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Notes

Introduction of Azobenzenes or Vinyl Groups into Ends of Rodlike Polymers

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Introduction

Macromolecules can take on some simple shapes, such as coils, spheres, and rods, as well as some simple architectures, such as flexible polymers, star-shaped polymers,[1,2] hyperbranched polymers,[3] ring polymers, and rodlike polymers. In both the shape and architectural categories, the rodlike polymers are characterized by high asymmetry.[4] Because of this asymmetric shape characteristic, the rodlike polymers have shown some unique physical properties such as liquid crystallinity,[5] anisotropic solution,[6] and dielectric and rheological behaviors.[7,8] Thus, rodlike polymers might be applied to new polymeric devices.[9−12] However, the self-diffusion coefficients of rodlike polymers, which are fundamental molecular parameters in chain dynamics, could not be determined by a forced Rayleigh scattering technique, although those coefficients of flexible polymers, such as polystyrene, have been reported for more than 15 years.[13] The difficulty arose in the attempt to synthesize dye-labeled rodlike polymers having desired molecular weights and narrow molecular weight distributions (MWDs).

One of the representatives of the rodlike polymers is poly(*n*-hexyl isocyanate) (PHIC). Living titanium-catalyzed coordination polymerization of isocyanates has been reported by Novac et al.[14,15] They prepared well-defined polyisocyanates (PICs) and block copolymers consisting of two different PIC blocks. To stabilize the resultant PIC, Novac et al. end-capped the polymerization using acetic anhydride derivatives,[16] and Hatada et al. did so by using acetyl chloride derivatives.[17] However, after Novac and Hatada reported the end-capping of PIC, the reaction of the living ends with other functional groups has not been studied. Therefore, the present study deals with this coupling reaction, introducing dye compounds into an end of living PHIC in order to employ the resultant dye-labeled PHIC in a forced Rayleigh scattering experiment. PHIC macromonomers might also be prepared using the same synthetic route, which is different from that of an earlier study reported by Novac et al.[18] When PHIC macromonomers are polymerized, star polymers having rodlike arms will be produced.[2] We call this polymer a chestnut bur-shaped star polymer,[19] and we expect it to show interesting physical properties.

To gain insight into methods to produce a coupling reaction of the living PHIC with halogen derivatives, two azobenzenes, two vinyl compounds, and a trichlorosilyl compound were tested as candidates for introduction into PHIC. Also, an interesting phenomenon of equilibrium polymerization of the isocyanates was applied to increase the coupling efficiencies (f_c) of the living PHIC with halogen derivatives.

Experimental Section

n-Hexyl isocyanate (HIC), $N(C_6H_{13}){=}C{=}O$, was purchased from Kanto Chemical Co., Inc. (Tokyo, Japan), and distilled under 20 mmHg, dried with calcium hydride (CaH_2) under high vacuum (10^{-6} mmHg), and then distilled into ampules with breakable seals. Just before polymerization, HIC was distilled into an ampule after being dried with an octylzenzophenone−sodium complex.[20,21] A titanium catalyst, $TiCl_3OCH_2CF_3$, was prepared according to Novac et al.[14,15] under high vacuum using a breakable-seal technique.

Two azobenzenes were prepared as follows:[22,23] (1) Nitrosobenzene was reacted with toluidine to produce 4-chloromethylazobenzene. 4-Chloromethylazobenzene was reacted with *N*-bromosuccinimide to prepare 4-bromomethylazobenzene (BrMAz), $Ph{-}N{=}N{-}C_6H_4{-}CH_2Br$. (2) Nitrosobenzene was reacted with *p*-aminobenzoic acid to produce *p*-aminoazobenzoic acid. The product was reacted with thionyl chloride to produce *p*-phenylazobenzoyl chloride (PAzCl), $Ph{-}N{=}N{-}C_6H_4{-}COCl$. Both azobenzenes were confirmed by ^1H NMR.

