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Anionic polymerization of isocyanates with optical functionalities

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Abstract

Polyisocyanates of 2-[4-(4-nitrophenylazo)-*N*-ethylphenyl amino]ethoxy carbonyl amino hexyl isocyanate, DR1NCO, and (*s*)-(−)-2-methyl-1-butyloxy carbonyl amino hexyl isocyanate, MBI, were synthesized by anionic polymerization using sodium naphthalenide as an initiator in THF at −98°C. In the polymerization reaction, crown ether (15C5) and octyl isocyanate (Oct-NCO) were used to suppress side reactions such as backbiting or chain transfer reaction. In the homopolymerization of DR1NCO, the polymers with high yield (~94%) were obtained due to suppression of backbiting by 15C5. In the random copolymerization of DR1NCO with MBI, the chain transfer reaction was suppressed due to the low reactivity of anionic chain end induced by octyl isocyanate. The random copolymers showed the optical activity in CD and ORD measurements, and specific rotations increased with increasing the component of MBI. © 2001 Published by Elsevier Science Ltd.

Keywords: Polyisocyanate; Anionic polymerization; Specific rotation

1. Introduction

Polyisocyanates are stiff polymers due to amide bond in the polymer main chain. These amide bonds have a partial double bond character due to which the polymer chains tend to be planar. However, the polyisocyanate chains are twisted into helical conformation because of steric reason [1]. While polypeptides have one helical preference due to chiral units in the main chain, polyisocyanates with achiral units are racemic mixtures of right- and left-handed helices. If chiral units are introduced to polyisocyanates, these polymers have one helical preference due to perturbation between main chain and chiral side chains [2]. Due to these structural properties, polyisocyanates have been studied in various fields such as chiral recognition materials, optical switches and liquid crystal materials [3–6].

Generally, polyisocyanates can be synthesized by anionic polymerization. Shashoua and co-workers first reported the polymerization of isocyanates, using *N*,*N*-dimethylformamide (DMF) and sodium cyanide (NaCN) as a solvent and an initiator, respectively. They found that the polymerization was favored at low temperature (−100 to −40°C) and with low concentration of initiator [7]. They also found that formation of cyclic trimer easily occurred when an anionic chain end attacked carbonyl groups in the main chain by backbiting. Another problem of the method is poor solubility of various aliphatic monomers in DMF. Even with the difficulties in the polymerization of isocyanates, many researchers have tried to synthesize the functional polyisocyanates. Goodman and co-workers first synthesized the optically active polyisocyanates with NaCN as an initiator in DMF at −78°C [2]. The polymer showed a high specific rotation, while the yield was low and MWD of the polymer was broad. Khatri and co-workers synthesized functional polyisocyanates using NaCN at −78°C in toluene [8]. Despite of low reaction temperature, the yield of polymer was not so high. Zentel and co-workers synthesized the optically active polyisocyantes with azobenzene side chains [3,4]. However, the yield was still low and a broad MWD was observed. To get over the solubility problem, Okamoto and co-workers used toluene as additive solvent in the polymerization of isocyanate in DMF [9,10].

In the case of polymerization of (meth)acrylates, depolymerization by backbiting had been one of the problems in the controlled polymerization as in the polymerization of isocyanates. However, the controlled polymerizations of (meth)acrylates have been performed successfully by stabilizing the chain end using suitable ligands such as LiCl [11], triethylborane [12], tetramethylethylenediamine [13], tetraalkylammonium salts [14], diethyl zinc [15] and crown ether [16], which interact coordinatively with the active initiating or propagating ion pairs. Among the controlled polymerizations of the meth(acrylates) using these ligands,

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Teyssie and co-workers reported the anionic living polymerization of MMA using dibenzo-18-crown-6 as an electron-donating σ-type ligand [16]. In the polymerization of MMA, the additive is effective to minimize the formation of trimer.

