aromatic polyamide and polystyrene with high molecular weight.[25]

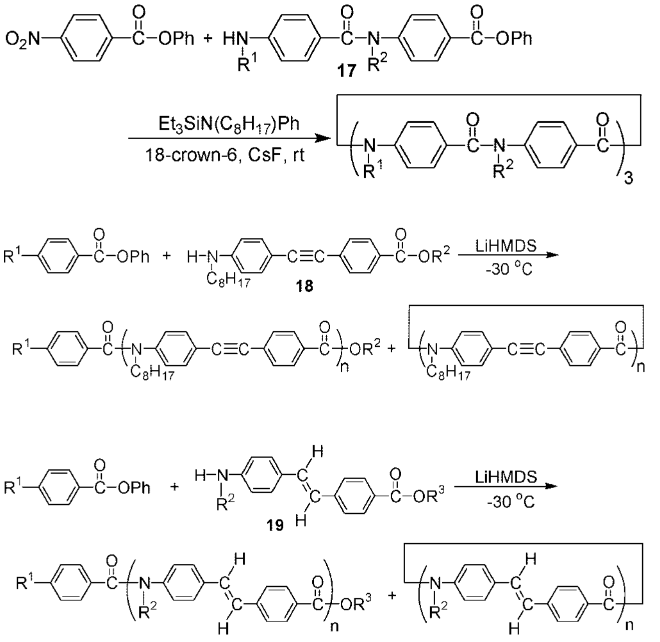
Scheme 19



Star-shaped condensation polymers have been prepared by copolycondensation of an A_n monomer with an AB-type monomer or with A_2 and B_2 monomers,[26] in which the arm lengths of the polymers obtained are not controlled. Well-defined star-shaped condensation oligomers have been synthesized by the coupling reaction between an A_n monomer and linear oligomers with monodispersity, which were prepared by a sequential condensation procedure.[27] We synthesized star-shaped aromatic polyamides with low polydispersity by the chain-growth condensation polymerization of **14a** from 1,3,5-tris(4-phenyloxycarbonylbenzyloxy)benzene (**16**) having the benzyloxy spacers (Scheme 19).[28] The benzyloxy linkages of the core of the star polymer were cleaved by hydrogenolysis to yield a polymer with low polydispersity, the M_n of which was one-third of that of the star polymer, indicating that the star polymer exactly possesses three arm chains of a uniform and controlled length. However, the polymerization at higher feed ratios of $[\mathbf{14a}]_0/[\mathbf{16}]_0$ afforded not only the three-armed polymer but also a linear polymer formed by self-polycondensation of **14a**. In the polymerization of **14a** with a monofunctional initiator, no self-polycondenation of **14a** takes place as long as the feed ratio of $[\mathbf{14a}]_0/[\text{initiator}]_0$ is 100 and less.[14] In the polymerization with trifunctional initiator **16**, however, the self-polycondensation occurred even at the feed ratio of $[\mathbf{14a}]_0/[\text{initiator site of } \mathbf{16}]_0 = 33$, which is much less than 100. Easy occurrence of the self-polycondensation in the polymerization of **14a** with multifunctional initiator **16** is presumably ascribed to the low local concentration of the initiator site in the whole solution except for the area around **16**. Thus, monofunctional initiators homogeneously exist in the solution, whereas multifunctional initiators make both the area of high local concentration of the initiator units and the area of low local concentration of them where self-polycondensation would be liable to occur.

The controlled polymerization of **14** led us to focus our attention on the condensation polymerization of two-aromatic monomers, 4-(alkylamino)benzoic acid dimer ester (**17**), diphenyacetylene monomer (**18**), and *trans*-stilbene monomer (**19**) (Scheme 20). Treatment of **17** with base (*N*-triethylsilyl-*N*-octylaniline/CsF/18-crown-6) in THF at room temperature

Scheme 20

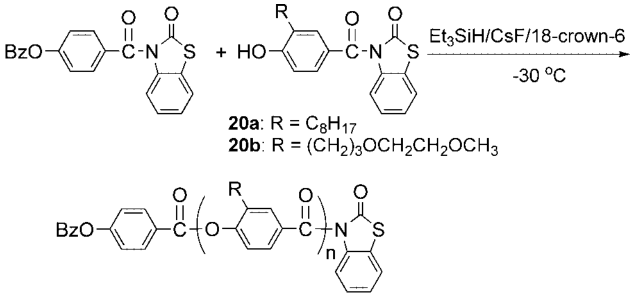


afforded not polymers but cyclic trimers in good yield.[29] On the other hand, the polymerization of **18** with LiHMDS at −30 °C gave a polymer with a relatively narrow molecular weight distribution (M_w/M_n = 1.43), as well as cyclic oligomers. Although complete control of the molecular weight was difficult due to the formation of the cycles, the molecular weight increased with a decrease in the amount of the initiator (M_n = 4780−5560). These results suggest that the main part of the reaction proceeded in a chain-growth polymerization manner, accompanied to some degree with step-growth polymerization.[30] Furthermore, in the polymerization of **19** under similar conditions, a polymer with narrower polydispersity (M_w/M_n = 1.22) was obtained, although a small amount of cyclic oligomers were formed. The M_n values of the polymer increased in proportion to the conversion of the monomer (M_n = 3880−5340), suggesting the involvement of chain-growth polymerization.[30] When a solution of **18** and **19** was slowly added to a solution of LiHMDS without using an initiator molecule, the corresponding cyclic trimers were selectively obtained.[31]

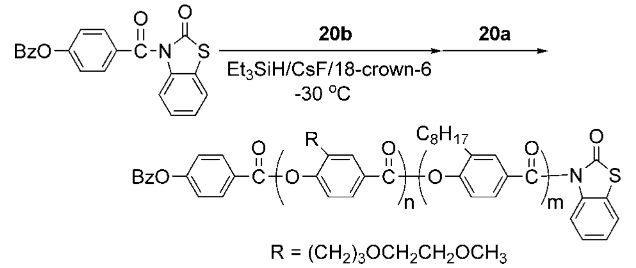
2.3. Polyesters

Synthesis of a well-defined aromatic polyester is more difficult than that of polyamide, because polyester easily undergoes transesterification, as mentioned above. The monomer can attack the polymer ester linkage to generate the cleaved chain with the phenoxide moiety and the acyl group at both ends, leading to conventional step-growth polycondensation. Actually, transesterification occurred in the condensation polymerization of monomer **20**, having an active amide moiety as a good leaving group, even with a weak base such as tertiary amine at room temperature.[32] However, when the polymerization of **20** was carried out at −30 °C with Et_3SiH, CsF, and 18-crown-6 as a base system, transesterification was almost completely suppressed and the molecular weight was controlled up to 7300 with low polydispersity ($M_w/M_n \leq 1.3$) (Scheme 21).[33] Under this condition, a block copolyester bearing various side chains was synthesized in one pot by the monomer addition method (Scheme 22).[33]

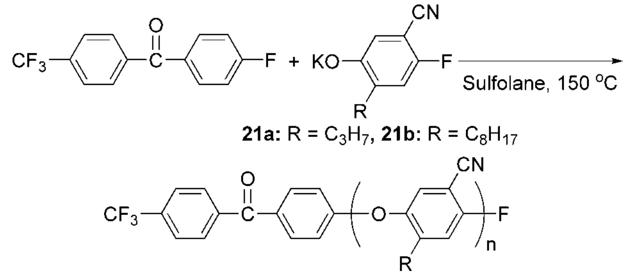
Scheme 21



Scheme 22



Scheme 23

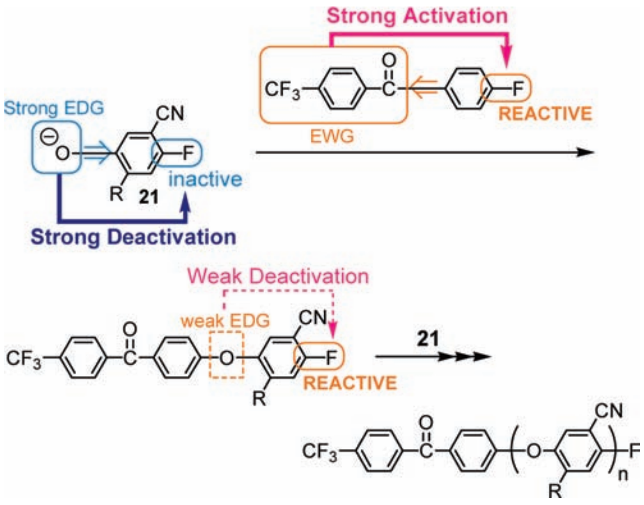


2.4. Polyethers

From the perspective of the advantages of different substituent effects between monomer and polymer for chain-growth condensation polymerization, the synthesis of well-defined polyethers seems to be difficult because the hydroxyl group in a monomer and the ether linkage of a polymer have similar electron-donating abilities. However, monomer **21a** bearing a phenoxide moiety underwent chain-growth condensation polymerization in sulfolane at 150 °C to yield an aromatic polyether with low polydispersity ($M_w/M_n \leq 1.1$). The molecular weight was controlled up to 3500, because polyether with higher molecular weight precipitated during polymerization.[34] Monomer **21b** with an octyl group instead of the propyl group in **21a** also afforded an insoluble polymer in sulfolane when preparation of higher molecular weight polymer was attempted (Scheme 23). In other solvents such as *N*,*N*-dimethylimidazolidinone (DMI) and tetraglyme, the polymerization proceeded homogeneously, but both chain-growth and step-growth polymerization took place to give a polyether with broad molecular weight distribution.[35]

The key to successful chain-growth condensation polymerization of **21** is the use of phenoxide in the monomer instead of phenol. The phenoxide moiety works as a stronger electron-donating group than does the phenol moiety and the ether linkage, and the carbon attached to the fluorine in monomer **21** is strongly deactivated to prevent **21** from reacting with another **21**. Accordingly, **21** reacts selectively with the initiator and the polymer end group, resulting in chain-growth condensation polymerization (Scheme 24).

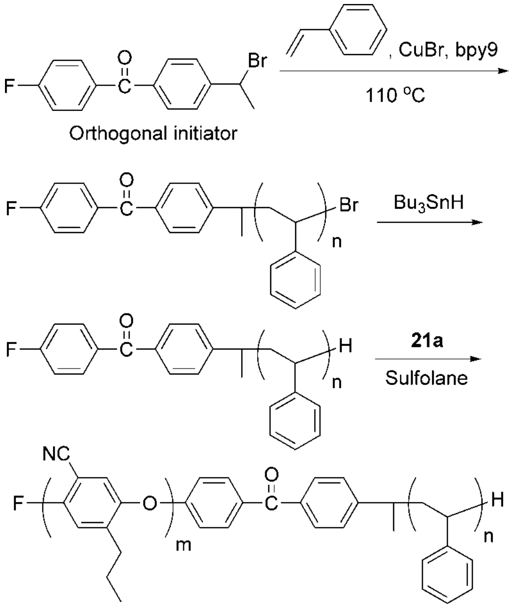
Scheme 24



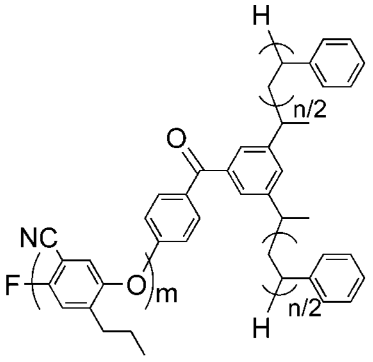
It is interesting that the polyether with low polydispersity from chain-growth condensation polymerization was more crystalline than the product with broad molecular weight distribution from conventional step-growth condensation polymerization. The powder X-ray diffraction (XRD) pattern of the former was more intense, and the differential scanning calorimetry (DSC) profile showed an exothermic peak at 172 °C (cold crystallization) on heating from the glassy state.[34b] This implies that the crystallinity of condensation polymers may be controlled by polydispersity.

