Synthesis of End-Functionalized Polymers by Means of Living Anionic Polymerization. 8. Reactions of Living Anionic Polymers with α,ω-Dihaloalkanes

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ABSTRACT: In order to prepare well-defined polymers with halogen end groups, anionic living polymers of isoprene and styrene were allowed to react with excess amounts of α,ω-dihaloalkanes in THF at −78 °C. The monosubstitution reactions of 1,3-dichloropropane with these anionic living polymers proceeded cleanly to afford quantitatively the polymers with chlorine end groups that possessed controllable molecular weights and narrow molecular weight distributions. On the other hand, the reactions of the anionic living polymers with either α,ω-dibromoalkanes or α,ω-diiodoalkanes proceeded competitively with side reactions leading to dimer formation of the starting living polymers. Thus, the bromine- and iodine-terminated polymers were obtained in 12−93% yields along with undesirable dimers. As side reaction candidates, we speculated on metal−halogen interchange and/or single electron transfer pathways followed by coupling reactions between the reaction intermediates generated by both pathways. By end-capping the polystyryl anion with 1,1-diphenylethylene, one could almost suppress the dimer formation, and the end-functionalized polystyrenes with bromine and iodine were successfully obtained in more than 95% yield.

Introduction

Polymers with halogen end groups are of great interest as prepolymers used in "liquid polymer" technology.[1] They are industrially prepared by free radical telomerization in the presence of some haloalkanes as transfer agents.[2] Use of the disulfide derivatives containing halogens is also useful for preparing such polymers.[3] Thus, synthetic methods used to prepare polymers with halogen end groups by free radical processes are well established. Unfortunately, free radical polymerization normally suffers from a broad distribution of molecular weights and from branching of the polymer. Moreover, inherent transfer and termination reactions lead to end-functionalities with greater or less than two end groups. These polymers may cause serious problems in further processes such as chain extension and network formation.

The anionic living polymers of styrene and 1,3-dienic monomers such as 1,3-butadiene and isoprene are very attractive precusors especially for the preparation of end-functionalized polymers with well-defined structures. First, these anionic living polymers have precisely controlled chain lengths with nearly uniform distributions. Second, they have highly reactive but stable carbanions at their polymer chain ends which can transform readily into other useful functional groups by reacting them with a variety of electrophiles. In fact, many successful examples have so far been reported on the preparation of well-defined end-functionalized polymers by using anionic living polymers.[4−7]

However, success has not been realized in the preparation of well-defined polymers with halogen end groups by the anionic route. Several attempts have so far been made by terminating the anionic living polymers with halogens and α,ω-dihaloalkanes. For example, direct halogenations of the polystyryl anion with both bromine and iodine were reported. These reactions proceeded competitively with coupling reactions to yield considerable amounts of dimeric side products.[8,9] The yield of brominated polystyrene was increased to some extents by converting polystyryllithium to the corresponding Grignard reagent.[10] Even in this case, the dimer formation by coupling could not be completely suppressed.

An alternative procedure for the preparation of end-functionalized polymers with halogens is to use difunctional α,ω-dihaloalkanes and the related dihalides. Richards and his co-workers previously reported the reaction of α,α′-dibromo-*p*-xylene with either polystyryllithium or polystyrylmagnesium bromide.[10] It was again observed that in addition to the desired termination reactions, coupling reactions to produce dimers occurred significantly under their reaction conditions. Watanabe and his co-workers reported the preparation of a styrene−2-vinylpyridine block copolymer with a chlorobenzyl end group by the reaction of the corresponding anionic living block copolymer with a large excess of α,α'-dichloroxylene.[11] Unfortunately, the degree of end-functionalization of the resulting polymer was not reported in this paper. The termination reactions of anionic living polymers of styrene and 1,3-butadiene with α,ω-dibromoalkanes and bis(halomethyl) ethers were previously attempted. Again, the detailed characterization of the resulting polymers was not carried out to give the degrees of end-functionalizations and molecular weight distributions of the resulting polymers.[12,13] Quirk and McFay reported the reaction of poly(1,3-butadienyl)lithium with an excess amount of 1,2-dibromoethane.[14] The reaction occurred to give the desired brominated polymer in only 24% yield with significant formation of the dimer.

