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ORIGINAL PAPER

Anionic polymerization of *N*-substituted maleimide with achiral and chiral amines as an initiator

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Abstract We have investigated anionic polymerization ability of *N*-substituted maleimides (RMI) with various amines as anionic initiator. As a result, anionic polymerizations of RMI proceed successfully in high polar solvents such as DMF and DMSO. The basicity and structure of amines influenced yields and number average molecular weights of polymers. Furthermore, using various chiral amines as an initiator, polymerizations of RMI were performed to obtain optically active polymers.

Keywords Anionic polymerization · *N*-Substituted maleimide · Amine · Optically active polymer

Introduction

Amines have been well known as anionic initiators to polymerize vinyl monomers with strong electron withdrawing groups. Previously, Pepper et al. [1–5] reported that cyanoacrylate esters could be polymerized by triethylamine, tribenzylamine, and pyridine. Moreover, Grodinsky et al. [6] and Jaacks et al. [7–10] reported on polymerizations of nitroethylene with pyridine and amine-initiated polymerizations of lactones, formaldehyde, and methylene malonic esters, respectively. On this polymerization system, a monomer attacked by amine forms zwitterionic species (an ammonium cation in initiation part and a carbanion in propagation part). The carbanion in the propagation reaction attacks a monomer, and anionic polymerization proceeds.

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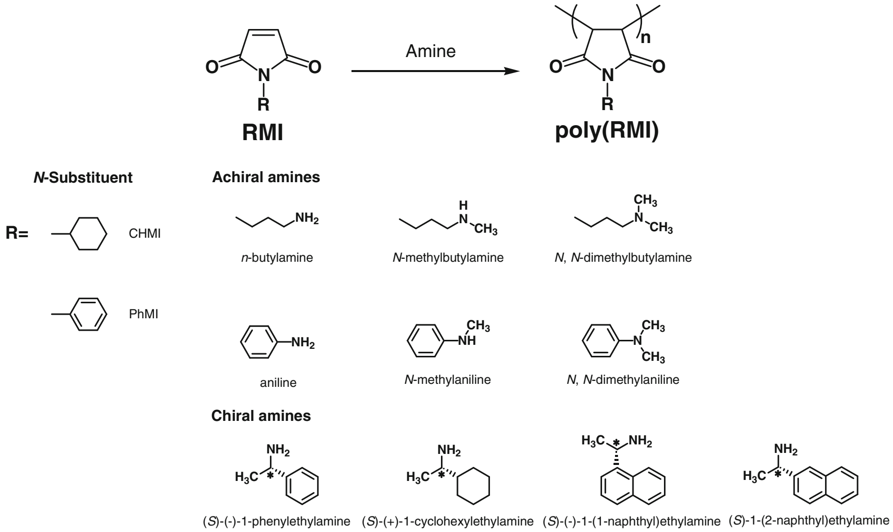
A number of researchers have investigated anionic and radical polymerizations of various *N*-substituted maleimides (RMIs) with anionic and radical initiator such as potassium *tert*-butoxide, *n*-butyllithium, diethylzinc, fluorenyllithium, 2,2′-azobis(isobutyronitrile) and benzoyl peroxide[11–29]. In these previous reports, strong bases such as organometals were used. In recent years, we focused on weak basic amines as a new anionic polymerization initiator of RMI. In general, amines are poor in reactivity as an initiator because the basicity of amines is much smaller in comparison with basicity of common organometals. However, we found that various amines behaved as an anionic polymerization initiator in highly polar solvents on the polymerizations of RMI. Because many amines are generally more stable than organometals in the atmosphere, the reactions (or polymerizations) with amines can proceed under relatively mild conditions. Moreover, using chiral amines as an initiator, optically active polymers can be synthesized without a chiral ligand. Therefore, amine compounds will be expected to be new initiators for asymmetric polymerizations of RMI.

In this paper, we report anionic polymerizations of *N*-cyclohexylmaleimide (CHMI) and *N*-phenylmaleimide (PhMI) with achiral and chiral amines (Scheme 1). This is the first report that RMI is polymerized with only amines.