β-Phenyl bromide was reacted with chloromethylmethyl ether to produce *p*-(*β*-bromoethyl)benzyl chloride. The product was dehydrated by potassium *tert*-butoxide to produce 4-vinylbenzyl chloride (VBCl), $CH_2{=}CH{-}C_6H_4{-}CH_2Cl$. Methacryloyl chloride (MACl), $CH_2{=}C(CH_3)COCl$, was purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). A four-functional coupling reagent, 1,2-bis(trichlorosilyl)ethane (BTCl), $Cl_3SiCH_2CH_2SiCl_3$, was purchased from Tokyo Kasei Industry Co. (Tokyo, Japan). BTCl was sublimed several times under high vacuum.[24] All reagents mentioned above, as well as the solvents employed in the preparation of the corresponding solutions and in polymerization, were purified by the same methods as for the anionic living polymerization technique, using breakable seals under high vacuum (10^{-6} mmHg).[20,21] The polymerization and coupling reactions were carried out under high vacuum using a breakable-seal technique.[25,26]

Molecular characterization of the resultant poly(*n*-hexyl isocyanate) (PHIC), $-[N(C_6H_{13}){-}CO]_n-$, was carried out using gel permeation chromatography equipped with low-angle laser light-scattering (GPC-LALLS) and new analytical equations we have presented elsewhere.[27]

The ratio of a number-average molecular weight (M_n) by GPC-LALLS to that by ultraviolet (UV) or NMR measurements (end-group analysis) for PHIC−MAz and PHIC−PAz, $M_n^{GPC-LALLS}/M_n^{UV}$ or $M_n^{GPC-LALLS}/M_n^{NMR}$, is defined as the coupling efficiency (f_c) that indicates the number of MAz or PAz groups per PHIC molecule. The coupling efficiency of PHIC−VB and PHIC−MA was determined by $M_n^{GPC-LALLS}/M_n^{NMR}$. The coupling efficiency of $(PHIC)_4{-}Si$ was determined by the ratio of the RI signal of the products to the RI signal of

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PHIC for the GPC chromatogram. On the other hand, the coupling efficiency at the ith elution volume of the GPC chromatogram for PHIC−PAz is defined as

$$(f_c)_i = \frac{(c_{\mathrm{PAz}})_i/M_{\mathrm{PAz}}}{(c_{\mathrm{PHIC}})_i/(M_{\mathrm{n,PHIC}})_i} \tag{1}$$

where $(c_{\mathrm{PAz}})_i$ and $(c_{\mathrm{PHIC}})_i$ are concentrations of PAz and PHIC for the resultant PHIC−PAz at the ith elution volume, respectively, and M_{PAz} and $(M_{\mathrm{n,PHIC}})_i$, determined by GPC-LALLS,[27] are molecular weights of PAz and PHIC at the ith elution volume, respectively. The UV signal of PHIC−PAz at 327 nm arises not from PHIC but PAz, because the molar absorptivity of PAz (4.1×10^4 mol^{-1} L cm^{-1}) is much larger than that of PHIC (∼0). Therefore, $(f_c)_i$ can be determined as follows:

$$(f_c)_i = \frac{[(H_{\mathrm{PHIC-PAz}}{}^{\mathrm{UV}})_i/k_{\mathrm{PAz}}{}^{\mathrm{UV}}]/M_{\mathrm{PAz}}}{[(H_{\mathrm{PHIC-PAz}}{}^{\mathrm{RI}})_i/k_{\mathrm{PHIC}}{}^{\mathrm{RI}}]/(M_{\mathrm{n,\,PHIC}})_i} \tag{2}$$

where $(H_{\mathrm{PHIC-PAz}}{}^{\mathrm{UV}})_i$ and $(H_{\mathrm{PHIC-PAz}}{}^{\mathrm{RI}})_i$ are the UV signal at 327 nm and the RI signal at the ith elution volume of the GPC chromatogram for PHIC−PAz, respectively, and $k_{\mathrm{PAz}}{}^{\mathrm{UV}}$ and $k_{\mathrm{PHIC}}{}^{\mathrm{RI}}$ are instrumental constants that were previously determined by the GPC measurements of PAz using the UV detector and of PHIC using the RI detector, respectively.