It is generally recognized that carbanions of organoalkali-metal compounds (RM) usually undergo nucleophilic substitution reactions with primary alkyl halides (R′X) to yield predominantly addition products (R−R′). Anionic living polymers of isoprene and styrene reacted efficiently with R′X in a similar fashion to afford the end-functionalized polymers with R′ groups normally in very good yields.[15−17] We have also demonstrated that anionic living polymers of both styrene and isoprene react nearly quantitatively with the ω-functional primary alkyl halides.[18−22] These results indicate

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that the reactions of the anionic living polymers with primary alkyl halides proceed smoothly without problem. Therefore, we consider that the preparation of end-functionalized polymers with halogens might be possible by the reactions of anionic living polymers with α,ω-dihaloalkanes, if the reaction conditions are carefully optimized. Since the related studies reported previously were not successful, as mentioned before, it is worthwhile to re-examine such reactions to explore their scope and limitations. Herein are reported our results on a systematic study of the reactions of anionic living polymers with a variety of α,ω-dihaloalkanes.

Experimental Section

Materials. Styrene and isoprene were purified according to the usual procedures. They were finally distilled over C_6H_5MgCl and *n*-butyllithium (*n*-BuLi), respectively, on the vacuum line into ampules with break seals that were prewashed with (1,1-diphenylhexyl)lithium in heptane. 1,1-Diphenylethylene was distilled over (1,1-diphenylhexyl)lithium on the vacuum line. α,ω-Dihaloalkanes were first distilled over CaH_2 and then distilled over C_6H_5MgCl on the vacuum line.

Polymerizations and Reactions of Anionic Living Polymers with α,ω-Dihaloalkanes. The polymerizations and reactions with α,ω-dihaloalkanes were carried out under high vacuum conditions (10^{-6} Torr) in sealed glass reactors with break seals. The reactors were always prewashed with initiator solution (*sec*-BuLi in heptane or potassium naphthalenide in THF) after being sealed off from the vacuum line and used for the polymerizations followed by the reactions. The anionic polymerization of styrene was carried out with either *sec*-BuLi or potassium naphthalenide in THF at −78 °C for 10 min. Isoprene was anionically polymerized with *sec*-BuLi in heptane at 40 °C for 2 h. In this case, an appropriate volume of THF was added to the heptane solution of poly(isoprenyllithium) at −78 °C prior to the reaction. The M_n values of the living polymers were in the range of 2000−3000 and were in good agreement with those calculated based on monomer to initiator ratios. The M_w/M_n values were less than 1.1 in all cases.

The living polymer solution freshly prepared was added dropwise into a THF solution of each α,ω-dihaloalkane at −78 °C over a period of 10 min. The reaction mixture was allowed to stand at −78 °C for additional 10 min and at 25 °C for 5 min for each of the bromides and the iodides. Since the reaction of poly(isoprenyllithium) with 1,3-dichloropropane was observed to proceed slowly, the reaction mixture was allowed to stand at −78 °C for 10 h. The polymers were then terminated with degassed methanol and precipitated in methanol. They were purified by repeated reprecipitation thrice to remove unreacted dihaloalkanes and freeze-dried.

The degrees of end-functionalization of the resulting polymers thus obtained were determined by comparison between the relative values of the ^1H NMR peak intensities. The resonance peaks for halomethylene protons (2.4−3.5 ppm) and methine proton of *cis*-1,4-polyisoprene, aromatic protons of polystyrene estimated from their M_n values by SEC, were used for this purpose. The peaks at 0.5−0.9 ppm corresponding to methyl protons from the residue of *sec*-BuLi are also useful probes for determining the degrees of end-functionalization. The errors for end-group analysis are less than 5%.

Measurements. ^1H and ^{13}C NMR spectra were recorded on JEOL FX-90Q (90 MHz) and JEOL GSX-500 (500 MHz) spectrometers in $CDCl_3$. Size exclusion chromatography (SEC) was obtained at 40 °C with a TOSOH HLC 8020 instrument with UV (254 nm) or refractive index detection. THF was a carrier solvent at a flow rate of 1.0 mL/min. Three polystyrene gel columns (TSKgel G4000H_{XL}, G3000H_{XL}, and G2000H_{XL}) were used. Calibration curves were made to determine M_n and M_w/M_n values with standard polystyrene and polyisoprene samples.

Results and Discussion

In the reactions examined here, the terminators chosen for our purpose were 1,3-dihalopropanes whose halogens were chlorine, bromine, and iodine. In addition, some α,ω-dihaloalkanes with different methylene chain lengths were used for comparison. Anionic living polymers employed were polyisoprenyllithium and polystyryllithium initiated with *sec*-BuLi, respectively. Difunctional living polystyrene was synthesized in THF at −78 °C with potassium naphthalenide as an initiator and used for the preparation of α,ω-di-end-functionalized polymers.

It should be noted that undesirable coupling to form dimeric product of the starting anionic living polymers was the predominant mode of reaction of polystyryllithium with the primary alkyl bromide in pure heptane in our previous paper.[23] On the other hand, such a dimer formation is completely suppressed by adding THF to the reaction system, while the THF proportions of the solvent mixture are usually not crucial to the success of the reactions. The reactions in this study were therefore carried out in THF or THF−heptane mixtures (1/1 to 1/4, v/v %) at −78 °C for appropriate times and then at 25 °C for additional 5 min.

