NOTES

Asymmetric Oligomerization of *N*-Substituted Isomaleimide

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Okamoto and co-workers¹ reported that anionic polymerizations of triphenylmethyl methacrylate (TrMA) were carried out with *n*-butyllithium (*n*-BuLi)/(-)-sparteine (Sp) as catalyst to obtain polymers with abnormally high specific rotation ($[\alpha]_D > 300^\circ$). It was considered that chirality was due to helical conformation of the TrMA polymer main chain. Okamoto *et al.*² reported that the asymmetric polymerization of *N*-phenylmaleimide (PhMI) was performed with *n*-BuLi/(-)-Sp catalyst to yield the chiral PhMI polymer having 12° of specific rotation. We reported asymmetric polymerizations of eleven types of *N*-substituted maleimide (RMI) with *n*-BuLi/(-)-Sp.³ The specific rotations of the resulting poly(RMI)s were -40° to $+11.3^\circ$, and asymmetry was due to a threodiisotactic structure of the poly(RMI) main chain, *i.e.*, helical structure and/or excess of chiral stereogenicity, (*S, S*) or (*R, R*).³

It has been reported that anionic polymerizations of *N*-substituted isomaleimide (RIMI) with *n*-BuLi give polymers consisting of both structures of isomaleimide (35—45 mol%) and maleimide (65—55 mol%).⁴ The resulting polymers were oligomers, and the degrees of polymerization for the poly(RIMI)s were 3 to 7. The specific rotation of the oligo(RIMI) of

very low molecular weight is interesting, since the oligo(RIMI)s are expected to have many maleimide ring units.

We report here the asymmetric oligomerizations of achiral RIMI [*N*-substituent(R) = *N*-*n*-butyl (nBIMI), *N*-isobutyl (iBIMI), *N*-*t*-butyl (tBIMI), *N*-cyclohexyl (CHIMI), *N*-phenyl (PhIMI), and *N*-DL- α -methylbenzyl (MBZIMI)] performed with BuLi/(-)-Sp in toluene, and the chirality of the resulting oligo(RIMI)s.

EXPERIMENTAL

Six RIMI were prepared from maleic anhydride and the corresponding primary amines, according to the method by Cotter *et al.*⁵ Boiling points and melting points of RIMI are as follows: nBIMI bp $96^\circ\text{C}/6\text{ mmHg}$, iBIMI bp $97^\circ\text{C}/17\text{ mmHg}$, tBIMI bp $32\text{—}36^\circ\text{C}/5.0 \times 10^{-2}\text{ mmHg}$, CHIMI bp $76\text{—}79^\circ\text{C}/5.0 \times 10^{-2}\text{ mmHg}$; mp $35\text{—}37^\circ\text{C}$, PhIMI mp $62\text{—}63^\circ\text{C}$, and MBZIMI bp $112\text{—}114^\circ\text{C}/5.0 \times 10^{-2}\text{ mmHg}$. RIMI monomers were identified by IR and NMR spectra.

Commercially available *n*-BuLi in hexane solution was used without further purification. Toluene (Tol), tetrahydrofuran (THF), and methanol were purified by the usual methods. (-)-Sp was purified by distillation under

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reduced pressure: bp 93–94°C/ 5×10^{-2} mmHg; $[\alpha]_D^{20} = -17.5^\circ$ ($c = 1.0 \text{ g dl}^{-1}$, ethanol). (–)-Sp and *n*-BuLi were mixed at room temperature just before use.

Anionic oligomerizations of RIMI were attained with *n*-BuLi/(–)-Sp as an initiator in toluene at several temperatures. Constant volumes of toluene and RIMI monomer were placed in a dry Schlenk's tube under nitrogen. The catalyst solution was added with a syringe to the monomer solution cooled to the temperature of polymerization (0 and –17°C). The reaction was terminated by the addition of a few drops of methanol. The oligomer was precipitated in a large amount of petroleum ether, separated by filtration and purified by reprecipitation from the THF solution containing a few drops of 0.1 *N* HCl to petroleum ether three times.

D-Line specific rotations, circular dichroism (CD), ^1H and ^{13}C NMR spectra were obtained as reported previously.⁶ In NMR measurement, tetramethylsilane was used as the

standard.