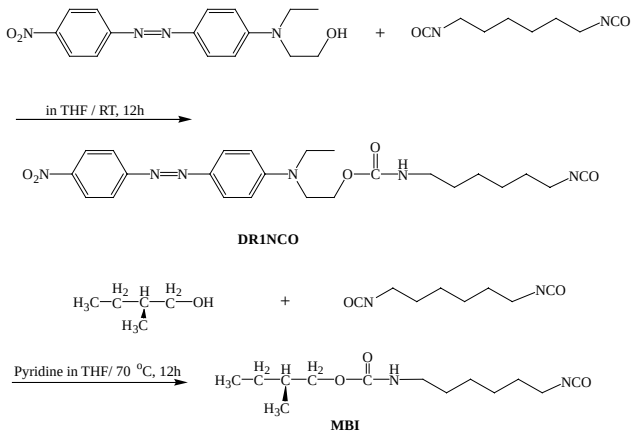
In the polymerization of isocyanates, polymerizations using additives have been reported. Endo and co-workers first introduced the samarium (II) or (III) iodide as an additive into the anionic polymerization of isocyanate [17]. Addition of samarium iodide suppressed the formation of trimer during the polymerization with alkyl lithium in THF at −78°C. However, they found that the MWD of the polymers were broad from 2.4 to 3.5 with low yield. Recently, Lee and co-workers succeeded in the synthesis of the well-defined poly(3-(triethoxysilyl)propyl isocyanate)) (PTESPI) by using sodium naphthalenide (Na-Naph) and crown ether (15C5) complex in THF at −98°C under high vacuum [18,19]. The system successfully prevented the backbiting of the anionic chain ends using a big counter cation, the complex of Na-Naph–15C5. Reports on polymerization of functional isocyanates have been very few because of limitations in variety of functional isocyanates and difficulties in the polymerization procedures. In addition, few functional polyisocyanates with narrow MWD have been synthesized until now.

Azo polymers have received increasing attention because they can be used as liquid crystal materials, nonlinear optical (NLO) materials, and optical storage materials. In this study, we first synthesized functional polyisocyanates containing asymmetric azo moiety via anionic polymerization. To suppress the formation of trimer and to synthesize the polymer having a narrow MWD in the polymerization, 15C5 was used as the bulky ligand. Octyl isocyanates were also used to prevent a chain transfer reaction by stabilizing the amidate anion. The optically active, random copolymers of 2-[4-(4-nitrophenylazo)-*N*-ethylphenylamino]ethoxy carbonyl amino hexyl isocyanate (DR1NCO) with (*s*)-(−)-2-methyl-1-butyloxy carbonyl amino hexyl isocyanate (MBI) were also synthesized.

2. Experimental

2.1. Materials

2-[4-(4-Nitrophenylazo)-*N*-ethylphenylamino]ethanol, commercially known as the disperse red 1 (DR1) (Aldrich) was recrystallized from benzene (Merck, 99.7%) and *n*-hexane (Mallin Crokdt, 100%). Crown ether (15C5, Aldrich), (*s*)-(−)-2-methyl-1-butanol (Aldrich) were used as received. 1,6-Diisocyanatohexane (Aldrich) was stirred with CaH_2 overnight and distilled under reduced pressure. Tetrahydrofuran (THF, Fisher, GR grade) was stirred with sodium overnight under reflux and distilled. The distilled THF was stirred with Na-Naph under high vacuum, and degassed by freezing.



Scheme 1.

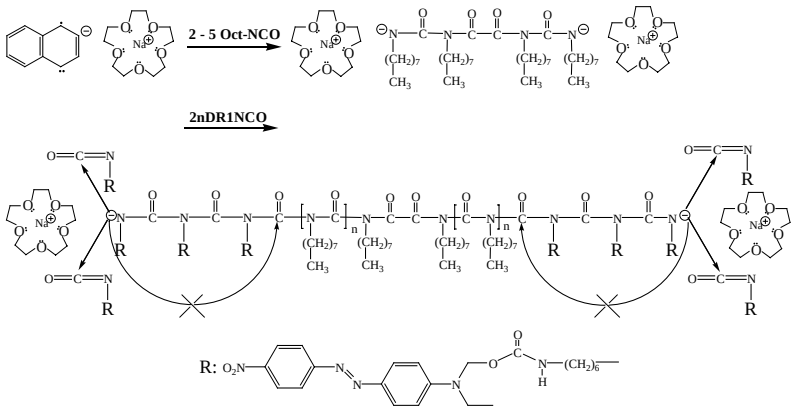
2.2. Initiator

Na-Naph in THF was prepared from the reaction of a small excess of naphthalene with sodium at room temperature. The reaction mixture turned green, and it was frozen by liquid nitrogen to remove gas by connecting to high vacuum line (10^{-6} Torr). After complete degassing of solution, the initiator obtained from this solution was stored in a glass ampoule with break-seal under high vacuum at −30°C.

