Isomerization Polymerizations of 4-Substituted Styrenes. Synthesis of Macromonomers with Amino and/or Silyl Groups

Yukio Nagasaki,*,† Ryota Ukai,† Masao Kato,† and Teiji Tsuruta‡

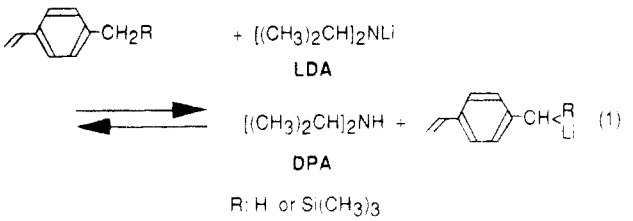
Department of Materials Science and Technology and Research Institute for Biosciences, Science University of Tokyo, Noda 278, Japan

Received June 10, 1994; Revised Manuscript Received September 6, 1994®

ABSTRACT: Lithium diisopropylamide (LDA) induced metalation reaction of styrenes with para substituents such as 4-methylstyrene (MST), 4-[(trimethylsilyl)methyl]styrene (SMS), and 4-[(dimethylamino)methyl]styrene (AMS) to form vinylbenzyllithium (VBL) derivatives. VBL derivatives initiated isomerization polymerizations to form oligomers with a polymerizable vinyl end and with functional groups such as amino groups and trimethylsilyl groups in the side chain. Cooligomerization of the 4-substituted styrenes gave macromonomers with a predicted extent of functional groups in the side chain.

Introduction

It is known that polymerization of vinyl monomers with active proton(s) often induces *isomerization polymerization* to form polymers with unique enchainments other than those from addition polymerizations.[1] For example, Heitz et al. reported polymerization of *p*-vinylbenzamide to form oligo(amide) with a polymerizable vinyl end group.[2] Oku and his co-workers reported an anionic isomerization polymerization of trimethylvinylsilane.[3]



We found previously that LDA induced metalation reaction of 4-methylstyrene derivatives such as MST and SMS to form 4-vinylbenzyllithium derivatives.[4] By using the metalation reaction of SMS, new types of macromonomers with organosilicon moieties were synthesized through anionic isomerization polymerizations as shown in Scheme 1.[5]

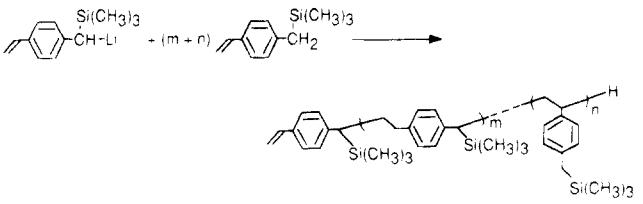
If this polymerization can be applied to other styrenic monomers having active hydrogen, new types of macromonomers can be synthesized through the isomerization polymerizations (Scheme 2). This paper deals with metalation and the isomerization polymerizations of AMS in the prsence of LDA. Copolymerizations of AMS with other monomers such as MST and SMS are also described.

Experimental Section

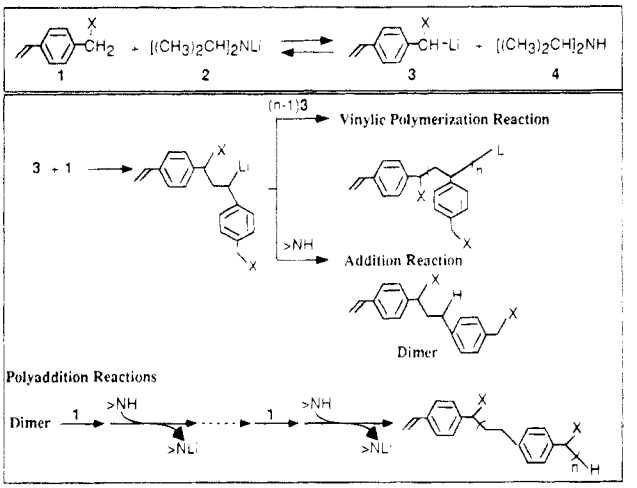
All experiments were carried out under an argon atmosphere in order to eliminate oxygen and moisture.

