Macromolecules

Volume 40, Number 12 June 12, 2007

Review

Converting Step-Growth to Chain-Growth Condensation Polymerization

Akihiro Yokoyama and Tsutomu Yokozawa*

Department of Material and Life Chemistry, Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan

Received June 19, 2006; Revised Manuscript Received March 9, 2007

ABSTRACT: The development and applications of chain-growth condensation polymerization are reviewed. Well-defined aromatic polyamides, polyesters, and polyethers have been synthesized via substituent effect-assisted chain-growth condensation polymerization, in which the polymer propagating ends are more reactive than the monomers due to resonance or inductive effects between the functional groups of the terminal monomer units. Chain-growth condensation polymerization for the synthesis of aromatic polyamides has been applied to the construction of well-defined block copolymers and star-shaped polymers. Nickel-catalyzed condensation polymerization of 5-metalated 2-halothiophene has been found to proceed in a chain-growth polymerization manner. Detailed investigations revealed that this polymerization is a catalyst-transfer condensation polymerization, in which the chain-growth nature is attributable to intramolecular catalyst transfer. Phase-transfer polymerization in a solid−solution biphasic system, in which the monomers are stored in an unpolymerizable solid phase, has been applied to the chain-growth condensation polymerization of potassium 4-bromomethyl-2-octyloxybenzoate.

I. Introduction

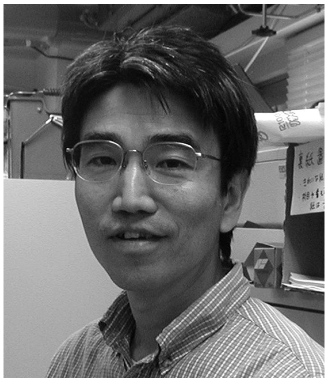
Polycondensation is a fascinating polymerization method to provide polymers having a variety of functional groups in their backbones and side chains. Because of strong intermolecular interactions between the polymer backbones, condensation polymers show strong mechanical properties with high thermal and chemical resistance, which make them potentially useful materials. Generally, polycondensation proceeds in a step-growth polymerization manner, in which condensation reactions between molecules of all degrees of polymerization occur. In the absence of side reactions or cyclization, the average degree of polymerization can be estimated according to the theory established by Carothers[1] and Flory,[2] and the molecular weight distribution approaches a value of 2. It has been difficult to synthesize condensation polymers having controlled molecular weight with a narrow molecular weight distribution in a step-growth polymerization manner.

In order to synthesize a polymer with controlled molecular weight and low polydispersity, the polymerization should start from an initiator unit and proceed in a chain-growth polymerization manner without disproportionation or termination. This is the case for so-called living polymerization. Since the discovery of anion living polymerization by Szwarc in 1956,[3] many kinds of living polymerizations have been developed and used to synthesize well-defined polymers with controlled molecular weight and a narrow molecular weight distribution. These polymerization methods have also afforded polymers of various shapes, such as block and graft copolymers, as well as star polymers, making it possible to construct self-assembled

* Corresponding author. E-mail: yokozt01@kanagawa-u.ac.jp. Telephone: +81-45-481-5661. Fax: +81-45-413-9770.

10.1021/ma061357b CCC: $37.00

Akihiro Yokoyama is currently an Assistant Professor of Material and Life Chemistry at Kanagawa University, Japan. He received his Ph.D. in Pharmaceutical Science from the University of Tokyo in 1997. After postdoctoral research at Osaka Prefecture University (1998−2000) and Tokyo Institute of Technology (2000−2001), he joined Kanagawa University in 2001. His research interests include development of novel polymerization methods and syntheses of polymers and supermolecules with well-defined three-dimensional structures.



Tsutomu Yokozawa received his Ph.D. in Organic Chemistry from the Tokyo Institute of Technology, Japan in 1987. In 1985, he had already started an academic career in the Research Laboratory of Resources Utilization, Tokyo Institute of Technology, as a Research Associate, and he was promoted to Assistant Professor in 1988. He joined the Department of Applied Chemistry, Kanagawa University, as a Lecturer in 1991, and he was promoted to Associate Professor in 1993. During 1997−1998, he worked as a visiting scientist at the University of Illinois at Urbana−Champaign. He was promoted to Full Professor in 1999. He was also a researcher for PRESTO, JST, during 2001−2005. His research interests cover controlled synthesis of polymers, supramolecular chemistry of polymers, and dynamic covalent chemistry, as well as organic chemistry.

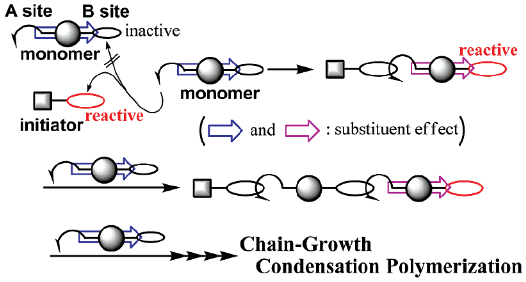
supramolecular architectures with defined shapes and properties. In general, however, living polymerization had been applicable only to addition polymerization of vinyl monomers and exothermic ring-opening polymerization of cyclic monomers, not to polycondensation and polyaddition.

If one can synthesize condensation polymers in a chain-growth polymerization manner from an initiator, the resulting polymers should possess controlled molecular weight, narrow polydispersity, and definite end group structures. Therefore, the characteristics of these polymers may be tunable by adjusting the molecular weight, and it should be easier to synthesize complex polymer architectures involving condensation polymer units. There are several reports of condensation polymerizations that proceed in a chain-growth polymerization manner, such as transition metal-catalyzed polymerization of α-amino acid *N*-carboxyanhydrides (NCA),[4,5] polyhomologation of dimethylsulfoxonium methylide,[6] polymerization of allylic arsonium ylides,[7] and anionic[8] and cationic[9,10] polymerization of phosphoranimines. As in the case of living polymerization of vinyl monomers, the chain-growth polymerization nature of these condensation polymerizations is based on the transfer of the reactive species, which is derived from the initiator, to the polymer end group. Aside from these polymerizations, we have been developing *chain-growth condensation polymerization* methods, in which selective activation of the polymer propagating terminal suppresses the reaction of monomers with each other, so that the monomer reacts only with the initiator and the polymer end group. Here, we highlight our development of chain-growth condensation polymerization. The approaches we have adopted are (1) change of substituent effect, (2) selective transfer of catalysts to the polymer end group, and (3) controlled transfer of monomer from an unpolymerizable solid phase to polymerizable solution phase.

