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Asymmetric polymerization of *N*-triphenylmethylmaleimide with chiral anionic initiators

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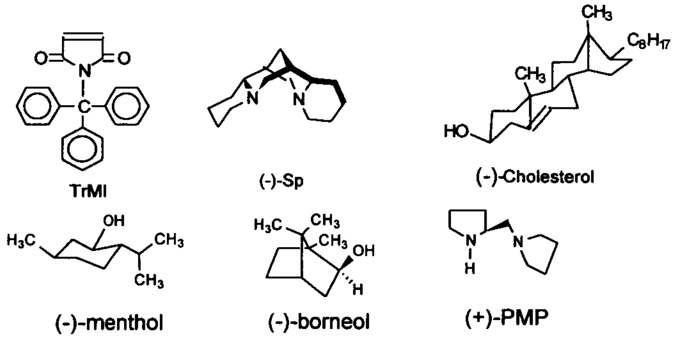
Summary

Asymmetric polymerization of N-triphenylmethylmaleimide(TrMI) is performed with chiral anionic initiators in tetrahydrofuran and toluene at -78 and 0°C to obtain optically active polymer. It is found that the (S)-(+)-1-(2-pyrrolidinylmethyl) pyrrolidinelithium [Li-(+)-PMP] and lithium (-)-menthoxide are effective for the asymmetric polymerization of N-triphenylmethylmaleimide in THF. The polymers obtained are characterized by circular dichroism(CD). It is inferred that the propagation reaction of polymerization of TrMI with Li-(+)-PMP is dominated by ion pair mechanism and meanwhile free ion mechanism cannot be ignored based on GPC analysis.

Introduction

N-Substituted maleimides(RMI) are interesting monomers which can be polymerized to yield two kinds of chiral center ,(S,S) or (R,R) in the polymer backbone. If one of these predominates over the other, the obtained polymers will exhibit optical activity. The optically active N-substituted maleimide polymers and copolymers have been obtained by polymerization and copolymerization of optically active N-substituted maleimide monomers,[1,2] radical copolymerizations of non-chiral RMI monomers with styrene in chiral solvents[3]or with chiral monomers[4] and asymmetric polymerization of non-chiral RMI monomers performed with n-butyllithium (n-BuLi)/ (-)-sparteine(Sp) in toluene.[5,6] In the last case, the optically active poly(N-cyclohexyl maleimide) showed the largest specific rotation($[\alpha]_D$=-40° in $CHCl_3$) in the 11 different kinds of RMI polymers reported by Oishi.[6] In our previous study,[7] optically active poly(N-diphenylmethyl maleimide) obtained with (-)-sparteine-fluorenyllithium complex[(-)Sp-FlLi] showed high positive specific rotation ($[\alpha]^{20}_D$= +64° in chloroform) and the polymer obtained with (S)-(+)-1-(2-pyrrolidinylmethyl)pyrrolidine-N,N'-Diphenylethylenediaminelithium [(+)PMP-DPEDALi] complex showed negative specific rotation ($[\alpha]^{20}_D$ = - 37.2° in chloroform). The optically active RMI polymers bearing different bulky substituents obtained with the same initiator system showed different specific rotations. This suggests that bulkiness of N-substituent plays an important role for the asymmetric polymerization.

The radical polymerization of N-triphenylmethylmaleimide(TrMI) was briefly reported by Otsu[8]. It was found that TrMI showed a lower polymerization reactivity, and the polymer yield was only 4.9%. Up to now, anionic and asymmetric polymerization of TrMI has not been reported. In the present study, anionic polymerization of TrMI is performed with (-)-sparteine-fluorenyllithium and chiral lithium alkoxides and amides as initiators. It is found that chiral lithium alkoxides and amides are effective initiators in THF for the asymmetric polymerization of TrMI and optically active poly(TrMI) is obtained. Gel permeation chromatography (GPC) and circular dichroism (CD) have been used to characterize the polymers.



Scheme 1

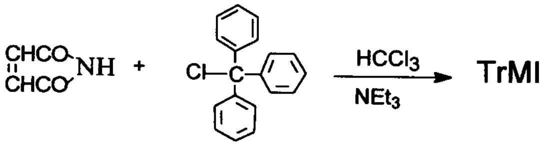
Experimental

Materials

Sp (Sigma Chem. Co.) and PMP (Aldrich Chem. Co.) were dried over calcium hydride and distilled under reduced pressure. Commercially obtained (-)-menthol, (-)-borneol were dried by evacuation before use. Cholesterol was recrystallized from absolute ethanol and then dried by evacuation at room temperature. Fluorene(Fl)(Aldrich Chem. Co.) was used as commercially available.