Experimental

Materials

Solvents used for polymerizations and measurements were purified in the usual manner and distilled over sodium metal. CHMI provided from NOF Corporation



Scheme 1 Anionic polymerizations of RMI

(Tokyo, Japan) was recrystallized by ethyl acetate/*n*-hexane (1/1). PhMI purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) was recrystallized by ethyl acetate/*n*-hexane (3/1). *N*,*N*-Dimethylbutylamine, (*S*)-(+)-1-cyclohexylethylamine ((*S*)-CHEA) and (*S*)-1-(2-naphthyl)ethylamine ((*S*)-2-NEA) were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). *N*-Methylbutylamine and (*S*)-(−)-1-(1-naphthyl)ethylamine ((S)-1-NEA) were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). Aniline and *N*,*N*-dimethylaniline were purchased from Ishizu Seiyaku (Osaka, Japan). *n*-Butylamine was purchased from Wako Pure Chemical Industries Co., Ltd. (Osaka, Japan). *N*-Methylaniline was purchased from Nakalai Tesque Inc. (Kyoto, Japan). (*S*)-(−)-1-phenylethylamine ((*S*)-PEA) was purchased from Yamakawa Chemical Industry Co., Ltd. (Tokyo, Japan). These amines were used without further purification.

Anionic polymerization

Anionic polymerizations of RMI were carried out in various solvents under a dry nitrogen atmosphere. An amine compound was added to a monomer solution heated to 30 °C. The reaction was terminated by the addition of a small amount of methanol. The polymer was precipitated in excess methanol containing a small amount of hydrochloric acid, separated by filtration, and purified by reprecipitation from chloroform–methanol systems three times.

Measurements

Specific optical rotations were measured in chloroform at 25 °C using a quartz cell (1.0 cm) by a JASCO DIP-1030 polarimeter (JASCO, Tokyo, Japan). CD and ultraviolet (UV) spectra were recorded in chloroform at 25 °C using a quartz cell with a path length of 0.1 cm by a JASCO J-805 spectropolarimeter (JASCO, Tokyo, Japan). The number-average molecular weights (M_ns) of the polymers were measured with gel permeation chromatography with a Shimadzu LC-10A instrument (Shimadzu Corp., Kyoto, Japan) equipped with an SPD-10A UV detector (Shimadzu Corp.), a JASCO OR-990 polarimetric (JASCO, Tokyo, Japan) detector and a C-R7Ae plus data processor. THF was used as the eluent. The molecular weight calibration curve was obtained with polystyrene standards. ^{1}H and ^{13}C NMR spectra were obtained by JEOL-EX270 (JEOL, Tokyo, Japan).

Results and discussion

Anionic polymerizaions of RMI using *n*-butylamine

To investigate the polymerization ability of RMI with an amine as an initiator, polymerizations of RMI were performed with *n*-butylamine in various solvents. The polymerization results are summarized in Table 1.

When *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were used for solvent, the polymers were obtained. In this instance, the polymerization

Table 1 Polymerizations of RMI with *n*-butylamine ($pK_b = 3.31$)

Run	RMI	Solvent[a]	Yield[b] (%)	M_n[c] ($\times 10^{-3}$)	M_w/M_n[c]
1	CHMI	THF	No polymerization		
2		DMF	10.5	3.5 (8.8, 2.5)	1.8 (1.3, 1.2)
3		DMSO	56.0	4.9 (18.6, 6.4, 2.2)	3.0 (1.5, 1.1, 1.2)
4	PhMI	THF	No polymerization		
5		DMF	14.0	1.7 (4.8, 1.5)	1.4 (1.1, 1.2)
6		DMSO	24.2	1.9	1.5

0.5 g, at 30°C for 24 h

[*n*-butylamine]/[Monomer] = 0.1

[a] 1.5 mL, *THF* tetrahydrofuran, *DMF N,N*-dimethyl formamide, *DMSO* dimethylsulfoxide