II. Chain-Growth Condensation Polymerization Using Substituent Effect

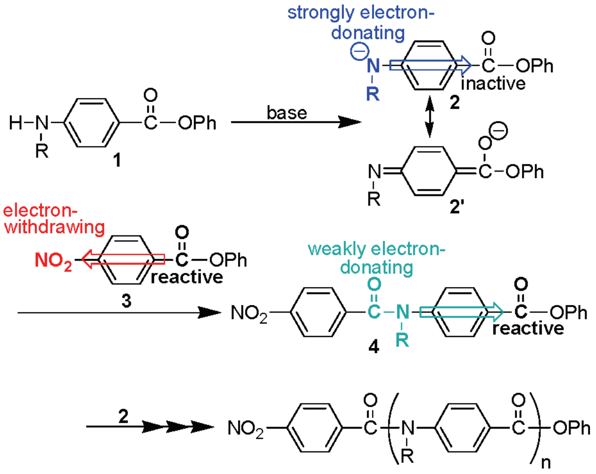
As in the case of living polymerization, condensation polymerization would proceed in a chain-growth polymerization manner if the monomer reacts only with the polymer propagating end, not with other monomers. One approach to chain-growth condensation polymerization is the selective activation of polymer end groups by utilizing a change of substituent effectsbetween the monomer functional groups. Scheme 1 shows a schematic illustration of this concept in the condensation polymerization of AB type monomers. In this monomer, the substituent effect of the A site diminishes the reactivity of the B site, suppressing undesired step-growth reaction between the monomers. When the monomer reacts with an initiator having a reactive site, the substituent effect changes. If the substituent effect of the formed bond enhances the reactivity of the polymer end group, the next monomer would react selectively with the polymer propagating end. This concept has been used to explain the polymerization behavior of para-substituted aromatic monomers, such as alkali metal salts of 4-halothiophenols,[11] 4-halo-2,6-dimethylphenols,[12] the potassium salt of 4-fluoro-4′-hydroxybenzophenone,[13] and sodium 4-fluorobenzenesulfinate.[14] Polymerization of methylphenyldichlorosilene with alkali metals[15] and condensation polymerization of dibromomethane with bisphenol[16] also showed such substituent effects. However, complete control of these condensation polymerizations was not attained owing to difficulties such as low solubility of the polymer formed, insufficient suppression of step-growth polymerization, or side reactions.

Scheme 1



The substituent effect-assisted chain-growth condensation polymerization differs significantly from living polymerization in terms of the reactivity of monomers: while living polymerization is generally conducted for monomers that are unable to

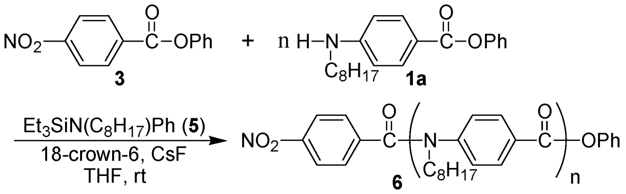
Scheme 2



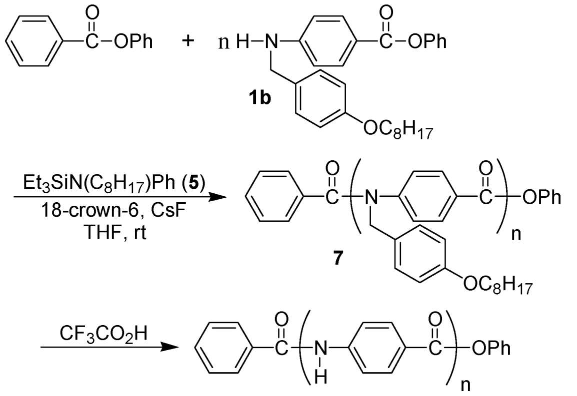
polymerize without initiators, the monomers used in the chain-growth condensation polymerization can polymerize without initiators, resulting in undesired step-growth polymerization if the conditions are not appropriately controlled. Therefore, suppression of the reaction between monomers is one of the key points of successful chain-growth condensation polymerization.

A. Polyamides. 1. Resonance Effect. Complete control of condensation polymerization by substituent effect-assisted chain-growth condensation polymerization was first demonstrated in the synthesis of *N*-alkylated poly(*p*-benzamide)s by polymerization of 4-(alkylamino)benzoic acid phenyl esters (**1**).[17] In this polymerization, the difference of resonance effects between the monomer amide anion and the polymer amide linkage was used to control the reactivity of the electrophilic ester unit. Scheme 2 illustrates our idea to activate the polymer end group in this condensation polymerization by using the difference of resonance effect. Deprotonation of the monomer **1** affords the amide anion **2**. As shown in the resonance structures of **2** and **2′**, the strongly electron-donating ability of the amide anion decreases the electrophilicity of the ester carbonyl group at the para position. This deactivation suppresses the reaction between the monomers to prevent from step-growth polymerization of **2**. In the presence of an initiator **3** having a reactive ester carbonyl group due to the presence of an electron-withdrawing substituent at the para position, **2** would react with **3** to give **4**. Because the amide linkage of **4** is a weakly electron-donating group and does not strongly deactivate the phenyl ester moiety at the para position, the ester carbonyl group of **4** has sufficient electrophilicity to react with another **2**. The polymer propagating group is activated in this manner, and the monomer **2** reacts selectively with the polymer end to result in chain-growth polymerization.

Scheme 3



Scheme 4



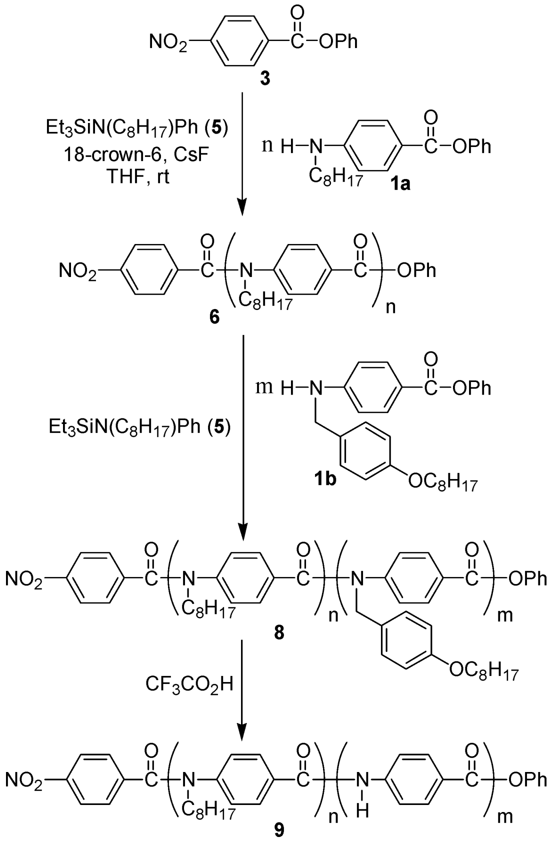
Polymerization of phenyl 4-(octylamino)benzoate (**1a**) was carried out in the presence of a base and the initiator **3**. When the combination of *N*-octyl-*N*-triethylsilylaniline (**5**)/CsF/18-crown-6 was used as a base, the polymerization gave a well-defined polyamide **6** with a narrow molecular weight distribution ($M_w/M_n \leq 1.1$) (Scheme 3). The molecular weight of **6** was controlled completely by the feed ratio of **1a** to **3** up to M_n = 22 000 and was in agreement with the value calculated on the assumption that all polymerization started from the initiator molecule **3**. An examination of the relationship between the M_n value of **6** and the conversion of **1a** in the condensation polymerization with 5 mol % of **3** demonstrated that M_n increased linearly in proportion to the monomer conversion. All of the results indicate that this polymerization proceeds in a chain-growth polymerization manner from the initiator **3**.

