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Protection and Polymerization of Functional Monomers. 12. Synthesis of Well-Defined Poly(4-aminostyrene) by Means of Anionic Living Polymerization of 4-(*N*,*N*-Bis(trimethylsilyl)amino)styrene

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ABSTRACT: Anionic polymerization of 4-(*N*,*N*-bis(trimethylsilyl)amino)styrene, 1, was investigated at −78 to 30 °C in tetrahydrofuran (THF) with lithium, sodium, and potassium as countercation. The living nature of the propagating end is substantiated by formation of the polymer of predictable molecular weight and narrow molecular weight distribution in quantitative yield. Anionic living poly(1) was allowed to react with styrene and isoprene to produce block copolymers with a well-defined chain structure. Acid hydrolysis of poly(1) and the block copolymers leads to poly(4-aminostyrene), 3, and block copolymers containing the primary amino group. Segregated microdomains of the resulting copolymers were observed by transmission electron microscopy.

Introduction

Preparative methods for linear functional polymers having a high uniformity of chain length and predictable molecular weight have been developed by anionic living polymerization of 4-hydroxystyrene,[1] 4-(2-hydroxyethyl)-styrene,[2] and 4-aminostyrene[3] masked with trialkylsilyl groups followed by removal of the protective groups from the produced polymer chain. Our investigation has been focused on exploring suitable masking groups and appropriate polymerization conditions that afford stable living polymers. In a previous paper,[3] we reported that the anionic polymerization of 4-(*N*,*N*-bis(trimethylsilyl)-amino)styrene, 1 (Scheme I), was initiated with lithium naphthalenide in tetrahydrofuran (THF) at −78 °C to give a living polymer of a predictable molecular weight and a narrow molecular weight distribution. The produced poly(1), 2, was hydrolyzed with 2 N HCl in THF followed by neutralization to afford poly(4-aminostyrene), 3, without cleavage of the main chain of 2. Formation of the stable living polymer of 1 leads to synthesis of the block copolymers of 1 with styrene and isoprene with controlled block lengths, which can be converted to block copolymers containing a primary amino group under mild conditions. Many reactive groups, such as aldehyde, ketone, acid chloride, and alkyl halide, could be allowed to react with the primary amino group attached to side chain of 3 and the block copolymers to produce a variety of functional polymers with well-defined chain structure.

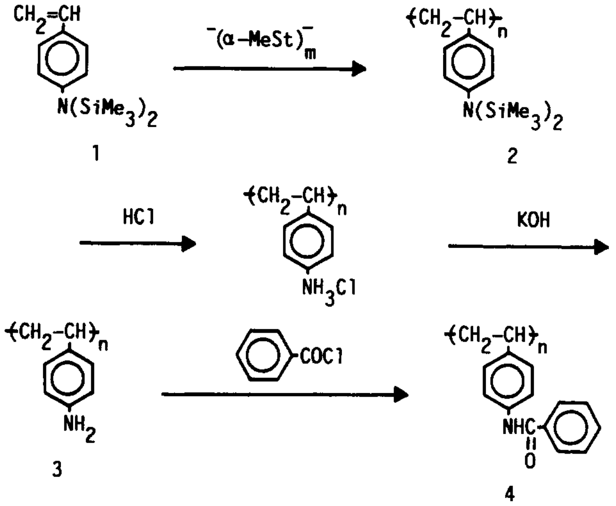
Experimental Section

Materials. THF was refluxed over sodium wire for 5 h, distilled over lithium aluminum hydride, and finally distilled from sodium naphthalenide solution.

Styrene, α-methylstyrene, and isoprene were distilled over calcium hydride. Prior to polymerization, they were distilled under high vacuum together with THF from benzylmagnesium chloride and stored in ampules equipped with breakseals.