Well-defined diblock copolymers of polystyrene and the aromatic polyether have been recently synthesized by the combination of atom transfer radical polymerization (ATRP) and this chain-growth condensation polymerization from an orthogonal initiator, which has two different initiating sites for two kinds of polymerization, with one of the initiating sites being inert with respect to polymerization from the other initiating site.[36] A polystyrene macroinitiator was first synthesized by the ATRP of styrene in the presence of the orthogonal initiator with the benzylic bromide moiety, and then the terminal C–Br of the polystyrene was reduced with Bu_3SnH. The chain-growth condensation polymerization of **21a** was then carried out with the polystyrene macroinitiator in sulfolane at 150 °C to afford well-defined polystyrene-*b*-aromatic polyether (Scheme 25). This diblock copolymer self-assembled in THF to form spherical aggregates. Block copolymer of the aromatic polyether and poly(methyl methacrylate) was prepared by a similar approach.[37] However, block copolymer of the aromatic polyether and polyacrylonitrile was synthesized in a reverse order of polymerization, because polyacrylonitrile macroinitiator underwent degradation with **21a** under the conditions for the polymerization of **21a**.[38]

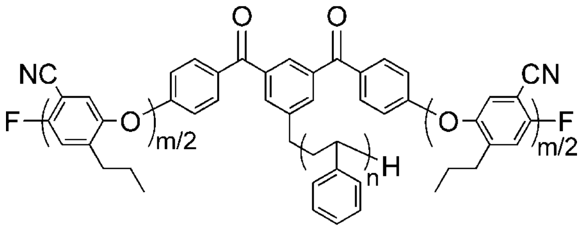
Scheme 25



Scheme 26



AB$_2$ type miktoarm star copolymer



A$_2$B type miktoarm star copolymer

This orthogonal approach was applied to the synthesis of AB$_2$ and A$_2$B type miktoarm star copolymers consisting of aromatic polyether arms as the A segment and polystyrene arms as the B segment, and their self-assembly was studied in comparison with that of the AB type diblock copolymer (Scheme 26).[39] As in the case of the AB type diblock copolymer, the AB$_2$ and A$_2$B type miktoarm star copolymers self-assembled to form spheres of 150−600 nm diameter when a THF solution of the copolymers was allowed to dry on a glass plate. Similar spherical aggregates were obtained from a THF−methanol solution of the A$_2$B type miktoarm star copolymer, whereas the AB$_2$ type afforded fiberlike structures under the same conditions (Figure 3). The solvent and polymer structure-dependent changes of morphology would be induced by the lower solubility of the polystyrene and poly**21a** segments in THF−methanol compared with THF solution. Because the AB$_2$ type miktoarm star copolymer contains two polystyrene arms, the fiber-like structure of the polymer would result from the combination of enhanced aggregability of the branched polystyrene unit and high crystallinity of the poly**21a** segment in THF−methanol. On the other hand, the enhancement of the aggregability of the A$_2$B type miktoarm star copolymer is thought to be insufficient to induce a change of self-assembled structure, probably due to intrinsically high solubility of this polymer in organic solvents.

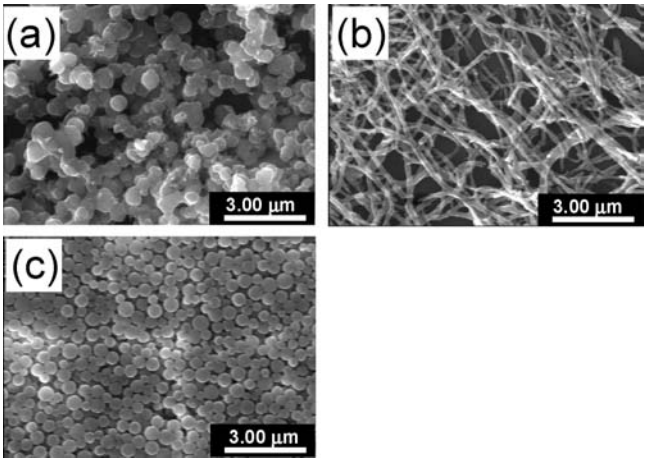


Figure 3. SEM images of self-assembled (a) AB type diblock copolymer ($M_n = 6700$, $M_w/M_n = 1.16$ (**21a**$_{14.3}$-*b*-St$_{28.8}$), (b) AB$_2$ miktoarm star copolymer ($M_n = 8360$, $M_w/M_n = 1.14$, **21a**$_{14.7}$-*b*-(St$_{17.5}$)$_2$), and (c) A$_2$B miktoarm star copolymer ($M_n = 7900$, $M_w/M_n = 1.08$, (**21a**$_{7.7}$)$_2$-*b*-St$_{37.0}$) in THF−MeOH (2/1, v/v). (Reprinted with permission from ref 39. Copyright 2009 American Chemical Society.)

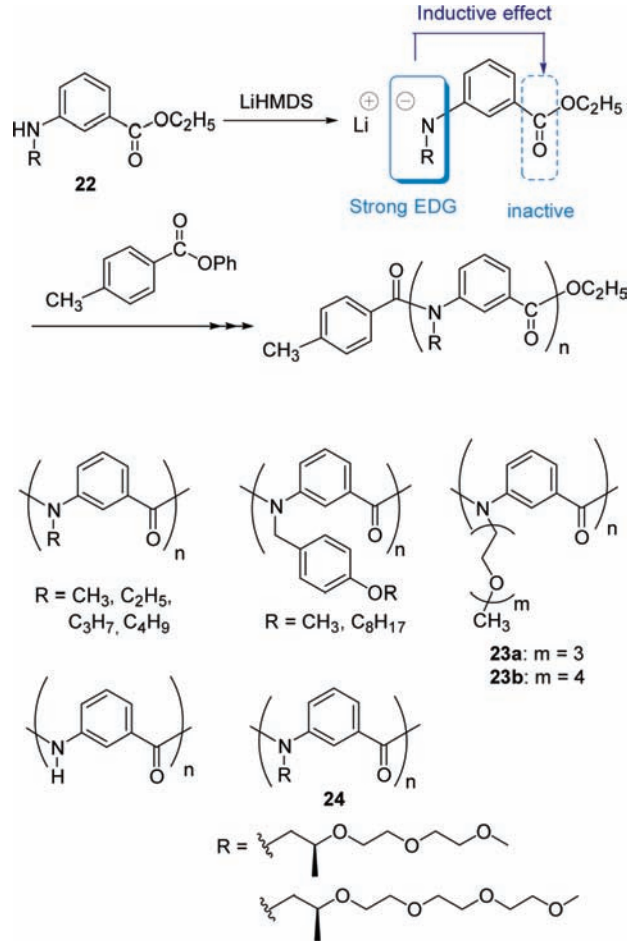
3. m-Substituted Aromatic Condensation Polymers: Polymerization through the Inductive Effect

In the chain-growth condensation polymerization of *p*-substituted monomers, the anionic nucleophilic site deactivates the electrophilic site on the *p*-position through the resonance effect (+*R* effect), resulting in suppression of self-condensation of the monomer but selective reaction with an initiator and the propagating end, leading to chain-growth polymerization. If this polymerization method can be applied to the condensation polymerization of *m*-substituted monomers, well-defined aromatic polymers with higher solubility compared to that of *p*-substituted aromatic polymers are formed. However, one might think that it would be difficult, because the anionic nucleophilic site of the monomer never deactivates the electrophilic site on the *m*-position through the +*R* effect, and there is a little of possibility of deactivation through the inductive effect (+*I* effect). The acidity of benzoic acid derivatives, however, shows that the −*I* effect of the *m*-nitro group, a strong electron-withdrawing substituent, is as strong as the −*R* effect of the *p*-nitro group: the pK_a of *m*-nitrobenzoic acid is 3.45, and that of *p*-nitrobenzoic acid is 3.44.[40] Therefore, the strong electron-donating nucleophilic site is expected to show an inductive effect (+*I* effect) on the reactivity of the electrophilic site at the *meta*-position as strong as the *R* effect, resulting in suppression of self-condensation of the monomer in a similar manner to the chain-growth condensation polymerization of *p*-substituted monomers.

3.1. Polyamides

We polymerized ethyl 3-(alkylamino)benzoate **22** in the presence of LiHMDS as a base and phenyl 4-methylbenzoate as an initiator in THF at 0 °C to obtain *N*-alkylated poly(*m*-benzamide)s with well-defined molecular weights and low polydispersities ($M_w/M_n \leq 1.1$) (Scheme 27). When the *N*-alkyl group was an octyl group, the M_n of the polymer was controlled up to 12 000 by the feed ratio of the monomer to initiator, and the polydispersity was quite narrow.[41a] In this polymerization, the aminyl anion of **22** deactivates the acyl group at the *meta* position through the strong +*I* effect, resulting in suppression of the self-polycondensation of **22**. The anion of **22** then selectively reacts with initiator and the polymer chain end, the acyl group of which is more reactive than that of the monomer with the aminyl anion, and growth would continue in a chain polymerization manner. To support this mechanism, density functional theory (DFT) calculations were performed. The activation energies for the propagation and self-condensation were 21.6 and 27.0 kcal/mol, respectively. On the basis of the geometries, energies, and vibrational frequencies obtained, the theoretical rate constants were then evaluated at 298.15 K and 1 atm. The reaction rate constant (1.1×10^{-3} s^{-1}) for the propagation is 8.6×10^3-fold greater than that for the self-condensation (1.3×10^{-7} s^{-1}) and, hence, is consistent with the experimental finding that propagation was observed exclusively over self-condensation; that is, chain-growth condensation polymerization of *m*-substituted aminobenzoic ester monomers proceeded. A variety of well-defined poly(*m*-benzamide)s were synthesized from the corresponding monomers. All these polymers have higher solubility than the *para*-substituted counterparts.[41b]

Scheme 27



Interestingly, poly(*m*-benzamide)s **23** having oligo(ethylene glycol) are soluble in water, and an aqueous solution of **23** showed a lower critical solution temperature (LCST) (Figure 4).[42] For **23a** (DP = 29.8, $M_w/M_n = 1.19$), a phase separation occurred at around 55 °C, where the solubility of the polymers sharply altered. In contrast, the phase separation

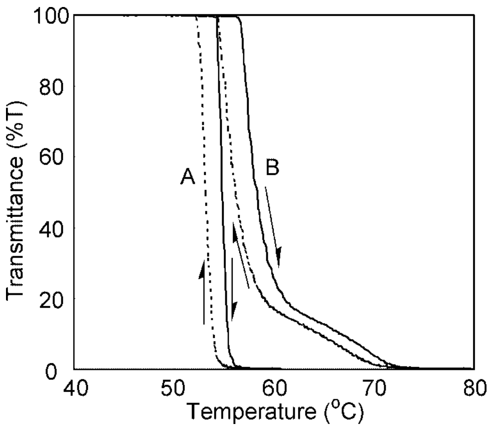
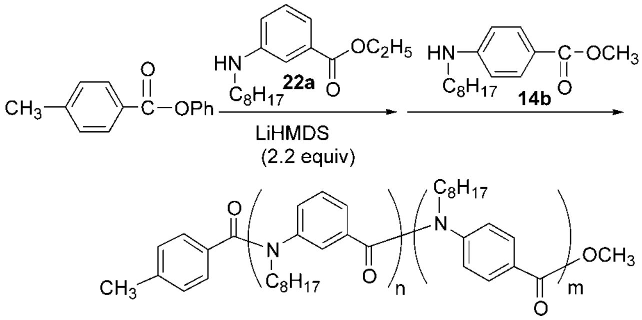


Figure 4. Transmittance vs temperature curves (500 nm, 0.5 °C/min; solid line, heating; dotted line, cooling) obtained for 0.5 wt % solutions of **23a** (curve A, DP = 29.8, M_w/M_n = 1.19) and **23b** (curve B, DP = 32.7, M_w/M_n = 1.15) in water.

Scheme 28



of **23b** (DP = 32.7, M_w/M_n = 1.15) gradually occurred between 58 and 72 °C, i.e., a higher temperature than that of **23a**. The temperature-dependent phase separation process of each polymer was actually reversible, but a hysteresis on temperature ($\Delta T > 1.5$ °C) was observed during heating and cooling cycles (±0.5 °C min^{-1}).[43] Poly(*m*-benzamide)s **24** having a chiral oligo(ethylene glycol) side chain adopt a chiral conformation in solution, depending on the solvent, the temperature, and the side chain.[44]

Under the conditions for the polymerization of ethyl 3-(alkylamino)benzoate (**22**) with LiHMDS as the base, a well-defined diblock copolymer of *m*- and *p*-substituted poly(benzamide) was synthesized.[41a] Ethyl 3-(octylamino)benzoate (**22a**) was polymerized with 2.2 equiv of LiHMDS at 0 °C to give a prepolymer. A fresh feed of methyl 4-(octylamino)benzoate (**14b**) was added to the prepolymer in the reaction mixture at the same temperature to obtain the block copolymer (Scheme 28). It should be noted that excess LiHMDS in the polymerization of **22a** as the first step did not react at all with the terminal ester moiety of poly**22a**, which was able to initiate the polymerization of **14b** as the second step.

