ELSEVIER

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 44 (2003) 3847–3854

polymer

www.elsevier.com/locate/polymer

Synthesis of well-defined block copolymers of *n*-hexyl isocyanate with isoprene by living anionic polymerization

Jun-Hwan Ahn, Yeong-Deuk Shin, Sun-Young Kim, Jae-Suk Lee*

Department of Materials Science and Engineering, Kwangju Institute of Science and Technology (K-JIST), 1 Oryong-dong, Buk-gu, Kwangju 500-712, South Korea

Received 19 February 2003; received in revised form 17 April 2003; accepted 18 April 2003

Abstract

n-Hexyl isocyanate (HIC) was polymerized at different reaction temperatures and times, using alkali metal naphthalenide, via anionic polymerization in THF. To prevent the formation of trimers, the polymerization of HIC was also performed utilizing sodium tetraphenylborate ($NaBPh_4$) as a common ion salt. As the reaction temperature decreases, yield of the polymer increases due to stabilization of the active amidate anion at low temperature. In the absence of the additive, a quantitative yield was obtained at −98 °C. However, after most of the monomer was polymerized, further reaction led to trimerization. This was prevented in the presence of $NaBPh_4$ effectively and the living polymerization was performed successfully at −98 °C. The reaction rate retarded with increasing concentration of $NaBPh_4$, the optimum concentration of $NaBPh_4$ was 10 times the concentration of the initiator for the living polymerization of HIC. The living system led to the polymers of molecular weight (MW) as high as 50,000 g/mol. The observed MW was well in agreement with the calculated one. At the higher reaction temperature, −78 °C, the quantitative yield was obtained at 2 min of the reaction time, however the living character was not observed at longer reaction time. The study indicated that the amidate anion was stabilized using $NaBPh_4$ having bulky contact ion pair. The block copolymer of HIC with isoprene, poly(HIC-*b*-isoprene-*b*-HIC), was synthesized with help of the living character of polyisoprene and $NaBPh_4$. The morphology and composition of the block copolymers were investigated using TEM and ^{1}H NMR, respectively.

Keywords: polyisocyanate; living polymerization; anionic polymerization

---

1. Introduction

Polyisocyanates are stiff polymers due to amide bond present in the polymer main chain. These amide bonds have a partial double bond character for which the polymer chains tend to be planar. However, the polyisocyanate chains are twisted into helical conformation because of the steric reason [1]. Due to the helical conformation, polyisocyanates have been studied for application fields such as chiral recognition materials, optical switches and liquid crystal materials [2–10].

It is well known that the polyisocyanates can be obtained readily via anionic polymerization [11–19]. However, the controlled polymerization of isocyanates is not easy to achieve. The main difficulty faced in retaining the living property in polymerization of isocyanates is the cyclic trimerization by backbiting of the amidate anions. The trimerization was accelerated up to 100% above −40 °C [1]. Therefore, it is necessary that the trimerization should be inhibited for the living polymerization of isocyanates to succeed. To suppress the trimerization, the variables such as reaction temperature, solvent, and initiator should be optimized.

In earlier reports, the polymerization of isocyanates was performed around −60 °C [2–7,11–19]. However, in these cases, the polymer yields were low and the trimerization was not completely suppressed because the active end anion is still unstable at this temperature. Khatri and co-workers polymerized functional isocyanates at −78 °C and yield of the polymer increased a little as compared with that of polymerization at −60 °C [11–20]. Okamoto and co-workers performed the polymerization of aliphatic isocyanates at −98 °C and yield of the polymer reached the quantitative value [21–22]. Thus, it was suggested that the reaction temperature should be brought down further to −98 °C. Except for broadness of MWD, their results were

---

* Corresponding author. Tel.: +82-62-970-2356; fax: +82-62-970-2304. *E-mail address:* jslee@kjist.ac.kr (J.-S. Lee).

0032-3861/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0032-3861(03)00325-2

advanced and indicated that the low reaction temperature could stabilize the active end anion resulting in the suppression of trimerization.

Among the anionic initiators in the polymerization of isocyanates, the initiators such as sodium cyanide, sodium *N*-methylacetamide, sodium benzophenone ketyl, butyl lithium, and sodium naphthalenide (Na-Naph) have been used [11–19]. Especially, NaCN in DMF had been a typical initiator for the anionic polymerization of isocyanates, because it was relatively less sensitive to moisture, which otherwise lead to side reactions [11–19]. However, its solubility is not so good in common solvents used for polymerization at low temperatures and the heterogenity due to low solubility resulted in broadness of MWD and low yields. Considering both reaction temperature and solubility, Na-Naph in THF was suggested to be a good alternative in the polymerization of isocyanates at low temperatures [21–26]. In this system, the polyisocyanates with quantitative yield and narrow MWD could be obtained within a very short time.