Materials. Commercial tetrahydrofuran (THF), diisopropylamine (DPA), 4-methylstyrene (MST), and methyl methacrylate (MMA) were purified by conventional methods.[6] Butyllithium was used as a hexane solution, the concentration of which was determined by Gilman's double titration method.[7] 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. 4-[(Dimethylamino)methyl]styrene (AMS)[8] and 4-[(trimethylsilyl)methyl]styrene (SMS)[9] were prepared according to the literature.

Scheme 1



Scheme 2. Isomerization Polymerizations



Isomerization Polymerization of AMS. In a typical procedure, butyllithium (1 mmol, 1.6 mL) was added to a THF (5 mL) solution of DPA (10 mmol, 1.0 g) in a 20-mL flask equipped with a three-way stopcock. After AMS (10 mmol, 1.6 g) was added, the mixture was allowed to react for 2 days at 50 °C. The resulting mixture was analyzed by gas chromatography and gel permeation chromatography to determine the monomer conversion and molecular weights of the oligomers formed. After volatile materials were evaporated completely, the products were analyzed by ^{1}H NMR.

Radical Copolymerization of AMS Macromonomers. MMA (0.25 g, 2.5 mmol), AMS macromonomers (0.5 g, 2.5×10^{-2} mmol; M_n = 2000), and AIBN (10 mg) were filled in a glass tube. After sealing off the tube under high vacuum, the mixture was allowed to react at 45 °C for 3 h, and then the tube was opened. The reaction mixture obtained was diluted by THF and analyzed by GPC after filtration by using 0.22-μm syringe filter.

Acid–Base Titration of AMS Macromonomers. A total of 15 mL of 0.1 mol/L hydrochloric acid was added to a AMS macromonomer (1.0 mmol as N atom) aqueous solution (30

* To whom correspondence should be addressed.
† Department of Materials Science and Technology.
‡ Research Institute for Biosciences.
® Abstract published in *Advance ACS Abstracts,* October 15, 1994.

0024-9297/94/2227-7236$04.50/0

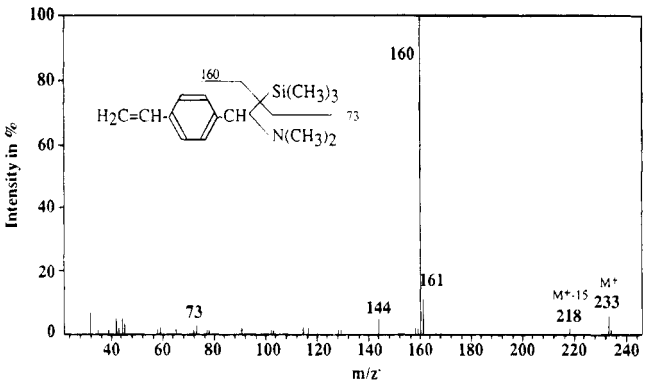


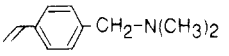
Figure 1. Mass spectrum of 4-[(trimethylsilyl)(dimethylamino)methyl]styrene prepared by the reaction of AMS by LDA.

mL). A titration curve was obtained by potentiometric titration using a 0.1 mol/mL NaOH aqueous solution as the titrant at 23 °C. Turbidity of the macromonomer solution was recorded simultaneously during titration using a UV/visible spectrometer at 500 nm.

Measurements. A Hewlett-Packard 5890 Series II GC was used (column: glass capillary column DB-1 0.25 μm ϕ × 30 m). GC/MS spectra were obtained using the Hewlett-Packard 5890 Series II, equipped with a 5971A mass selective detector. GPC measurements were performed on a Shimadzu LC 6A liquid chromatograph with a RID-6A IR detector and TSK-Gel G4000H8 + G3000H8 + G2500H8 columns. A total of 2% of triethylamine was added to an eluent (THF) to avod adsorption of the AMS macromonomers on the gel. 399.65-MHz ^{1}H NMR spectra were measured on a JEOL EX400 spectrometer using $CDCl_3$ as a solvent at room temperature. Chemical shifts relative to $CHCl_3$ (^{1}H NMR: δ 7.26) were employed. Turbidity titration was carried out by means of a Hitachi 557 UV/vis spectrometer.

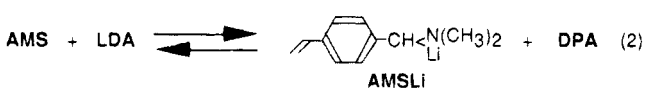
Results and Discussion

As we reported previously,[10] the isomerization polymerization of SMS proceeds through the following three steps: (i) metalations of SMS by LDA (eq 1); (ii) additins of SMSLi to the double bond of the monomers and/or preformed oligomers; (iii) transmetalations by DPA. To generalize this polymerization system, polymerizations of other 4-methylstyrene with active hydrogens such as AMS were examined.