When the polymerization was carried out with a monomer bearing a chiral tri(ethylene glycol) unit as the *N*-alkyl 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. Because the chain-growth condensation polymerization gives *N*-alkylated 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 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]

This polymerization provides not only *N*-alkylated poly(*p*-benzamide)s, but also *N*-unsubstituted ones when the monomer has a removable *N*-alkyl group as a protecting group. Because *N*-unsubstituted poly(*p*-benzamide)s are soluble only in strong acid and are essentially insoluble in common organic solvents, complete deprotection should be carried out under homogeneous conditions in strongly acidic media. A suitable protecting group is the octyloxybenzyl group, not only because it can be easily removed by treatment with trifluoroacetic acid, but also because the octyloxy group enhances the solubility of the protected polymer. If the solubility of the protected polymer is insufficient, control of the condensation polymerization is difficult because of precipitation of the polymer, as in the case of the polymerization of *N*-methoxybenzyl monomer. Polymerization of the *N*-octyloxybenzyl monomer **1b** gave the polyamide **7** with controlled molecular weight and low polydispersity. Treatment of this polyamide with trifluoroacetic acid resulted in complete removal of the 4-octyloxybenzyl group from **7**. However, it was difficult to characterize the resulting poly(*p*-benzamide) due to its extremely low solubility in organic solvents (Scheme 4).

The chain-growth polymerization nature of this condensation polymerization also makes it easy to synthesize well-defined block copolymers. An example is the synthesis of block copolymers consisting of *N*−H and *N*-alkylated poly(*p*-benza-

Scheme 5

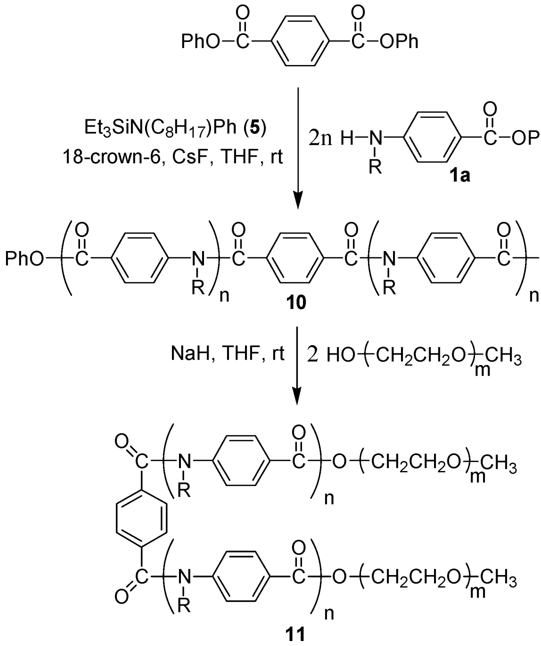


mide)s, as shown in Scheme 5. Thus, after polymerization of **1a** in the presence of the base and a small amount of **3**, a fresh feed of **1b** and **5** was added to the reaction mixture. The added **1b** feed smoothly polymerized from the prepolymer **6** to give a well-defined poly**1a**-*b*-poly**1b** block copolymer **8**. Treatment of **8** with trifluoroacetic acid afforded the block copolymer **9**, which self-assembled to construct bundle and flake structures, presumably due to hydrogen bonding between the polymer backbones.[19]

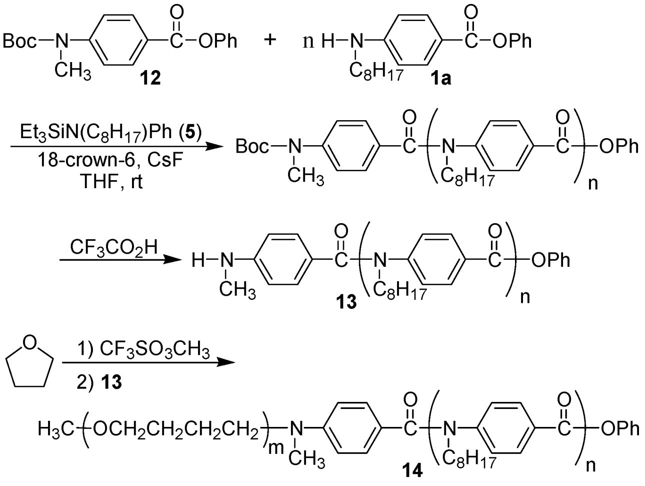
Because this condensation polymerization always proceeds from initiators, block copolymers with a variety of sequences can be synthesized by using multifunctional initiators. Furthermore, in contrast to general living polymerizations, the reactivity of the polymer end groups obtained by the chain-growth condensation polymerization remains after isolation. For example, polymerization of **1a** with phenyl terephthalate as an initiator proceeded in two directions from the initiator. The isolated polyamide **10** has two electrophilic ester moieties at the polymer ends, and treatment with PEG alkoxide gave an ABA triblock copolymer **11** (Scheme 6).[20] Polymerization from a trifunctional initiator afforded star-shaped aromatic polyamides.[21]

When the polymerization of **1a** was carried out in the presence of *N*-protected 4-(methylamino)benzoic acid ester **12** as an initiator, deprotection after the polymerization gave telechelic-type polyamide **13**, in which one of the polymer ends is the electrophilic ester moiety and the other is a nucleophilic amino group. The terminal amino group of **13** reacted with the living cationic propagating group of poly(THF) to afford the diblock copolymer **14** (Scheme 7). When the polymerization of THF was initiated by trifluoromethanesulfonic anhydride and the polymer was quenched with **13**, a poly(THF)−polyamide−poly(THF) triblock copolymer was obtained.[22]