Results and Discussion

A portion of the toluene solution of the HIC monomer was introduced into the toluene solution containing $TiCl_3OCH_2CF_3$, whose polymerization rate has been found to be very fast. After the initiation was finished in 15 min, a few percent of THF was added to the polymerization solution to introduce the living end to be solvated by coordination with THF. This small amount of THF was found to slow the propagation rate to a few hundredths of the initial rate. The residual monomer in the toluene/THF mixture was then added to the oligomeric living PHIC solution to propagate the polymer slowly. By this seed polymerization technique, we have prepared living PHIC having desired molecular weights and narrow MWDs. The toluene-rich solvent was exchanged for a THF-rich solvent under high vacuum, and then five halogen derivatives were added to the living PHIC solution. A typical procedure of the coupling reaction was as follows. A THF (10 mL) solution of PAzCl (0.76_8 g, $2.1_5 \times 10^{-3}$ mol) was added to a THF/toluene solution (130 mL/10 mL) of a living PHIC ($17._8$ g, $M_n = 1.1_0 \times 10^5$, $1.6_2 \times 10^{-4}$ mol) to prepare PHIC−PAz at −5 °C for 740 h under high vacuum (10^{-6} mmHg). The precursor was taken out of the glass apparatus at a given time by the same methods as for the anionic living polymerization technique,[20,21] so as to determine the coupling efficiency.

Table 1 shows the results of the coupling of the living PHIC with each of the five halogen derivatives and describes the maximum values of coupling efficiency (f_c) and the corresponding molecular characteristics. When the living PHIC was reacted with each of two azobenzenes (BrMAz and PAzCl), both azobenzenes were introduced into PHIC with low f_c values (less than 2.3% and less than 27.6%, respectively). When the living PHIC was reacted with each of two vinyl compounds (VBCl and MACl), MACl was introduced into PHIC with high f_c values (less than 77%), as compared with a f_c value of 0% for VBCl. To prepare four-arm star polymers having rodlike arms, the living PHIC was allowed to react with BTCl.[24] Despite the long reaction times, no coupling of the living PHIC with BTCl was found.

Table 1. Molecular Characteristics and Coupling Efficiency (f_c) of the Resultant Polymers

polymers	halogens	$10^{-4}M_k$[a]	$10^{-4}M_n$[b]	M_w/M_n[b]	f_c (%)
PHIC−MAz	BrMAz	0.34_5	0.40_9	1.1_6	2.3
PHIC−PAz	PAzCl	9.9_4	$11._0$	1.2_4	$27._6$
PHIC−VB	VBCl	8.7_6	9.2_2	1.1_3	0
PHIC−MA	MACl	1.0_2	1.0_4	1.1_0	77
PHIC−MA[c]	MACl	1.0_2	1.0_4	1.1_1	100[c]
$(PHIC)_4$−Si	BTCl	$11._4$	2.8_3	1.2_7	0

[a] Determined from the amounts of monomer and initiator by considering polymer yield. [b] Determined by GPC-LALLS using new analytical equations.[27] [c] A mixture (23 g) of HIC monomer, the living PHIC, and PHIC−MA was first prepared. After the depolymerization was carried out at 50 °C for 2 days under high vacuum, PHIC−MA (17 g) was isolated as precipitate when the resultant product was poured into methanol.

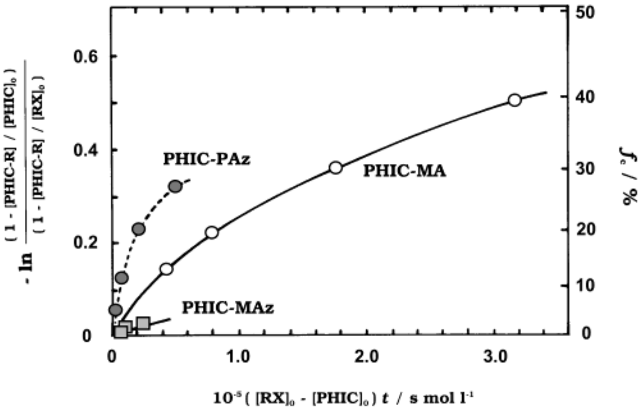

Figure 1. Second-order plots of the coupling reaction for the living PHIC with halogen derivatives. $[RX]_0$ and $[PHIC]_0$ are initial concentrations of the halogen derivatives and living PHIC, respectively. [PHIC−R] is a concentration of the resultant polymers at a given coupling time.