[b] Methanol—insoluble part

[c] By GPC (THF)

solution changed to a red color as soon as the amine was added. After the reaction was terminated, this color disappeared rapidly. This phenomenon indicated that this polymerization proceeded by the mechanism of anionic polymerization. The yields and M_n of the polymers were 10.5–56.0% and 1700–4900, respectively. As the polarity of solvent was higher, the yields of the polymers tended to increase. In the case of low polar solvent such as tetrahydrofurane (THF), while the reactions gave no polymers, byproducts formed by Michael addition reaction of the monomer with the amine. The byproduct and unreacted monomers were confirmed by ^{1}H NMR spectra. In the cases of highly polar solvents such as DMF and DMSO, it seems that DMF or DMSO solvated to the zwitterion molecule generated from the amine and the maleimide monomer. Therefore, the zwitterion molecule was stabilized by high polar solvents, and the polymerization successfully proceeded. On the other hand, in 1990, Hagiwara et al. [16] reported that anionic polymerization of PhMI initiated with potassium *tert*-butoxide in THF at −72 °C gave 100% of polymer yield in only 20 min. However, the polymerization initiated with *n*-butylamine in DMSO at 30 °C gave 56% of polymer yield in 24 h. The basicity of potassium *tert*-butoxide that is strong base was much higher than that of *n*-butylamine that is very weak base. These indicated that anionic polymerization ability of RMI greatly depends on the basicity of the initiator. Compared with the results of each RMI, the yields and M_ns of poly(CHMI) were higher than those of poly(PhMI). Electron density of C=C bond in PhMI having an electron-rich phenyl group is higher than that in CHMI. Thus, the electron density of the C=C bond in RMI may affect polymerization ability.

Anionic polymerizations of RMI using various amines

The effects of basicity (pK_b) and structures of the primary, secondary, and tertiary amines on the polymerization ability of RMI are summarized in Table 2. As a result of utilizing various amines, all the amines initiated the polymerizations of RMI. The yields and number average of molecular weights (M_ns) of polymers were 0.7–66.8%

Table 2 Polymerizations of RMI with various amines

Run	RMI	Initiator[a] pK_b	Yield[b] (%)	M_n[c] ($\times 10^{-3}$)	M_w/M_n[c]
1	CHMI	Aniline (9.42)	11.0	11.5 (14.8, 2.9)	2.0 (1.7, 1.1)
2	PhMI		4.1	4.6	1.8
3	CHMI	*N*-methylbutylamine (3.17)	66.8	3.9 (15.8, 6.3, 2.1)	2.3 (1.3, 1.1, 1.2)
4	PhMI		14.5	2.1	1.4
5	CHMI	*N*-methylaniline (9.30)	12.2	13.9 (16.0, 3.0)	1.9 (1.7, 1.1)
6	PhMI		1.0	12.5	1.6
7	CHMI	*N*,*N*-dimethylbutylamine (4.17)	35.7	13.2	1.8
8	PhMI		23.6	1.7	1.4
9	CHMI	*N*,*N*-dimethylaniline (8.94)	14.4	18.0	1.8
10	PhMI		0.7	17.2	1.8

0.5 g, in DMSO (1.5 mL) at 30 °C for 24 h

[a] [Initiator]/[Monomer] = 0.1

[b] Methanol—insoluble part

[c] By GPC (THF)

and 1700–18000, respectively. Poly(CHMI) initiated by *N*-methylbutylamine showed the highest yield. The yields of polymers initiated with high basicity amines were higher than those of polymers initiated with low basicity amines. On the other hand, in the case of low basicity amines, M_ns were higher. These results indicated that the basicity of amines influenced the propagation reaction of polymerization.

As shown in Fig. 1, the polymers obtained by *n*-butylamine (c) and *N*-methylbutylamine (b) showed a bimodal or a trimodal molecular distribution. While the polymers obtained by *N*,*N*-dimethylbutylamine (a) depicted a monomodal molecular distribution. Therefore, we proposed the mechanism for propagation reaction showed in Scheme 2. Using the primary amines or the secondary amines, the propagation reaction proceeded via route A and route B. In the process of route B, the obtained polymers showed a bimodal or trimodal molecular distribution because of the termination reaction between a proton of quaternary ammonium salt in the initiation part and a carbanion of the propagation species. On the other hand,