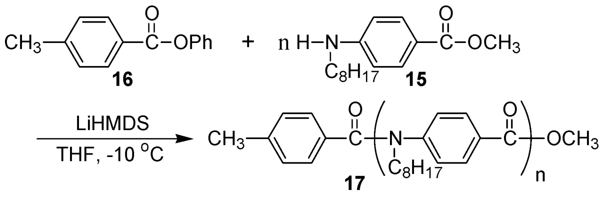
Scheme 6



Scheme 7

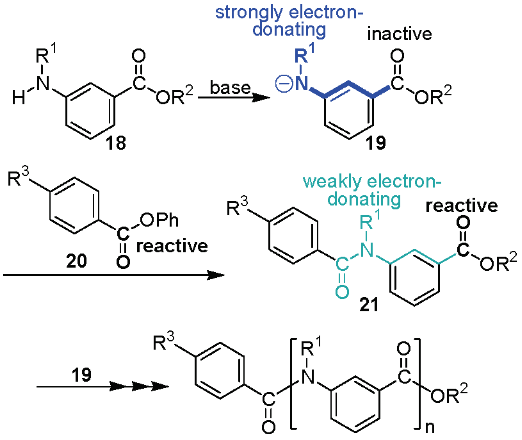


Scheme 8

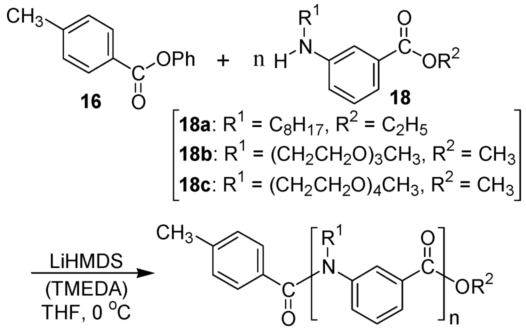


The chain-growth condensation polymerizations mentioned above were carried out using the phenyl ester monomers and the combination of *N*-octyl-*N*-triethylsilylaniline (**5**), CsF, and 18-crown-6 as a base. Phenyl esters are not common compared with methyl and ethyl esters, and **5** must be synthesized. Furthermore, phenol and *N*-octylaniline were formed as byproducts, removal of which usually required HPLC. In order to prepare well-defined poly(*p*-benzamide)s more conveniently, we investigated the polymerization of the methyl ester monomer **15** with several kinds of commercially available bases, and found that **15** polymerized in a chain-growth manner in the presence of lithium 1,1,1,3,3,3-hexamethyldisilazide (LiHMDS) and **16** as a base and an initiator, respectively (Scheme 8). When the polymerization was quenched by the addition of an aqueous

Scheme 9



Scheme 10

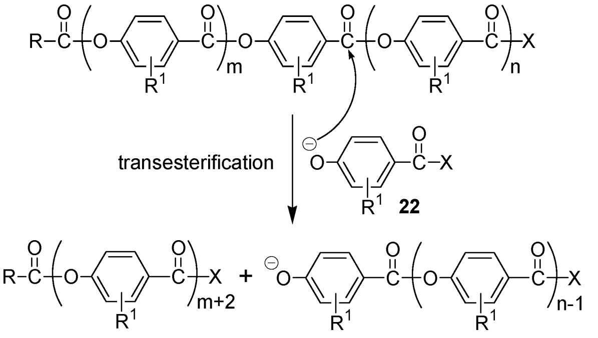


solution of NH_4Cl, the mixture contained the polymer and byproducts, such as methanol, ammonia, and phenol. The mixture was extracted with CH_2Cl_2, and the organic layer was treated with aqueous NaOH solution and concentrated by evaporation, then the byproducts were removed to afford well-defined *N*-octyl poly(*p*-benzamide) **17** in pure form.[23] Ueda and co-workers reported a similar chain-growth condensation polymerization using 3-acyl-2-benzothiazolethione monomer in the presence of Grignard reagent as a base. Byproducts of this polymerization could be removed by washing with water.[24]

2. Inductive Effect. In the polymerization of 3-(alkylamino)-benzoic acid esters **18** for the synthesis of *N*-alkylated poly(*m*-benzamide)s, the key substituent effects between the amino group and the ester carbonyl group of the monomer are not resonance, but inductive effects. Although inductive effects are generally weaker than resonance effects, we thought that the negative charge of the amide anion of **19** formed by deprotonation of **18** would deactivate the ester carbonyl group sufficiently to suppress the reaction between **19**'s. Because the reaction of **19** with an initiator **20** converts the strongly electron-donating amide anion of **19** into the weakly electron-donating amide linkage of **21**, the ester carbonyl group of **21** is more reactive than that of the monomer. As in the case of resonance effect-assisted chain-growth condensation polymerization of the para-substituted monomer **2**, the meta-substituted monomer **19** would react selectively at the polymer propagating end to result in chain-growth condensation polymerization (Scheme 9).

We investigated the bases and the leaving groups at the ester linkage in the polymerization of 3-(octylamino)benzoic acid esters, and found that polymerization of the ethyl ester monomer **18a** in the presence of the initiator **16** using LiHMDS as a base proceeded in a chain-growth polymerization manner in THF at 0 °C (Scheme 10). The obtained *N*-octylated poly(*m*-benzamide)s had narrow molecular weight distributions ($M_w/M_n \leq 1.1$) and controlled molecular weights which were almost identical to the values calculated from the feed ratio of the initiator **16** to the monomer **18a** ($[\mathbf{18a}]_0/[\mathbf{16}]_0$).[25] The methyl ester monomer also polymerized in a chain-growth polymerization manner, but prolongation of the reaction time resulted in a small shoulder in the GPC chromatogram.

Scheme 11

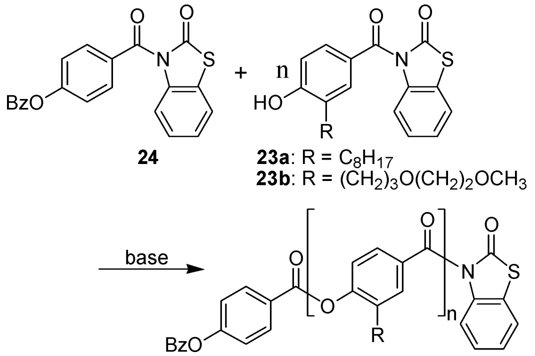


Poly(*m*-benzamide)s with a variety of *N*-substituents were synthesized.[26] They showed higher solubility than the corresponding para-substituted counterparts. When the *N*-alkyl group of **18** was oligo(ethylene glycol) monomethyl ether such as **18b** and **18c** in Scheme 10, the controlled polymerization required the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) as an additive: polymerization without TMEDA resulted in formation of polymer with a broad molecular weight distribution, probably due to the association of the multidentate oligo(ethylene glycol) moiety with the lithium cation.[27] The obtained polyamide was soluble in water, and the aqueous solution showed reversible clouding on heating. Poly(*m*-benzamide)s having a chiral *N*-alkyl group adopt a chiral conformation in solution, depending on the solvent, temperature, and the *N*-alkyl group.[28]

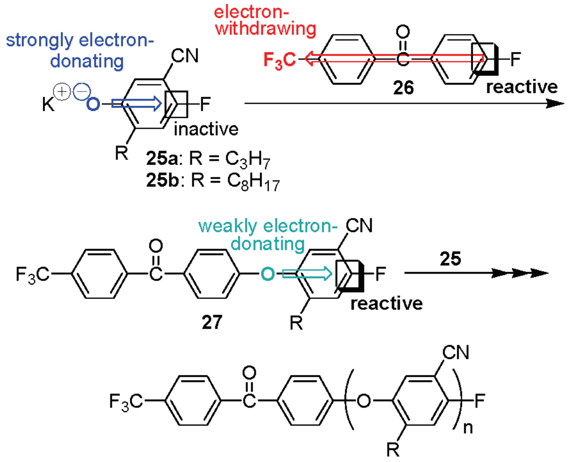
B. Polyesters. One might think that it would be easy to synthesize well-defined aromatic polyesters, such as poly(4-hydroxybenzoate)s, by chain-growth condensation polymerization of 4-hydroxybenzoic acid derivatives **22** in a similar manner to that shown in Scheme 2. However, controlled condensation polymerization for the synthesis of aromatic polyesters is more difficult than in the case of aromatic polyamides, because the ester linkages of the polyester backbone react with nucleophiles much more easily than do amide linkages. When the phenoxy group of the monomer **22** reacts not with the polymer propagating end, but with the polyester backbone, transesterification occurs and cleavage of the propagating polymer results in broadening of the molecular weight distribution of the polymer (Scheme 11).