2.3. Synthesis of monomers

DR1NCO was prepared from the reaction between 1,6-diisocyanatohexane and disperse red 1 (Scheme 1). To 1,6-diisocyanatohexane (HDI, 8.17 g, 48.60 mmol, the molar ratio of HDI to DR1 was around 9:1) in the reactor at room temperature in nitrogen atmosphere, solution of disperse red 1 (DR1, 1.70 g, 5.40 mmol) in THF (60 ml) was added dropwise with vigorous stirring. After the addition of DR1, the reaction mixture was vigorously stirred for 12 h, and reaction temperature was decreased to −78°C by using acetone bath with dry ice for 5 min. The precipitate was filtered off. To the filtrate still under N_2, a large amount of dry *n*-hexane was added to precipitate the crude monomer. It was washed with dry *n*-hexane and dried in vacuo. The yield was 50.0% (1.3 g, 2.69 mmol). The purified monomer was stored in a glass ampoule under high vacuum at −30°C. Anal. calcd for $C_{24}H_{30}N_6O_5$: C, 59.74; H, 6.27; N, 17.42. Found: C, 59.49; H, 6.25; N, 17.46. ^{1}H NMR ($CDCl_3$) (ppm): δ 1.20 (t, 3H, CH_3), 1.30–1.59 (m, 8H, CH_2), 3.15 (q, 2H, CH_2–NH), 3.03 (t, 2H, –CH_2–NCO), 3.50 (t, 2H, –N–CH_2–), 3.67 (t, 2H, –N–CH_2–CH_3), 4.27 (t, 2H, –CH_2–O–), 4.70 (s, 1H, –NH–), 6.80 (d, 2H, Ar–H), 7.90 (t, 4H, Ar–H), 8.30 (d, 2H, Ar–H); ^{13}C NMR ($CDCl_3$) (ppm): δ 156.7 (–NHCOO–), 122.0 (–NCO). FTIR (neat, cm^{-1}): 859, 823 (aromatic, *p*-disubstituted), 1269 (C–O, s, ester), 1389 (Ar–NO_2), 1423 (N=N), 1518 (N–H), 1689 (C=O), 2272 (N=C=O).

MBI was prepared from the reaction between 1,6-diisocyanatohexane and (*s*)-(−)-2-methylbutanol (Scheme 1).



Scheme 2.

To a mixture of 1,6-diisocyanatohexane (22.85 g, 136.0 mmol) and pyridine (2 ml), a solution of (*s*)-(−)-2-methylbutanol (6.20 ml, 56.70 mmol) in *n*-hexane (20 ml) was added drop by drop with stirring at 70°C under nitrogen atmosphere. The reaction mixture was stirred under reflux for 7 h. The solvent was removed from the mixture under reduced pressure at room temperature. The residue was distilled twice under reduced pressure (126°C, 1 mmHg) and the distillate is the pure MBI. The yield was 58.0% (8.38 g, 32.86 mmol). Anal. calcd for $C_{13}H_{24}N_2O_3$: C, 60.91; H, 9.44; N, 10.93. Found C, 60.85; H, 9.41; N, 10.83. ^{1}H NMR ($CDCl_3$) (ppm): δ 0.80 (t, 6H, CH_3), 1.10 (m, 1H, –CH(CH_3)–CH_2), 1.28 (m, 4H, –CH_2–), 1.42 (m, 2H, –CH_2–CH_3), 1.52 (m, 4H, –CH_2–), 3.05 (q, 2H, –CH_2–NH–), 3.20 (t, 2H, –CH_2–NCO), 3.75 (t, 2H, –CH_2–O–), 4.70 (s, 1H, –NH–); ^{13}C NMR ($CDCl_3$) (ppm): δ 156.8 (–NHCOO–), 121.8 (–NCO), FTIR (neat, cm^{-1}): 1525 (N–H), 1704 (C=O), 2273 (N=C=O).