Alkali-metal naphthalenides were prepared from 1.2 equiv of naphthalene and the corresponding alkali metals in THF under high vacuum and stored at −30 °C in ampules equipped with breakseals. The concentration of metal naphthalenide was determined by titration with standardized 1-octanol in a sealed reactor as described previously.[1] Just prior to polymerization, the oligo(α-methylstyrene) dilithium, disodium, and dipotassium were freshly prepared by the reaction of the corresponding metal naphthalenides with 2–4 equiv of α-methylstyrene at 30 °C, and then the mixture was kept at −78 °C for 10 min to complete the reaction.

Scheme I



4-Aminostyrene. A mixture of 2-(4-aminophenyl)ethyl alcohol (10 g, 73 mmol), KOH (25 g), and *tert*-butylcatechol (0.1 g) was heated in a flask at 220–250 °C/50–30 mmHg. Distillation of the contents under reduced pressure gave crude 4-aminostyrene, which was extracted with ether and dried over NaOH. After evaporation of ether, 4-aminostyrene (6.3 g, 53 mmol) was obtained by fractional distillation ((bp 60–62 °C/0.5 mmHg) (lit.[4] 92 °C/3.5 mmHg)).

4-(*N*-(Trimethylsilyl)amino)styrene. 4-Aminostyrene (6.3 g, 53 mmol), hexamethyldisilazane (16.1 g, 100 mmol), and trimethylsilyl chloride (1.0 g, 10 mmol) were refluxed at 140 °C for 4 h. After removal of unreacted hexamethyldisilazane, 4-(*N*-(trimethylsilyl)amino)styrene (8.4 g, 44 mmol) was obtained by fractional distillation (bp 58–60 °C/0.2 mmHg): ^{1}H NMR ($CDCl_3$) δ 6.59, 7.26 (4 H, 2d, *J* = 8.4 Hz, Ar), 6.66 (1 H, dd, =CH—), 5.53, 5.05 (2 H, 2d, *J* = 16, 11 Hz, =CH_2), 3.75 (1 H, s, NH), 0.30 (9 H, s, $SiCH_3$); ^{13}C NMR ($CDCl_3$) δ 0.11 ($SiCH_3$), 109.6 (=CH_2), 115.0 (Ar C1) 116.1 (Ar C3), 127.4 (Ar C2), 136.8 (=CH—), 147.4 (Ar C4).

4-(*N*,*N*-Bis(trimethylsilyl)amino)styrene (1). To a solution of ethylmagnesium bromide in THF (0.6 M, 150 mL) was added dropwise 4-(*N*-(trimethylsilyl)amino)styrene (8.4 g, 44 mmol) with stirring. The mixture was stirred at 40 °C for 12 h. To the resulting solution was added trimethylsilyl chloride (13 g, 120 mmol) with stirring at 40 °C for 6 h. The crude product was obtained by distillation from the mixture. 1 (8.5 g, 32 mmol) was purified by fractional distillation (bp 60–65 °C/0.5 mmHg): ^{1}H NMR ($CDCl_3$) δ 7.28, 5.85 (4 H, 2d, *J* = 8.1 Hz, Ar), 6.70 (1 H, dd, =CH—), 5.66, 5.17 (1 H, 2d, *J* = 18, 11 Hz, =CH_2—), 0.08

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Table I
Anionic Polymerization of 1 with Various Initiators in THF at -78 °C for 30 min[a]

1, mmol	initiator type	initiator mmol	α-methylstyrene,[b] mmol	$10^{-4}\bar{M}_n$(calcd)	$10^{-4}\bar{M}_n$(obsd)[c]	$\bar{M}_w/\bar{M}_n$[d]
5.32[e]	Li-naph	0.0715	0.000	1.8	1.6	1.16
3.38	Li-naph	0.0614	0.000	3.0	2.7	1.15
2.73	Li-naph	0.0357	0.000	4.2	5.3	1.12
3.67	Na-naph	0.101	0.000	2.0	2.0	1.28
3.53	K-naph	0.0792	0.000	2.4	2.1	1.21
2.33	Li-naph	0.0779	0.271	1.7	1.6	1.15
2.06	Na-naph	0.0764	0.408	1.6	1.5	1.45
2.89	K-naph	0.0782	0.423	2.2	1.9	1.33