For the synthesis of well-defined poly(4-hydroxybenzoate)s by transesterification-suppressing chain-growth condensation polymerization, we investigated appropriate leaving groups of the monomer acyl moiety by means of model reactions, and designed the monomer **23a** bearing a 3-acyl-2-benzothiazolone unit as an electrophilic acyl moiety, as well as an octyl group to increase the solubility of the polymer. When the polymerization of **23a** in CH_2Cl_2 at room temperature was carried out in the presence of 20 mol % of the initiator **24** and an amine as a base, the polymerization proceeded in a chain-growth polymerization manner and yielded the polyester with a controlled molecular weight and a narrow molecular weight distribution (Scheme 12). However, polymerization with smaller amounts of the initiator resulted in uncontrolled condensation polymerization due to transesterification between the polymer backbone and monomer.[29] The transesterification was reduced at lower temperature, and the polymerization of **23a** with **24** in THF at

Scheme 12



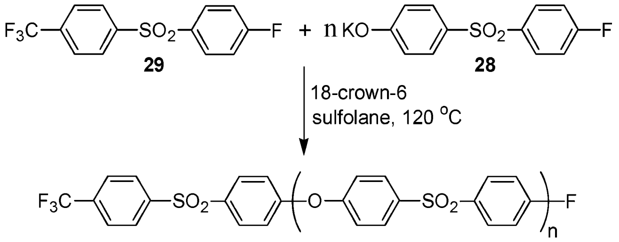
Scheme 13



−30 °C using a combination of Et_3SiH/CsF/18-crown-6 as a base gave well-defined polyester of up to $M_n = 3500$: however, attempts to obtain longer polyesters resulted in uncontrolled polymerization due to precipitation of the polymer. The solubility of the polyester was improved by using the monomer **23b** bearing a 4,7-dioxaoctyl group instead of the octyl group, and a well-defined polyester was obtained up to $M_n = 7250$. A diblock copolymer of poly**23a** and poly**23b** with a narrow molecular weight distribution was also synthesized.[30]

C. Polyethers. Substituent effect-assisted chain-growth condensation polymerization can also be applied to the polymerization of monomers without a carbonyl group. The condensation polymerization of potassium 4-fluorophenolate **25**, which proceeds via aromatic nucleophilic substitution between phenoxide and aryl fluoride, was controlled as shown in Scheme 13. The strongly electron-donating ability of the phenoxide of **25** presumably reduces the electrophilicity of the aromatic carbon at the para position. Indeed, **25a** did not polymerize at all in sulfolane at 150 °C. When the reaction was carried out in the presence of an initiator **26** bearing an electron-withdrawing group, **25** reacted with **26** to yield an ether **27**. Because the electron-donating ability of the ether linkage is much weaker than that of the phenoxide, the fluorine-connected aromatic carbon of **27** would be more reactive than that of **25**, resulting in reaction of **27** with the next monomer. The activation of the aromatic carbon was supported by the lower-field shift of the fluorine signal of **27** in the ^{19}F NMR spectra. Polymerization proceeded in a chain-growth manner, and the molecular weight of the obtained polyether was controlled precisely by the feed ratio of **25a** to **26** up to $M_n = 3600$, with a M_w/M_n ratio of less than 1.1. However, polyether of higher molecular weight was not soluble in the polymerization solvent, and could not be synthesized in a controlled manner.[31]

Scheme 14



The solvent effect on the polymerization was investigated using the more soluble monomer **25b**.[32] In *N*,*N*′-dimethylimidazolidinone (DMI) and tetraglyme, the polymerization of **25b** in the presence of the initiator **26** at 150 °C proceeded homogeneously, but the obtained polyether had a broad molecular weight distribution. The matrix-assisted laser desorption ionization time-of-flight (MALDI−TOF) mass spectrum of the polyether obtained in DMI revealed that the product consisted of two species: one without the initiator unit, and the other with the initiator unit. On the other hand, polymerization of **25b** with **26** in sulfolane gave the polyether with a narrow molecular weight distribution, and the MALDI−TOF mass spectrum showed only the initiator-containing polyether. In this polymerization, transetherification between the polymer and monomer was not observed. Interestingly, polymerization of **25b** in sulfolane in the absence of the initiator predominantly afforded macrocycles. Polyethers with narrow molecular weight distributions obtained by the chain-growth condensation polymerization method showed higher crystallinity than did polyethers having broad molecular weight distributions.[33]

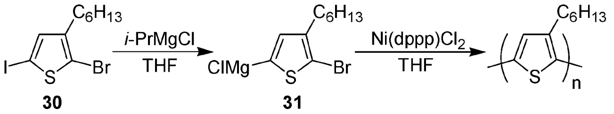
Aromatic poly(ether sulfone)s were similarly synthesized in a controlled manner by chain-growth condensation polymerization. In this case, the nucleophilic and electrophilic sites of the monomer **28** are located on different benzene rings connected by a sulfone group, and the substituent effect should be transmitted through these units. Polymerization of the two-aromatic monomer **28** was carried out in the presence of the initiator **29** and 18-crown-6 in sulfolane at 120 °C, and proceeded in a chain-growth polymerization manner to afford the poly(ether sulfone)s with $M_w/M_n < 1.3$ (Scheme 14).[34] Recently, well-defined poly(ether ketone)s were also synthesized in a similar manner.[35]

III. Catalyst-Transfer Condensation Polymerization

Various π-conjugated polymers have been synthesized via metal-mediated polycondensation reactions.[36] Among these polymers, regioregular poly(3-alkylthiophene)s[37] show unique properties such as light-emitting ability and high field-effect mobility, and have received increasing attention. Regiocontrolled synthesis of poly(3-alkylthiophene)s has been developed by McCullough[38] and Rieke,[39] who found that transition metal-catalyzed polycondensation of 5-metalated 2-halo-3-alkylthiophenes afforded head-to-tail poly(3-alkylthiophene)s. However, the molecular weight and polydispersity of the products were not well controlled: poly(3-alkylthiophene)s with narrow molecular weight distributions were obtained only after fractionation with Soxhlet extraction.[40]

Chain-growth condensation polymerization for the synthesis of head-to-tail poly(3-alkylthiophene)s was first reported by us (Scheme 15).[41] After the bromoiodothiophene **30** was transformed into the Grignard-type monomer **31** by treatment with 1 equiv of isopropylmagnesium chloride in THF at 0 °C, the condensation polymerization of **31** was carried out by addition of $Ni(dppp)Cl_2$ (dppp = 1,3-bis(diphenylphosphino)propane).