RESULTS AND DISCUSSION

Oligomerization of RIMI

Anionic oligomerizations of RIMI by *n*-BuLi/(–)-Sp in toluene proceeded homogeneously throughout. The results are shown in Table I. It is considered that the resulting oligomers consisted of both structures of isomaleimide and maleimide, and contained about 40 mol% of isomaleimide units, as judged from IR and NMR spectra. The signal assigned to a methine proton located at $\text{H}-\text{C}=\text{N}-\text{O}$ in lactone ring shifted to a lower magnetic field (about 3.7 ppm) than that for another methine proton (3.35 ppm). Two methine protons of maleimide ring also appeared at about 3.35 ppm. According to ^1H NMR, ratios of RIMI/([RIMI] + [RMI]) were estimated, as shown in Table I. Decrease of characteristic peaks assigned to a lactone ring at 1780 cm^{-1} was observed in IR spectra for

Table I. Anionic polymerization of *N*-substituted isomaleimide with *n*-BuLi/(–)-sparteine system in toluene^a

RIMI	Solvent toluene	Temp	Cat. × 10 ²	Polym. time	Yield	[α] _D ^b	$\bar{M}_n$ ^c	$\bar{M}_w$ ^c	$\bar{M}_n$ ^d	Content of RIMI unit ^e	
mol l ⁻¹	ml	°C	mol l ⁻¹	h	%	deg				%	
PhIMI	0.57	5	0	6.0	12	50.9	−5.5	370	610	720	46
PhIMI	0.72	4	0	6.0	48	85.1	−5.8	390	750		42
PhIMI	0.72	4	−17	6.0	48	64.2	−6.0	490	1080	770	42
CHIMI	1.11	5	0	6.0	12	15.8	−2.6	660	740	570	40
CHIMI	1.11	5	0	6.0	48	27.3	−4.8	630	910		
CHIMI	1.39	4	−17	6.0	48	61.9	+1.4	230	400		41
nBIMI	6.52	2	0	6.0	24	2.8	−2.2	530	1490		
nBIMI	6.52	2	0	6.0	48	2.5	−6.9	620	910		
iBIMI	6.52	2	0	6.0	24	3.7	−22.3	420	760		
tBIMI	1.86	3.5	0	6.0	20	22.8	−3.8	1400	1960	1920	40
MBZIMI	2.48	2	0	6.0	24	3.6	+16.6	640	870		
MBZIMI	2.48	2	−17	6.0	48	2.7	−0.4	470	770		

^a $[n\text{-BuLi}]/[(\text{–})\text{-Sp}] = 1.0/1.2$.

^b $C = 0.2\text{--}1.0 \text{ g dl}^{-1}$; $l = 5$ or 1 cm ; THF.

^c By GPC.

^d By VPO.

^e $[\text{RIMI}]/([\text{RIMI}] + [\text{RMI}])$; by NMR.

the polymer. This is consistent with the results of anionic oligomerization of RIMI only with *n*-BuLi, as reported previously.⁴ Molecular weights ($\bar{M}_n$) for the oligomers were very low and the degrees of polymerization were 3 to 9. The poly(RIMI)s were oligomers. All oligomers obtained in toluene were optically active. The specific rotations of oligo(RIMI) were -22° (iBIMI) to $+16.6^\circ$ (MBZMI), and influenced by *N*-substituents and polymerization temperature. However, specific rotations could not be correlated with the steric and polar character of the *N*-substituent, according to the Taft equation.⁷

The obtained oligomers revealed obvious CD at peaks from 220 to 275 nm, attributed to the $n \rightarrow \pi^*$ transition of the carbonyl groups, as shown in Figure 1. CD patterns were different among the polymers. This suggests that asymmetry of the oligo(RIMI) was affected by

N-substituents. The magnitude of molecular ellipticity for the oligo(RIMI)s was much smaller than for poly(RIMI)s reported previously.³

The oligomerization of PhIMI and chiroptical properties of the oligo(PhIMI)s were investigated. The yields of oligomers obtained at 0°C were over 80% in about 24 h. Specific rotations for the oligomers obtained at over 12 h of polymerization were constant. The degrees of polymerization of the oligo(PhIMI) at 0°C were constant (3–4), and not correlated with polymerization time. Relationships between yields of oligomers and $[\alpha]_D$, $\bar{M}_n$ are shown in Figure 2. $[\alpha]_D$ increased with yield. $\bar{M}_n$ was independent of yield, and constant.