Synthesis of TrMI monomer

Attempts to synthesize TrMI were unsuccessful according to the usual preparation method of RMI from maleic anhydride and the corresponding primary amine described in the literature^9. But it could be prepared from triphenylmethyl chloride and heavy metal salts of maleimide in benzene or maleimide in the presence of triethylamine in chloroform as shown in Scheme 2.^{10} Maleimide(9.7g, 0.10mol) and triphenylmethyl chloride(28.7g, 0.10mol) were mixed together in 100ml of chloroform, and then triethylamine(30.3g, 0.30mol) was added dropwise to the reaction mixture over a period of 20 minutes. After stirring for one hour at refluxing temperature, chloroform and triethylamine were evaporated. The crude product was dissolved in THF and the insoluble part was filtered off. After THF was evaporated, the crude product was recrystallized three times from ethyl acetate to obtain pure TrMI. Yield, 49%; mp, 226-228°C. The TrMI monomer was identified on the basis of elemental analysis, IR and ^{1}H-NMR spectra.



Scheme 2

Elemental analysis: Found, C=81.25%, H=5.10%, N=4.10%; Calcd. for $C_{23}H_{17}NO_2$, C=81.42%, H=5.01%, N=4.13%. ^1H NMR [δ in ppm from $Si(CH_3)_4$ in $CDCl_3$]: 7.15-7.42 (m, 15H in phenyl group), 6.58(s, 2H, -CH=CH-). IR spectrum(KBr pellet) [wave number(cm^{-1})]:3450, 3000-3100,1700, 1670, 1600 1490, 1450, 1320, 830, 750, 700.

Polymerization procedure

Fluorenyllithium (FlLi) prepared from Fl and butyllithium was mixed with (-)Sp in toluene at room temperature to prepare the complex. The lithium amide of (+)-PMP(Li-PMP) and lithium alkoxides of (-)-menthol, (-)-borneol and cholesterol(Li-menthoxide, Li-borneoxide, and Li-cholesteroxide) were prepared by adding equimolar amounts of butyllithium to the solutions of optically active amine and alcohols in THF at room temperature. The polymerization was carried out in toluene or THF under dry nitrogen. An initiator solution was added to the monomer solution cooled to -78°C or 0°C. The reaction was terminated with a small amount of methanol. The polymer was precipitated in a large amount of methanol containing small amount of hydrochloric acid, collected by filtration or centrifugation, washed with methanol three times and dried under vacuum at 55°C.

Measurements

Optical rotation was measured with Perkin-Elmer 141 MC polarimeter at the wavelength 589 nm of a sodium lamp at 25°C. UV spectrum was recorded at room temperature in 1,4-dioxane solution on Shimazu UV-3000 spectrophotometer. Circular dichroism(CD) spectra were recorded in a 1.0-cm cell at room temperature on JASCO J-500C spectropolarimeter. ^1H NMR spectra were measured in deuterium chloroform at room temperature with a Varian XL-200 spectrometer. The gel permeation chromatographic(GPC) analysis was accomplished on Waters 201 with a μ-styragel column and tetrahydrofuran as solvent, and the molecular weight was calibrated with standard polystyrene.

Results and discussion

Table 1 Polymerization of TrMI with the complex of (-)Sp-FlLi at 0°C for 24h.[a)]

Run	Solvent	Yield(%)	$[\alpha]_D^{25}$ [b)]	$\bar{M}_W X10^{-3}$	$\bar{M}_W/\bar{M}_n$
1	TOL	8	0	1.21	1.94
2	TOL/THF (3/1,v/v)	11	0	1.51	1.77
3	TOL/THF (1/1,v/v)	16	0	1.47	1.72
4	THF	23	0	5.80	5.52

a) TrMI 0.50g, Solvent 20ml, [M]/[I]=20/1, [FlLi]/[Sp]=1.2. b) Specific rotation in units deg·dm^{-1}·g^{-1}·cm^3, Measured in THF.