Furthermore, we synthesized *N*-alkyl poly(*m*-benzamide)-*b*-*N*-H poly(*m*-benzamide), *N*-alkyl poly(*m*-benzamide)-*b*-*N*-H poly(*p*-benzamide), and *N*-alkyl poly(*p*-benzamide)-*b*-*N*-H poly(*m*-benzamide) by the above sequential chain-growth condensation polymerization of *N*-alkyl and *N*-octyloxybenzyl monomers, followed by removal of the octyloxybenzyl group with trifluoroacetic acid. These block copolymers showed gelating properties at low concentration in various solvents.[45] The SEM analysis of the dried CH_2CH_2 gel revealed that the block copolymers self-assembled to form a three-dimensional network structure, in which the solvent might be confined to afford a gel (Figure 5). The gelating properties are dependent on the substitution position (*meta*- or *para*-) and the composition ratio of the *N*-H poly(benzamide) segment in these block copolymers. Among them, the block copolymer containing *N*-H poly(*p*-benzamide) showed extensive gelating properties in solvents ranging from aromatic to aprotic polar solvents.

There are several reports on the synthesis of block copolymers composed exclusively of rigid or semirigid condensation oligomer or polymer,[46−53] and these block copolymers appear to have unique and intriguing characteristics due to strong intermolecular interaction. In general, however, such block copolymers have been composed of polymers with a broad molecular weight distribution or oligomers synthesized in a stepwise manner. Synthesis of well-defined diblock condensation copolymer with controlled molecular weight and narrow polydispersity remains a challenging topic. We synthesized diblock copolymers composed of poly(*m*-benzamide) and aromatic polyether by means of successive chain-growth condensation polymerizations.[54] When an orthogonal initiator for the synthesis of the polyamide and aromatic polyether segments was used, side reactions occurred at the 4-fluorobenzophenone unit of the initiator or the macroinitiator. On the other hand, polymerization of polyamide monomer **22a** with a monofunctional initiator afforded well-defined polyamide, which was subsequently converted to a macroinitiator **25** bearing the terminal 4-fluorobenzophenone unit. Polymerization of polyether monomer **21a** in the presence of **25** proceeded in a chain-growth condensation manner from the initiation site of **25** to yield the diblock copolymers of aromatic polyamide and polyether with controlled molecular weight and narrow polydispersity (Scheme 29).

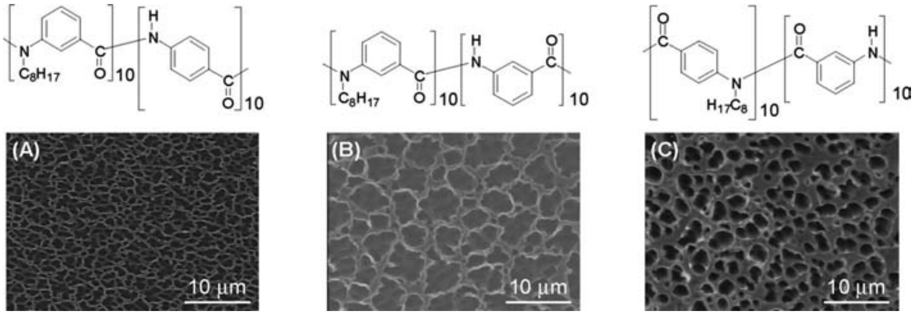
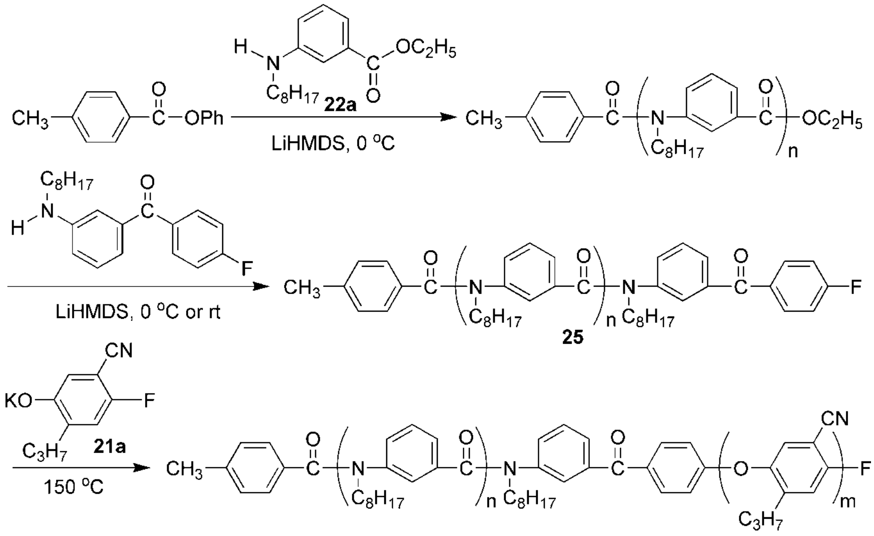


Figure 5. SEM images of (A) dried CH_2Cl_2 gel at 5 wt % of diblock copolymer and (B, C) structures after drying a 5 wt % solution of diblock copolymer in CH_2Cl_2. (Reprinted with permission from ref 45. Copyright 2008 American Chemical Society.)

Scheme 29



3.2. Hyperbranched Polymers

Most of hyperbranched polymers are synthesized by polycondensation or polyaddition, which proceeds through a step-growth polymerization mechanism, so that they generally possess uncontrolled molecular weight and broad molecular weight distribution. The synthesis of hyperbranched polymers with low polydispersity has been tried by slow monomer addition to a core molecule[55,56] or by the use of a highly reactive core molecule.[57] In both methods, however, the polydispersity increased when attempts were made to synthesize polymer with higher molecular weight, because self-polycondensation of the monomer was not fully suppressed. For the synthesis of hyperbranched polymers with defined molecular weight and low polydispersity, irrespective of the amount of the core molecule, the AB_m monomer needs to be polymerized in a chain-growth polymerization manner. On the basis of the above successful chain-growth condensation polymerization of *m*-substituted monomer, the aminyl anion of 5-(methylamino)isophthalic acid ethyl ester (**26**) as an AB_2 monomer would also deactivate both the ester moieties through the inductive effect to suppress self-polymerization of the anion of **26**, leading to chain-growth polymerization of AB_2 monomer (Scheme 30). Thus, the monomer **26** was polymerized with LiHMDS as a base in the presence of a core initiator and LiCl at −30 °C to yield hyperbranched aromatic polyamide (HBPA) with low polydispersity ($M_w/M_n \leq 1.14$) and a degree of branching of about 0.5.[58] The matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra showed that all HBPAs with different molecular weights contained the initiator unit. The M_n value of HBPA increased linearly in proportion to the ratio of $[\mathbf{26}]_0/[\text{initiator}]_0$ up to 40000, while the M_w/M_n ratio remained at 1.14 or less. Therefore, the polymerization of **26** proceeds through a chain-growth polymerization mechanism from the initiator without side reactions.

Taking advantage of the character of chain-growth polymerization of AB_2 monomer, we tried to synthesize a well-defined diblock copolymer of linear and hyperbranched polymer. Thus, methyl 3-(4-octyloxybenzylamino)benzoate (**22b**) was polymerized in the presence of an initiator, LiHMDS, and LiCl to give a prepolymer. A fresh feed of **26** was added to the prepolymer in the reaction mixture. The added **26** feed was smoothly polymerized, resulting in successful production of the linear-hyperbranched block copolymer (Scheme 31).

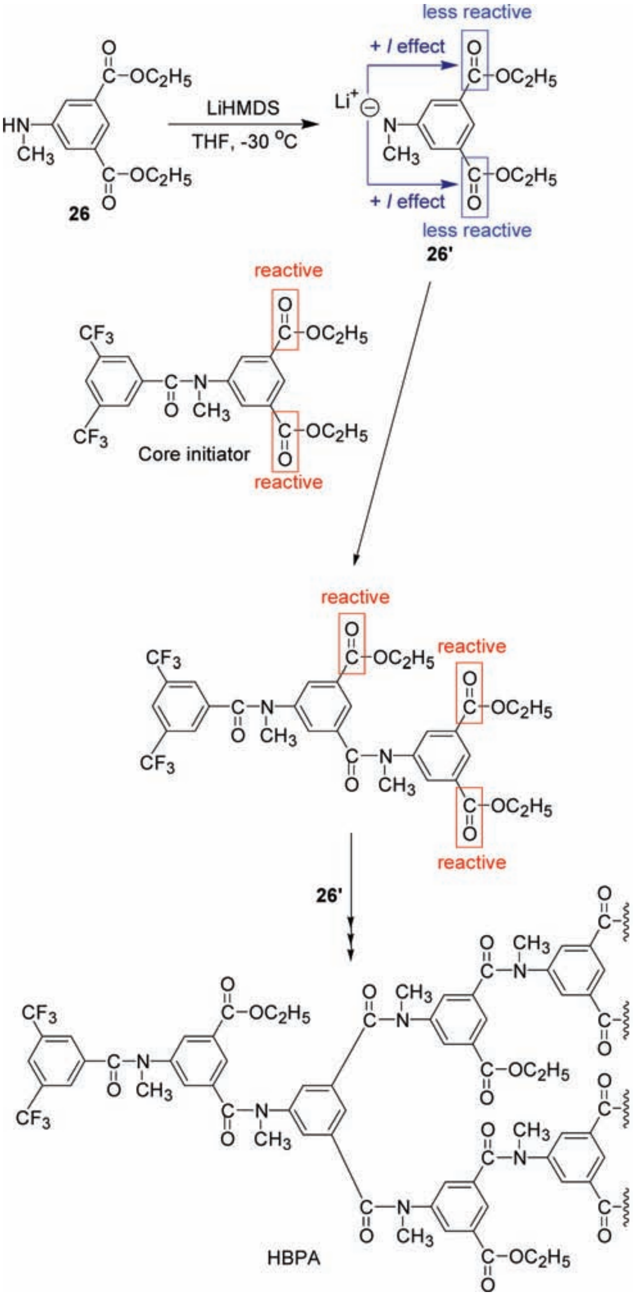
4. Nonaromatic Condensation Polymers

4.1. Polysulfides and Polyesters: Polymerization in Biphasic Systems

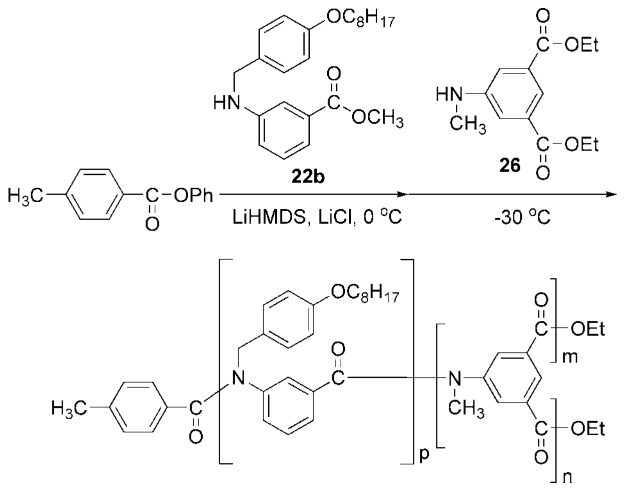
In the early 1980s, Percec et al. pointed out that biphasic phase transfer catalyzed condensation polymerization showed the behavior of chain-growth condensation polymerization.[59] High molecular weight polymers were usually obtained at low conversions. In several cases, even at 100% conversion, the polydispersity of the obtained polymers was low ($M_w/M_n \leq 1.3$). At any conversion, the organic phase contained only polymers with electrophilic chain ends, even when the nucleophilic monomer was used in excess. They speculated that when the nucleophilic anion monomer becomes a polymer chain end, the extraction constant of its onium salt should be molecular weight dependent, based on the fact that the hydrophobicity of the nucleophilic anion increases with the increase of the polymer molecular weight. In several cases, the electrophilicity of the polymer end group should be enhanced by n-participation (anchimeric assistance) (Scheme 32).[60] They applied this chemistry to the synthesis of ABA triblock copolymers and $(A\text{-}B)_n$ alternating block copolymers.[61]

Shaffer studied the phase transfer catalyzed-polymerization of sodium sulfide and a variety of α,*ω*-dibromoalkanes in detail and found that very high molecular weight polysulfide with low polydispersity ($M_n = 683\,000$, $M_w/M_n = 1.24$) was obtained when 1,8-dibromooctane **27** was used as a monomer, together with a catalytic amount of tetrahydrothiophene (THT).[62] In the proposed polymerization mechanism, THT served as an inverse phase transfer catalyst (PTC). THT reacted with **27** to afford a sulfonium salt, which reacted with sodium sulfide in the water phase. The resulting sulfide was extracted into the organic phase as a quaternary ammonium salt of 8-bromooctyl sulfide by virtue of the PTC QX. Last, the transferred ammonium salt reacted with the

Scheme 30



Scheme 31



reactive sulfonium polymer chain end in the organic phase. This chain-end sulfonium was electrophilically more reactive to polymerization than the monomer. This may explain the high molecular weight and narrow polydispersity (Scheme 33). However, controlling molecular weight by addition of a chain initiator was not attempted in this study.