[a] Yields of polymers were nearly quantitative in each case. [b] Oligo(α-methylstyrene) dianions prepared from naphthalenides and α-methylstyrene were used as initiator. [c] Observed molecular weights of polymers were obtained by VPO. [d] Values of $\bar{M}_w/\bar{M}_n$ were estimated from the GPC curves by using the calibration curve of standard polystyrene. [e] GPC curve of the polymer is shown in Figure 4.

(18 H, s, $SiCH_3$); ^{13}C NMR ($CDCl_3$) δ 136.7 (=CH—), 133.0 (Ar C4), 130.2 (Ar C2), 126.4 (Ar C3), 112.2 (=CH_2), 2.1 ($SiCH_3$). After several fractional distillations, 1 was distilled under high vacuum together with a THF solution of ethylmagnesium bromide and second with benzylmagnesium chloride.

Polymerization. The polymerization was carried out by mixing an initiator and 1 in THF in a glass apparatus equipped with breakseals and by shaking the mixture occasionally at -78 to 30 °C under high vacuum. The polymerization of 1, where the monomer was usually depleted within 1 min, was terminated with methanol after 10–30 min. Poly(1), 2, was precipitated by adding the reaction mixture to a large excess of methanol and collected by filtration. The polymer was redissolved in THF, precipitated into methanol two additional times, and freeze-dried from benzene.

Block copolymerization and isolation of the resulting polymers were performed in a similar manner. The molecular weight of the central block was estimated by measuring that of the corresponding homopolymer by vapor pressure osmometry. The molecular weight of the block copolymer was evaluated from the molecular weight of the central block and the molar ratio of the segments measured by NMR.

Evaluation of the Surviving End. Polymerization of 1 (0.80 mmol in 5.0 mL of THF) was initiated with oligo(α-methylstyrene) dianion as a difunctional initiator at the ratio of [1]/[initiator] = 10 at -78 °C. After the solution was allowed to stand for 30 min at -78, 0, and 30 °C, 2.0 mmol of styrene was added to the solution as a second monomer. The mixture was kept at the temperature for 10 min and treated with methanol to terminate the reaction. The gel permeation chromatogram (GPC) of the reaction product was resolved to three Gaussian curves as shown in Figure 3.

Removal of the Protective Group. To a dispersion of poly(1) in methanol was dropwise added 2 N methanolic hydrogen chloride solution at room temperature until the polymer was completely dissolved. The clear solution was poured into a large excess of ether, and the precipitated poly(aminostyrene hydrochloride) was collected by filtration. It was redissolved in methanol containing 5 times excess of KOH over that of the hydrochloride. The neutralized poly(4-aminostyrene), 3, was precipitated by pouring the methanol solution into a large excess of water containing triethylamine and freeze-dried from dioxane.

Deprotection of the block copolymer containing 2 block was carried out by a method similar to that for the homopolymer except for employment of a mixture of methanol and THF in place of methanol as a reaction medium.

Benzoylation of 3. To a solution of poly(aminostyrene hydrochloride) (5.0 mmol) in pyridine (2 mL) was added dropwise benzoyl chloride (10 mmol) with stirring at 0 °C. The reaction mixture was stirred for 12 h at room temperature and poured into 0.1 N methanolic KOH solution to precipitate the amidopolymer. Complete conversion was confirmed by ^1H NMR.

Measurements. ^1H NMR and ^{13}C NMR spectra were recorded with a JEOL FX-90Q instrument. Gel permeation chromatograms were obtained with Toyo Soda HLC-802 instrument with UV and/or refractive index detection at 40 °C. THF was used as a carrier solvent at a flow rate 1.4 mL min^{-1}. Vapor pressure osmometry (VPO) measurements were made with a Corona 117 instrument in benzene solution. Glass transition temperatures (T_g) of polymers were evaluated from the differential scanning calorimetry (DSC) diagrams recorded on a Perkin-Elmer DSC-2 instrument with a 10 °C/min heating rate. Transmission electron micrographs of the block copolymer were observed by a JEOL 100CX.