Since difunctional electrophiles always require selective monosubstitution reactions in the termination reactions with anionic living polymers, the addition order as well as the quantity of the dihalide should be very important. The anionic living polymer was normally added dropwise to α,ω-dihaloalkane to avoid a subsequent reaction of the living polymer with the end-haloalkyl group of the polymer once introduced. α,ω-Dihaloalkane was used in a large excess (ca. 10-fold excess). Use of a small excess (ca. 1.5-fold excess) of reagent was also examined in view of the synthetic advantage.

The reactions of anionic living polymers with excesses of α,ω-dihaloalkanes were carried out, and the results are summarized in Tables 1 and 2. The variation of anionic living polymer, stoichiometry, halogen, and methylene chain length of α,ω-dihaloalkanes was ex-

Table 1. Reactions of Anionic Living Polymers with $X(CH_2)_nX$[a]

living polymer[c]	$X(CH_2)_nX$ X	$X(CH_2)_nX$ *n*	method[d]	T/C[e]	SEC of reaction product[b] P, %	SEC of reaction product[b] P−P, %	functionality, % ^1H NMR
Pl−Li	Cl	3	N	11	100	0	99
Pl−Li	Cl	3	N	1.5	99	1	97
Pl−Li	Cl	3	R	1.4	100	0	94
PS−Li	Cl	3	N	1.2	100	0	99
PS−Li	Cl	3	R	1.2	100	0	100
Pl−Li	Br	3	N	11	93	7	92
Pl−Li	Br	3	N	2.5	93	7	91
Pl−Li	Br	3	R	1.1	72	28	69
PS−Li	Br	3	N	12	66	34	56
PS−Li	Br	3	N	1.1	42	58	38
PS−Li	Br	3	R	1.3	13	87	10
PS−Li	Br	4	N	11	79	21	83
PS−Li	Br	5	N	13	65	35	70
PS−Li	Br	10	N	9.0	56	44	69
Pl−Li	I	3	N	11	30	70	30
Pl−Li	I	3	N	1.1	12	88	10
PS−Li	I	3	N	10	29	71	19
PS−Li	I	3	N	1.1	17	83	22
Pl−Li	I	5	N	13	73	27	62
Pl−Li	I	5	R	1.2	68	32	72
PS−Li	I	5	N	1.5	34	66	27

[a] Reactions were carried out in THF or THF−heptane mixtures at −78 °C for 20 min to 10 h and then at 25 °C for 5 min. M_n values of starting living polymers were in the range 2000−3000. M_w/M_n values were less than 1.10. [b] P indicates the yield of end-functionalized polymer, and P−P indicates the yield of dimeric product. [c] Pl−Li and PS−Li indicate polyisoprenyllithium and polystyryllithium, respectively. [d] N indicates a normal addition order, while R indicates a reverse addition order where dihalide is added into living polymer. [e] T/C indicates the molar ratio of dihalide to the living polymer end.

Table 2. Reactions of Anionic Living Polymers with $X(CH_2)_3X'$ [a]

living polymer[c]	$X(CH_2)_3X'$ X	$X(CH_2)_3X'$ X′	method[d]	T/C[e]	SEC of reaction product[b] P, %	SEC of reaction product[b] P−P, %	functionality, % ^{1}H NMR
Pl−Li	Cl	Br	N	1.6	100	0	97
PS−Li	Cl	Br	R	1.1	100	0	94
Pl−Li	Cl	I	N	1.2	85	15	77
PS−Li	Cl	I	R	1.2	100	0	100
Pl−Li	Br	I	N	1.3	33	67	28
PS−Li	Br	I	N	1.3	55	45	45

[a] Reactions were carried out in THF or THF−heptane mixtures at −78 °C for 20 min and then at 25 °C for 5 min. M_n values of starting living polymers were in the range 2000−3000. M_w/M_n values were less than 1.10. [b] indicates the yield of end-functionalized polymer, and P−P indicates the yield of dimeric product. [c] Pl−Li and PS−Li indicate polyisoprenyllithium and polystyryllithium, respectively. [d] N indicates a normal addition order, while R indicates a reverse addition order where dihalide is added into living polymer. [e] T/C indicates the molar ratio of dihalide to living polymer end.

amined to find suitable conditions for the preparation of polymers with halogen end groups.