AMS

To initiate the isomerization polymerization, AMS must be metalated by LDA. When AMS was added to a THF solution of LDA at 20 °C ([AMS]$_0$/[LDA]$_0$/[DPA]$_0$ = 0.5/0.5/0.5 mol/L), the color of the mixture turned pale yellow immediately, suggesting carbanion formation. After the mixture was treated with trimethylsilyl chloride (TMSCl), the reaction mixture was analyzed directly by GC/MS spectroscopy. As can be seen in Figure 1, trimethylsilylated AMS was detected by mass spectroscopy (M^+ = 233), indicating a formation of lithiated AMS (AMSLi) by the metalation reaction of AMS by LDA (eq 2).



AMSLi

When the mixture of AMS and LDA in THF was allowed to react for 48 h at 50 °C with stirring ([AMS]$_0$/[LDA]$_0$/[DPA]$_0$ = 1.0/0.1/0.9 mol/L), nonvolatile materials were obtained. Figure 2 shows GPC patterns of the

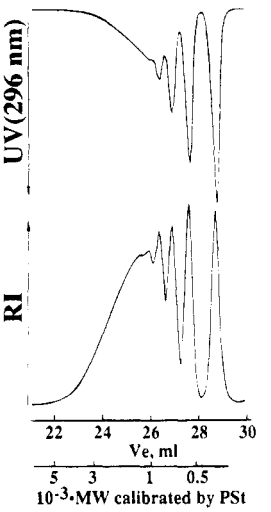


Figure 2. GPC trace of the AMS macromonomers obtained by the isomerization polymerization of AMS in the presence of LDA in THF (the same conditions as run 5 Table 1).

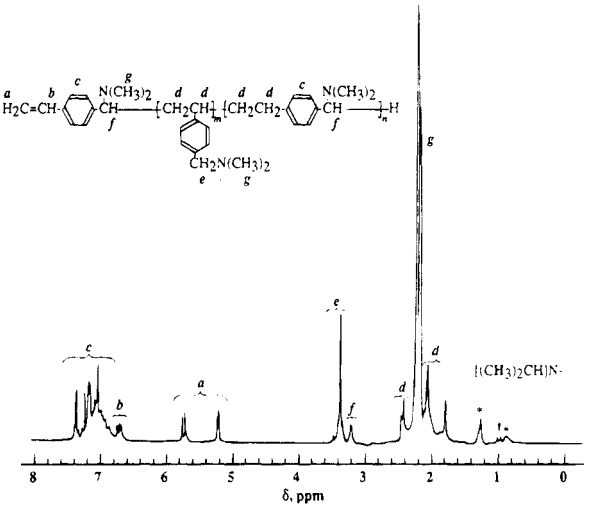


Figure 3. ^{1}H NMR spectrum of the AMS macromonomers (the same sample as in Figure 2). An asterisk denotes an impurity.

products, in which oligomeric mixtures with molecular weights from a few hundred to 5000 were detected by RI detector. Figure 2 also shows that the oligomers thus formed have a UV absorption at 296 nm, which is a typical absorption band originating from vinylbenzyl conjugation, and the intensity of the peaks decreased with increasing molecular weight, which suggests that the oligomers obtained have vinylbenzyl end groups. Figure 3 shows an ^{1}H NMR spectrum of these oligomers, in which signals originating from LDA (1 ppm) were extremely small, indicating almost no initiation took place with LDA. Around 5–6 ppm in the figure, four signals originating from styrenic protons appeared, which strongly indicated that AMSLi initiated the polymerizations. Results of polymerization reactions under several conditions are summarized in Table 1. M_n of the oligomers determined by ^{1}H NMR signals (olefinic protons around 5–6 ppm vs phenyl protons around 6.8–7.5 ppm) agreed well with that by GPC patterns. On the basis of these results, the oligomers thus obtained were identified as AMS macromonomers.