To extend the living character, the use of an additive is helpful and it prevents depolymerization. Endo and coworkers introduced samarium iodide as an additive into the polymerization of isocyanates [27–28]. The use of samarium iodide drastically suppressed the trimerization of isocyanates during the polymerization with alkyllithiums in THF at −78 °C, resulting in polymer with higher molecular weights. However, the MWD was relatively broad, in the range of 2.4–3.5, in addition to a large variation in yields from 0 to 70%. It was thought that samarium iodide was not satisfactory as an additive as it did not effectively react with alkyl lithium initiator. Thus, the selection of proper additive and initiator is very important in living polymerization of isocyanates.

Synthesis of polyisocyanates with the bulky alkoxysilyl groups, (poly(3-(triethoxysilyl) propyl isocyanate)) and azobenzene chromophore by anionic polymerization was recently reported by us using sodium naphthalenide (Na-Naph) and 15-crown-5 (15C5) complex as an initiator in THF at −98 °C [23–24]. The growing chain ends of the polymer could not attack the carbonyl groups in the backbone because of the steric hindrance resulting from the interaction between the bulky cation–ligand complexes (Na-Naph-15C5) and the bulky side chains. Thus, formation of the trimer could be effectively suppressed. However, in this case, the fast propagation attributed to the stretch between the chain ends and sodium-15C5 complexes so that fast backbiting occurred after yield of the polymer reached the quantitative value. It means that the stability of living character in the polymerization system does not last for a long time. *n*-Hexyl isocyanate (HIC) was also polymerized by us via anionic polymerization using sodium naphthalenide in THF at −98 °C [25–26]. The formation of trimers was prevented by utilizing sodium tetraphenylborate ($NaBPh_4$) as a common ion salt which formed a tight ion pair with amidate anion and stabilized it with excess sodium cations. The living polymerization was performed successfully during the prolonged time range of 20–40 min, using $NaBPh_4$ [25–26].

In this study, the polymerizations of HIC were performed with different reaction times, temperatures, and initiators in the presence of $NaBPh_4$. Also, the synthesis of PHIC was carried out with changing concentration of $NaBPh_4$ to investigate the effect of $NaBPh_4$. To examine the living condition at a higher temperature, the polymerizations were performed at −78 °C in the presence of $NaBPh_4$. The block copolymers of HIC with isoprene were synthesized to further investigate the living character of PHIC. The morphology of the film cast from the block copolymers was studied with TEM to investigate the structure of the block copolymer synthesized by living anionic polymerization.

2. Experimental

2.1. Materials

n-Hexyl isocyanate (HIC, Aldrich Chemical Co. Inc., 97%) and isoprene (Aldrich Chemical Co. Inc.) were dried over CaH_2 and distilled under vacuum. Tetrahydrofuran (THF, Fisher Scientific Co. GR grade) was distilled under N_2 after refluxing with sodium for 5 h and distilled again under vacuum from sodium naphthalenide (Na-Naph) solution. Sodium (Na, Aldrich Chemical Co. Inc., 99%), potassium (K, Aldrich Chemical Co. Inc., 98%), lithium (Li, Aldrich Chemical Co. Inc., 99.9%), calcium hydride (CaH_2, Junsei Chemical Co., Ltd., 95%), sodium tetraphenylborate ($NaBPh_4$, Aldrich Chemical Co. Inc., 99.5%), naphthalene (Naph, Aldrich Chemical Co. Inc., 99%), and *n*-octyl alcohol (Octyl-OH, Duksan Pharmaceutical Co., First Grade) were used without further purification. The glassware (Iwaki Glass Co. PYREX®) used in fabrication of the apparatus, were rinsed with tap water and finally with triply distilled water and dried in an oven before use.

2.2. Initiators

Li-, Na-, and K-Naph, in THF were prepared by the reaction of small excess of naphthalene with lithium, sodium, potassium, respectively, at room temperature. The reaction solution which turned green, was degassed by connecting to high vacuum (10^{-6} Torr) after freezing in liquid nitrogen. After complete degassing of the solution, the initiator so obtained was stored in glass ampules with break seals under the same vacuum condition at −30 °C.