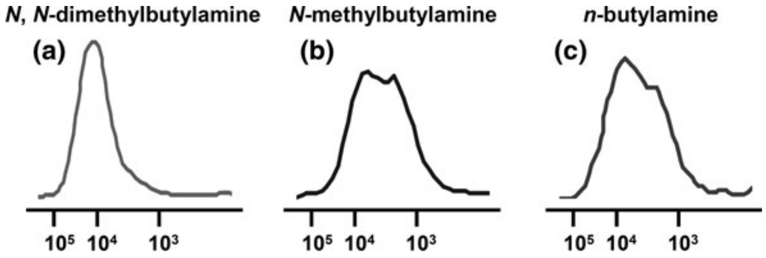
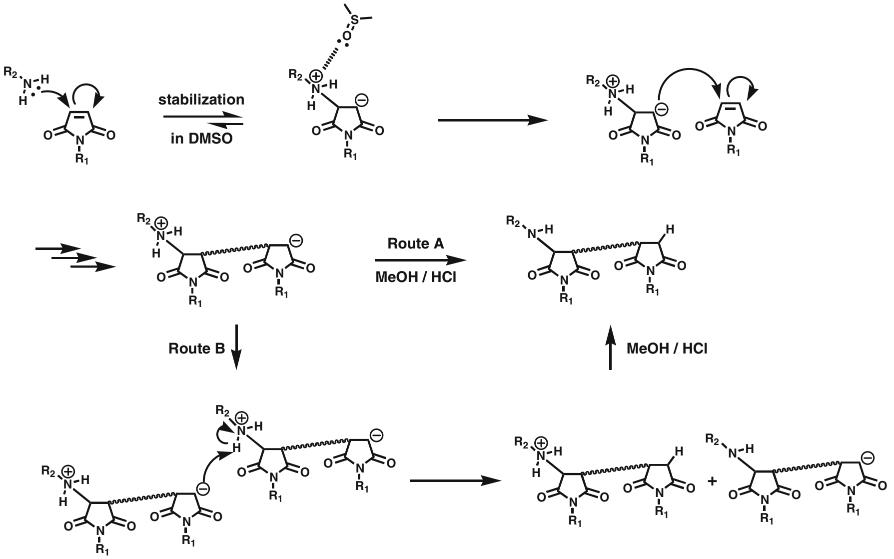


Fig. 1 GPC curves of poly(CHMI) obtained by **a** *N*, *N*-dimethylbutylamine, **b** *N*-methylbutylamine, **c** *n*-butylamine



Scheme 2 Polymerization mechanism of RMI with amine

the tertiary amines have no hydrogens at nitrogen atom of the amine, and the propagation reaction consequently proceeded via only route A. This suggested that the structure of amines significantly influenced the propagation reaction of polymers.

Asymmetric anionic polymerization of RMI using chiral amines

Table 3 summarizes the results of poly(RMI)s obtained with (*S*)-PEA. The yields and M_ns of polymers were 24.3–92.5% and 1200–17000, respectively. The specific optical rotations of the polymers obtained were −40.7° to +2.8°. Increasing the amount of initiator, molecular weights of each polymer decreased.

Moreover, in accordance with decrease of molecular weights, the specific optical rotations of poly(CHMI) changed to positive from negative sign. It was indicated that optical rotation of the polymer main chain in the proximity to initiation part showed positive.

Figure 2 shows CD and UV spectra of poly(CHMI) and poly(PhMI) obtained with (*S*)-PEA. In CD spectrum of poly(CHMI), a negative cotton effect appeared around 270 nm due to $\pi \rightarrow \pi^*$ transition of phenyl group in (*S*)-PEA of initiation part. In poly(PhMI), a negative cotton effect appeared around 240–280 nm, which could be attributed to carbonyl groups of maleimide ring and phenyl groups of *N*-substituent and (*S*)-PEA of initiation part. These results suggested that an asymmetric induction partially took place on the main chain of poly(PhMI).