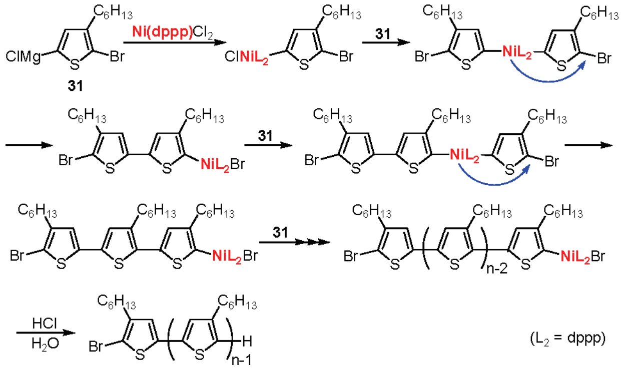
Scheme 15



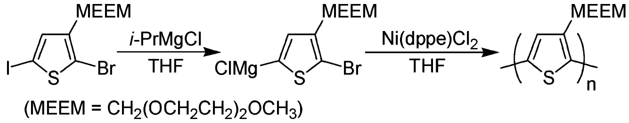
The polymerization proceeded smoothly at room temperature, and the molecular weight of the growing polymer increased linearly in proportion to the conversion of **31**, maintaining M_w/M_n in the range of 1.30−1.39. Furthermore, the molecular weight of the head-to-tail poly(3-hexylthiophene)s obtained was controlled by the feed ratio of **31** to Ni(dppp)Cl_2. All the points described above, as well as a result of a monomer-addition experiment, showed that this polymerization proceeds in a chain-growth polymerization manner. In order to control the polymerization completely, both the purity of the monomer and the reagents, and the polymerization conditions are crucial: if the purity of the monomer or the reagents is insufficient, or if the polymerization is carried out under inadequate conditions, the polythiophenes formed have a broad molecular weight distribution. Soon after our report, McCullough and co-workers also reported the chain-growth polymerization of 2-bromo-5-chlorozinc-3-hexylthiophene instead of **31**.[42]

Although the polymerization of **31** showed chain-growth polymerization behavior, the GPC elution curve of the obtained polymer showed a small shoulder in the higher molecular weight region, and the molecular weight distribution of the crude polymer was more than 1.2. Investigation of the polymerization conditions and workup procedures revealed that the molecular weight distribution of the product depended on the quenching reagent. When the polymerization was quenched with water, the GPC profiles of the obtained polymer showed the small shoulder. However, the polymer obtained by quenching with 5 M hydrochloric acid showed a unimodal elution curve and a narrower molecular weight distribution ($M_w/M_n \leq 1.15$). The small shoulder of the GPC elution curve is thought to be caused by disproportionation reaction between the polymer growing ends.[43]

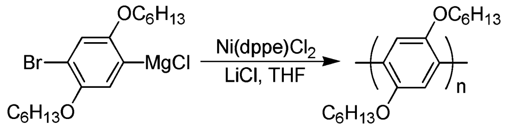
Scheme 16



Scheme 17



Scheme 18

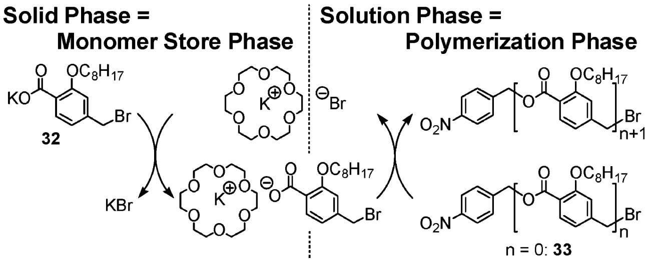


We examined the chain-growth polymerization mechanism by means of polymer end group analysis.[44] The MALDI−TOF mass spectra of poly(3-alkylthiophene)s prepared by insufficiently controlled polymerization showed several series of peaks,[45] but controlled polymerization of **31** afforded polymer whose MALDI−TOF mass spectrum showed only one series of peaks corresponding to the poly(3-hexylthiophene) bearing a bromine atom and a hydrogen atom at the two ends. When 3,4-dimethylphenylmagnesium chloride was added to the reaction mixture at the late stage of polymerization of **31**, the MALDI−TOF mass spectrum of the product also consisted of one series of peaks, corresponding to poly(3-hexylthiophene) with 3,4-dimethylphenyl units at both ends. The average number of repeat units of the arylated polymer could be determined easily from the ^{1}H NMR integral ratio of the methyl proton of the repeating hexylthiophene unit relative to that of the dimethylphenyl unit at the two ends, and was the same as the value calculated from the feed ratio of the converted monomer **31** to the Ni catalyst used. These results indicate that the polymer propagating group is a nickel complex, and that one Ni molecule forms one polymer chain. Furthermore, the reaction of **31** in the presence of 50 mol % of Ni(dppp)Cl_2 afforded mainly 4,4′-dihexyl-5-bromo-2,2′-bithiophene. On the basis of the above results, we proposed the chain-growth mechanism shown in Scheme 16. Thus, the polymerization is initiated by the reaction of the Ni catalyst with two molecules of the monomer **31**. After formation of the bithiophene by reductive elimination, the Ni catalyst transfers intramolecularly to the terminal C−Br bond. Propagation would proceed through reaction of **31** with the Ni complex at the polymer growing end, followed by intramolecular transfer of the Ni catalyst. In this way, the monomer reacts selectively at the polymer propagating end to result in chain-growth polymerization. We call this type of polymerization *catalyst-transfer condensation polymerization*. We recently demonstrated that polythiophene with oxyethylene side chains (Scheme 17)[46] and poly(*p*-phenylene) with hexyloxy side chains (Scheme 18)[47] can be synthesized in a controlled manner via catalyst-transfer condensation polymerization, and that the best ligand for the nickel catalyst to control the polymerization depended on the monomer: catalyst-transfer condensation polymerization for the synthesis of the conjugated polymers required Ni(dppe)Cl_2 (dppe = 1,2-bis(diphenylphosphino)-ethane) as a catalyst, not Ni(dppp)Cl_2, which was used for the synthesis of well-defined poly(3-hexylthiophene). A few other reactions involving similar intramolecular transfer of metal catalysts have been reported,[48−50] but chain-growth polymerization via the catalyst-transfer mechanism has not been demonstrated. McCullough and co-workers proposed a similar chain-growth mechanism on the basis of end group analysis by ^{1}H NMR spectroscopy.[51]

IV. Biphasic System

In order to carry out condensation polymerization in a chain-growth polymerization manner, it is crucial to prevent the reaction of monomers with each other. If insoluble solid monomers, which are unable to react with each other in the solid phase, are dispersed in an organic solvent and transferred to the solution phase at an appropriate rate with the aid of a phase-transfer catalyst, the monomer would polymerize in a chain-growth polymerization manner. This type of polymerization was demonstrated in the condensation polymerization of potassium 4-bromomethyl-2-octyloxybenzoate (**32**) in acetone in the presence of 4-nitrobenzyl bromide (**33**) and 18-crown-6 as an initiator and a phase-transfer catalyst, respectively (Scheme

Scheme 19



19).[52] Because the rate of monomer transfer from the solid phase to the solution phase was affected by the amount of the phase-transfer catalyst, polymerization with smaller or larger amounts of the catalyst afforded polymers with broad molecular weight distributions, while the use of equimolar amounts of 18-crown-6 and **33** gave polymer with a narrow molecular weight distribution. When the polymerization was carried out using 7 mol % of **33** and 18-crown-6, the molecular weight of the growing polymer increased linearly in proportion to the conversion of **32** with a narrow molecular weight distribution throughout ($M_w/M_n < 1.3$), and the ratio of the polymer growing end to the initiator unit was unity over the whole conversion range. These results suggest that this condensation polymerization proceeds in a chain-growth polymerization manner. Polymerization of **32** in acetone with tetrabutylammonium iodide instead of 18-crown-6 also proceeded in a chain-growth polymerization manner.[53]