We expected that the solid phase of the monomer would prevent the reaction of monomers with each other and that the monomer dissolving in an organic solvent with the aid of a PTC in a certain amount would react with an initiator and the polymer end group in the solution phase. The solid monomer potassium 4-bromomethyl-2-octyloxybenzoate (**28**) was polymerized in the presence of 18-crown-6 as a PTC and 4-nitrobenzyl bromide (**29**) as the initiator in acetone (Scheme 34).[63] The polymerization successfully proceeded by chain-growth to yield polyesters with M_w/M_n less than 1.3 until the feed $[\mathbf{28}]_0$:$[\mathbf{29}]_0$ reached 15. With a ratio of 20 or above, the control of polymerization was not perfect: polymers having M_n values close to the calculated ones were obtained as well as oligomers without the initiator **29** unit. Similar chain-growth polymerization was also attained with tetrabutylammonium iodide as the PTC instead of 18-crown-6.[64]

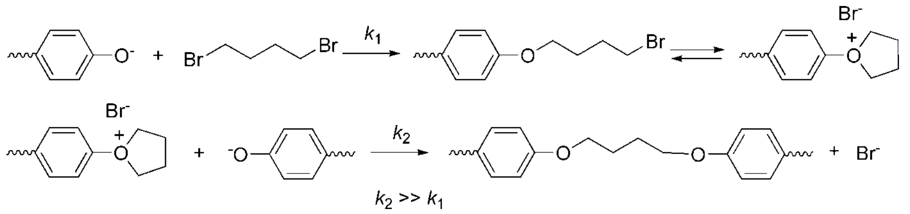
4.2. Polysilanes and Polyphosphazenes: Polymerization through Substituent Effect

The silicon atom in polysilanes is conjugated through the d-orbital of silicon, so that the terminal chlorosilyl group is preferentially reduced with alkali metal, followed by reaction with monomer, dichlorosilane. Matyjaszewski et al. reported that monomodal polysilanes with relatively narrow molecular weight distributions ($M_w/M_n < 1.5$) were synthesized by the reductive coupling of methylphenyldichlorosilane **30** with alkali metals in toluene at ambient temperature in the presence of ultrasound (Scheme 35).[65] The sonochemical synthesis was accompanied by selective degradation, which decreased the molecular weight to the limiting value of $M_n \approx 50\,000$ and also reduced polydispersities ($M_w/M_n < 1.2$). High molecular weight polysilane was formed at low conversion, indicating that the polymerization resembled a chain-growth polymerization.

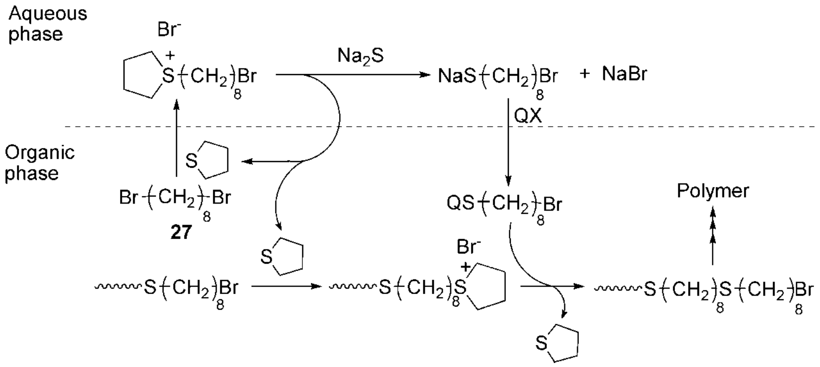
In this polymerization, cyclic oligomers were also formed in high yields by end-biting of silylsodium with chloro-terminated oligosilanes. To reduce the intramolecular cyclization, Ph(n-Hex$_2$Si)$_4$I was used as a chain initiator. The polymer yield increased, but the cyclics were still formed in high yield (≈80%). The ^{1}H NMR spectrum of the polymer showed that 15−20% of the initiator was incorporated into the polymer. These results were explained by the coupling reaction between the initiator and by the competitive reactions of the monomer and initiator with sodium.

Initiation may proceed by the coupling of monomeric radicals at the surface of sodium and subsequent reactions to form chloro-terminated oligosilanes of a length sufficient to have a reductive coupling potential similar to that of chloro-terminated polymer chains. Propagation involves the sequential reactions in Scheme 36. A chloro-terminated chain rapidly takes up one electron to form a radical anion and eventually a silyl radical. The silyl radical takes a subsequent electron from a metallic sodium particle to form polymeric silylsodium. Silylsodium reacts preferentially with the monomer possessing two electron-withdrawing chloride atoms rather than with the chloro-terminated chain end.

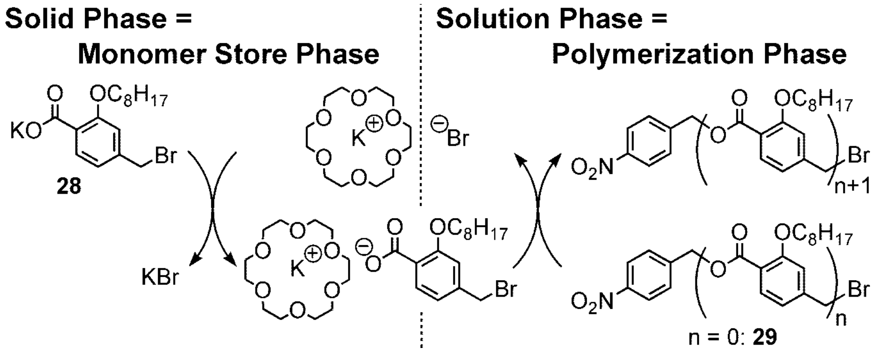
Scheme 32



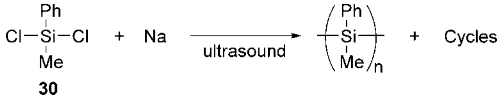
Scheme 33



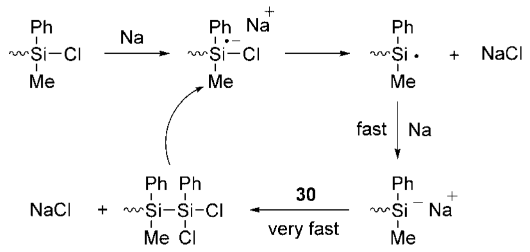
Scheme 34



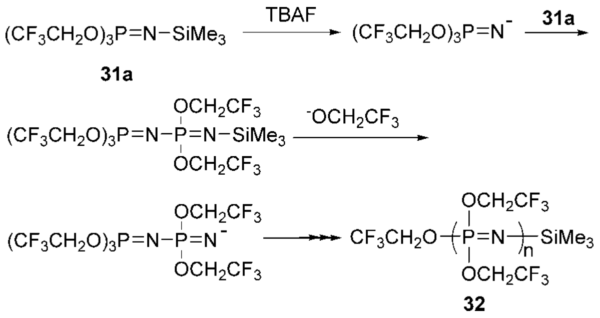
Scheme 35



Scheme 36



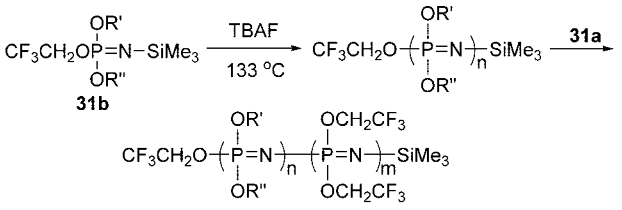
Scheme 37



The polymerization of *N*-silylated phosphoranimine **31a** for the synthesis of polyphosphazenes proceeds with a fluoride ion catalyst via a chain-growth process. Montague and Matyjaszewski reported that **31a** was polymerized with tetrabutylammonium fluoride (TBAF) at 95 °C to yield polyphosphazene **32** with M_w/M_n of about 1.5.[66a] The proposed polymerization mechanism is as follows. The polymerization is initiated by the abstraction of the silyl group from **31a** with TBAF, followed by attack of the resulting phosphazene anion on another monomer. Propagation then proceeds through the attack of the resulting trifluoroethoxide on the silyl group of the growing polymer chain, producing an anion which can then attack another monomer molecule (Scheme 37). Selective desilylation of the polymer end group can be explained by the possibility that the strength of the N−Si bond on a polymer end group is weaker than that on a monomer molecule, owing to the conjugation length of the polymer.[66b]

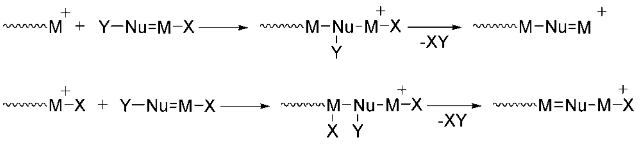
Polyphosphazene block copolymers were synthesized by this chain-growth polymerization method. The successive anionic polymerization of *N*-silylphosphoranimines **31b** and **31a** at 133 °C yielded the block copolymer with M_w/M_n of 1.4−2.3 (Scheme 38).[66b,67] However, due to the presence of two possible leaving groups in **31b**, this approach yielded

Scheme 38

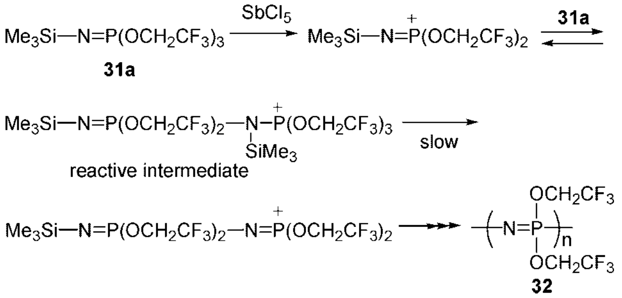


R', R'' = $CH_3OCH_2CH_2OCH_2CH_2$-, $CH_3OCH_2CH_2$- and/or CF_3CH_2-

Scheme 39



Scheme 40



block copolymers where one of the block segments contained a mixture of side groups.

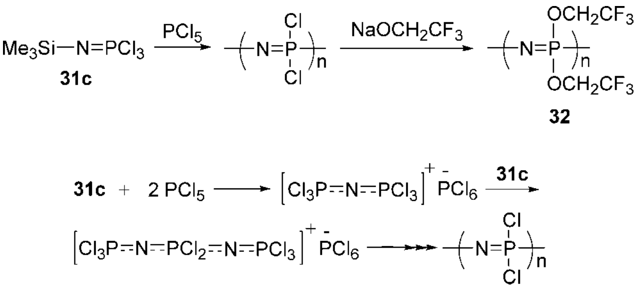
4.3. Polyphosphazenes and Polymethylenes: Polymerization by Transfer of Reactive Species

4.3.1. Polymerization of N-Silylated Phosphoranimine

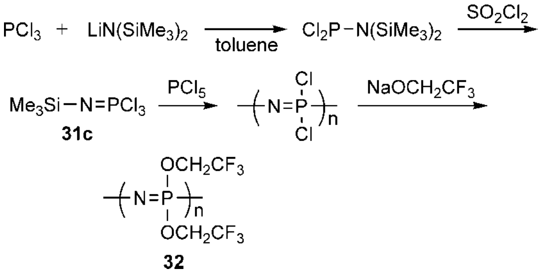
N-Silylated phosphoranimine, mentioned above, is also polymerized with a cationic catalyst in a chain-growth polymerization manner through transfer of cationic species, stemmed from the initiator. A general scheme of the propagation can be described as Scheme 39.