Table 4 summarizes the results of poly(CHMI)s obtained with various chiral amines((*S*)-PEA, (*S*)-CHEA, (*S*)-1-NEA, and (*S*)-2-NEA). The yields and M_ns of polymers were 71.8–92.5% and 3700–7300, respectively. The polymers had the

Table 3 Polymerizations of RMI with (*S*)-PEA ($pK_b = 4.25$)

Run	RMI	Initiator [(*S*)-PEA]/[RMI]	Yield[a] (%)	M_n[b] ($\times 10^{-3}$)	M_w/M_n[b]	[α]25 435[c] deg.
1	CHMI	0.01	57.7	17.0	1.5	−40.7
2		0.10	92.5	7.3 (11.6, 3.3)	1.8 (1.4, 1.1)	−20.2
3		0.50	56.3	3.9 (7.3, 2.2)	1.7 (1.2, 1.2)	+2.7
4		1.00	54.1	3.2 (7.7, 2.5)	1.5 (1.2, 1.1)	+2.8
5	PhMI	0.01	24.3	4.1	1.5	−11.6[d]
6		0.10	44.7	1.9	1.5	−13.5[d]
7		0.20	50.0	1.9	1.7	−11.3[d]
8		0.40	48.4	1.6	1.7	−35.0[d]
9		0.60	41.8	1.2	1.9	−17.4[d]
10		0.80	44.2	1.2	1.8	−7.7[d]

0.5 g, in DMSO(1.5 mL) at 30 °C for 24 h

[a] Methanol—insoluble part

[b] By GPC (THF)

[c] $c = 1.0$ g/dL, $l = 1$ cm, in THF

[d] $c = 1.0$ g/dL, $l = 1$ cm, in $CHCl_3$

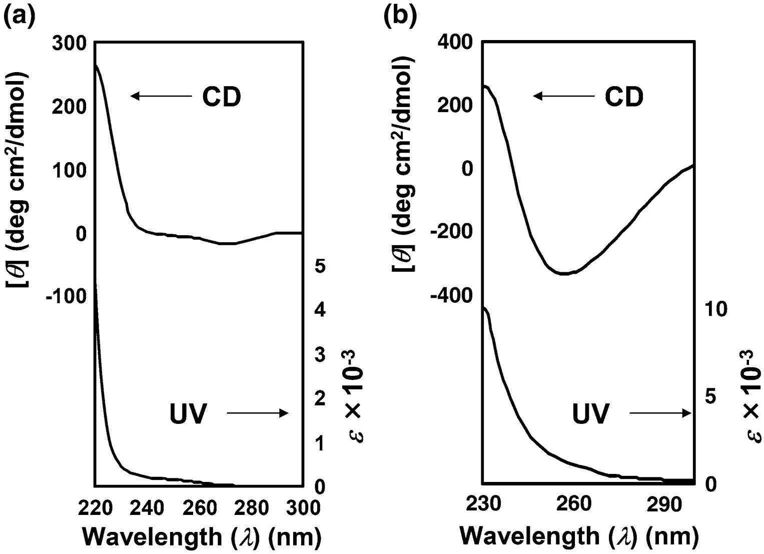


Fig. 2 CD and UV spectra of **a** poly(CHMI) initiated with (*S*)-PEA (run2, Table 3), and **b** poly(PhMI) initiated with (*S*)-PEA (run 8, Table 3)

specific optical rotations of −20.2° to +17.9°. The optical rotations of polymers obtained with (*S*)-CHEA and (*S*)-1-NEA showed opposite sign to those of the corresponding amines. It seems that steric hindrance of substituent groups of the amines affected optical rotations of polymers in the initiation reaction by amines.

Table 4 Polymerizations of CHMI with various chiral amines

Run	Initiator[a] pK_b	Yield[b] (%)	M_n[c] ($\times 10^{-3}$)	M_w/M_n[c]	$[\alpha]25\ 435$[d] deg.
1	(*S*)-CHEA (3.11)	74.0	3.7 (10.2, 2.4)	2.1 (1.3, 1.3)	−3.5
2	(*S*)-PEA (4.25)	92.5	7.3 (11.6, 3.3)	1.8 (1.4, 1.1)	−20.2
3	(*S*)-2-NEA (4.64)	71.8	3.9 (11.4, 4.9, 2.1)	2.0 (1.2, 1.1, 1.1)	−9.1
4	(*S*)-1-NEA (4.74)	85.2	5.0 (10.7, 2.6)	2.1 (1.4, 1.2)	+17.9

0.5 g, in DMSO(1.5 mL) at 30 °C for 24 h

[a] [CHMI]/[initiator] = 10, (*S*)-CHEA: (*S*)-cyclohexylethylamine

(*S*)-PEA: (*S*)-phenylethylamine, (*S*)-2-NEA : (*S*)-1-(2-naphthyl)ethylamine

(*S*)-1-NEA : (*S*)-1-(1-naphthyl)ethylamine

[b] Methanol—insoluble part

[c] By GPC (THF)