2.3. Anionic polymerization of n-hexyl isocyanate

All polymerizations were carried out under high vacuum in a glass apparatus equipped with break-seals. In a typical polymerization procedure, the initiator solution, Na-Naph

(0.015 g, 0.10 mmol) in THF, was transferred into the reaction flask through a break-seal followed by 10-fold excess of $NaBPh_4$ (0.319 g, 1.00 mmol) to the initiator in THF. The solution temperature was brought to −98 °C. When the polymerization was carried out by adding HIC (0.720 g, 5.64 mmol) in THF to the initiator solution, the color of the reaction solution changed to light brown. The polymerization was terminated after 20 min by adding 20-fold excess HCl in methanol to the polymer solution, and the polymer was precipitated into methanol, filtered, and dried in vacuo. Methanol soluble part was analyzed quantitatively by weighing the residue after evaporation of the solvent and using ^{1}H NMR to check the presence of unreacted monomer and/or trimer. The yield of poly(*n*-hexyl isocyanate) (PHIC) was 99%.

PHIC. ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm): 0.9 (3H, CH_3), 1.0–2.0 (8H, $(CH_2)_4$), 3.7 (2H, $N{-}(CH_2){-}$). ^{13}C NMR ($CDCl_3$, 75 MHz), δ (ppm): 14.5 (CH_3), 22.5 (CH_2), 26.2 (CH_2), 28.5 (CH_2), 31.5 (CH_2), 48.6 ($N{-}CH_2{-}$), 156.8 (C=O). IR (KBr, cm^{-1}): 3441 (–NH), 2959, 2932, 2860, 1700 (C=O), 1349/1297 (disubstituted amide), 1227, 1175, 1092, 785, 728.

2.4. Block copolymerization

In a typical block copolymerization procedure, homopolymerization of isoprene (0.150 g, 2.31 mmol) as a first polymer to initiate subsequent polymerization of HIC was performed with Na-Naph (0.006 g, 0.04 mmol) as an initiator in THF, in a glass apparatus under high vacuum, at −78 °C using frozen acetone bath. The solution assumed the characteristic light yellow color of isoprenyl anion. After homopolymerization, some amount of polyisoprene was taken into a receiver to characterize the polyisoprene, and the reactor was cooled to −98 °C using frozen methanol bath. $NaBPh_4$ (0.134 g, 0.42 mmol) was added to the solution before adding HIC (0.446 g, 3.51 mmol) as the second monomer. The reactions were terminated by adding methanol, and the homo and the block copolymers were precipitated into methanol, filtered, and dried in vacuo.

Poly(HIC-b-isoprene-b-HIC). ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm): 0.8–2.3 (aliphatic units of HIC and isoprene, hydrocarbon backbone of isoprene), 3.6–3.9 (2H, $N{-}CH_2{-}$), 4.5–4.8 (2H, $C(CH_3){=}CH_2$), 4.8–5.1 (2H, $CH{=}CH_2$), 5.6–6.0 (1H, $CH{=}CH_2$). ^{13}C NMR ($CDCl_3$, 75 MHz), δ (ppm): 14.5 (CH_3), 18.3, 22.5 (CH_2), 26.2 (CH_2), 28.5 (CH_2), 31.5 (CH_2), 41, 43, 48.6 ($N{-}CH_2{-}$), 112, 148, 156.8 (C=O). IR (KBr, cm^{-1}): 3441 (–NH), 3074, 2959, 2932, 2860, 1700 (C=O), 1644, 1464, 1349/1297 (disubstituted amide), 1227, 1175, 1092, 1025, 1002/910 ($CH{=}CH_2$), 886 ($C(CH_3){=}CH_2$), 785, 754, 728, 683.

2.5. Measurements

Infrared spectra (KBr disk) were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer. ^{1}H NMR and ^{13}C NMR were recorded on a JEOL JNM-LA300WB in $CDCl_3$. Chemical shifts are reported in ppm downfield relative to tetramethylsilane (δ 0) for ^{1}H NMR and to $CDCl_3$ (δ 77.1) for ^{13}C NMR as standard. Molecular weights of the PHIC were calculated from the response of a multi-angle laser light scattering detector (Wyatt Technology) that was connected to a size exclusion chromatograph (MALLS/SEC). The d*n*/d*c* value for PHIC in THF at 40 °C was measured with an LED (Optilab DSP) source. The phase separations of the block copolymers were characterized by energy filtering transmission electron microscope (EF-TEM, EM 912 OMEGA [ZEISS, Germany]). For TEM, thin films of each rod-coil were cast from dilute THF solution (10 wt%) onto carbon support films and stained with OsO_4 vapors for 1 h.

3. Results and discussion

3.1. Effect of temperature and time on polymerization

Several variables which influence the formation of the polymer were taken into consideration. These were the polymerization temperature, the polymerization time, concentration of the monomer, and concentration of the initiator. In case when polymerization was executed at 0 °C, only trimer was observed as shown in Fig. 1. It means that the growing oligomer chains trimerized due to backbiting competitively to reacting with the monomer. Yield of the PHIC increased with the decreasing reaction temperature as shown in Fig. 1. A quantitative yield of PHIC was obtained at the low temperature of −98 °C.