Matyjaszewski and co-workers found that *N*-silylated phosphoranimine **31a** polymerized with $SbCl_5$ at 100 °C to yield polyphosphazene **32** with M_n of 10000−50000 and M_w/M_n of 1.2−2.5.[68] The molecular weight reached a maximum at partial conversion and leveled off, most likely because of transfer reactions. However, the inverse relationship of molecular weight and the amount of $SbCl_5$, the appearance of high molecular weight polymer at partial conversion, and the first-order kinetics in $SbCl_5$ of the reaction supported the conclusion that $SbCl_5$ was the true initiator and that polymerization proceeded by chain-growth. The mechanism of polymerization is shown in Scheme 40. The zero-order kinetics in monomer of the reaction indicates that a reactive intermediate is formed in rapid equilibrium with monomer, followed by slow unimolecular elimination of trimethylsilyl trifluoroethoxide.

Scheme 41



Scheme 42



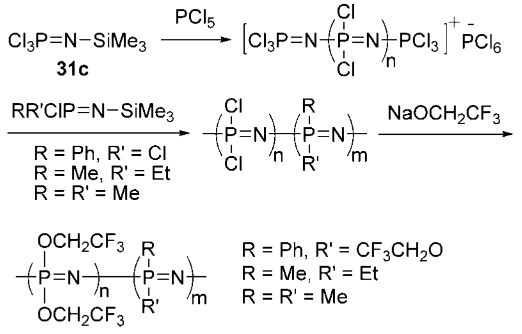
Allcock and co-workers reported that trichloro(trimethylsilyl)phosphoranimine **31c** polymerized with PCl_5 at ambient temperature with elimination of trimethylsilyl chloride. The resulting poly(dichlorophosphazene) was treated with an excess of $NaOCH_2CF_3$ to give polymer **32** (Scheme 41). When the polymerization was carried out in dichloromethane, the molecular weight increased with increasing ratio of **31c** to PCl_5 (M_w = 7000−14000), and the molecular weight distribution remained narrow (M_w/M_n = 1.04−1.20).[69] The polymerization proceeded faster in toluene than in dichloromethane to give polymers with high molecular weights in the range of 10^5 with low polydispersities (<1.3).[70] Phenyl-substituted monomer **31d**, $PhCl_2P{=}NSiMe_3$, also underwent controlled polymerization until the feed ratio of **31d** to PCl_5 was 100. Other related initiators such as $SbCl_5$, $TaCl_5$, or $PhPCl_4$ also appear to initiate the ambient temperature polymerization of **31c** and **31d**. The polymerization is initiated by the reaction of **31c** and 2 equiv of PCl_5 with elimination of Me_3SiCl to generate a salt, with which **31c** successively reacts with elimination of Me_3SiCl, resulting in the elongated cation.

Monomer **31c** was synthesized by the reaction of PCl_5 with either $LiN(SiMe_3)_2$ or $N(SiMe_3)_3$. These methods give relatively low product yields, because PCl_5 is an initiator for the polymerization of **31c**. To circumvent this concurrent polymerization, a new method for synthesizing **31c** and the subsequent polymerization in one pot has been reported.[71] PCl_3 was reacted with $LiN(SiMe_3)_2$ to afford $Cl_2P{-}N(SiMe_3)_2$, which was oxidized with SO_2Cl_2 to yield **31c**. To the mixture, mainly containing **31c**, Me_3SiCl, and LiCl, PCl_5 was added to produce the polyphosphazene. Under optimized conditions, the polymer **32** showed a relatively narrow molecular weight distribution (M_w/M_n = 1.24) even in this one-pot reaction from PCl_3 (Scheme 42).

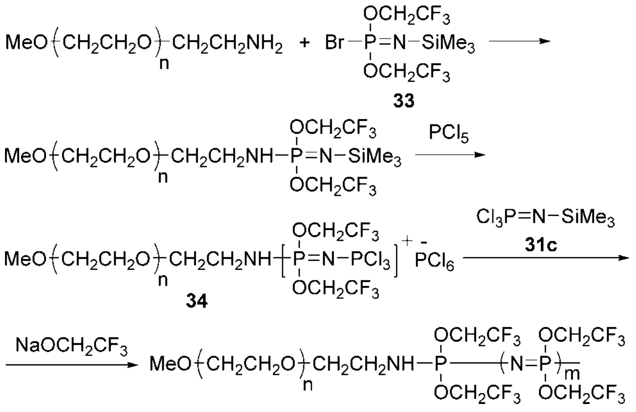
Cationic successive polymerization of phosphoranimines with different side chains yields block copolymers, where each block segment has one kind of side chain, contrary to the anionic block copolymerization mentioned in Scheme 38. For example, the polymerization of **31c** with PCl_5 was carried out at ambient temperature, followed by addition of a second phosphoranimine to yield a block copolymer with M_w/M_n of 1.1−1.4 (Scheme 43).[72]

Some block copolymers of polyphosphazene and coil polymers have been reported by Allcock and co-workers. An example is block copolymer of polyphosphazene and PEG. Amino-terminated PEG was reacted with bromophosphoranimine **33** in the presence of triethylamine to give PEG-phosphoranimine, which was treated with 2 equiv of PCl_5

Scheme 43



Scheme 44

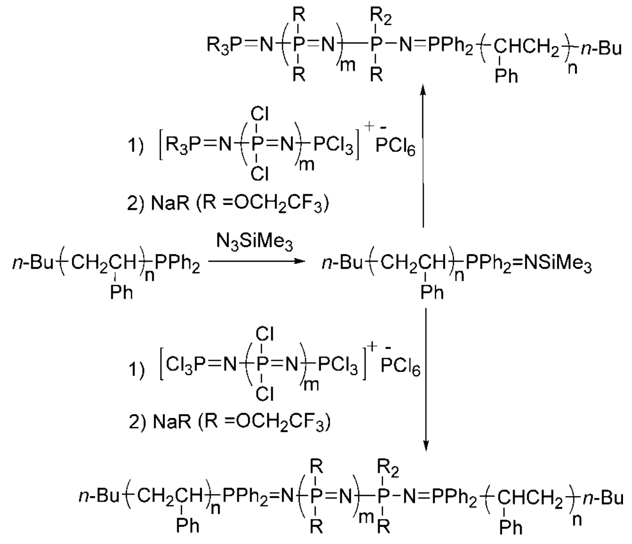


at −78 °C, resulting in the formation of macroinitiator **34**. This macroinitiator induced living cationic polymerization of **31c** to yield the diblock copolymer. Following termination, the chlorine atoms were replaced with trifluoroethoxide groups (Scheme 44). When difunctional amino-terminated PEG was used, the triblock copolymer was obtained.[73] The micellar characteristics of this amphiphilic diblock copolymer were studied.[74] Triblock copolymers consisting of PEG and two kinds of polyphosphazenes were also synthesized.[75]

Diblock and triblock copolymers of polyphosphazene and polystyrene were prepared by the macroterminator method. Phosphine-terminated polystyrene, prepared by quenching anionic living polystyrene with Ph_2PCl, was treated with N_3SiMe_3 to afford polystyryl phosphoranimine. This species was used as a macromolecular terminator for monofunctional and difunctional living poly(dichlorophosphazene), derived from the cationic polymerization of **31c**, to yield the diblock and triblock copolymers, respectively. Following termination, the chlorine atoms were replaced with trifluoroethoxide groups (Scheme 45).[76] Monofunctional poly(dichlorophosphazene) was prepared by using nonhalogen phosphoranimines, such as **31a**, to generate the initiating species with PCl_5 for the living polymerization of **31c**.[77] Diblock copolymers of polystyrene and polyphosphazene with a diethylene glycol monomethyl ether side chain were also synthesized. The self-association behavior of the block copolymers in aqueous media was investigated.[78]

Since the procedure for the formation of macroinitiator by using **33**, mentioned in regard to the synthesis of block copolymers of polyphosphazene and PEG, enabled the synthesis of monofunctional polyphosphazenes,[79] monoallyl functional polyphosphazene was prepared and treated by hydrosilylation with dihydride-terminated poly(dimethylsiloxane) to produce polyphosphazene−polysiloxane−polyphosphazene triblock copolymer (Scheme 46). When phosphoranimine-terminated polysiloxane was used, polysiloxane−polyphosphazene−polysiloxane triblock copolymer was obtained in a similar manner as in the synthesis of the block copolymer of polyphosphazene and polystyrene.[80]

Scheme 45



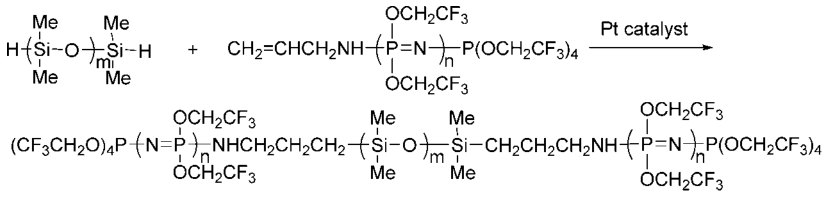
Graft copolymers of polynorbornene, polystyrene, or poly(methyl methacrylate) (PMMA) with polyphosphazene were reported by Allcock et al. Monotelechelic polyphosphazene with a norbornene end group was synthesized through the termination of living poly(dichlorophosphazene) with norbornenyl phosphoranimine. This material was employed as a macromonomer for the synthesis of graft copolymer via ring-opening metathesis polymerization of the terminal norbornenyl moiety (Scheme 47).[81] By a similar approach, styryl-telechelic polyphosphazene was prepared and radically copolymerized with styrene or MMA to yield the graft copolymer of polystyrene[76] or PMMA[82] with polyphosphazene (Scheme 48). Triarm star polyphosphazene was also synthesized by the cationic chain-growth polymerization of **31c** from a trifunctional cationic species. This multifunctional initiator was prepared by the reaction of tridentate primary amine with **33**, as mentioned in the synthesis of the block copolymer of polyphosphazene and PEG.[83]

4.3.2. Polymerization of Ylides

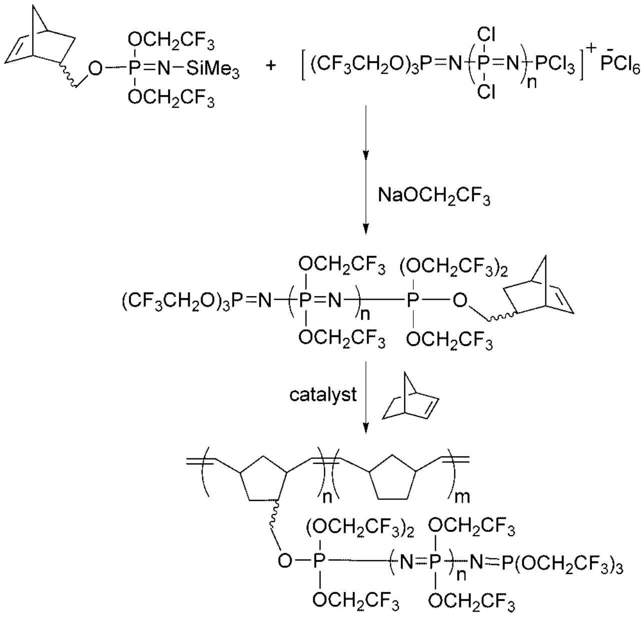
Ylide is polymerized with a trialkylborane initiator accompanying elimination of a neutral compound from the ylide. As shown in a general scheme (Scheme 49), the propagation involves insertion of the ylide monomer to the terminal M-BR_2 bond, so that the propagating end group and the initiator have the same structure, and the polymerization proceeds in a chain-growth polymerization manner.