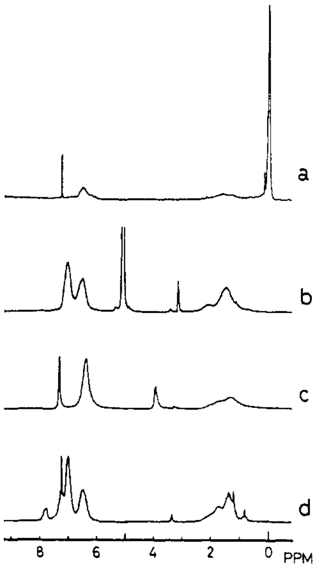

Figure 1. NMR spectra of poly(1), a; poly(aminostyrene hydrochloride), b; poly(aminostyrene), c; poly(p-vinylbenzanilide), d.

Results and Discussion

Anionic Homopolymerization. Anionic polymerization of 1 was initiated with lithium, sodium, and potassium naphthalenides in THF at -78 °C. On addition of 1 to an initiator solution, the color of the reaction mixture changed rapidly to orange or dark red corresponding to lithium or potassium countercation, respectively. The resulting colored solution suggests the formation of stable living polymers at -78 °C in THF. These characteristic colors remain unchanged after 24 h at -78 °C and immediately fade on addition of small amounts of methanol. In each case complete disappearance of the monomer in the solution was confirmed by gas chromatography (GC), and the yield of polymer was almost quantitative. α-Methylstyrene oligomer dianions were also able to initiate the polymerization of 1 and to afford the living polymer. The ^1H NMR spectrum of the resulting polymer is shown in Figure 1, where the ratio of the signal intensities for trimethylsilyl and aromatic protons was found to be 18:4 exactly. No trace of hexamethyldisiloxane, which might be formed as a condensate of trimethylsilanol produced by cleavage of the N–Si bond, was detected by GC in the filtrate of the workup procedure. These results indicate that N–Si linkage is stable enough toward water and methanol under mild alkaline and neutral conditions. Consequently, spe-

Table II
Block Copolymerization of 1 with Styrene and Isoprene at −78 °C in THF[a]

type of block copolymer[b]	A monomer	block copolymer (homopolymer)[c] $10^{-4}\bar{M}_n$(calcd)	$10^{-4}\bar{M}_n$(obsd)[d]
A–B–A[e]	styrene	3.5 (1.8)	3.2 (1.6)
A–B–A	styrene	5.5 (1.3)	6.0 (1.4)
B–A–B	styrene	2.7 (0.54)	2.9 (0.54)
B–A–B	styrene	4.7 (2.5)	4.8 (2.8)
A–B–A	isoprene	6.9 (2.9)	7.1 (2.7)
B–A–B	isoprene	5.2 (1.6)	4.5 (1.8)

[a] First monomer was polymerized with oligo(α-methylstyrene) dipotassium. Yields of homopolymers and block copolymers were quantitative. [b] B-block refers to poly(1). [c] Homopolymer corresponds to central block. [d] Molecular weights were measured by VPO and NMR measurement. [e] GPC curves of homopoly(1) and the block copolymer are shown in Figure 2. A transmission electron micrograph of the deprotected block copolymer is shown in Figure 5.