2.4. Polymerization

Anionic polymerizations were carried out in a glass apparatus equipped with break-seals under high vacuum (10^{-6} Torr) at −98°C in the usual manner [18,19]. The reactors were pre-washed with the initiator solutions after sealing off from the vacuum line. The initiator was introduced to the reactor, and cooled to −98°C in a frozen methanol bath. The polymerization was initiated by adding octyl isocyanate to the initiator–15C5 solution to make oligo-octyl amidate anion. After 1 or 2 min, the monomer was added to the solution containing the oligo-octyl amidate anion with vigorous stirring (Scheme 2). The reaction was terminated with the addition of methanol to the reaction solution. The mixture was then poured into a large amount of methanol, and the precipitated polymer was filtered and dried under reduced pressure. To check the weight of unreacted monomers or trimers, the methanol soluble part was concentrated by evaporating it under reduced pressure and dried in vacuo.

2.5. Measurements

The elemental analysis of the monomers were done using EA 1110 Analyzer (CE instrument, Italy).

NMR spectra were obtained with JEOL JNM-LA300WB system operating in the FT mode at 300 MHz, using $CDCl_3$. ^{1}H chemical shifts were referred to $(CH_3)_4Si$.

FTIR spectra were carried out on a Perkin Elmer 2000 spectrophotometer. The samples were prepared as KBr pellets.

Size exclusion chromatography (SEC) was accomplished on a Waters M 77251, M 510 SEC system equipped with three columns and refractive index detector. Polystyrene standard samples (Scientific Polymer) were used for calibration, and THF was the elution solvent at a flow rate of 1.0 ml min^{-1}.

Thermal gravimetric analysis (TGA) was performed on a TA instrument series DSC 2010 at a heating rate of 10°C min^{-1} under nitrogen atmosphere.

Optical activity measurements were carried out at 25°C on a JASCO 715 spectrometer using a cell path length of 1 dm. Specific rotation values at sodium D-line are expressed as deg dm^{-1} g^{-1} dl. Specific ellipticity values are expressed in deg ml g^{-1} dm^{-1}.

UV absorption spectra of the samples were recorded at 25°C in THF solution on a Varian UV–Vis spectrophotometer (Cary 1-E).

3. Results and discussion

3.1. Homo polymerization of DR1NCO

Poly(DR1NCO) was synthesized with changing time and additives. Table 1 shows the results of polymerization of DR1NCO with changing additives in THF at −98°C. In the case of polymerization with no additives (run 1 in Table 1), the product was assigned to be a trimer by SEC and ^{1}H NMR. In the case of polymerization without 15C5

Table 1
The effect of 15C5 and octyl isocyanate on the anionic polymerization of DR1NCO in THF at −98°C

Run	Na-Naph[a] (mmol)	15C5 (mmol)	Oct-NCO[b] (mmol)	DR1NCO (mmol)	Time (min)	M_n ($\times 10^{-3}$)		M_w/M_n	Yield[c] (%)
						Calculated	Observed[d]		
1	0.040	–	–	0.89	30	15.9	1.7	1.06	74[e]
2	0.061	–	0.178	1.53	30	6.5	1.8	1.09	26[e]
3	0.104	0.950	–	1.24	30	6.3	7.5	1.23	55
4	0.092	0.950	0.216	1.24	30	8.6	10.4	1.07	62

[a] Sodium naphthalene as an initiator.
[b] Octyl isocyanate as an additive.
[c] Yield of polymers.
[d] Determined by SEC using polystyrene standard in THF at 40°C.
[e] Yield of trimers.

(run 2 in Table 1), the product was also proved to be cyclic trimer by SEC and ^{1}H NMR. The yield of trimer was low due to relatively low reactivity of the anionic chain end induced by octyl isocyanate. However, the polymerization using only 15C5 (run 3 in Table 1) showed no trimer-formation, even though the MWD was broader than that of polymer using both additives. The methanol-soluble part was proved to be an unreacted monomer by ^{1}H NMR, SEC, and FTIR. It suggests that 15C5 strongly disfavored trimer-formation by the steric hindrance of bulky Na–15C5 complex.