The f_c values increased as coupling time increased. Figure 1 shows the second-order plots of the time−conversion curves for the living PHIC's coupling reactions with three halogen derivatives. In conclusion, the coupling reactivity of the alkyl halides (BrMAz > VBCl = BTCl = 0) was less than that of the acid chlorides (PAzCl > MACl).

The two azobenzenes tested had much higher adsorption coefficients than that of PHIC. Even if only a slight amount of azobenzene was introduced into PHIC, the coupling efficiency was detected easily when RI and UV detectors were used for GPC measurement. Therefore, the distribution of f_c among the elution volume of the GPC chromatogram was determinable. Figure 2 shows the resultant f_c distribution of the product (PHIC−PAz). The f_c value did not depend on the elution volume; that is, it did not depend on the molecular weight of PHIC. The azobenzene was homogeneously introduced into PHIC.

Even if the dye-labeled PHIC has lower f_c values than those appearing here, the sample can be employed in a forced Rayleigh scattering experiment because labeling by even a few percent of azobenzene is sufficient to gain scattering intensity from PHIC due to a high UV coefficient. In contrast, when preparing macromonomers, the vinyl groups have to be introduced into PHIC in 100% coupling efficiency because it is difficult to remove PHIC from the product of poly(PHIC) star polymers prepared by polymerization of the PHIC

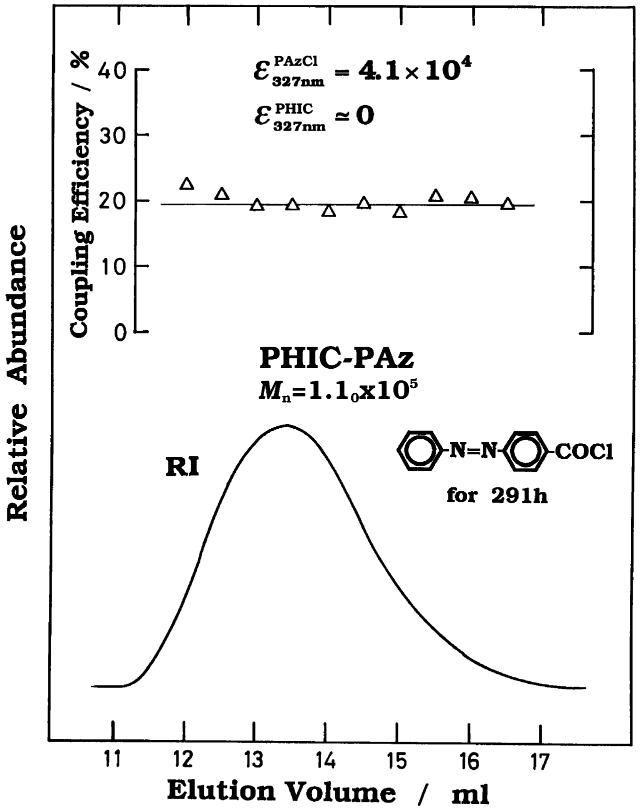

Figure 2. GPC chromatogram and distribution of the coupling efficiency (f_c) for PHIC−PAz.

macromonomers. A PHIC macromonomer having the methacryl group could be prepared at high coupling efficiency (77%), but this efficiency would remain below 100%, even after a long time (∼740 h).