Reactions of Anionic Living Polymers with α,ω-Dihaloalkanes Containing the Same Halogen Atom. (1) Reaction of Polyisoprenyllithium or Polystyryllithium with 1,3-Dichloropropane. The reaction of polyisoprenyllithium with $Cl(CH_2)_3Cl$ was first attempted with a large excess (an 11-fold excess) of the reagent. The reaction was not rapid as evidenced from the observation that a yellow color characteristic of the polyisoprenyl anion still remained after 0.5 h. Taking a longer reaction time to 10 h caused the yellow color to completely disappear, indicating that the reaction was complete. After removal of unreacted $Cl(CH_2)_3Cl$ from the polymer by three reprecipitations, the resulting polymer was analyzed by ^{1}H NMR in which the resonance peaks for chloromethylene protons were clearly present at 3.5 ppm.

The degree of end-functionalization was found to be almost quantitative in the sample obtained by quenching after 10 h, while it was 73% in the case after 0.5 h. The SEC analysis of the resulting polymer showed it to possess a M_n value calculated by the [M]/[I] ratio and a unimodal distribution without any shoulders and tailings, the value of M_w/M_n being 1.05. The formation of a dimeric product suggested by the previous reports was not observed at all under the conditions. These results clearly indicate that only one side of the chloroalkyl moiety of $Cl(CH_2)_3Cl$ predominantly reacts with polyisoprenyllithium to afford the polyisoprene with a chloro (or chloropropyl) end group. It was also found that the use of a slight excess (a 1.5-fold excess) of $Cl(CH_2)_3Cl$ was enough to permit the expected monosubstitution reaction. This result is of particular importance from the viewpoint of practical synthesis. Surprisingly, quantitative end-functionalization could also be achieved even by a reverse addition order where the dichloride was added to polyisoprenyllithium.

In contrast, the reaction of polystyryllithium with $Cl(CH_2)_3Cl$ was very rapid and was completed within 5 min at −78 °C even with the use of a 1.2-fold excess of the dichloride. After 5 min, it was found that polystyryllithium was quantitatively end-functionalized to give the polystyrene with a chlorine end group. The resulting polymer possessed a well-controllable M_n value and a narrow distribution of molecular weight (M_w/M_n = 1.05). Coupling to produce the dimeric product was also negligible in this reaction. Similarly, a satisfactory result was obtained by the reverse addition of the reagent. Thus, quantitative end-functionalization of living polymers of isoprene and styrene was successful with $Cl(CH_2)_3Cl$ in THF (or mixed solvents containing THF) at −78 °C.

(2) Reaction of Polyisoprenyllithium or Polystyryllithium with α,ω-Dibromoalkanes. With the use of $Br(CH_2)_3Br$ under the identical condition, the reaction with polyisoprenyllithium was virtually instantaneous as evidenced from the observation that the characteristic yellow color varnished as soon as the living polymer was added to the dibromide. An excellent degree of end-functionalization was indicated by the ^{1}H NMR analysis of the resulting polymer as shown in Table 1. A similar result was obtained by the use of a 2.5-fold excess of the dibromide. In both cases, however, small but detectable amounts of dimer were observed by the SEC traces to be 7%, respectively, estimated by their peak areas.[24] As expected, the dimer quantity was increased to 28% by adding the dibromide into polyisoprenyllithium in a reversed addition order. In the same sample, the degree of end-functionalization determined by ^{1}H NMR was 69%, which is a fair agreement with the yield (100 − 28 = 72%) of end-functionalized polymer estimated by SEC. This strongly indicates that the polymer obtained is quantitatively end-functionalized, while no bromine end group is introduced in the dimer.

The dimer formation was more significant in the reaction with $Br(CH_2)_3Br$ when polystyryllithium was used. Amounts of the dimer were 34% and 58%, respectively in the reactions with 12-fold and 1.1-fold excesses of the dibromide. Furthermore, the dimer was predominantly produced in 87% by the reverse addition of the reagents. The yield of end-functionalized polymer was only 13% in this case. In each case, there is a good agreement between the degrees of end-functionalization measured by ^{1}H NMR and the yields of end-functionalized polymer estimated by SEC as listed in Table 1.

We next examined the effect of methylene chain length of α,ω-dibromoalkanes on the reaction with polystyryllithium. In addition to $Br(CH_2)_3Br$, $Br(CH_2)_4Br$, $Br(CH_2)_5Br$, and $Br(CH_2)_{10}Br$ were employed for this purpose. In all reactions with polystyryllithium in THF at −78 °C, considerable amounts of dimer formation were observed by their SEC charts and the desired end-functionalized polystyrenes were obtained in 69−83% yields. Thus, the yield was not improved by changing the methylene chain length of α,ω-dibromoalkane. Accordingly, the dimer formation appears be inherent in the reactions of anionic living polymers of isoprene and, in particular, styrene with α,ω-dibromoalkanes under our reaction conditions in THF at −78 °C.