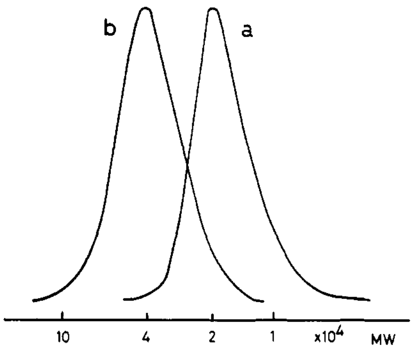

Figure 2. GPC curves for homopoly(1) (a) and the block copolymer of 1 with styrene (b). Molecular weights of the polymers are shown in Table II (footnote *e*).

cial care is not required for the characterization of the masked polymer with the trimethylsilyl group. The number-average molecular weights and polydispersity indexes of 2's produced with various ratios of monomer to initiator are listed in Table I. The predictable molecular weights based on ratios of grams of monomer to moles of initiator fairly agree with the values of molecular weight measured by vapor pressure osmometry. The ratios of $\bar{M}_w/\bar{M}_n$ are around 1.1–1.3. These results indicate that the anionic polymerization of 1 proceeds without termination and transfer reactions and that the initiation reaction proceeds rapidly compared with the propagation reaction.

Block Copolymerization. The formation of block copolymer is of great importance from the viewpoint of carbanion chemistry. The stability and reactivity of the propagating carbanion can be discussed on the basis of the formation of block copolymer. The block copolymers with a regulated block chain having a primary amino group are very interesting materials, which may have specific association behavior through hydrogen bonding and high reactivity of the amino group.

ABA-type triblock copolymers, where A and B blocks are polystyrene and poly(1), respectively, are prepared by addition of styrene to THF solution of difunctional living poly(1) that was initiated with lithium naphthalene and kept for 30 min at −78 °C. The yields of the copolymers were almost quantitative in all cases. As shown in Table II, the molecular weights of block copolymers and central blocks agree with those calculated. The GPC curve of block copolymer shown in Figure 2 clearly shifts toward the higher molecular weight side and no peak or shoulder is observed at the lower molecular weight side where the GPC curve of the homopoly(1) has a peak. The polydispersity index, $\bar{M}_w/\bar{M}_n$, was estimated from the GPC curve to be around 1.2. These facts indicate that the carbanions at propagating chain end of poly(1) are stable at −78 °C at least for 30 min and are able to initiate polymerization of styrene rapidly without any side reactions. As can be seen in Table II, isoprene is also polymerized with the carbanion derived from 1 to yield the corresponding block copolymers with a well-defined chain structure.

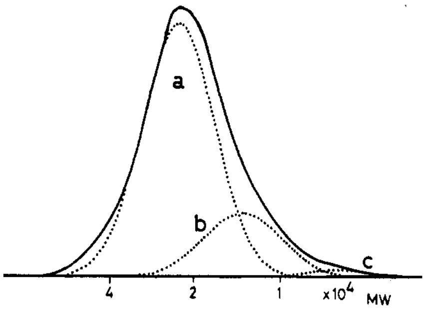

Figure 3. GPC curve of the reaction product of living poly(1) and styrene at 0 °C: countercation, Li$^+$; triblock copolymer, a; diblock copolymer, b; homopoly(1), c.

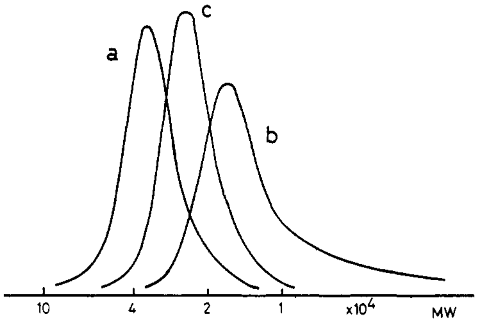

Figure 4. GPC curve of poly(1), $\overline{DP}_{obsd}$ = 65 (a); poly(4-aminostyrene) (b), and poly(4-(benzoylamino)styrene) $\overline{DP}_{obsd}$ = 63 (c). The polymerization condition is shown in Table I.

Therefore the reactivity of the propagating chain end of poly(1) is considered as high as that of polystyryl living anion. The block copolymers of reversed sequence were similarly prepared by addition of monomer 1 to the THF solutions of living polystyrene and polyisoprene.