The results of the polymerization of HIC using Na-Naph with varying reaction time at −98 °C are summarized in Table 1. The yield of PHIC increased rapidly with reaction time of 2, 5, and 10 min. The polymerization was completed at 10 min of the reaction time giving the quantitative yield of the polymer. As the reaction time increased from 10 min, yield of the PHIC decreased with formation of trimer. The results indicate that the growing active chain ends react with

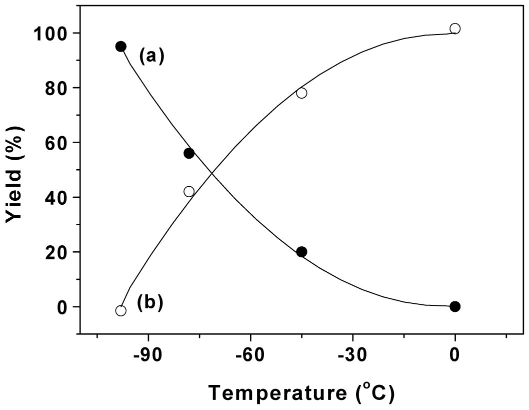


Fig. 1. Temperature dependence on the yield of (a) polymer and (b) trimer.

Table 1
Anionic polymerization of HIC as a function of time in THF at −98 °C

Counter cation	$[HIC]_0/[M\text{-}Naph]_0$	Time (min)	$M_n \times 10^{-3}$		M_w/M_n [a]	Yield of polymer, %
			Calcd[b]	Obsd[a]		
Li^+	50.2	5	4.0	22.0	3.92	33(67)[c]
Li^+	50.1	10	7.0	34.0	3.59	56(44)[c]
Li^+	56.9	20	13.5	42.0	2.95	95(4)[c]
Na^+	40.3	2	7.5	26.5	1.26	74(26)[c]
Na^+	49.2	5	12.0	44.4	1.14	95(5)[c]
Na^+	55.2	10	14.0	36.5	1.21	100
Na^+	44.3	20	10.5	29.6	1.26	92(8)[d]
Na^+	52.3	30	12.0	39.0	1.19	89(11)[d]
Na^+	48.2	60	10.5	72.8	1.24	86(14)[d]
K^+	52.4	5	13.0	53.0	3.62	96(4)[d]
K^+	57.6	10	12.3	49.8	2.43	87(13)[d]
K^+	52.8	20	11.0	67.0	2.11	81(18)[d]

[a] M_n and M_w/M_n were measured by SEC-LS in THF at 40 °C.
[b] Calculated M_n is computed by [HIC]/[M-Naph] × 2 × molecular weight of HIC.
[c] The amounts of unreacted monomer are presented in parentheses.
[d] The yields of trimer are presented in parentheses.

the monomer rather than attack the carbonyl carbon in backbone, as long as the monomer exists in the reaction mixture. From these results, it can be concluded that the polymer with a high yield can be obtained by a proper control over the reaction time, and at low temperature using Na-Naph as an initiator.

3.2. Effect of counter cations on polymerization

The results of polymerization of HIC using various alkali metal naphthalenide initiators such as Li-, Na-, and K-Naph in THF at −98 °C are shown in Table 1. The propagation rate is affected by the nature of the counter cation; low for Li^+ and high for K^+. These results are consistent with the observation in polymerization of other polar monomers such as methyl methacrylate and ethylene oxide and can be explained by the push-pull mechanism [29–31]. It shows that the rate of polymerization increases with increasing size of the counter cation, a general tendency in polymerization of polar monomers in polar solvents [29].

The kinetics of initiation and propagation of PHIC is not clear, but is related with the nature such as size and electron affinity of the counter cation. The molecular weight distribution (MWD) of PHIC, synthesized by anionic polymerization in THF at −98 °C, is affected by the separation of amidate anion and counter cation, due to solvation in the polar solvent THF and the pull-push theory. The dimerization rate of the resulting radical anion from the metal naphthalenide initiator increases with increasing size of the counter cation [29]. Thus, the initiation rate with K-Naph becomes relatively fast compared with other cases, while polar solvents accelerate the rate of propagation. When Li^+ and K^+ are used as the counter cations in the polymerization of HIC, the distance between the amidate anion and the counter cation is too close or too far, respectively, resulting in heterogeneous propagation and broad MWD due to the discordance between the rates of propagation and initiation. In the case of polymerization with Na-Naph, the reaction rate shows intermediate properties compared with the above two cases. The MWD also shows relatively narrow due to the favorable distance between the amidate anion and Na^+. From these results, it is suggested that Na^+ is the best among three as the counter cations in the polymerization of isocyanate.