As shown in Figure 3, the magnitude of specific rotation was remarkably affected by rise of temperature and measurement solvents. This suggests that the main chains of oligo(PhIMI)s take different conformations depending on the temperature and solvent. The specific rotations of oligomers were not correlated with the dielectric constants of solvents.

Cubbon⁸ reported that free radical and anionic polymerizations of RMI gave rise to polymers not completely stereoregular but

Figure 1. CD curves for RIMI oligomers: (1) PhIMI, (2) CHIMI, (3) nBIMI, (4) iBIMI, (5) tBIMI, and (6) MBZMI oligomers.

Figure 2. Relationships between yield of oligomer and specific rotations ($[\alpha]_D$) and $\bar{M}_n$ of oligo(PhIMI) obtained with *n*-BuLi/(–)-Sp at 0°C .

Figure 3. Effects of measurement temperature on specific rotation $[\alpha]_D$ of oligo(PhIMI) in solvents: (○) dichloromethane, (●) dioxane, (■) chloroform, (□) benzene, and (△) THF.

predominantly *threo*-diisotactic polymers. In the case of poly(RIMI)s, the degrees of polymerization were so small that a helical structure resulting from the *threo*-diisotactic addition of RIMI may scarcely be present.

IR and ^1H NMR spectra of some RIMI oligomers were measured. NMR spectra for the oligomers obtained with *n*-BuLi and *n*-BuLi/(–)-Sp were different from that for the oligomer obtained with AIBN, as shown in Figure 4. Judging from the NMR spectra, oligomers obtained with anionic initiators may contain different structural oligomers. But oligomers could not be separated from the mixture. Signals due to initiator fragments (*n*-butyl and isobutyronitrile groups) from 2.5 to 0.5 ppm were observed, as shown in Figure 4. Two signals assigned to methine protons of RMI and RIMI were detected at about 3.35 ppm (RIMI and RMI) and 3.70 (RIMI) ppm, respectively.

Figure 4. ^1H NMR spectra for oligo(PhIMI)s obtained with (a) *n*-BuLi/(–)-Sp at 0°C, (b) *n*-BuLi at 0°C, and (c) AIBN in toluene at 70°C; (d) poly(PhIMI) obtained with AIBN at 70°C.

Scheme 1.

The cause of optical activity of the RIMI oligomer may be as follows (1), (2), (3), and (4).

Farina⁹ reported that polymerizations of cycloalkene derivatives yield two *trans*-additions, *i.e.*, chiral centers of (*S*, *S*) and (*R*, *R*), and that if one is produced more than the other, the obtained polymer is optically active. (1) According to this concept, it is considered that the chirality of the RIMI oligomer is attributable to the excessive chiral center of (*S*, *S*) or (*R*, *R*), as shown in Scheme 1. (2)

The RIMI unit possesses not a symmetric structure like RMI but an unsymmetrical olefin like benzofuran. Accordingly, different combinations (*i.e.*, head to head and head to tail) give optically active oligomers even in the absence of *threo*-diisotactic additions. (3) The presence of RIMI and RMI units in the oligomer produce optical activity because the oligomer *i.e.*, poly(RIMI-*co*-RMI) has no symmetry. (4) Chirality in both oligomer chain-ends can not be neglected.

The cause of optical activity of the RIMI oligomer is not clear, but the main contributions may be (2) and (3).

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REFERENCES

1. Y. Okamoto, K. Suzuki, and H. Yuki, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 3043 (1980).
2. Y. Okamoto, Y. Nakano, H. Kobayashi, and K. Hatada, *Polym. Bull.*, **25**, 5 (1991).
3. T. Oishi, H. Yamasaki, and M. Fujimoto, *Polym. J.*, **23**, 795 (1991).
4. T. Oishi, M. Fujimoto, N. Yoshimoto, and T. Kimura, *Polym. J.*, **21**, 655 (1989).
5. R. J. Cotter, C. K. Sauers, and J. M. Whelan, *J. Org. Chem.*, **26**, 10 (1961).
6. T. Oishi and M. Fujimoto, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 2789 (1984).
7. R. W. Taft, Jr., in "Steric Effect in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N.Y., 1956, p 556.
8. R. C. P. Cubbon, *Polymer*, **6**, 419 (1966).
9. M. Farina, "The Stereochemistry of Linear Macromolecules," Topics in Stereochemistry, Vol. 17, E. L. Eliel and S. H. Wilen, Ed., John Wiley & Sons, Inc., 1987.