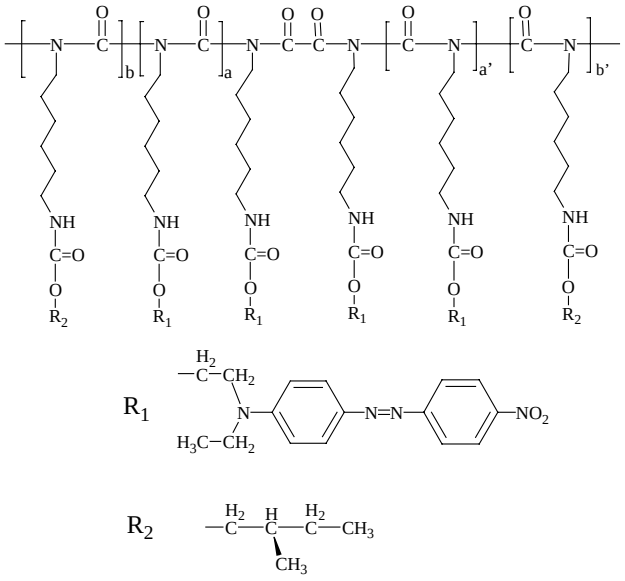
The polymers obtained from polymerization with additives (run 4 in Table 1) have a relatively narrow MWD, and the yield of each polymer has a tendency to increase with reaction time (Table 2). When the reaction time reached at 120 min, the yield of polymer had the highest value of 94% (run 6 in Table 2). Most methanol-soluble part obtained from the polymerization within 100 min was assigned to unreacted monomers from ^{1}H NMR. The molecular weights of polyisocyanates measured by SEC using polystyrene standards generally have a higher value than the real molecular weight, because polyisocyanate has the rigid backbone [20]. However, the expected molecular weights based on the yield fit well with observed molecular weights even though polystyrenes were used as reference standard in SEC studies. The possibility for well agreement in molecular weights is that the polymer has long and bulky side chains. Lee and co-workers reported that the calculated molecular weights of poly(TESPI) with bulky side chains were very similar to the measured molecular weight by SEC [18]. Zentel and co-workers also reported that the polyisocyanates with bulky azobenzene side chains have a small molecular weight measured by SEC using PS standards as compared with the molecular weight using polyisocyanate standards [21]. Thus, it indicates that the molecular weights of the poly(DR1NCO) were well fitted with theoretical molecular weights due to bulky side chains in the low ranges.

After 120 min, the yield of polymer decreased with increasing reaction time, and trimers were observed. The polymer obtained from the polymerization for 230 min (run 8 in Table 2) showed the bimodal SEC curve despite of its narrow MWD. This means that the effect of 15C5 on the suppression of trimer got weakened with time. The above result suggests that the active anionic chain end selectively not attacks the carbonyl groups in the polymer

Table 2
Anionic polymerization of DR1NCO as a function of reaction time in THF at −98°C

Run	Na-Naph[a] (mmol)	15C5 (mmol)	Oct-NCO[b] (mmol)	DR1NCO (mmol)	Time (min)	M_n ($\times 10^{-3}$)		M_w/M_n	Yield[c] (%)
						Calculated	Observed[d]		
1	0.067	0.620	0.110	2.10	5	10.8	9.4	1.20	35
2	0.092	0.950	0.216	1.24	30	8.6	10.4	1.07	62
3	0.072	0.725	0.227	1.26	60	12.4	10.6	1.17	69
4	0.087	0.853	0.525	0.99	80	12.8	11.6	1.25	84
5	0.154	0.832	0.786	2.47	100	15.2	14.4	1.22	90
6	0.154	1.400	0.516	1.39	120	9.8	12.4	1.28	94
7	0.164	1.450	0.694	2.38	160	13.9	15.7	1.24	87(11)[e]
8	0.164	1.525	0.736	2.24	230	13.1	12.0	1.20	72(23)[e]

[a] Sodium naphthalene as an initiator.
[b] Octyl isocyanate as an additive.
[c] Yield of polymers.
[d] Determined by SEC using polystyrene standard in THF at 40°C.
[e] Yield of trimer in parenthesis.



Scheme 3.

chain but the isocyanate when many isocyanates still exist. Anionic chain end attacks the carbonyl group after most isocyanates were consumed due to stretch between anionic chain end and bulky cation–ligand complex. Lee and co-workers reported that the effect of 15C5 on the protection of backbiting of poly((3-triethoxysilyl)propyl isocyanate) lasted for around 2 h and the yield of polymer started decreasing once the polymerization is complete [18].