3.3. The living polymerization using $NaBPh_4$

The results of the polymerization of HIC using $NaBPh_4$ as an additive in various concentrations in THF at −98 °C for 20 min are summarized in Table 2. Yield of the polymer decreased with increasing concentration of $NaBPh_4$. When the concentration was 10 times larger than that of the initiator, the quantitative yield was obtained at 20 min and the calculated molecular weight of the polymer agreed well with the observed value by SEC-LS, even though the observed molecular weights of the polymer obtained in polymerization without $NaBPh_4$ were larger than that of the calculated one. The addition of $NaBPh_4$ increased the efficiency of Na-Naph because tetraphenylborates pulled the sodium cations resulting in the promotion of the reactivity of naphthalene anions. As the concentration of $NaBPh_4$ increased, the observed molecular weights tended to be close to the calculated values. When the concentration of $NaBPh_4$ was 10 times larger than that of the initiator, the observed molecular weights of the polymer and the calculated values agreed nicely. It means that the optimum concentration of $NaBPh_4$ for the controlled polymerization is around 10 times than that of the initiator. When more than 10 times of $NaBPh_4$ compared with the initiator was used, the yields of the polymer decreased and the methanol

Table 2
Anionic polymerization of HIC in the presence of $NaBPh_4$ in THF at − 98 °C

$[NaBPh_4]_0/[Na\text{-}Naph]_0$	$[HIC]_0/[Na\text{-}Naph]_0$	Time (min)	$M_n \times 10^{-3}$		M_w/M_n[a]	Yield of polymer, %
			Calcd[b]	Obsd[a]		
9.7	48.9	10	11.0	12.8	1.08	89 (11)[c]
0	44.3	20	10.5	29.6	1.26	92 (8)[d]
2.8	59.2	20	14.4	23.4	1.22	96
4.7	54.5	20	13.3	17.5	1.17	96
9.6	45.3	20	11.5	11.7	1.09	99
14.5	84.3	20	11.8	18.5	1.10	55 (45)[c]
26.2	63.8	20	6.0	20.9	1.15	36 (64)[c]
10.0	56.4	20	13.9	14.6	1.06	97
10.0	88.1	20	21.5	22.2	1.11	96
10.3	138.3	20	34.4	31.0	1.07	97
9.7	163.4	20	40.3	42.7	1.12	97
10.0	200.4	20	50.9	54.5	1.11	97
9.9	48.0	40	11.8	12.8	1.12	96
9.5	49.6	60	11.5	10.8	1.13	93 (7)[d]

[a] M_n and M_w/M_n were measured by SEC-LS in THF at 40 °C.

[b] Calculated M_n is computed by [HIC]/[Na-Naph] × 2 × molecular weight of HIC.

[c] The amounts of unreacted monomer are presented in parentheses.

[d] The yields of trimer are presented in parentheses.

soluble parts were assigned to the unreacted monomer. It means that the higher concentration of the bulky common ion salt hinders the propagation reaction. From the above results, 10 times excess of $NaBPh_4$ relative to initiator was used for further studies in the polymerization of HIC.

In the presence of $NaBPh_4$, the polymer was obtained with the yield of 89% (Table 2) in 10 min, while the 100% (Table 1) yield of PHIC was achieved in the polymerization without $NaBPh_4$ at the same reaction time [25–26]. This means that the polymerization rate decreased because of a tight contact ion pairs with $NaBPh_4$. Especially, the calculated molecular weights of PHIC, obtained using $NaBPh_4$ agreed well with the values observed by SEC-LS. Trimerization was not observed until the reaction time of 40 min. It means that the amidate anions were stable at least for 40 min without trimerization when 10 times of $NaBPh_4$ was used in the polymerization. The trimerization gradually proceeded after 40 min and 7% trimer was observed after 60 min. The polymerizations with high molecular weights in range from 30,000 to 50,000 g/mol were also performed and the results are shown in Table 2. As in the case with the low molecular weight range, the absolute molecular weight of the polymer coincide with the calculated one which means that the living polymerization is possible regardless of molecular weight at least in the observed range.