Shea et al. reported the polymerization of dimethylsulfoxonium methylide **35** initiated by trialkylborane. Propagation involves insertion of **35** at the terminal C−B bond with elimination of dimethylsulfoxide (DMSO). The polymerization was carried out in toluene at 70−80 °C, followed by oxidative workup to yield hydroxyl terminated polymethylene (Scheme 50). The M_n values were very close to the calculated values from the feed ratio of **35** to trialkylborane, and M_w/M_n ranged from 1.04 to 1.17. These results are consistent with a living polymerization. The insertion mechanism involves an initial attack of the ylide on the alkylbo-

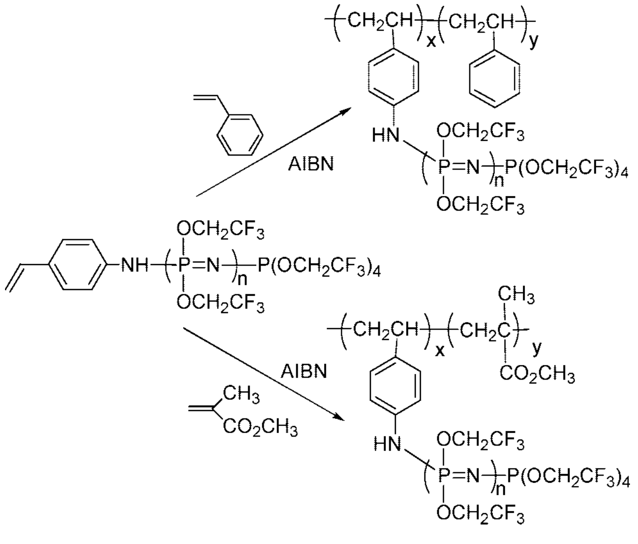
Scheme 46



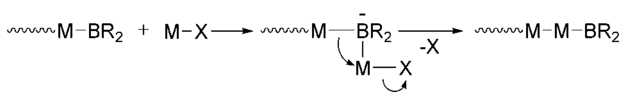
Scheme 47



Scheme 48



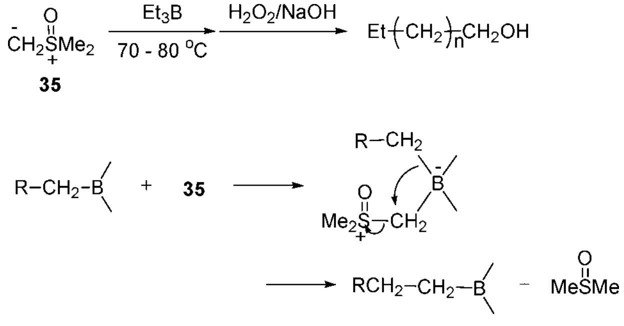
Scheme 49



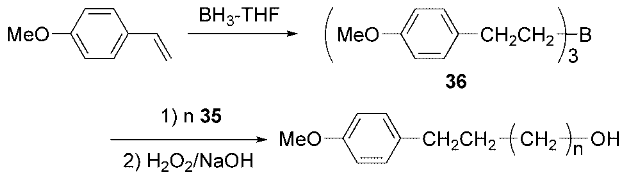
rane. The borate complex undergoes 1,2-migration of the alkyl group to produce the homologated alkylborane and a molecule of DMSO.[84]

This polyhomologation with alkylboranes is amenable to the synthesis of telechelic polymethylene, because alkylboranes can be prepared by hydroboration of a variety of α-olefins. For example, polymethylene with 4-methoxyphenyl and hydroxy groups at both ends was synthesized from initiator **36** prepared by hydroboration of 4-vinylanisole with $BH_3 \cdot THF$ (Scheme 51).[84a] Other functional groups, including biotin, carbohydrates, primary and secondary amines, and dansyl and pyrene fluorescent groups, were also introduced as end groups from the corresponding α-olefins.[85] When *B*-thexylboracycloheptane **37**, prepared by the hydroboration of 1,5-heptadiene with thexylborane, was used as an initiator, methylene was inserted only into the C−B bond of boracyclane, not the thexyl-B bond, resulting in ring expansion. The expanded boracycle was treated with sodium cyanide, followed by benzoyl chloride and then peroxide oxidation to yield cyclic ketone (Scheme 52).[86]

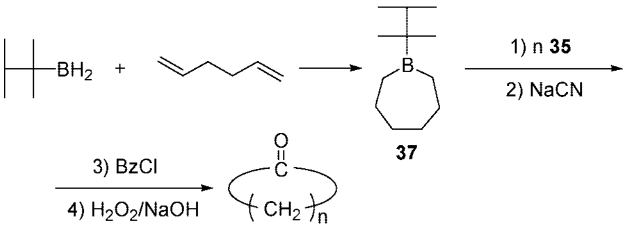
Scheme 50



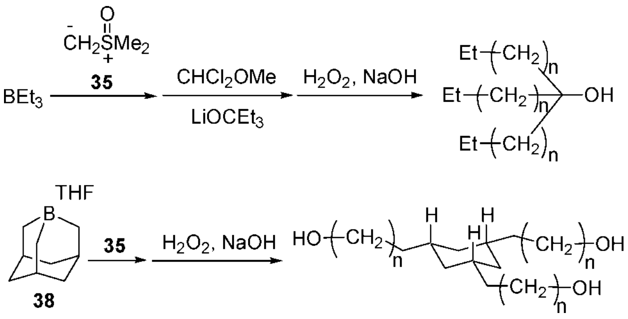
Scheme 51



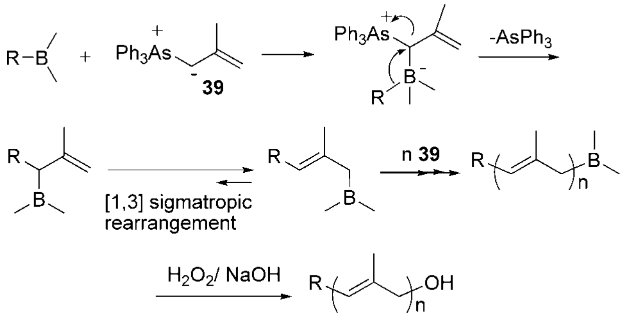
Scheme 52



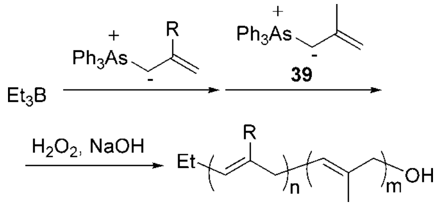
Scheme 53



Scheme 54



Scheme 55



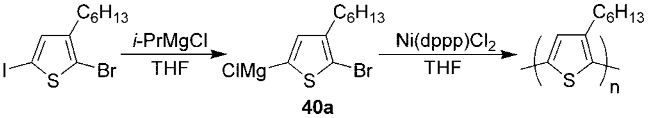
Shea et al. also synthesized star polymethylenes (Scheme 53). Polymethylene from **35** was reacted with α,α-dichloromethyl methyl ether, followed by treatment with $LiOCEt_3$, and oxidation with H_2O_2 and NaOH to give the star polymethylene methanol. The M_n of the polymer obtained agreed well with the calculated value based on the feed ratio of **35** to triethylborane, and M_w/M_n ranged from 1.02 to 1.13. GPC revealed the absence of linear polymethylene.[87] When 1-boraadamantane·THF **38** was used as the initiator for polymerization of **35**, star polymethylene triol was formed.[88]

Moskowski and co-workers reported similar polymerization of arsonium ylide **39** initiated by trialkylborane.[89] The reaction of **39** at 0 °C in THF did not lead to polymers with substitutions on every carbon atom like the polymerization of sulfoxonium ylide **35**, but rather to a polymer in which the main chain has been elongated by three carbon atoms at a time (Scheme 54). Polymers of varying degree of polymerization (DP) were obtained by using varying ratios of ylide **39** to trialkylborane, but the DP was larger than expected from these ratios. The M_w/M_n ranged from 1.21 to 1.58. This suggests that the initiation of the polymerization was not completely efficient, but the propagation was controlled. The polymerization mechanism is different from that of the polymerization of ylide **35**; it involves [1,3] sigmatropic rearrangement after 1,2-migration of the alkyl group of borate. This is the reason for the elongation by three carbons at each step of this insertion polymerization. Block copolymers were also synthesized by successive polymerization of different arsonium ylides (Scheme 55).[89b]

5. π-Conjugated Polymers: Polymerization by Catalyst Transfer

Condensation polymerization with a catalyst can involve another mechanism for chain-growth condensation polymerization, that is a catalyst-transfer mechanism, in which the catalyst activates the polymer end group, followed by reaction with the monomer and transfer of the catalyst to the elongated polymer end group, in a similar manner to biological condensation polymerization.

Scheme 56



5.1. Polythiophenes

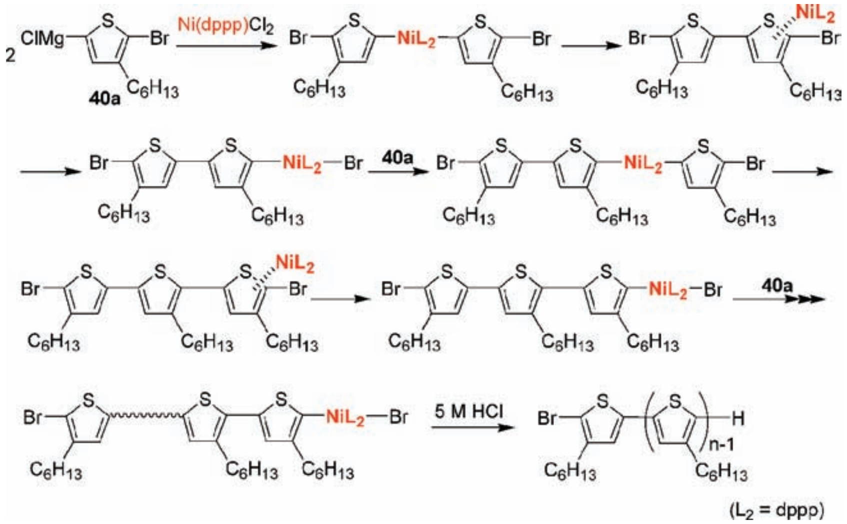
Poly(alkylthiophene) has received much attention in recent years because of its small band gap, high electrical conductivity,[90] and interesting properties, such as light emitting ability[91] and high field effect mobility.[92] The polymerization of Grignard thiophene monomer **40a** with $Ni(dppp)Cl_2$ (dppp = 1,3-bis(diphenylphosphino)propane) was well-known as a regioregulated synthetic method for poly(alkylthiophene)s developed by McCullough et al., but the polymers obtained possessed a broad molecular weight distribution.[93] However, we found that the M_n values of polymers increased in proportion to monomer conversion, with narrow polydispersities bring retained, and were controlled by the amount of the Ni catalyst; the M_n values were proportional to the feed ratio of $[\mathbf{40a}]_0/[\text{Ni catalyst}]_0$ when the polymerization was carried out at room temperature, with care to use the exact amount of isopropylmagnesium chloride for generation of monomer **40a** from the corresponding bromoiodothiophene (Scheme 56).[94] Furthermore, the M_w/M_n ratios were around 1.1 up to M_n of 28 700 when the polymerization of **40a** was quenched with hydrochloric acid.[95] McCullough and co-workers also reported that a similar zinc monomer[96] and **40a** from the corresponding dibromothiophene showed the same polymerization behavior.[97]

After a detailed study of the polymerization of **40a**, four important points were clarified: (1) the polymer end groups are uniform among molecules; one end group is Br and the other is H; (2) the propagating end group is a polymer-Ni-Br complex; (3) one Ni molecule forms one polymer chain; and (4) the chain initiator is a dimer of **40a** formed in situ. On the basis of these results, we have proposed a catalyst-transfer condensation polymerization mechanism (Scheme 57). Thus, $Ni(dppp)Cl_2$ reacts with 2 equiv of **40a**, and the coupling reaction occurs with concomitant generation of a zero-valent Ni complex. The Ni(0) complex does not diffuse to the reaction mixture but is inserted into the intramolecular C−Br bond. Another **40a** reacts with this Ni, followed by the coupling reaction and transfer of the Ni catalyst to the next C−Br bond. Growth would continue in such a way that the Ni catalyst moves to the polymer end group.[98]

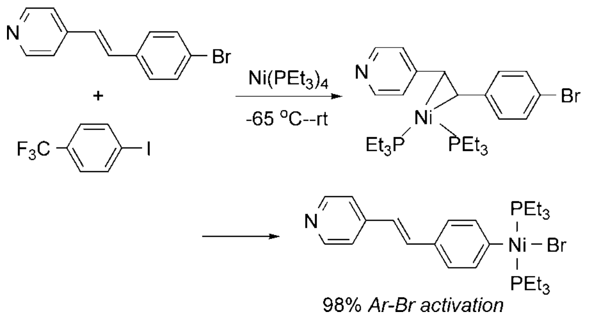
Several other reactions involving similar intramolecular transfer of metal catalysts have been reported.[99−102] Van der Boom and co-workers demonstrated that the reaction of $Ni(PEt_3)_4$ with a brominated vinylarene results in selective η^2-C=C coordination, followed by intramolecular "ring-walking" of the metal center and aryl-bromide oxidative addition, even in the presence of aryl-I containing substrates (Scheme 58).[101c] Nakamura and co-workers studied the Ni-catalyzed cross-coupling reaction by analysis of kinetic isotope effects and theoretical calculations, and they indicated that the first irreversible step of the reaction is the π-complexation of the Ni catalyst on the π-face of haloarene. In other words, once a Ni/haloarene π-complex forms through ligand change, it does not dissociate and proceeds quickly to the oxidative addition step in an intramolecular manner.[102]