In the ^{1}H NMR spectra of poly(DR1NCO), the peak corresponding to CH_2 group adjacent to nitrogen in the main chain was observed at 3.08 ppm, while the peaks corresponding to protons attached to phenyl rings were observed at 8.30, 7.90, 6.70 ppm. The broad signals of ^{1}H NMR spectrum indicate that the mobility of side chain decreases due to polymer backbone. The peak corresponding to the proton of the carbamate in ^{1}H NMR spectrum was at 5.50 ppm and it was shifted down field to that of the monomer. Okamoto and co-workers also reported a similar result [5].

To confirm the existence of nitro group in DR1 moiety, UV spectra of polymer and monomer were taken in solution at room temperature. The typical maximum absorbance (λ_{max}) of disperse red 1 observed at 488 nm was registered at 482 nm for DR1NCO while λ_{max} of the polymer was observed at 476 nm. The λ_{max} of the polymer shifted to short-wavelength region due to the attachment of side chains to the rigid polymer backbone. The similar shift of the λ_{max} in the polyisocyanide system as that in the polyisocyanate system was also reported by Kaurannen and co-workers [22]. Thus, it became clear that the azobenzene structure with nitro group was intact after polymerization.

The thermal analysis of poly(DR1NCO) was also measured. The poly(DR1NCO) exhibited a glass transition temperature (T_g) of 50°C and the melting temperature (T_m) of 110°C determined by DSC. Generally, polyisocyanates show very low T_g. The T_g of poly(hexyl isocyanates) is around −50°C and most polyisocyanates have similar T_g [23]. However, the poly(DR1NCO)s have more elevated T_g than other polyisocyanates, because the polymer has the bulky and rigid azo-benzene side chains. The degradation temperature of the poly(DR1NCO)s measured by TGA was around 295°C at which 5% of polymer decomposed.

3.2. Random copolymerization

Scheme 3 shows the structure of the random copolymer of DR1NCO with MBI and the results of random copolymerization are provided in Table 3. When the reaction time is 1 h (run 1 in Table 3), the polymer is nearly homopolymer of DR1NCO determined by ^{1}H NMR spectra, and it does not show optical rotation. This means that most MBIs do not polymerize within 1 h. If the given reaction time is 2 h, with similar feed ratio as the previous one, the yield was 73% with composition of MBI in copolymer about 10% ($[\alpha]_D = +10$) (run 2 in Table 3). It shows that the reactivity of MBI was lower than that of DR1NCO in this system and that reaction time for random copolymerization should be longer than at least 2 h.

Table 3
Anionic random copolymerization from DR1NCO and MBI in THF at −98°C

Run	Na-Naph[a] (mmol)	15C5 (mmol)	Oct-NCO[b] (mmol)	MBI/DR1NCO (mmol)	Time (h)	M_n ($\times 10^{-3}$)		M_n/M_w	Yield[c] (mmol)	$[\alpha]_D$[d]
						Calculated	Observed[e]			
1	0.08	0.14	0.17	2.68/1.96	1	17.0	11.0	1.10	42 (<1)[f]	0
2	0.09	0.18	1.18	2.86/1.59	2	24.0	15.0	1.86	73 (10)[f]	+10
3	0.07	0.18	–	2.04/2.16	2	33.0	20.0	3.34	74 (26)[f]	+15
4	0.15	1.34	0.35	2.20/0.58	2	4.0	15.0	1.32	34 (29)[f]	+17
5	0.09	0.84	0.54	4.41/0.20	2	4.5	27.0	1.89	15 (33)[f]	+21
6	0.07	1.10	0.17	2.97/0.56	2	29.0	18.0	1.59	56 (34)[f]	+27

[a] Sodium naphthalene as an initiator.
[b] Octyl isocyanate as an additive.
[c] Yield of polymers.
[d] Optical rotations were measured at room temperature and at 589 nm using ORD spectrometer.
[e] Determined by SEC using polystyrene standard in THF at 40°C.
[f] Composition (%) of MBI in random copolymers in parentheses.