V. Summary and Outlook

We have demonstrated that chain-growth condensation polymerization can be achieved by utilizing substituent effects, intramolecular catalyst transfer, or a biphasic system. Substituent effect-assisted chain-growth condensation polymerization is applicable to the synthesis of well-defined aromatic polyamides, polyesters, and polyethers. Because the growth of the condensation polymer starts from an initiator, and both ends of the obtained polymer have definite and stable structures, it is easy to synthesize well-defined block copolymers and star-shaped polymers involving these condensation polymer units. Although we have demonstrated only the synthesis and self-assembly of several polymer architectures involving aramides, a variety of polymer architectures involving other condensation polymer units should be obtainable using this condensation polymerization approach, and these products are expected to show interesting and novel self-assembly properties. Chain-growth condensation polymerization with the aid of intramolecular catalyst transfer or the use of a biphasic system has been demonstrated in the condensation polymerization of 5-metalated 3-alkyl-2-halothiophenes and potassium 4-bromomethyl-2-octyloxybenzoate, respectively. We believe that these chain-growth condensation polymerization methods have generality for the synthesis of a variety of condensation polymers, and studies on the synthesis of well-defined π-conjugated polymers, as well as on condensation polymerization with other biphasic systems, are in progress. Chain-growth condensation polymerization with nonaromatic monomers also remains an interesting target.

References and Notes

(1) Carothers, C. H. *Trans. Faraday Soc.* **1936**, *32*, 39.
(2) Flory, P. J. *Chem. Rev.* **1946**, *39*, 137.
(3) Szwarc, M. *J. Am. Chem. Soc.* **1956**, *78*, 2656.
(4) For a recent review of polymerization of α-amino acid *N*-carboxyanhydrides, see: Kricheldorf, H. R. *Angew. Chem. Int. Ed.* **2006**, *45*, 5752.
(5) For controlled polymerization of α-amino acid *N*-carboxyanhydrides using transition metals, see: (a) Deming, T. J. *J. Am. Chem. Soc.* **1997**, *119*, 2759. (b) Deming, T. J. *Nature (London)* **1997**, *390*, 386. (c) Deming, T. J. *Macromolecules* **1999**, *32*, 4500. (d) Curtin, S. A.; Deming, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 7427. (e) Cheng, J.; Deming, T. J. *Macromolecules* **1999**, *32*, 4745. (f) Deming, T. J.; Curtin, S. A. *J. Am. Chem. Soc.* **2000**, *122*, 5710. (g) Deming, T. J. *J. Polym. Sci., Part A Polym. Chem.* **2000**, *38*, 3011. (h) Cheng, J.; Deming, T. J. *J. Am. Chem. Soc.* **2001**, *123*, 9457. (i) Brzezinska, K. R.; Deming, T. J. *Macromolecules* **2001**, *34*, 4348. (j) Cheng, J.; Deming, T. J. *Macromolecules* **2001**, *34*, 5169. (k) Brzezinska, K. R.; Curtin, S. A.; Deming, T. J. *Macromolecules* **2002**, *35*, 2970. (l) Seidel, S. W.; Deming, T. J. *Macromolecules* **2003**, *36*, 969.
(6) (a) Shea, K. J.; Walker, J. W.; Zhu, H.; Paz, M.; Greaves, J. *J. Am. Chem. Soc.* **1997**, *119*, 9049. (b) Shea, K. J.; Busch, B. B.; Paz, M. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 1391. (c) Shea, K. J.; Lee, S. Y.; Busch, B. B. *J. Org. Chem.* **1998**, *63*, 5746. (d) Shea, K. J.; Staiger, C. L.; Lee, S. Y. *Macromolecules* **1999**, *32*, 3157. (e) Shea, K. J. *Chem.—Eur. J.* **2000**, *6*, 1113. (f) Zhou, X.-Z.; Shea, K. J. *J. Am. Chem. Soc.* **2000**, *122*, 11515. (g) Wagner, C. E.; Shea, K. J. *Org. Lett.* **2001**, *3*, 3063. (h) Busch, B. B.; Paz, M. M.; Shea, K. J.; Staiger, C. L.; Stoddard, J. M.; Walker, J. R.; Zhou, X.-Z.; Zhu, H. *J. Am. Chem. Soc.* **2002**, *124*, 3636. (i) Busch, B. B.; Staiger, C. L.; Stoddard, J. M.; Shea, K. J. *Macromolecules* **2002**, *35*, 8330.
(7) (a) Goddard, J.-P.; Lixon, P.; Le Gall, T.; Mioskowski, C. *J. Am. Chem. Soc.* **2003**, *125*, 9242. (b) Mondière, R.; Goddard, J.-P.; Carrot, G.; Le Gall, T.; Mioskowski, C. *Macromolecules* **2005**, *38*, 663.
(8) (a) Montague, R. A.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1990**, *112*, 6721. (b) Matyjaszewski, K.; Moore, M. K.; White, M. L. *Macromolecules* **1993**, *26*, 6741. (c) White, M. L.; Matyjaszewski, K. *Macromol. Chem. Phys.* **1997**, *198*, 665.
(9) (a) Honeyman, C. H.; Manners, I.; Morrissey, C. T.; Allcock, H. R. *J. Am. Chem. Soc.* **1995**, *117*, 7035. (b) Allcock, H. R.; Crane, C. A.; Morrissey, C. T.; Nelson, J. M.; Reeves, S. D.; Honeyman, C. H.; Manners, I. *Macromolecules* **1996**, *29*, 7740. (c) Allcock, H. R.; Nelson, J. M.; Reeves, S. D.; Honeyman, C. H.; Manners, I. *Macromolecules* **1997**, *30*, 50. (d) Nelson, J. M.; Allcock, H. R. *Macromolecules* **1997**, *30*, 1854. (e) Allcock, H. R.; Reeves, S. D.; Nelson, J. M.; Crane, C. A. *Macromolecules* **1997**, *30*, 2213. (f) Allcock, H. R.; Reeves, S. D.; Nelson, J. M.; Manners, I. *Macromolecules* **2000**, *33*, 3999. (g) Allcock, H. R.; Reeves, S. D.; de Denus, C. R.; Crane, C. A. *Macromolecules* **2001**, *34*, 748.
(10) Wang, B. *Macromolecules* **2005**, *38*, 643.
(11) Lenz, R. W.; Handlovits, C. E.; Smith, H. A. *J. Polym. Sci.* **1962**, *58*, 351.
(12) (a) Risse, W.; Heitz, W.; Freitag, D.; Bottenbruch, L. *Makromol. Chem.* **1985**, *186*, 1835. (b) Percec, V.; Wang, J. H. *J. Polym. Sci., Part A Polym. Chem.* **1991**, *29*, 63.
(13) Hibbert, D. B.; Sandall, J. P. B.; Lovering, J. R.; Ridd, J. H.; Yousaf, T. I. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1739.
(14) Robello, D. R.; Ulman, A.; Urankar, E. J. *Macromolecules* **1993**, *26*, 6718.
(15) Matyjaszewski, K.; Greszta, D.; Hrkach, J. S.; Kim, H. K. *Macromolecules* **1995**, *28*, 59.
(16) Miyatake, K.; Hlil, A. R.; Hay, A. S. *Macromolecules* **2001**, *34*, 4288.
(17) Yokozawa, T.; Asai, T.; Sugi, R.; Ishigooka, S.; Hiraoka, S. *J. Am. Chem. Soc.* **2000**, *122*, 8313.
(18) Tanatani, A.; Yokoyama, A.; Azumaya, I.; Takakura, Y.; Mitsui, C.; Shiro, M.; Uchiyama, M.; Muranaka, A.; Kobayashi, N.; Yokozawa. T. *J. Am. Chem. Soc.* **2005**, *127*, 8553.
(19) Yokozawa, T.; Ogawa, M.; Sekino, A.; Sugi, R.; Yokoyama, A. *J. Am. Chem. Soc.* **2002**, *124*, 15158.
(20) Sugi, R.; Hitaka, Y.; Sekino, A.; Yokoyama, A.; Yokozawa, T. *J. Polym. Sci., Part A Polym. Chem.* **2003**, *41*, 1341.
(21) Sugi, R.; Hitaka, A.; Yokoyama, A.; Yokozawa, T. *Macromolecules* **2005**, *38*, 5526.
(22) Sugi, R.; Yokoyama, A.; Yokozawa, T. *Macromol. Rapid Commun.* **2003**, *24*, 1085.
(23) Yokozawa, T.; Muroya, D.; Sugi, R.; Yokoyama, A. *Macromol. Rapid Commun.* **2005**, *26*, 979.
(24) Shibasaki, Y.; Araki, T.; Okazaki, M.; Ueda, M. *Polym. J.* **2002**, *34*, 261.
(25) Sugi, R.; Yokoyama, A.; Furuyama, T.; Uchiyama, M.; Yokozawa, T. *J. Am. Chem. Soc.* **2005**, *127*, 10172.
(26) Ohishi, T.; Sugi, R.; Yokoyama, A.; Yokozawa, T. *J. Polym. Sci., Part A Polym.* **2006**, *44*, 4990.