The influence of the phosphine ligand of the Ni catalyst on the catalyst-transfer condensation polymerization was investigated.[103,104] The M_n value and the M_w/M_n ratio of

Scheme 57



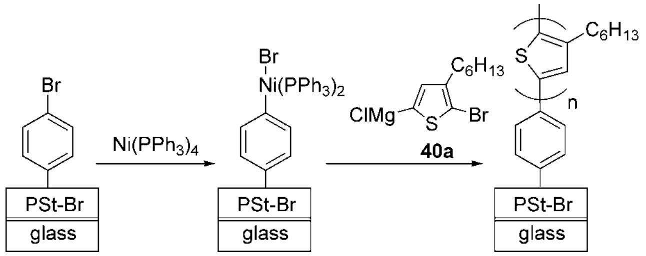
Scheme 58



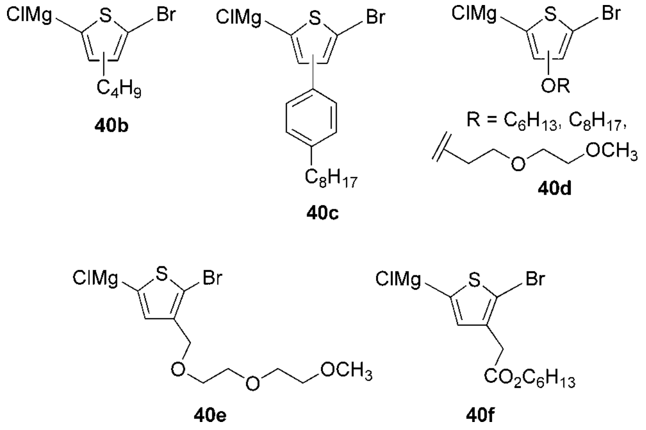
polymer were strongly affected by the ligands of the Ni catalyst: Ni(dppe)Cl_2 (dppe = 1,2-bis(diphenylphosphino)ethane), and Ni$(PPh_3)_4$ gave a polymer with a slightly lower M_n and a slightly broad molecular weight distribution, whereas Ni$(PPh_3)_2Cl_2$, Ni(dppb)Cl_2 (dppb = 1,4-bis(diphenylphosphino)butane), and Ni(dppf)Cl_2 (dppf = 1,1′-bis(diphenylphosphino)ferrocene) gave polymers with low M_n's and broad molecular weight distributions. After all, Ni(dppp)Cl_2 resulted in the M_n value close to the theoretical value based on the feed ratio of monomer to the catalyst and the narrowest M_w/M_n ratio. The influence of the molecular weight and molecular weight distribution of poly(3-hexylthiophene) on the characteristics of the field effect transistor (FET)[105] and photovoltaic cells[106] was investigated.

Taking advantage of the polythiophene end group containing the Ni complex, McCullough and co-workers introduced functional groups on one or both ends of the polymer by Grignard reagents. Allyl, ethynyl, and vinyl Grignard reagents afford monofunctionalized polythiophenes, whereas aryl and alkyl Grignard reagents yield difunctionalized polythiophenes. By utilizing the proper protecting groups, hydroxyl, formyl, and amino groups can also be incorporated onto the polymer chain ends.[107] Kiriy and co-workers used $(PPh_3)_2$Ni(Ph)Br as an initiator and synthesized Ph-terminated poly(3-hexylthiophene).[108] This method was applied to growing conductive polymer brushes of poly(3-hexylthiophene) via surface-initiated chain-growth condensation polymerization of **40a**. Thus, the Ni(II) macroinitiator was prepared by the reaction of Ni$(PPh_3)_4$ with photo-cross-linked poly(4-bromostyrene) films. Exposure of the initiator layers to the monomer solution led to the polymerization from the surface, resulting in poly(3-hexylthiophene) brushes (Scheme 59).

Scheme 59

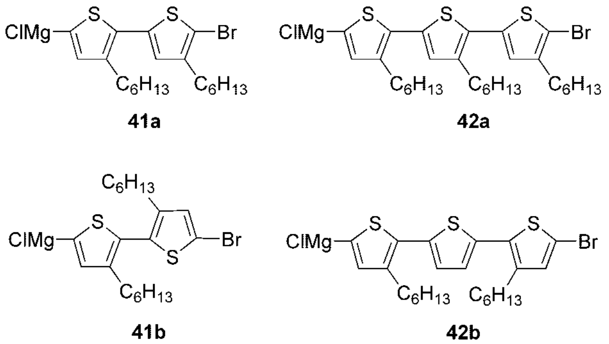


Scheme 60



The chain-growth polymerization of other substituted thiophene monomers instead of **40a** with the hexyl group was investigated (Scheme 60). The polymerization of butylthiophene monomer **40b** with Ni(dppp)Cl_2 afforded polymer with low polydispersity (M_w/M_n = 1.33−1.43), although the M_n value is less than 5500 due to the low solubility of poly**40b**.[109] Aryl-substituted monomer **40c**, the polymer of which may have a stabilized π-conjugated main chain system by virtue of the pendent aromatic group, gave a polymer with M_w/M_n = 2.15, probably due to the low solubility of the conjugated poly**40c** in the reaction solvent.[110] The polymers from alkoxy-substituted monomers **40d** possessed M_w/M_n of 1.5−1.7.[111] The polymerization of alkoxymethyl-substituted monomer **40e** with Ni(dppp)Cl_2 gave a polymer

Scheme 61



41a 42a 41b 42b

Table 1. Ph-Ni(PPh$_3$)$_2$-Br initiated polymerization

monomer	M_n[a]	M_w/M_n[a]	Ph/H and Ph/Br, %[b]
41a	5300	1.67	87
42a	5700	1.74	69
41b	3300	1.91	45
42b	4200	2.0	31

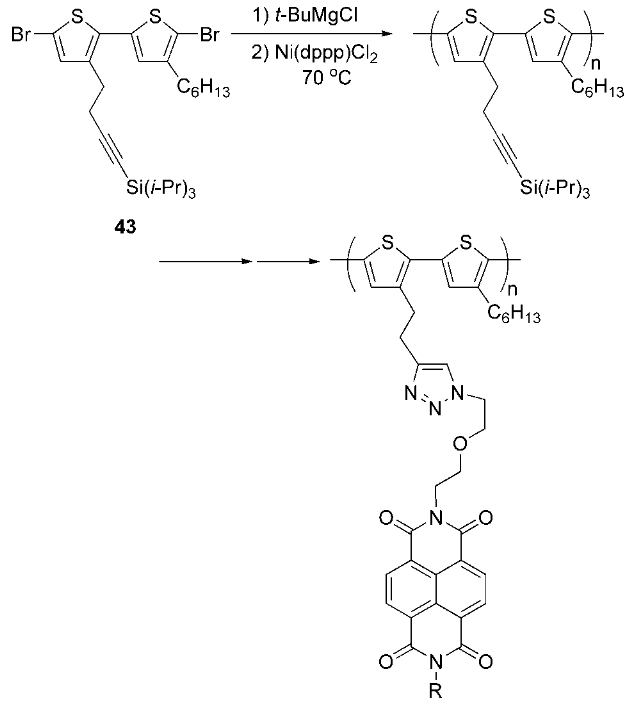
[a] GPC data. [b] ^{1}H NMR data.

with M_w/M_n of 1.42, whereas the polymerization with Ni(dppe)Cl$_2$ instead of Ni(dppp)Cl$_2$ resulted in a decrease of the M_w/M_n up to 1.15.[112] The polymerization of a thiophene monomer **40f** containing an ester moiety also showed chain-growth polymerization behavior to afford polymers with M_w/M_n of 1.25−1.5.[113]

Kiriy and co-workers studied the polymerization of thiophene dimer **41** and trimer **42** with (PPh$_3$)$_2$Ni(Ph)Br as an initiator to see how far intramolecular catalyst transfer takes place (Scheme 61, Table 1).[114] The polymerization of **41a** and **42a** led predominantly to Ph-terminated polymers, indicating the chain-growth polymerization mechanism, although an increase of the monomer molecular length somewhat decreased the fraction of the Ph-terminated products. However, the polymerization of **41b** and **42b** gave less than half the fraction of the Ph-terminated products. Accordingly, the chain-growth performance turns out to be sensitive to the substitution pattern of the polymerized monomers. The monomers having alkyl substituents in an ortho (respective to the growing site) position gave better results, possibly due to higher stability of intermediate ortho-substituted aryl-nickel complexes.

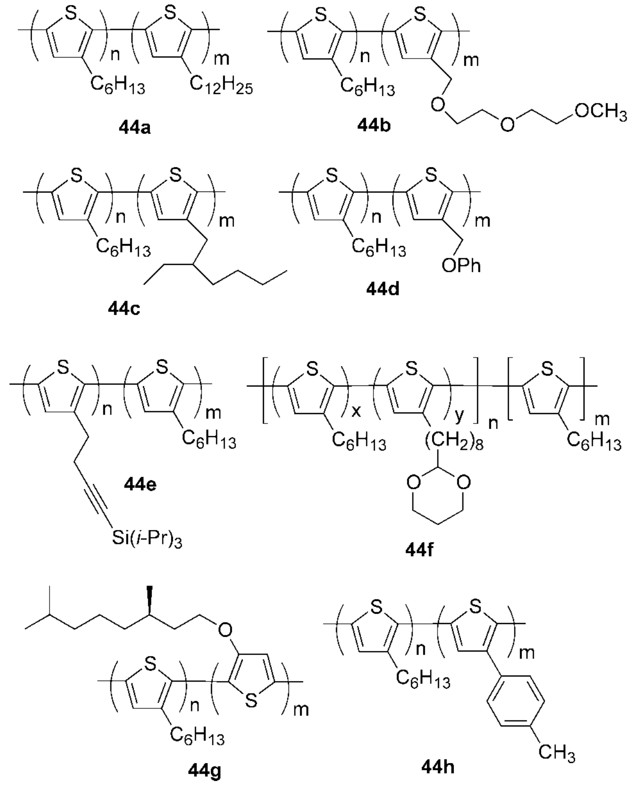
Venkataraman and co-workers tried the polymerization of another thiophene dimer **43** with Ni(dppp)Cl$_2$.[115] The polymerization at ambient temperature afforded very little of the desired polymer, but the polymerization at 70 °C yielded the polymer bearing alternating protected butynyl and hexyl side chains. The M_n value was 15 300, and the M_w/M_n was 1.28−1.35. The obtained polymer was functionalized by azide bearing a naphtalimide moiety under "click chemistry" conditions (Scheme 62).