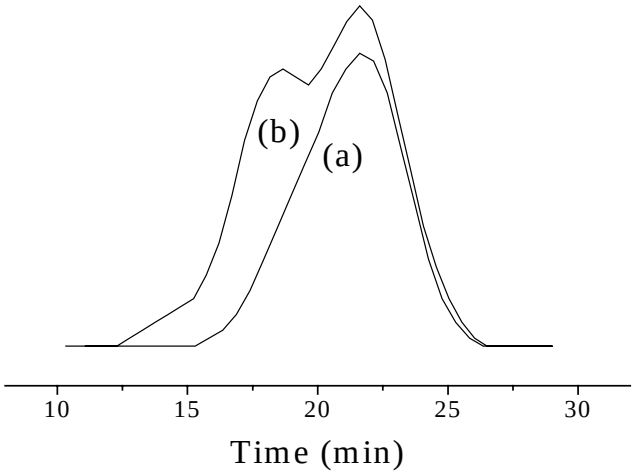


Fig. 1. SEC curves of poly(DR1NCO-*r*-MBI)s: (a) with octyl isocyanate (run 2 in Table 2); (b) without octyl isocyanate (run 3 in Table 2).

It was observed that copolymer without octyl isocyanate has bimodal shape in the SEC curve and has broad MWD, M_w/M_n 3.34 (run 3 in Table 3, Fig. 1b). The possible explanation is that the side reaction occurred easily in the random copolymerization without octyl isocyanate in two possible ways. The first side reaction is the reaction between sodium naphthalenide and carbamate bonds of monomers. The second side reaction is the chain transfer reaction from amidate anion to the amine groups of carbamate bonds. The above two side reactions may result in broad MWD. However, in the random copolymerization using octyl isocyanate as an additive, the side reaction could be suppressed because oligo-octyl amidate anion makes less reactive anionic chain end than that of DR1NCO and/or MBI. Table 3 shows the results of copolymerizations changing the compositions of both monomers to make optically active polymers. Specific rotations of the polymers increase with increasing chiral contents and show a higher value than that of chiral monomer (MBI, $[\alpha]_D^{25} = -5.4$). The CD absorption bands were observed in two regions. The first region (240–320 nm) was due to the absorption of the main chain and the aromatic group. Generally, the poly(alkylisocyanate) shows the absorption bands around 254 nm. However, in this case, the absorption of aromatic group overlapped into this region. Okamoto and co-workers also reported similar results in the polymerization of aromatic isocyanates [24]. The CD bands in this region were positive and the sense of the helix is assigned to be left-handed from the sign of the Cotton effect. The second region (370–600 nm) was due to the absorption of azo-benzene side chains. Fig. 2 shows the CD and UV spectra of random copolymer in this range. The λ_{max} of the polymer due to azo-benzene side chains was observed at 476 nm and the CD band of the polymer shows induced optical activity.

To make low light scattering optical devices, block copolymers with styrene were synthesized and studied for induced optical properties in our previous works [25,26].

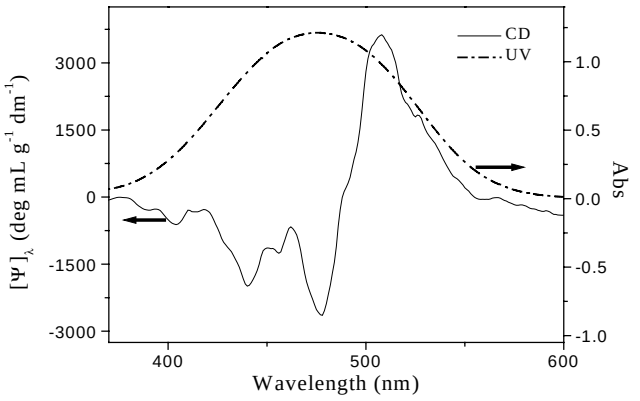


Fig. 2. The circular dichroism (CD) and UV spectra of poly(DR1NCO).

The random copolymers reported in this paper show low T_g around 30°C. Due to low T_g, the copolymer will be applied to photo-refractive materials by introducing carbazole derivatives, which will enhance optical conductivity of the polymers.

4. Conclusions

The poly(DR1NCO) with high yield and narrow molecular weight distribution could be synthesized despite of difficulties in polymerization. The random copolymers of DR1NCO with MBI were also synthesized. The anionic chain end could be successfully protected from backbiting by using the 15C5 as a counter cation ligand until most monomers were consumed. The chain transfer reaction from anion chain end to carbamate group was also suppressed by using oligo-octyl amidate anion with weak reactivity. Thus, it suggested that polyisocyanates containing optical functionalities could be synthesized with high yield, by using crown ether and octyl isocyanate. The CD and ORD spectra confirm the induced optical activity of the random copolymer and specific rotation of the polymer increased as the contents of MBI increased.

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