The molecular weights of the AMS macromonomers were controlled by [AMS]$_0$/[DPA]$_0$. Actually, the macromonomers with M_n of a few hundred to 2000 were obtained in good yield. The extent of isomerization enchainments in the AMS macromonomers can be measured by ^{1}H NMR patterns using phenyl methylene

Table 1. Isomerization Polymerizations of AMS in the Presence of LDA in THF

run	$[AMS]_0$ (mol/L)	$[LDA]_0$ (mol/L)	$[DPA]_0$ (mol/L)	time (days)	temp (°C)	conv[a] (%)	$M_n \times 10^{-2}$ GPC	$M_n \times 10^{-2}$ NMR	MWD[b]	extent of isomerization[c] (%)
1	1.0	0.1	2.9	2.0	50	31.8	3.5	nd	1.0	nd
2	1.0	0.1	1.9	2.0	50	51.3	4.1	nd	1.2	nd
3	1.0	0.1	0.9	2.0	50	89.7	6.0	8.4	1.4	46.4
4	1.0	0.1	0.9	4.0	50	96.1	8.0	11.9	1.5	40.9
5	1.0	0.1	0.9	2.0	25	70.8	6.9	6.3	1.3	23.0
6	1.0	0.1	0.9	4.0	25	80.5	6.7	6.1	1.3	27.7
7	1.0	0.1	0.5	2.0	50	96.7	10.4	nd	1.4	nd
8	1.0	0.1	0.4	2.0	50	96.7	12.2	12.0	1.4	1.0
9	1.0	0.1	0.1	2.0	50	99.5	20.1	nd	1.4	nd
10	1.0	0.1	0.05	2.0	50	99.9	18.2	nd	2.0	nd
11	0.5	0.1	2.9	2.5	50	23.3	3.7	4.3	1.1	42.6
12	0.5	0.05	0.95	2.0	50	84.7	6.3	6.0	1.3	37.4
13	0.5	0.05	0.45	2.0	50	95.1	9.4	nd	1.4	nd
14	0.5	0.05	0.45	4.0	50	97.1	10.4	nd	1.4	nd
15	3.0	0.1	0.9	2.0	50	61.7	5.2	9.6	1.3	76.7

[a] Determined by GC. [b] Molecular weight distribution determined by GPC. [c] Determined by ^1H NMR (see text).

Table 2. Isomerization Copolymerizations of 4-Methylstyrene Derivatives in the Presence of LDA in THF[a]

run	$[AMS]_0$ (mol/L)	$[MST]_0$ (mol/L)	$[LDA]_0$ (mol/L)	$[DPA]_0$ (mol/L)	conv[b] (%)	$M_n \times 10^{-2}$ GPC	$M_n \times 10^{-2}$ NMR	MWD[c]	mole fraction of AMS in the copolym[d] (%)
1	1.0	0	0.1	0.9	89.7	6.0	8.4	1.4	100
2	0.8	0.2	0.1	0.9	83.0	5.7	7.1	1.3	89
3	0.5	0.5	0.1	0.9	96.1	6.6	8.0	1.8	57
4	0.2	0.8	0.1	0.9	87.0	5.5	7.9	1.3	25
5	0	1.0	0.1	0.9	88.8	6.9	8.6	1.3	0
6[e]	0.5	0.5	0.1	0.4	94.0	8.2	10.7	1.4	55
7	0.5	0.5	0.1	0.4	99.7	12.4	13.9	1.6	nd
8	0.5[f]	0.5	0.1	0.9	89.2	9.7	11.2	1.2	52.1[g]
9	0.5	0.5[f]	0.1	0.9	91.9	5.0	5.3	1.2	53.0

[a] Temp: 50 °C. Time: 2 days. [b] Determined by GC. [c] Molecular weight distribution determined by GPC. [d] Determined by ^1H NMR (see text). [e] Time: 1 days. [f] SMS was used instead of MST. [g] SMS extent in the copolymer.

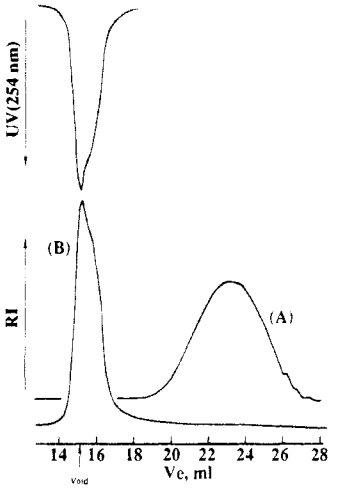


Figure 4. GPC trace of a reaction mixture of AMS macromonomers (the same sample as run 9 in Table 1) with MMA in THF (A) before and (B) after copolymerization.