(3) Reaction of Polyisoprenyllithium or Polystyryllithium with α,ω-Diiodoalkanes. Both of the termination reactions of polyisoprenyllithium and polystyryllithium with $I(CH_2)_3I$ were very fast and were completed almost instantaneously on mixing of the reagents. Similar to the reactions with α,ω-dibromoalkanes, coupling to produce dimeric products was occurring predominantly in either system. The results of the SEC and ^{1}H NMR analyses showed that the yields of the end-functionalized polymers were very low and 20−30% yields were obtained even by the most preferred method using a large excess of the diiodide as shown in Table 1. It appeared however that the yield was improved to some extents with the use of $I(CH_2)_5I$. For example, about 70% of the end-functionalized polymer was obtained in the reaction of polyisoprenyllithium with $I(CH_2)_5I$, although the result was still far from success. Thus, the reactions of anionic living polymers

with α,ω-diiodides as well as α,ω-dibromides do not provide a practical route to the end-functionalized polymers with bromine and iodine.

We first considered that the dimers were formed as a result of a coupling of the anionic living polymer with either the bromopropyl or iodopropyl group at the polymer chain end produced in the reaction. That bromide and iodide are better leaving groups than chloride may be a key factor to facilitate the coupling reaction. If this is true, the quantities of such dimers should be greatly decreased by using large excesses of the dihalides since the dihalides are always present much more than those of the polymeric halides. However, no improvement was observed on the yield of end-functionalized polymer with the use of greater than a 10-fold excess of dihalide. It is therefore not likely that the dimers would be formed by the coupling between the living polymer and the resulting polymeric halide. Accordingly, another reaction pathway should be considered to account reasonably for the dimer formation. This will be discussed later.

In summary, the chlorine (or, to be more exact, the chloropropyl) group could be quantitatively introduced at the chain ends of both living polymers of isoprene and styrene by reactions with $Cl(CH_2)_3Cl$ in THF at −78 °C. The resulting polymers possessed controllable molecular weights and very narrow molecular weight distributions. On the other hand, coupling to form dimeric products of the starting living polymers was always competitive with the desired termination reactions in the reactions of the anionic living polymers with $Br(CH_2)_nBr$ or $I(CH_2)_nI$. In these cases, the end-functionalized polymers were obtained in 10−90% yield along with dimeric side products.

Reactions of Anionic Living Polymers with 1,3-Dihaloalkanes Containing a Different Halogen Atom. In the preceding section, we have found that α,ω-dibromides and diiodides behave in a different manner than $Cl(CH_2)_3Cl$ in the reaction with anionic living polymers. Unfortunately, significant amounts of dimers were formed along with the desired end-functionalized polymers in the reactions with the use of dibromides or diiodides. In this section, we will react $Cl(CH_2)_3Br$, $Cl(CH_2)_3I$, or $Br(CH_2)_3I$ with anionic living polymers of isoprene and styrene under identical conditions in order to examine such a halogen effect on the reaction. The results are summarized in Table 2.

The reaction of polyisoprenyllithium with $Cl(CH_2)_3Br$ was found to proceed very rapidly as evidenced by the observation that a yellow color of polyisoprenyllithium disappeared immediately on mixing. This observation suggests that the reaction takes place possibly at the bromoalkyl moiety of $Cl(CH_2)_3Br$. A careful 500 MHz ^{1}H NMR analysis of the resulting polymer showed only a signal at 3.53 ppm corresponding to the chloromethylene protons, while no resonance peak for bromomethylene protons (3.39 ppm) was observed. From the peak area, the degree of end-functionalization was nearly quantitative. Accordingly, polyisoprenyllithium reacts virtually with the bromoalkyl part in a complete chemoselective manner to afford the polyisoprene with a chlorine end group. The polymer thus obtained possessed a unimodal peak with a narrow distribution. No dimer formation was observed at all.

Use of a small excess (a 1.6-fold) of the dihalide is enough to see to the success of the reaction, as can be seen in Table 2. Quantitative end-functionalization was also achieved by reversely adding the halide into the living polymer. Similarly, a well-defined polystyrene with chlorine end group was obtained by the less preferred method, i.e., the reverse addition with the use of a 1.1-fold excess of $Cl(CH_2)_3Br$.

The reaction of polyisoprenyllithium with $Cl(CH_2)_3I$ proceeded very fast and finished almost as soon as they were mixed. The ^{1}H NMR showed that the chloromethylene protons were only present in the resulting polymer. No resonance peak for iodomethylene protons (2.80 ppm) was observed. The degree of end-functionalization determined by the NMR was however found to be 77%. The SEC analysis exhibited that the resulting polymer consisted of 85% of the major desired product along with 15% of the dimeric product. In contrast, the reaction of polystyryllithium with this halide took place cleanly to afford quantitatively the polystyrene with a chlorine end group. No dimer was formed in this case.