Stability of the Propagating End. To determine the concentration of living ends, the colorimetric titration previously employed for the living polymers of 4-vinylphenol[1] and 4-(vinylphenyl)dimethyl-2-propoxysilane[5] was applied to this system. However, the end point of titration was not clear enough to obtain accurate data. Therefore, the amount of propagating ends of poly(1) surviving at −78, 0, and 30 °C for 30 min was estimated by block copolymerization with styrene. The resulting polymers were characterized by GPC. Resolution of the GPC curve into three components is shown in Figure 3. The resolved Gaussian curves, a, b, and c, are assigned to ABA- and AB-type block copolymers and homopoly(1), respectively, where A and B are polystyrene and poly(1) blocks. The tri- and diblock copolymers were produced from difunctional living poly(1) and the monofunctional one, where one propagating end was deactivated. The homopoly(1) with both propagating ends destroyed did not react with styrene any more.

Because the absorbance of poly(1) block (ϵ_{254} = 1790) is much larger than that of polystyrene (ϵ_{254} = 176), the intensity of the GPC detected at 254 nm is nearly proportional to the amount of poly(1) block, and hence areas of the resolved curves correspond to numbers of the respective polymer chains by neglecting absorption of polystyrene block. Accordingly, the relationship between

Table III
Stability of Living Poly(1)[a]

	surviving carbanion, %		
countercation	−78 °C	0 °C	30 °C
Li	100	70	20
Na	100	90	80
K	100	100	100

[a] Mole fraction of surviving carbanion after polymerization for 30 min was estimated from eq 1 or 2.

the fraction of living end surviving after 30 min and areas of the resolved curves is expressed as follows:

$$s(1)/S = (1 - x)^2$$

$$s(2)/S = 2x(1 - x)$$

$$s(3)/S = x^2$$

$$S = s(1) + s(2) + s(3)$$

where x is the mole fraction of the living end of poly(1) and S, $s(1)$, $s(2)$, and $s(3)$ are areas of the overall GPC curve, those resolved for triblock, diblock copolymers, and homopoly(1), respectively. From these equations, x is given by

$$x = 2s(3)/[s(2) + 2s(3)] \quad (1)$$

$$x = s(2)/[2s(1) + s(2)] \quad (2)$$

The values of x calculated by eq 1 and 2 agree well with each other in all cases. The results are summarized in Table III. Living ends are stable during polymerization of 1 at −78 °C for 30 min regardless of countercations. At elevated temperatures, the stability of propagating end depends upon the countercations. Living poly(1) with potassium cation is stable, and loss of the living ends cannot be detected even at 30 °C for 30 min. On the other hand, the propagating ends with lithium and sodium cations at higher temperature were partly deactivated. Especially with lithium countercation, most of the carbanion was killed at 30 °C in 30 min.

Deprotection of Homopolymers. As described in a previous paper,[3] samples of poly(1) were converted to poly(4-aminostyrene)s (**3**) by hydrolysis followed by neutralization. The complete removal of trimethylsilyl groups was confirmed by NMR and IR spectroscopies.

To ascertain whether or not cleavage of the main chain occurs during the deprotection process, accurate evaluation of the molecular weight and molecular weight distribution of **3** is essential. However, GPC curves of **3** showed marked tailing presumably due to adsorption of the polymer with primary amino groups on the polystyrene gel packed in the GPC column. Similar phenomena were observed in the case of amine-terminated polystyrene.[6] The primary amino group of **3** was allowed to react with benzoyl chloride to form the amido polymer, **4**, which showed a symmetrical distribution curve without tailing as shown in Figure 4. The degrees of polymerization of **4** estimated by using a calibration curve of standard polystyrene agree with those of corresponding poly(1)s. The polydispersity index of **4**, 1.15, is almost the same as that of **2**. This indicates that the trimethylsilyl group is removed quantitatively without degradation of the main chain of the polymer.