(27) Sugi, R.; Ohishi, T.; Yokoyama, A.; Yokozawa, T. *Macromol. Rapid Commun.* **2006**, *27*, 716.

(28) Yamazaki, K.; Yokoyama, A.; Yokozawa, T. *Macromolecules* **2006**, *39*, 2432.

(29) Yokoyama, A.; Iwashita, K.; Hirabayashi, K.; Aiyama, K.; Yokozawa, T. *Macromolecules* **2003**, *36*, 4328.

(30) Iwashita, K.; Yokoyama, A.; Yokozawa, T. *J. Polym. Sci., Part A Polym. Chem.* **2005**, *43*, 4109.

(31) Yokozawa, T.; Suzuki, Y.; Hiraoka, S. *J. Am. Chem. Soc.* **2001**, *123*, 9902.

(32) Suzuki, Y.; Hiraoka, S.; Yokoyama, A.; Yokozawa, T. *J. Polym. Sci., Part A Polym. Chem.* **2004**, *42*, 1198.

(33) Suzuki, Y.; Hiraoka, S.; Yokoyama, A.; Yokozawa, T. *Macromolecules* **2003**, *36*, 4756.

(34) Yokozawa, T.; Taniguchi, T.; Suzuki, Y.; Yokozawa, T. *J. Polym. Sci., Part A Polym. Chem.* **2002**, *40*, 3460.

(35) Shibasaki, Y.; Araki, T.; Nagahata, R.; Ueda, M. *Eur. Polym. J.* **2005**, *41*, 2428.

(36) For a review, see: Yamamoto, T. *Macromol. Rapid Commun.* **2002**, *23*, 583.

(37) For a review, see: McCullough, R. D. *Adv. Mater.* **1998**, *10*, 93.

(38) (a) McCullough, R. D.; Lowe, R. D. *J. Chem. Soc., Chem. Commun.* **1992**, 70. (b) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904. (c) Loewe, R. S.; Khersonsky, S. M.; McCullough, R. D. *Adv. Mater.* **1999**, *11*, 250. (d) Loewe, R. S.; Ewbank, P. C.; Liu, J.; Zhai, L.; McCullough, R. D. *Macromolecules* **2001**, *34*, 4324.

(39) (a) Chen, T.-A.; Rieke, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 10087. (b) Chen, T.-A.; O'Brien, R. A.; Rieke, R. D. *Macromolecules* **1993**, *26*, 34623. (c) Chen, T.-A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233.

(40) Trznadel, M.; Pron, A.; Zagorska, M.; Chrzaszcz, R.; Pielichowski, J. *Macromolecules* **1998**, *31*, 5051.

(41) Yokoyama, A.; Miyakoshi, R.; Yokozawa, T, *Macromolecules* **2004**, *37*, 1169.

(42) Sheina, E. E.; Liu, J.; Iovu, M. C.; Laird, D. W.; McCullough, R. D. *Macromolecules* **2004**, *37*, 3526.

(43) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *Macromol. Rapid Commun.* **2004**, *25*, 1663.

(44) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *J. Am. Chem. Soc.* **2005**, *127*, 17542.

(45) Liu, J.; Loewe, R. S.; McCullough, R. D. *Macromolecules* **1999**, *32*, 5777.

(46) Adachi, I.; Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *Macromolecules* **2006**, *39*, 7793.

(47) Miyakoshi, R.; Shimono, K.; Yokoyama, A.; Yokozawa, T. *J. Am. Chem. Soc.* **2006**, *128*, 16012.

(48) (a) Nomura, N.; Tsurugi, K.; Okada, M. *Angew. Chem. Int. Ed.* **2001**, *40*, 1932. (b) Nomura, N.; Tsurugi, K.; RajanBabu, T. V.; Kondo, T. *J. Am. Chem. Soc.* **2004**, *126*, 5354.

(49) (a) Sinclair, D. J.; Sherburn, M. S. *J. Org. Chem.* **2005**, *70*, 3730. (b) Dong, C.-G.; Hu, Q.-S. *J. Am. Chem. Soc.* **2005**, *127*, 10006.

(50) (a) Reinhold, M.; McGrady, J. E.; Perutz, R. N. *J. Am. Chem. Soc.* **2004**, *126*, 5268. (b) Strawser, D.; Karton, A.; Zenkina, O. V.; Iron, M. A.; Shimon, L. J. W.; Martin, J. M. L.; Boom, M. E. *J. Am. Chem. Soc.* **2005**, *127*, 9322.

(51) Iovu, M. C.; Sheina, E. E.; Gil, R. R.; McCullough, R. D. *Macromolecules* **2005**, *38*, 8649.

(52) Yokozawa, T.; Suzuki, H. *J. Am. Chem. Soc.* **1999**, *121*, 11573.

(53) Yokozawa, T.; Maeda, D.; Hiyama, N.; Hiraoka, S. *Macromol. Chem. Phys.* **2001**, *202*, 2181.

MA061357B