(e in Figure 2; 3.4 ppm) and phenyl methine (f in Figure 2; 3.2 ppm) protons according to our previous paper,[9] the results of which are listed in Table 1. Polyaddition extents in isomerization polymerizations of AMS in the presence of LDA were found to be in the range of 17–77%.

To examine if the AMS macromonomers thus obtained can easily be incorporated in the copolymers, a radical copolymerization of the macromonomers with MMA was carried out. The copolymerization proceeded smoothly until 100% consumption of MMA (nondetectable by GC). As can be seen in the GPC pattern in Figure 4, AMS macromonomers were also almost diminished after the polymerization and the polymer obtained has a UV absorption at 254 nm. These facts indicate that AMS macromonomers incorporated in the polymer easily through the radical copolymerization with MMA to form poly(MMA-*g*-AMS).

It is well-known that anionic copolymerizations of vinylic monomer pairs are normally very difficult because monomer reactivities toward a growing anion are seriously changeable depending on a minute variation in the monomer structure. In the present anionic isomerization polymerization, however, the copolymerizability was governed by not only the reactivities of the vinyl groups of the comonomers toward carbanions but also the concentrations of lithiated comonomers, in other words, the stability of the lithiated comonomers. Thus, the monomers with high metalation ability by LDA have an opportunity to be incorporated into the preformed oligomers competitively though the vinyl group of the monomer may not have enough reactivity to the carbanion as compared to its comonomers. The copolymerization of MST with AMS in the presence of LDA gave oligomeric products, the molecular weight of which was a few hundred to 1300 (Table 2). Time–conversion curves of AMS in the copolymerization (Figure 5) were almost similar to those of MST, indicating the resulting copolymer had an almost random sequence, though AMS contents in the copolymer were slightly higher than those in the feed. ^1H NMR of the oligomers shows signals originating from both comonomers (Figure 6), with no signal originating from LDA, indicating the resulting oligomers are regarded as copoly(AMS–MST) macromonomers. Anionic copolymerizations of SMS with other 4-methylstyrene derivatives such as MST and AMS proceeded to form comacromonomers with almost the same monomer contents as in the feed (runs 8 and 9 in Table 2).

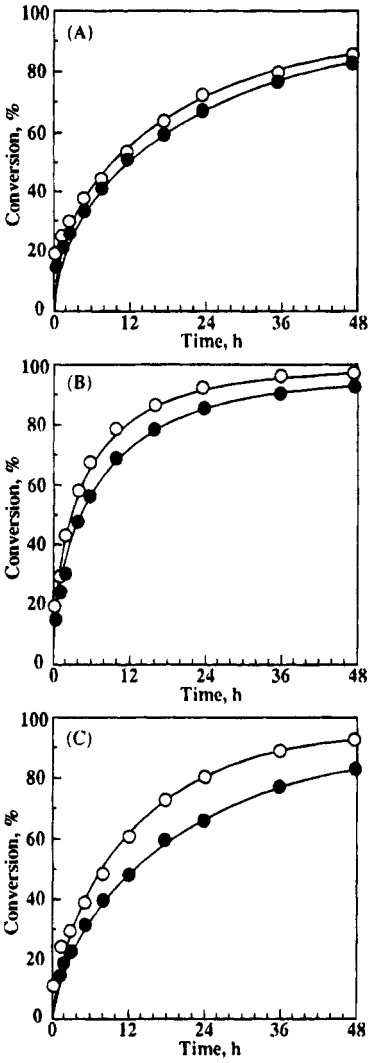


Figure 5. Time–conversion curves of AMS (○) and MST (●) in the isomerization copolymerization in THF: (A) run 2 in Table 2; (B) run 3 in Table 2; (C) run 4 in Table 2.

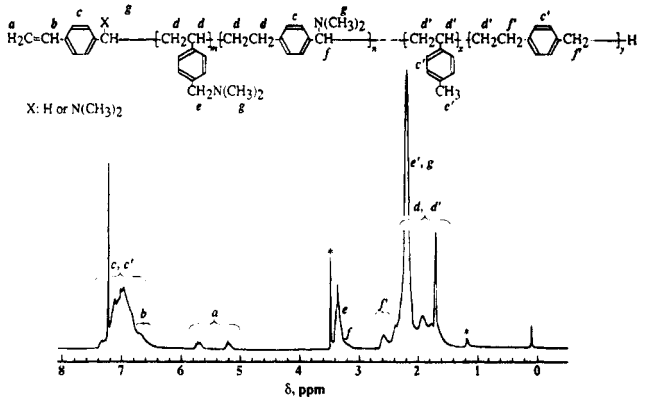


Figure 6. ^{1}H NMR spectrum of poly(AMS-*co*-MST) (the same sample as in Figure 5B). An asterisk denotes an impurity.