The results obtained here seem to be somewhat curious. If only the bromo- or iodoalkyl moiety of the halide participates in the reactions with anionic living polymers, then significant dimer formation should have occurred. However, no dimers were formed at all in the reactions with either $Cl(CH_2)_3Br$ or $Cl(CH_2)_3I$ except for the reaction of polyisoprenyllithium with $Cl(CH_2)_3I$. Even in the latter case, the quantity of dimer was much less than that produced by the reaction with $I(CH_2)_3I$. Thus, the elucidation of the reaction pathway is further complicated by the results obtained here which are not consistent with those for the corresponding dibromides and diiodides.

The reaction of $Br(CH_2)_3I$ with either polyisoprenyllithium or polystyryllithium was observed to occur very rapidly and was completed within a few seconds. It was found by ^{1}H NMR analysis that only bromomethylene protons were present in each of the resulting polymers. Their degrees of end-functionalization were low in both cases. As was seen in Table 2, considerable quantities of dimeric products were formed in these reactions. The results with $Br(CH_2)_3I$ were reasonable because they were in between those obtained with use of $Br(CH_2)_3Br$ and $I(CH_2)_3I$.

Reactions of Polystyryl Anions End-Capped with 1,1-Diphenylethylene with 1,3-Dibromopropane or 1,3-Diiodopropane. As mentioned above, a major limitation of this anionic approach to end-functionalized polymers with halogens is the failure of the quantitative end-functionalization of anionic living polymers with α,ω-dibromo and α,ω-diiodopropanes. Very fortunately, this limitation may be circumvented by modifying the polystyrylanion with 1,1-diphenylethylene to transform it into a bulky, less nucleophilic anion.

Polystyryllithium was end-capped with 1,1-diphenylethylene to transform it into a 1,1-diphenylalkyl-type carbanion, which was then allowed to react with a 13-fold excess of $Br(CH_2)_3Br$. The dark red color disappeared immediately on mixing, indicating that the reaction was rapid. The SEC trace indicated that the resulting polymer possessed a sharp unimodal peak without any tailings and shoulders. Virtually no dimer formation was observed in this reaction. It was further found that the end-functionalization degree determined by ^{1}H NMR was quantitative. Thus, the end-functionalized polystyrene with bromine could successfully be prepared by using the modified anion. The reaction of this modified anion also proceeded efficiently even with the use of a slight excess (a 1.3-fold excess) of $Br(CH_2)_3Br$ to give a bromine-terminated polystyrene whose end-functionalization degree by ^{1}H NMR was almost quantitative. Unfortunately, the SEC analysis of the resulting polymer showed that a trace amount (4%) of dimer

Table 3. Reactions of polystyrylanion End-Capped with 1,1-Diphenylethylene with $X(CH_2)_3X$[a]

living polymer[c]	$X(CH_2)_3X$ X	method[d]	T/C[e]	SEC of reaction product[b] P, %	SEC of reaction product[b] P−P, %	functionality, % ^{1}H NMR
PS−Li	Br	N	12	66	34	56
PS−K	Br	N	12	20	80[f]	
PS(DPE)Li	Br	N	13	100	0	100
PS(DPE)Li	Br	N	1.3	96	4	100
PS(DPE)K	Br	N	1.3	100	0	100
PS−Li	I	N	10	29	71	19
PS−K	I	N	10	30	70[f]	
PS(DPE)Li	I	N	11	95	5	95
PS(DPE)K	I	N	6.0	100	0	95

[a] Reactions were carried out in THF or THF−heptane mixtures at −78 °C for 20 min and then at 25 °C for 5 min. M_n values of starting living polymers were in the range 2000−3000. M_w/M_n values were less than 1.10. [b] P indicates the yield of end-functionalized polymer, and P−P indicates the yield of dimeric product. [c] PS−Li and PS−K indicate polystyryllithium and polystyryldipotassium (difunctional). PS(DPE)Li and PS(DPE)K indicate polystyryllithium and dipotassium endcapped with 1,1-diphenylethylene. [d] N indicates a normal addition order. [e] T/C indicates the molar ratio of dihalide to living polymer end. [f] P−P in this case indicates yield of high molecular weight materials greater than the dimeric product of the starting living polystyrene.

was formed.[24] These results are summarized in Table 3.