The solubility of poly(1) is remarkably changed by removal of the protective group; the masked polymer is soluble in hexane, benzene, and acetone, whereas the unmasked polymer, **3**, does not dissolve in these solvents and swells in methanol and water. The masked polymer, where the Si–N linkage is stable in aqueous basic and neutral conditions as described above, can be kept in air for several months and under N_2 for over 1 year. However, the deprotected polymer **3** is less stable and becomes insoluble in solvents in air within a few days presumably due to the reaction of the primary amino group with carbon dioxide.[7] Furthermore, the possibility of the oxidative cross-linking, which was not cleaved by hydrolysis, might be also suggested.

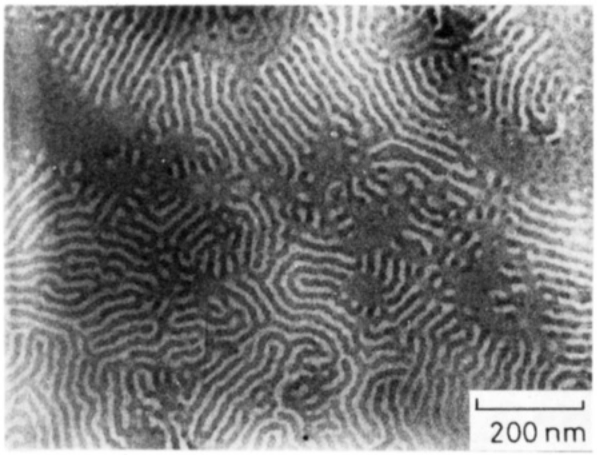

Figure 5. Transmission electron micrograph of poly(styrene-*block*-4-aminostyrene-*block*-styrene). The molecular weight of the protected block copolymer is shown in Table II (footnote *e*).

Deprotection of Block Copolymers. Removal of the protective group from block copolymer was carried out similarly to the case of the homopolymer. ^{1}H NMR, ^{13}C NMR, and GPC measurements revealed that the masking group was completely removed from the polymer chain via acid hydrolysis and that neither cleavage of the main chain nor addition of hydrogen chloride to the carbon–carbon double bonds of polyisoprene block occurred. The resulting block copolymers contain hydrophilic and hydrophobic segments with narrow molecular weight distributions. Block lengths of these segments are easily controlled by the feed ratio of the monomers to initiator. Such copolymers with segregated microdomains can be designed for biocompartible materials.

The morphological study of the block copolymers was performed by electron microscopy. Lamellar-type microphase separation was observed for $(\text{styrene})_{78}$–$(\text{4-aminostyrene})_{61}$–$(\text{styrene})_{78}$ as shown Figure 5. The periodicity distance of the lamella is estimated to be 20–22 nm, which is a reasonable value for the molecular weight of the copolymer, 2.3×10^4.

Glass transition temperatures determined by DSC are 150–160 °C for poly(1) and **2**, and 170–180 °C for deprotected polymer, **3**. The high T_g's may be caused by steric hindrance of the bulky trimethylsilyl group for **2** and by hydrogen bonding for **3**. A pair of T_g's, 109 and 160 °C, were measured for poly[(styrene)-*block*-(1)-*block*-styrene]. The higher T_g is attributable to the poly(1) block and the lower one to that of the polystyrene block, which indicates clear separation of the microdomains.

Registry No. 1, 85967-70-0; 2, 85967-71-1; 2·2Li, 119365-94-5; 2·2Na, 119365-95-6; 2·2K, 119365-93-4; (2)(styrene) (block copolymer), 119298-29-2; (2)(isoprene) (block copolymer), 119298-30-5; 4-aminostyrene, 1520-21-4; hexamethyldisilazane, 999-97-3; trimethylsilyl chloride, 75-77-4; 4-(*N*-(trimethylsilyl)amino)styrene, 85968-77-0.