[d] $c = 1.0$ g/dL, $l = 1$ cm, in THF

Figure 3 shows CD and UV spectra of poly(CHMI)s initiated with various chiral amines. With (*S*)-PEA (Fig. 3a), small negative cotton effect appeared at 260–280 nm due to $\pi \rightarrow \pi^*$ transition of phenyl group in (*S*)-PEA of initiation part. With (*S*)-CHEA (Fig. 3b), negative cotton effect appeared around 250 nm due to $n \rightarrow \pi^*$ transition of carbonyl groups in maleimide ring. With (*S*)-1-NEA (Fig. 3c), the CD spectra showed peaks around 220–240 nm and 270–300 nm, which could be ascribed to the ^1B_b (long axis) and ^1L_a (short axis) electron transition of naphthalene in (*S*)-1-NEA of initiation part, respectively. Additionally, positive cotton effect appeared around 250 nm due to $n \rightarrow \pi^*$ transition of carbonyl

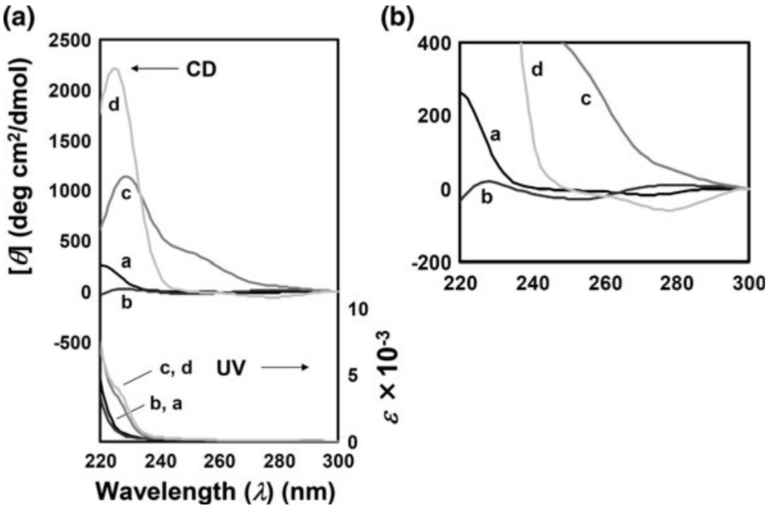


Fig. 3 CD and UV spectra of **a** poly(CHMI)s initiated with (*a*) (*S*)-PEA, (*b*) (*S*)-CHEA, (*c*) (*S*)-1-NEA, and (*d*) (*S*)-2-NEA, and **b** enlarged illustration of **a**

group in maleimide ring. With (*S*)-2-NEA (Fig. 3d), the CD spectra showed peaks around 220–240 nm, 270–300 nm, which could be attributed to the ^1B_b (long axis) and ^1L_a (short axis) electron transition of naphthalene in (*S*)-2-NEA of initiation part, respectively. Previously, we reported that the cotton effect due to carbonyl group in maleimide ring appeared around 250 nm when asymmetric induction took place on polymer main chain [22–24]. The CD spectra of the poly(CHMI) obtained with (*S*)-CHEA and (*S*)-1-NEA showed negative and positive cotton effects due to carbonyl groups. These two polymers obtained with (*S*)-CHEA and (*S*)-1-NEA showed opposite sign to the specific optical rotation of the corresponding amines. Therefore, these results suggested that the specific optical rotations of the polymers were changed by asymmetric induction on the polymer main chain.

Conclusions

The polymerizations of CHMI and PhMI were performed with various amines as an initiator. As a result, poly(RMI)s were successfully synthesized in only high polar solvents. The basicity and structure of amines significantly affected yields and M_ns of the polymers. The optically active poly(CHMI)s and poly(PhMI)s could be prepared by using chiral amines as an initiator. The optical rotations of poly(CHMI)s obtained with (*S*)-CHEA or (*S*)-1-NEA showed opposite sign to those of the corresponding amines. This study revealed that the structure of chiral amines affected the specific optical rotations of the polymers.

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