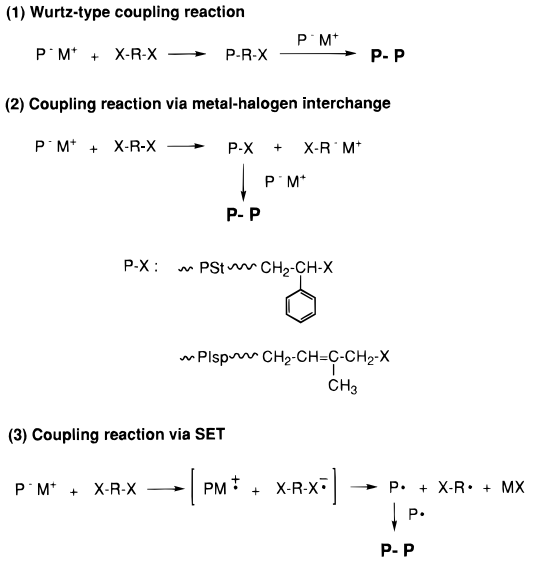
Similarly, treatment of the modified anion with $I(CH_2)_3I$ (a 10-fold excess) gave the polystyrene with an iodine end group in 95% yield and gave 5% dimer formation, which both were estimated by the SEC analysis.

The use of 1,1-diphenylalkyl-type anion is thus remarkably effective in the reaction with $Br(CH_2)_3Br$ or even $I(CH_2)_3I$ to prepare the end-functionalized polystyrenes with bromine and iodine. More optimization should be needed for the quantitative preparation, since the dimer formation was not completely suppressed in some cases.

We next attempted the preparation of difunctional halogen-terminated polymers by the reaction of a difunctional living polymer with either $Br(CH_2)_3Br$ or $I(CH_2)_3I$. At first, to evaluate the effect of countercation on the reaction, difunctional polystyryldipotassium was reacted with each of these dihalides. The reactions were fast and completed within a few minutes. The SEC analyses of the resulting polymers showed multimodal peaks in addition to small sharp unimodal peaks (ca. 20−30%) possibly corresponding to the difunctionalized polystyrenes with bromo and iodo end groups. Accordingly, the termination reactions were competitive with coupling reactions, similar to the cases using polystyryllithium. Thus, changing the countercation from Li^+ to K^+ did not improve the yields of the end-functionalized polymers.

Difunctional polystyrylpotassium was then end-capped with 1,1-diphenylethylene, followed by the reaction with $Br(CH_2)_3Br$. The effectiveness in the use of the modified anion is again demonstrated. A difunctional bromine terminated polystyrene with a predictable molecular weight and a narrow distribution was quantitatively obtained, as shown in Table 3. A small excess (a 1.3-fold excess) of $Br(CH_2)_3Br$ is enough for achieving the quantitative preparation. Similarly, a difunctional polystyrene with an iodine end group could be prepared quantitatively by the reaction of the modified anion with a 6.0-fold excess of $I(CH_2)_3I$. Thus, the end-capping of difunctional polystyrylpotassium with 1,1-diphenylethylene is also effective for quantitative preparation of well-defined α,ω-dibromo and α,ω-diiodopolystyrenes. Moreover, an additional advantage

Scheme 1



of this method is that it is essentially accessible to any another anionic living polymers that can be end-capped with 1,1-diphenylethylene.

We will examine in more detail these reactions in the near future, because the etiology of such a dramatic effect of the modified anion on the reaction remains obscure. In addition, more optimization should be needed for a practical approach to end-functionalized polymers with bromine and iodine.

In the methodology developed here on the preparation of end-functionalized polymers with halogens by means of the reactions of anionic living polymers of isoprene or styrene with α,ω-dihaloalkanes, an unfortunately unavoidable consequence is the formation of dimeric side products formally derived from coupling between polymers. The coupling reaction was observed to occur predominately in the reactions with α,ω-dibromides and α,ω-diiodides. We therefore presume that the three reaction pathways shown in Scheme 1 are possible candidates leading to the formation of dimeric products.

The first pathway involves the Wurtz-type coupling reaction of a living polymer anion with the terminal haloalkyl group of polymer produced during the reaction. The second pathway is a metal−halogen interchange followed by the coupling between the remaining living polymer anion and the halobenzyl end group generated by the interchange reaction. Single-electron transfer (SET) is also a possible mechanistic pathway leading to the dimer. In this case, the dimer may be produced by the coupling between the generated polymer radical intermediates. This is the third candidate.

As mentioned in the preceding section, the first reaction pathway via Wurtz-type coupling is considered to be unlikely. The second and third pathways are well-known reactions often occurring between alkyl halides and organolithium compounds.[25] As illustrated in Scheme 1, a highly reactive halobenzyl terminus in the case of living polystyrene (or haloallyl terminus in the case of living polyisoprene) is generated by metal−halogen interchange. The halobenzyl terminus thus generated may readily undergo coupling with the living polymer anion to form the dimer. If the interchange reaction had indeed occurred, the dimer would have formed considerably even under the condition where a large excess of dihalide was used, since the halobenzyl (or haloallyl) terminus is more reactive than the haloalkyl group. This can provide a reasonable explanation for the results obtained with the uses of dibromides

and the diiodides. Furthermore, the occurrance of the metal−halogen interchange is suggested from the fact that the ease of metal−halogen interchange reactions of alkyl halides is generally recognized to be in the order RI > RBr > RCl.