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Spectroscopic Analysis of Discotic Liquid-Crystalline Molecules and Polymers on External Surfaces

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ABSTRACT: The molecular orientation of two discotic liquid crystals, hexahydroxybenzene hexa(*n*-octanoate-6,6-d_2) (BH8-6,6-d_2) and a poly(benzene hexa-*n*-alkanolate) (PBHA-18), on external surfaces has been measured by unpolarized infrared radiation. The method allows the orientation of molecules in a cast film to be obtained as a function of temperature without tilting the sample. Discotic cores in the crystal phase of the cast film orient predominantly parallel to the external surface. The measured orientation function decreases when the temperature is raised and can be used to follow changes in molecular orientation with temperature through various phase changes and to characterize some of the accompanying structural changes. Orientation of the flexible hydrocarbon chains in the crystal phase of the oriented film is nearly parallel to the disklike cores, indicating that the gauche conformation of the C–O–C*O*–C bond is more stable than the trans one. Significant disordering of the flexible side chains occurs at the solid–solid phase transition, and the chain ends disorient much more readily than do groups near the aromatic core. Polarization characteristics of observed infrared bands are reported.

Introduction

Disklike (discotic) molecules or polymers often form thermotropic liquid-crystalline phases. The chemical structures of the molecules used in this work are well defined, and their phase transitions occur at temperatures less than 100 °C. This fact allows many experiments to be carried out to characterize the structural changes that accompany temperature and phase changes in these materials.

A number of liquid-crystalline molecules or polymers have been reported in the literature. Perhaps the most well characterized is the family of hexasubstituted benzenes, although there are other interesting candidates available.[1-4] Previous structural characterization studies of the disklike molecules used in this investigation include scattering,[5,6] thermal analysis,[7-9] nuclear magnetic resonance spectroscopy,[10] and vibrational spectroscopy.[11-13] Each of these experiments provides different structural information. Vibrational spectroscopy has provided a measure of the temperature-induced change in conformation of the side chains attached to the central core,[11] and the amount of conformational or orientational disorder in the hydrocarbon side chains has been obtained as a function of temperature by using site-specific deuterium-labeled samples prepared in these laboratories.[11,12]

Several aspects of the structures of these disklike molecules or polymers remain unclear. For example, the conformation of the C*O*–C bond orientation relative to the central plane is not understood, where C* is the carbon of the ester group. How the central cores pack relative to the principal axis of individual columns or how these parameters change as a function of temperature and at phase transitions also remain as open questions.

Highly oriented discotic systems are difficult to obtain. Under certain experimental conditions, these liquid-crystalline molecules orient significantly on external surfaces.[13] At least two different approaches have been proposed to characterize such oriented films.[14,15] These involve tilting the oriented film in the incident beam in order to obtain polarized spectra as a function of tilt angle. Since the signal intensity decreases rapidly with tilt angle, the method has been found more suited to determination of true absorbance than to orientation when dispersive infrared spectrometers are used.[15] Even with the greater light flux of Fourier transform infrared instrumentation, the method is of limited utility for orientation studies. The need to use bulky heating stages imposes an additional constraint, for the stages stop the beam incident on the sample at relatively small tilt angles.

In the current study, we have developed a useful and simple spectroscopic technique to characterize the structures of these discotic molecules. The conformations have been characterized in each phase, and changes have been followed as a function of temperature, allowing association of structural changes with the transitions observed by other techniques. These results are reported here.

Experiment

Synthesis and Characterization of Disklike Molecules and Polymer. Disklike molecules, a series of hexahydroxybenzene hexa-*n*-alkanoates (denoted BHn), have been prepared in our laboratories.[11-13] To probe local conformations of side chains, BHn's were prepared with site-specific deuterium labels. In the work reported here, BH8-6,6-d_2 is used. Each of the six side chains carries two deuterium atoms at the sixth carbon in the eight carbon chain. Mass spectrometric analysis using fast-atom bombardment with direct chemical ionization showed that the sample contains 85% d_{12} and 15% d_{11}. Discotic polymer was synthesized by

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