3.4. Polymerization at − 78 °C

To check the effect of $NaBPh_4$ on the stability of the amidate anion in the polymerization at a higher temperature, the anionic polymerizations of HIC with or without $NaBPh_4$ were performed at − 78 °C as shown in Table 3. In the polymerization without $NaBPh_4$, yield of the polymer reached 39% at 10 min and the formation of the trimer was the dominant reaction. After 20 min, yield of the polymer decreased to 11% and the portion remaining was the trimer. It showed that fast backbiting occurred at − 78 °C compared with the case at − 98 °C. In the presence of 10-fold concentration of $NaBPh_4$ to that of initiator, yield of the polymer was quantitative (99%) at 2 min of the reaction time. As the reaction time increased, yield of the polymer decreased and formation of the trimer was observed. However, as compared with the results of polymerization without $NaBPh_4$, the backbiting rate was retarded and yield of the polymer was relatively high in the presence of $NaBPh_4$, while the observed molecular weights of the polymer formed in the presence of $NaBPh_4$ do not agree well with the calculated ones. It means that at − 78 °C, $NaBPh_4$ stabilized the end anion and protected the backbiting for a very short time that was insufficient to maintain the living character.

To study the effect of a higher concentration of the additive on the stability of the living polymer at − 78 °C, 15-fold $NaBPh_4$ was used. As a result, at 5 min of the reaction time, nearly quantitative yield (96%) was obtained and the methanol soluble part was assigned to unreacted monomer, which could not polymerize due to the increased concentration of $NaBPh_4$. However, the observed molecular weights were much different from the calculated ones. At 10 min of the reaction time, yield of the polymer was 80%, more compared to the polymer isolated at the same time with 0- or 10-fold concentration of $NaBPh_4$. It indicates that high concentration of $NaBPh_4$ retards the backbiting rate as well as the progressing of the polymerization. Thus, at − 78 °C, $NaBPh_4$ decreased the propagation rate and prevented backbiting, while the living character of PHIC could not be observed due to the inhomogeneity of polymerization system.

Table 3
Anionic polymerization of HIC in the presence of NaBPh$_4$ in THF at −78 °C

$[NaBPh_4]_0/[Na\text{-}Naph]_0$	$[HIC]_0/[Na\text{-}Naph]_0$	Time (min)	$M_n \times 10^{-3}$		M_w/M_n[a]	Yield of polymer, %
			Calcd[b]	Obsd[a]		
0	54.3	10	5.5	37.0	1.56	39 (58)[c]
0	56.3	20	1.6	28.0	1.64	11 (88)[c]
10.0	49.0	2	9.2	12.0	1.12	99
10.0	49.9	5	11.1	14.7	1.11	85 (12)[c]
10.3	50.7	10	9.4	10.6	1.14	73 (26)[c]
14.5	34.5	5	8.4	16.3	1.12	96(4)[d]
14.5	40.4	10	6.7	14.5	1.24	80(16)[c]

[a] M_n and M_w/M_n were measured by SEC-LS in THF at 40 °C.
[b] Calculated M_n is computed by [HIC]/[Na-Naph] × 2 × molecular weight of HIC.
[c] The yields of trimer are presented in parentheses.
[d] The amounts of unreacted monomer are presented in parentheses.

3.5. Block copolymerization

The rod-coil-rod ABA block copolymers, poly(HIC-*b*-isoprene-*b*-HIC)s (P(HIC-*b*-I-*b*-HIC)), were synthesized with changing composition of each block using living property of polyisocyanates. The results are shown in Table 4. The quantitative yield of the block copolymers was obtained with narrow MWD and the composition and molecular weight of each block in polymers agreed well with the feed ratio of both the monomers as estimated by ^{1}H NMR. Thus, it was possible to synthesize the block copolymers, P(HIC-*b*-I-*b*-HIC)s, as intended using the living character of PHIC paving the way for the synthesis of block copolymers of HIC with other vinyl monomers. In Fig. 2, the peak in the SEC spectra clearly shifted from base polyisoprnyl anion with Na$^+$ counter cation toward high molecular weight without tailing and the chromatograms showed that the obtained copolymer has unimodal and narrow MWD. While the isocyanates have high reactivity, reactivity of the amidate anions, formed after initiation, is very weak. Due to this, block copolymerization of the isocyanate as first monomer did not progress and the polyisocyanate anionic chain end could not initiate vinyl monomers [32].

Fig. 3 shows the TEM micrographs obtained from bulk samples of P(HIC-*b*-I-*b*-HIC)s with various compositions cast from THF. The dark regions are the polyisoprene (PI) domains, which have been preferentially stained with OsO$_4$ and the white regions are the PHIC domains. Two layers of PI and PHIC domains showed the lamellae morphology (Fig. 3(a) and (b)) and there were a few zigzag patterns which also had been reported for poly(styrene-*b*-HIC) by Ober and co-workers [33–34]. In Fig. 3(a), the PI domains show the lamellae form, and the size of each domain was nearly constant. This confirmed that the structure of the block copolymers could be well-controlled. As the content of isoprene increased from 42 to 67%, the size of the PHIC domains (Fig. 3(b)) reduced compared with that in Fig. 3(a). In our case, when the composition of PI reached to 83% (Fig. 3(c)), the perforated lamellae morphology was observed. It suggests that the morphology might have been changed