Scheme 62



43

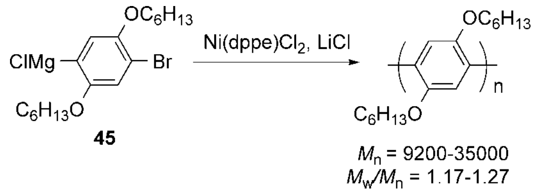
Scheme 63



44a 44b 44c 44d 44e 44f 44g 44h

Since several substituted thiophene monomers undergo chain-growth polymerization in a living polymerization fashion, a lot of block copolythiophenes **44**[97,115−121] have been synthesized by successive polymerization in one pot (Scheme 63). Of these block copolymers, **44a** was first synthesized by McCullough and co-workers.[97] We synthesized block copolymer **44b**, having both hydrophobic and hydrophilic side chains in each segment.[116] The thin films of **44c**,[117] **44d**,[118] and **44h**[121] showed nanofiber structures after annealing, probably because of microphase separation of the crystalline poly(hexylthiophene) segment and the other amorphous segment. The side chain of block copolymer **44e**[115] was converted to the naphthalimide moiety, as shown in Scheme 62. The diblock copolymer **44f**[119] consists of a block made from a random copolymerization of hexylthiophene monomer and (1,3-dioxan-2-octyl)thiophene monomer and the pure poly(hexylthiophene) block. The acetal moiety was converted to the formyl group, followed by introduction of fullerene C$_{60}$ with the aide of *N*-methylglycine. In the block copolymer **44g**, the chiral segment

Scheme 64



influences the supramolecular organization of the poly(hexylthiophene) segment.[120]

5.2. Polyphenylenes

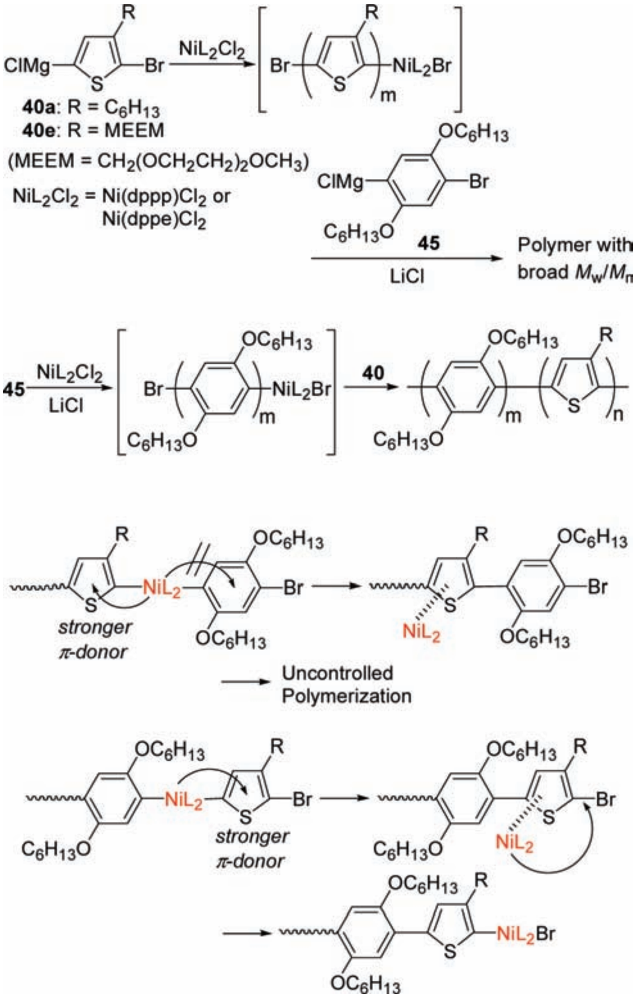
It is important to clarify whether catalyst-transfer condensation polymerization is specific to polythiophene or whether it is generally applicable to the synthesis of well-defined π-conjugated polymers. We investigated the synthesis of poly(*p*-phenylene), to see whether a monomer **45** containing no heteroatom in the aromatic ring would undergo catalyst-transfer polymerization. However, all polymers obtained in the polymerization with Ni(dppp)Cl_2, Ni(dppe)Cl_2, or Ni(dppf)Cl_2 possessed low molecular weights and broad polydispersities. Nevertheless, we found that LiCl was necessary for optimizing the chain-growth condensation polymerization, leading to poly(*p*-phenylene) with low polydispersity, and that the molecular weight was controlled by the feed ratio of **45** to the Ni catalyst (Scheme 64).[122]

We next tried to synthesize block copolymers of polythiophene and poly(*p*-phenylene) by the successive catalyst-transfer condensation polymerization of monomers **40a** or **40e** and **45** with a Ni catalyst.[123] This is the first example of the successive catalyst-transfer condensation polymerization for the synthesis of block copolymers consisting of different types of π-conjugated polymers. The polymerization of **40** and then **45** with a Ni catalyst yielded polymers with broad molecular weight distribution, whereas the reverse order of polymerization resulted in well-defined block copolymers of poly(*p*-phenylene) and polythiophene (Scheme 65). Successful block copolymerization of **45** and then **40** may be accounted for by the π-donor ability of polythiophene and poly(*p*-phenylene) because the π-electrons of the polymers are considered to assist the transfer of the Ni catalyst in catalyst-transfer polymerization. When **45** is added to the reaction mixture of polythiophene as a prepolymer, the Ni catalyst would be difficult to move to the terminal C−Br bond of the phenylene ring of the elongated **45** unit, because the thiophene ring has stronger π-donor ability than the phenylene ring. On the other hand, when **40** is added to poly(*p*-phenylene) as a prepolymer, the Ni catalyst would smoothly move to the C−Br bond of the thiophene ring with stronger π-donor ability (Scheme 65).

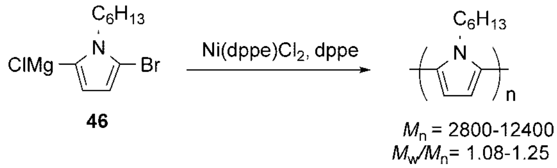
5.3. Polypyrroles

We also investigated the condensation polymerization of Grignard-type *N*-hexylpyrrole monomer **46** with a Ni catalyst (Scheme 66). When Ni(dppp)Cl_2 was used as a catalyst in a similar manner to the case of polymerization of hexylthiophene monomer **40a**, a polymer with the M_w/M_n of 1.26 was obtained, accompanied with low-molecular-weight oligomers. On the other hand, polymerization with Ni(dppe)Cl_2 afforded the polymer with a narrower polydispersity ($M_w/M_n = 1.19$), though oligomeric byproducts were still formed. To suppress the formation of the oligomeric byproduct, we examined the effect of several additives and found that polymerization of **46** with Ni(dppe)Cl_2 in the presence of additional dppe equimolar to the catalyst at 0 °C gave the polypyrrole with a narrow molecular weight distribution ($M_w/M_n = 1.11$) without formation of byproduct. The conversion-M_n and feed ratio−M_n relationships indicated that this polymerization proceeded in a catalyst-transfer polymerization manner.[124]

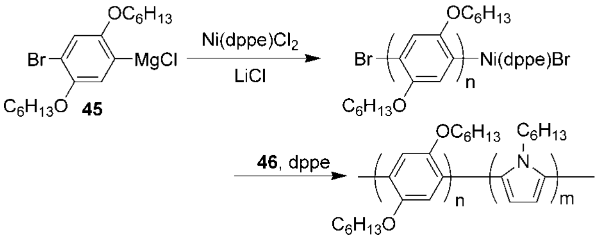
Scheme 65



Scheme 66

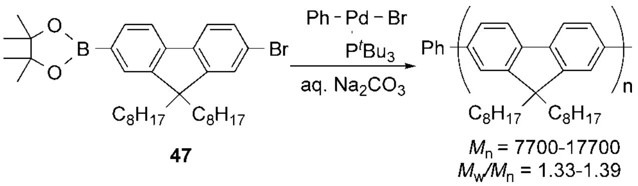


Scheme 67



A block copolymer of poly(*p*-phenylene) and polypyrrole was similarly synthesized. The *p*-phenylene monomer **45** was polymerized first with Ni(dppe)Cl_2 in the presence of LiCl, followed by addition of **46** and dppe to yield the desired

Scheme 68



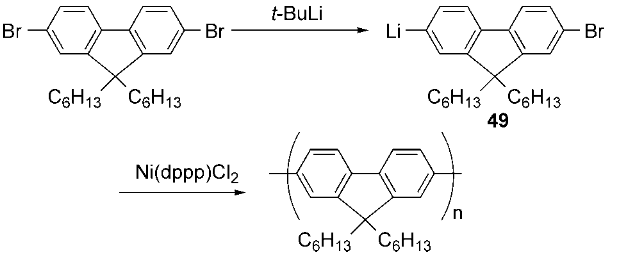
block copolymer with a narrow polydispersity (M_w/M_n = 1.16) (Scheme 67). The block copolymerization in reverse order afforded polymer with a somewhat broader polydispersity (M_w/M_n = 1.38).

5.4. Polyfluorenes

Furthermore, we investigated chain-growth Suzuki−Miyaura coupling polymerization. In this polymerization, stable arylpalladium(II) halide complex was used as an externally added initiator, and the aryl group of the complex served as an initiator unit of the polymer. The polymerization of a fluorene monomer **47** was carried out in the presence of ^{t}Bu$_3$PPd(Ph)Br as a catalyst to yield polyfluorene with a narrow polydispersity (Scheme 68). The molecular weight of the obtained polymer increased linearly in proportion to the conversion of monomer with low polydispersity throughout the polymerization, and it also increased linearly in proportion to the feed ratio of **47** to the initiator, up to 17 700 with low polydispersity, indicating that this Suzuki−Miyaura coupling condensation polymerization proceeded through a chain-growth polymerization mechanism,[125] as shown in the model reactions.[100] The MALDI-TOF mass spectrum of the obtained polyfluorene showed that all the polymers bore the phenyl group at one end. This observation strongly supported the view that ^{t}Bu$_3$PPd(Ph)Br served as an initiator. The catalyst-transfer polymerization with an externally added initiator would provide surface-grafted π-conjugated polymers with defined molecular weight and low polydispersity by the use of a surface-bound Pd complex initiator.

Geng and co-workers have recently reported the polymerization of Grignard-type fluorene monomer **48** with Ni(dppp)Cl$_2$.[126] The monomer **48** was generated from the corresponding bromoiodofluorene with *i*-PrMgCl/LiCl (1:1). The polymerization proceeded very fast at 0 °C and was almost over in 10 min. High molecular weight polyfluorene (M_n = 18 800−86 000) was obtained in the very beginning, and the M_n almost remained identical at different conversions of monomer **48**. The M_w/M_n of the resulting polymers was in the range of 1.49−1.77. The behavior of this polymerization resembles that of conventional radical polymerization, which proceeds in a chain-growth polymerization manner, accompanying the chain transfer reaction. The ^{1}H NMR spectrum of the polymer indicated that a noticeable amount of polymers were the Br/Br ended polyfluorene, which would be formed by reductive elimination followed by intermolecular transfer of the Ni(0) catalyst that can initiate polymerization of another chain (Scheme 69).

Scheme 70

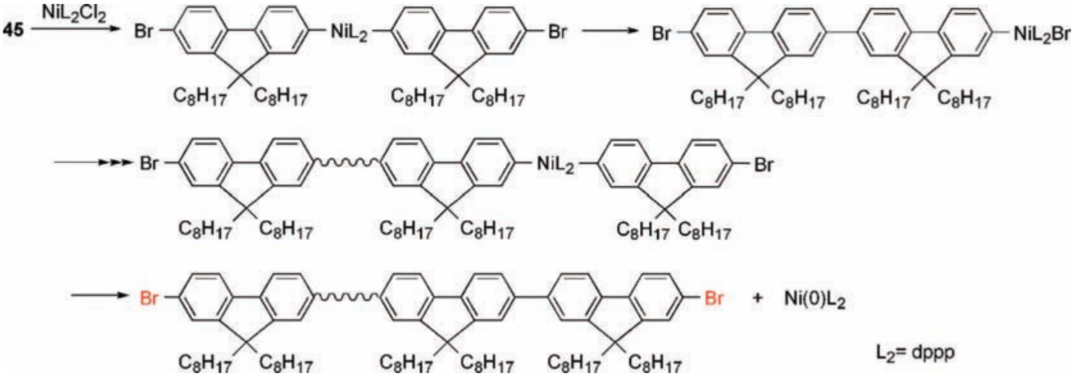


Carter and co-workers conducted the polymerization of lithiated fluorene monomer **49**, obtained by the reaction of the corresponding dibromofluorene with *t*-BuLi in situ, with Ni(dppp)Cl$_2$ (Scheme 70).[127] The ratio of *t*-BuLi to the dibromofluorene had a direct effect on the molecular weight; use of an excess amount of *t*-BuLi decreased the molecular weight. Furthermore, the observed polydispersity indexes were around 2. Accordingly, they proposed a step-growth polymerization mechanism.

6. Conclusion

We have described development and application of chain-growth condensation polymerization. The change of the polymerization mechanism from a step-growth to a chain-growth process has been attained in several ways: (1) activation of the polymer end group by differing substituent effects between the monomer and the polymer; (2) phase-transfer polymerization in a biphase system comprising a monomer storage phase and a polymerization phase; (3) transfer of the reactive species, derived from the initiator, to the polymer end group; and (4) activation of the polymer end group by transfer of the catalyst to it. Chain-growth condensation polymerization enables us to produce architectures containing well-defined condensation polymers, such as block copolymers, star polymers, graft copolymers, etc. Some of these self-assemble to form supramolecular nano- to micro-order structures by virtue of the strong intermolecular forces between condensation polymer units. Furthermore, architectures containing π-conjugated polymers have been rapidly developed and

Scheme 69



applied to organic electrical materials for photovoltaic devices and field effect transistors. Future research efforts will be directed toward the development of chain-growth condensation polymerization of AA and BB monomers, which is a more general condensation polymerization than that of AB monomers, as well as discovery of specific physical properties of condensation polymers with narrow molecular weight distribution.

7. Acknowledgments

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