As a PHIC chain forms a helical conformation and the resonance structure of the main chain, a ceiling temperature of 43 °C appears.[16] Therefore, the solution of the coupling reaction was left standing above the ceiling temperature for 2 days. The living PHIC unreacted with MACl was depolymerized to yield the corresponding monomer and/or trimer, and the PHIC-MA was transferred intact due to the absence of livingness. Therefore, the f_c value became 100%, as shown in Table 1. This technique to depolymerize the living PHIC is a remarkable method for preparing a macromonomer having a 100% coupling efficiency, and it should be useful for other applications. For example, when the polymerization solution of a living PHIC was left standing for 2−5 days at a certain temperature below the ceiling temperature (in a case where the equilibrium HIC concentration was close to that of the living PHIC), the M_w/M_n values came close to 1.00 with an increase in the retention time, even if the polymer yield and molecular weight were transferred intact.[28]

When PHIC−MA and methyl methacrylate (MMA) were copolymerized by 2,2′-azobis(isobutyronitrile) (AIBN), the PHIC weight percent of the resultant PHIC-*co*-PMMA branched copolymers was less than 25%, even with an 85% PHIC−MA in the feed. In addition, the number of rodlike branches in a copolymer chain was found to be less than 3.2. The methacryl group of PHIC−MA does not seem to be quantitatively polymerized due to steric hindrance of the N,N-disubstituted methacrylamide.[29]

These findings can be explained by the NMR spectra in which PHIC−MA shows additional ^{1}H NMR signals of the vinyl protons that are different from but close to those of MACl. As shown in Figure 3, although each of the two vinyl protons of the methacrylamide of PHIC−MA was split into doubles at 24 °C, at 70 °C each of them was observed as a line. At intermediate temperatures (a spectrum observed at 55 °C is shown in Figure 3), the spectra observed are superpositioned in varying proportions of the two limiting spectra. Thus, a symmetrical displacement or rotation about a C−CO bond of the methacryl group can be performed at 70 °C.[30,31] Hence, a small amount of PHIC−MA can be polymerized, even though the N,N-disubstituted methacrylamide has been reported to be not quantitatively polymerizable.[29] A systematic study of the polymerization of the PHIC−MA macromonomer is in progress. To prepare PHIIC macromonomers, N-monosubstituted methacrylamide should be introduced into an end of PHIC.

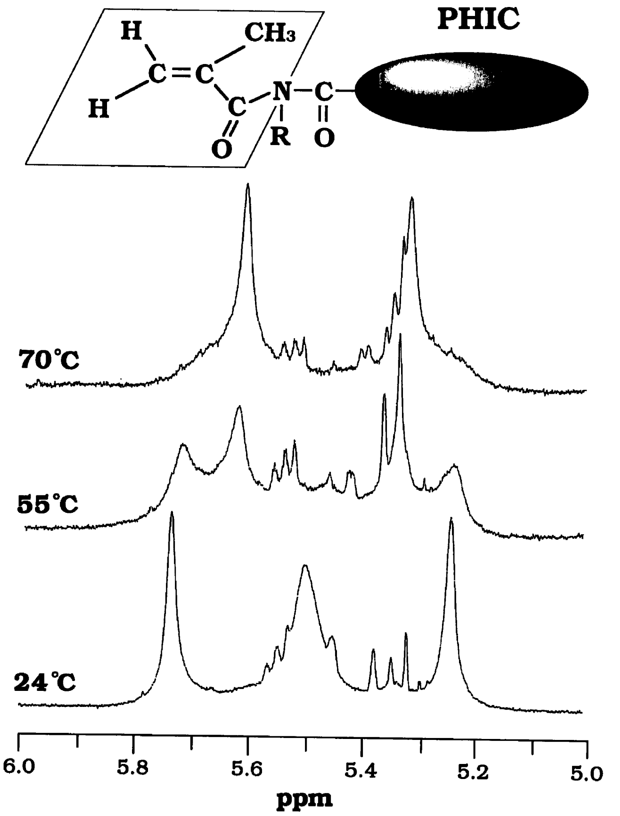

Figure 3. Temperature dependence of the ^{1}H NMR spectra for a vinyl group of PHIC−MA.

In conclusion, dye-labeled rodlike polymers, such as PHIC−PAz and PHIC−MAz, having desired molecular weights and narrow MWDs were prepared for use in a forced Rayleigh scattering experiment. A well-defined PHIC−MA having a f_c value of 100% was prepared for preparation of new star polymers having rodlike arms.

References and Notes

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