Table 4
Block copolymerization of HIC with isoprene in the presence of NaBPh$_4$ in THF at −98 °C

	$[isoprene]_0/[Na\text{-}Naph]_0$	$[NaBPh_4]_0/[Na\text{-}Naph]_0$	$[HIC]_0/[Na\text{-}Naph]_0$	Time (min)	$M_n \times 10^{-3}$		M_w/M_n[a]	Yield of polymer, %
					Calcd[b]	Obsd[a]		
1H[c]	14.0	–	–	240	2.0	2.4	1.05	100
1B[d]	11.5	11	90.0	20	24.0	25.0	1.19	97
2H[c]	57.7	–	–	240	7.7	8.5	1.07	100
2B[d]	27.8	10.5	87.7	20	26.0	28.0	1.14	98
3H[c]	49.7	–	–	240	6.7	7.2	1.14	100
3B[d]	49.1	9.7	21.3	20	12.0	12.8	1.23	97
4H[c]	71.4	–	–	240	9.7	10.5	1.05	100
4B[d]	94.8	10.9	18.9	20	17.5	21.7	1.03	98

[a] M_n and M_w/M_n were measured by SEC-LS in THF at 40 °C.
[b] Calculated M_n is computed by {[isoprene]/[Na-Naph] × 2 × molecular weight of isoprene + [HIC]/[Na-Naph] × 2 × molecular weight of HIC}.
[c] Homopolymers of isoprene which were obtained from at the first-stage polymerization.
[d] Block copolymers of isoprene with HIC; 1B, isoprene/HIC (12%/88%) in molar composition calculated by ^{1}H NMR, 2B, (42/58), 3B, (67/33), 4B, (83/17).

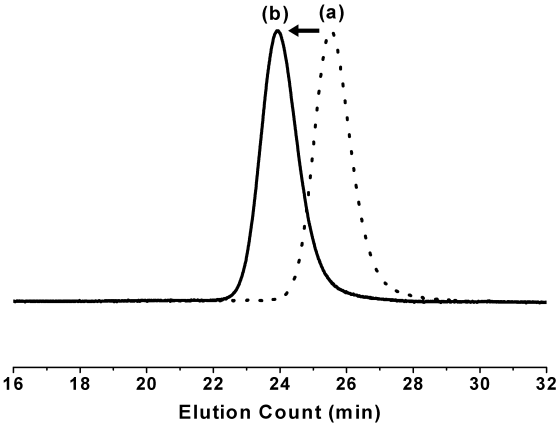
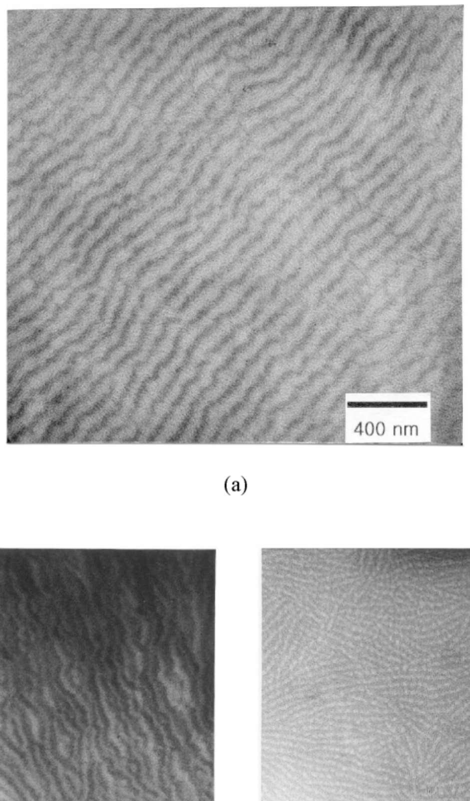


Fig. 2. SEC curves of PI and P(HIC-*b*-I-*b*-HIC) obtained by homo polymerization and block copolymerization, respectively: (a) base PI, 4H; M_n: 10,500, $M_w/M_n = 1.05$, (b) P(HIC-*b*-I-*b*-HIC), 4B; M_n: 21,700, $M_w/M_n = 1.03$.

from the lamellae to the cylinder form, when the content of PI blocks increased. The results of the block copolymerization of HIC with isoprene, was successful in order to demonstrate the living character of the polymerization and the chain length of each block could be effectively controlled by the monomer/initiator feed ratios.