The reaction pathway mediated by a SET process is also a possible scheme to account for dimer formation. If SET is involved in the reaction, the polymer radicals could be produced from the living polymer anion and the dihalide. This newly produced reactive radical intermediate may readily undergo radical coupling to form the dimer. Obviously, from the mechanism, the dimer formation can not be suppressed even by using a large excess of dihalide. The ease of a SET process of alkyl halides has been reported to be in the order RI > RBr > RCl,[26] which is exactly what is observed for metal−halogen interchange. Accordingly, a SET-mediated process is also likely to occur in the reactions with α,ω-dibromides and α,ω-diiodides. Thus, the second and the third pathways are considered to be the most probable mechanisms for the dimer formation.

We have found that dimers are neither formed nor nearly suppressed to be formed in the reactions with $Br(CH_2)_3Br$ and $I(CH_2)_3I$ by transforming the styryl anion into a 1,1-diphenylalkyl anion with 1,1-diphenylethylene. It appears that if a terminal 1,1-diphenylhaloalkyl group is generated by metal−halogen interchange, it is probably difficult for it to undergo a coupling with the 1,1-diphenylalkyl anion due to steric bulkiness. Moreover, it may be probable that metal−halogen interchange reaction is not facilitated with the more stabilized diphenylalkyl anion. Radical coupling between polymer radicals generated by SET is also not likely to occur due to the same steric hindrance even if a SET-mediated pathway is operable.

On the other hand, we have obtained several disparate results in which dimers are not formed in the reactions of anionic living polymers with bromides and iodides. For example, no dimer formation was observed in the reactions of the anionic living polymers with $Cl(CH_2)_3Br$ and $Cl(CH_2)_3I$, except for the reaction of polyisoprenyllithium with $Cl(CH_2)_3I$, where 15% dimer was formed. If indeed the Li−halogen interchange and/or a SET process occurs during the reactions, both $Cl(CH_2)_3Br$ and $Cl(CH_2)_3I$ should give results similar to $Br(CH_2)_3Br$ and $I(CH_2)_3I$ in the reactions. We also observed that no dimers were formed in the reactions of both polyisoprenyllithium and polystyryllithium with n-C_4H_9I. The *n*-Butyl group was introduced quantitatively at each polymer chain end. Thus, Li−I interchange as well as SET followed by coupling leading to dimer formation is negligible in these systems. We previously reported several end-functionalization reactions of anionic living polymers of isoprene and styrene with a variety of ω-functionalized bromides and iodides.[18−23]. Once again, dimer formation was not normally observed in each of these reactions. Accordingly, the results of the reactions with α,ω-dibromides and α,ω-diiodides obtained here are inconsistent with those using $Cl(CH_2)_3Br$ and $Cl(CH_2)_3I$, *n*-butyl iodide, and the ω-functional alkyl bromides and iodides. At the present time, unfortunately no consensus has emerged between the two results.

Conclusions

The reactions of α,ω-dihaloalkanes with anionic living polymers of styrene and isoprene have been utilized to introduce halogens (or haloalkyl groups) to the polymer chain ends. Quantitative end-functionalizations have been achieved only in the reactions of anionic living polymers with $Cl(CH_2)_3Cl$. On the other hand, undesirable dimeric products have been more or less formed in addition to the end-functionalized polymers in the reactions with the use of $Br(CH_2)_nBr$ or $I(CH_2)_nI$. The metal−halogen interchange and/or a SET process is considered to be the probable reaction pathway leading to the dimer formation. By transformation of the polystyryl anion into the 1,1-diphenylalkyl anion with 1,1-diphenylethylene, dimer formation was greatly reduced or completely suppressed in the reactions with $Br(CH_2)_3Br$ and $I(CH_2)_3I$. The end-functionalized polystyrenes with bromine or iodine were obtained in yields of more than 95%.

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(24) It was observed under the conditions employed here that the dimer was not always but often formed in yields of less than 3% even by quenching with degassed methanol. This is probably produced as a result of an elimination of LiH from the living polymer to afford the polymer with a C=C end group, followed by a reaction with another living polymer to produce the dimer. The dimer thus formed is difficult to be distinguished from that produced by the coupling reaction of α,ω-dihaloalkane with 2 equiv of living polymer. The results should be therefore evaluated to take this into consideration.
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