On the basis of these results, it is concluded that the anionic polymerizations of 4-methylstyrene derivatives gave macromonomers with functional groups such as dimethylamino and/or trimethylsilyl groups with predicted extents.

To estimate the response of AMS macromonomers against pH change, acid–base and turbidity titrations

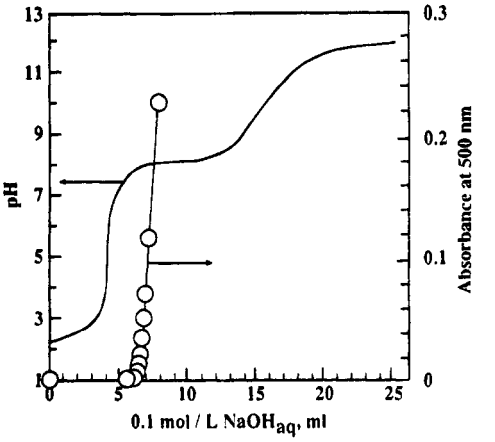


Figure 7. Acid–base and turbidity titrations of AMS macromonomers (the same sample as run 9 in Table 1).

were carried out. As shown in Figure 7, the apparent pK value of the macromonomers was 8.05 which was lower that of the AMS monomer (pK = 8.55) owing to the shielding effect of the polyamines.[11] The solubility of the macromonomers was drastically changeable depending on the extent of protonation of amino groups (α). With increasing pH, the macromonomers started to precipitate at around α = 0.9 (pH = 7.9), and then the turbidity of the solution increased drastically up to α = 0.8 (pH = 8). This was in sharp contrast to the poly(silaamine) oligomers with diamine units in the main chain.[12] This macromonomer, poly(silaamine), usually shows a turbidity point at around α = 0.5, indicating a higher hydrophobicity of AMS macromonomers than that of poly(silaamine) oligomers.

Acknowledgment. Y. N. expresses his sincere appreciation to the Tokyo Ouka Foundation, for financial support of a part of this research. A part of this study was also supported financially by Grant-in-Aid for Encouragement of Young Scientists, the Ministry of Education, Science and Culture, Japan (No. 04855186).

References and Notes

(1) (a) Asahara, T.; Yoda, N. *Polym. Lett.* **1966**, *4*, 921. (b) Yuki, H.; Kosai, K.; Ohtsu, K. *Kogyo Kagaku Zasshi* **1967**, *70*, 1963.
(2) Jung, H.; Heiz, W. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 373.
(3) Asami, R.; Oku, J.; Takeuchi, M.; Nakamura, K.; Takaki, M. *Polym. J.* **1988**, *20*, 699.
(4) Nagasaki, Y.; Tsuruta, T. *Makromol. Chem.* **1986**, *187*, 1583.
(5) Nagasaki, Y.; Tsuruta, T. *Makromol. Chem., Rapid Commun.* **1989**, *10*, 403.
(6) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; 2nd ed.; Pergamon Press: Oxford, U.K., 1980.
(7) (a) Gilman, H.; Langham, W.; Moor, F. W. *J. Am. Chem. Soc.* **1940**, *62*, 2327. (b) Gilman, H.; Haubeim, A. H. *J. Am. Chem. Soc.* **1944**, *66*, 1515.
(8) Higo, Y.; Chosi, H.; Fujimoto, T.; Nagasawa, M. *Polym. J.* **1980**, *12*, 729.
(9) Nagasaki, Y.; Tsuruta, T. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 437.
(10) Nagasaki, Y.; Tsuruta, T. *Macromol. Chem., Phys.*, in press.
(11) Elias, H.-G. *Macromolecules. I. Structure and Properties*; Stafford, J. W., Translator; Plenum Press: New York, 1977.
(12) Nagasaki, Y.; Honzawa, E.; Kato, M.; Kihara, Y.; Tsuruta, T. *J. Macromol. Sci., Pure Appl. Chem.* **1992**, *A29*, 457.