4. Conclusions

The PHIC was synthesized via living anionic polymerization at −98 °C in THF using Na-Naph as an initiator in the presence of $NaBPh_4$ as a common ion salts. The living polymerization of HIC was made possible by applying $NaBPh_4$ as a common ion salt in THF at −98 °C from 20 to 40 min and the molecular weights of the polymer was successfully controlled by modulating the feed ratio of the monomer to initiator. In the presence of $NaBPh_4$, the polymer with quantitative yield was obtained at −78 °C within 2 min. Due to short lifetime the proof for the living character could not be obtained. The rod-coil-rod block copolymers, P(HIC-*b*-I-*b*-HIC)s, were successfully synthesized with quantitative yields and controlled molecular weights at −98 °C. From the results and the morphology of the block copolymers, it was confirmed that the living



(a)

(b)

(c)

Fig. 3. TEM micrographs of P(HIC-*b*-I-*b*-HIC) in a bulk thin film cast from THF, the lighter regions are the PHIC domains and the darker regions are PI domains stained with OsO_4. (a) 2B; (b) 3B; (c) 4B.

polyisocyanates were successfully obtained by the living anionic polymerization using $NaBPh_4$.

Acknowledgements

National R&D project for Nano Science and Technology (M10214000169-02B1500-02710), Korea Science and Engineering Foundation (contract no. 20016-301-02-2), and Ministry of Education (BK21) of Korea.

References

[1] Bur AJ, Fetters L. J Chem Rev 1976;76:727.
[2] Goodman M, Chen S. Macromolecules 1970;3:398.
[3] Goodman M, Chen S. Macromolecules 1971;4:625.
[4] Green MM, Gross RA, Crosby IIIC, Schilling FC. Macromolecules 1987;20:992.
[5] Lifson S, Andreola C, Peterson NC, Green MM. J Am Chem Soc 1989;111:8850.
[6] Green MM, Khatri CA, Reidy MP, Levon K. Macromolecules 1993; 26:4723.
[7] Shibaev PV, Tang K, Genack AZ, Kopp V, Green MM. Macromolecules 2002;35:3022.
[8] Muller M, Zentel R. Macromolecules 1994;27:4404.
[9] Maeda K, Okamoto Y. Macromolecules 1998;31:1046.
[10] Aharoni SM, Walsh EK. Macromolecules 1979;12:271.
[11] Shashoua VE. J Am Chem Soc 1959;81:3156.
[12] Shashoua VE, Sweeny W, Tietz RF. J Am Chem Soc 1960;82:866.
[13] Lecomte L, Marchal E. Eur Polym J 1976;12:741.
[14] Aharoni SM. Macromolecules 1979;12:94.
[15] Berger MN, Tidswell BM. J Polym Sci Symp 1973;42:1063.
[16] Schneider NS, Furusaki S, Lenz RW. J Polym Sci Part A 1965;3:933.
[17] Turunen T, Tenhu H, Samarianov B, Timofeev VP. Polymer 1995;36: 4097.
[18] Beaman RG. US Patent 1962; No. 3048566.
[19] Shmueli U, Traub W, Rosenheck K. J Polym Sci Part A-2 1969;7:515.
[20] Khatri CA, Vaidya MM, Levon K, Jha SK, Green MM. Macromolecules 1995;28:4719.
[21] Okamoto Y, Nagamura Y, Hatada K, Khatri C, Green MM. Macromolecules 1992;25:5536.
[22] Maeda K, Matsunaga M, Yamada H, Okamoto Y. Polym J 1997;29: 333.
[23] Lee JS, Ryu SW. Macromolecules 1999;32:2085.
[24] Shin YD, Ahn JH, Lee JS. Polymer 2001;424:7979.
[25] Shin YD, Kim SY, Ahn JH, Lee JS. Macromolecules 2001;34:2408.
[26] Shin YD, Ahn JH, Lee JS. Macromol Rapid Commun 2001;22:1041.
[27] Wang J, Nomura R, Endo T. Chem Lett 1996;909.
[28] Wang J, Nomura R, Endo T. Macromolecules 1996;29:2707.
[29] Szwarc M. Adv Polym Sci 1983;49:1.
[30] Bohn LL, Chmelir M, Lohr G, Schmitt BJ, Schultz GV. Adv Polym Sci 1972;9:1.
[31] Sigwalt P, Boileau S. J Polym Sci Symp 1978;62:51.
[32] Godfrey RA, Miller GW. J Polym Sci Part A: Polym Chem 1969;7:2387.
[33] Chen JT, Thomas EL, Ober CK, Hwang SS. Macromolecules 1995; 28:1688.
[34] Chen JT, Thomas EL, Ober CK, Mao Gp. Science 1996;273:343.