Table 1 shows the results of the polymerization of TrMI with the complex of (-)Sp-FlLi at 0°C. Only oligomers which consist of a large amount of dimer are obtained in toluene and don't exhibit optical activity. This may be ascribed to the fact that the oligomer contains the chiral centers of (S,S) equal to those of (R,R) as reported by Oishi. The yield in toluene is lower than that in THF. With an increase of solvent polarity, the polymer yield increases. The polymer obtained in THF consists of a small amount of higher molecular weight and a large oligomer parts, so the molecular weight distribution is very broad. In addition, the asymmetric induction cannot occur with the complex initiator in such a polar solvent as THF which possesses better solubility than toluene for some of RMI monomers because the complex initiator system might be destroyed by THF.[6,11] Hence, the polymers obtained in the solvent containing THF do not show optical activity even if the polymers contain high molecular weight part.

Table 2 shows the results of the asymmetric polymerization of TrMI with Li-(-)-menthoxide, Li-(-)-borneoxide and Li-cholesteroxide in THF at 0°C. The polymerizations are homogeneous. The conversion of monomer and the molecular weight of the polymer are relatively low. Hagiwara[12] has reported that the anionic polymerization of N-phenyl maleimide with lithium tert-butoxide is initiated by the so-called "slow initiation mechanism" and its propagation reaction is dominated by the ion pair mechanism even in such a polar solvent as THF. According to above mechanism, It can be inferred that the polymerization should be sluggish for TrMI bearing sterically hindered bulky substituent. This also explains why the molecular weight and yields are low. In addition, higher concentrations of monomer and initiator are beneficial to improving the polymer yield as shown in run 2 of Table 2.

Table 2 Polymerization of TrMI with chiral lithium alkoxides and amide in THF for 24h.[a)]

Run	Initiators	T(°C)	Yield(%)	$[\alpha]_D^{25}$ [b)]	$\bar{M}_w$X10-3	$\bar{M}_w/\bar{M}_n$
1	Li-(-)-menthoxide	0	14	+9.4	1.25	1.53
2 [c)]	Li-(-)-borneoxide	0	32	-2.6	1.88	2.31
3	Li-cholesteroxide	0	16	0	2.58	3.31
4	Li-(+)-PMP	0	20	-8.6	6.14	6.08
5	Li-(+)-PMP	-78	21	-10.0	8.04	7.86

a) TrMI 0.50g, Solvent 10ml, [M]/[I]=20/1. b) Specific rotation in units deg·dm^{-1}·g^{-1}·cm^{3}, Measured in THF. c) Solvent 4 ml.

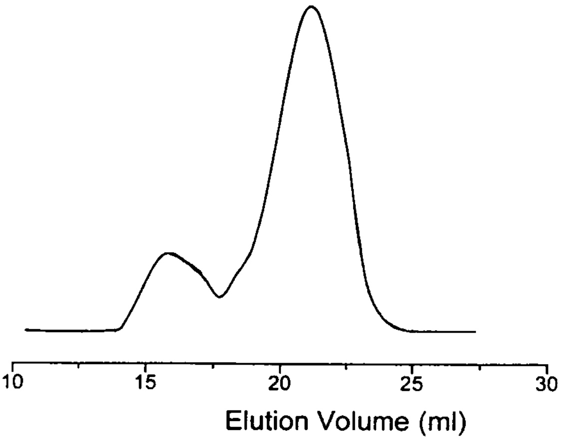


Figure 1. GPC profile of poly(TrMI) obtained with Li-(+)-PMP (run 5 in Table 2).

TrMI is also polymerized with Li-(+)-PMP in THF. The yield and molecular weight of the polymer are slightly improved in THF with Li-(+)-PMP comparing the lithium alkoxides system. Figure 1 shows GPC profile of poly(TrMI) obtained with Li-(+)-PMP. The high molecular weight part in the polymer is observed, and the low molecular weight part constitutes the majority. The molecular weight distribution is very broad when both parts are taken into account. This also illustrates that there are two kinds of mechanisms in the polymerization with Li-(+)-PMP. It is inferred that the propagation reaction of polymerization of TrMI with Li-(+)-PMP is dominated by ion pair mechanism and meanwhile free ion mechanism cannot be ignored.

The optically active poly(TrMI) obtained with Li-(-)-menthoxide shows positive specific rotation which is opposite in sign to that of the initiator. This indicates that the Li-(-)-menthoxide exhibits an effective asymmetric induction in the polymerization of TrMI in THF. The poly(TrMI) obtained with Li-cholesteroxide does not exhibit optical activity. This may be ascribed to that the anionic species is rather far away from the chiral center and the long-distance effect may be too weak to induce the asymmetric polymerization.

Li-(+)-PMP is a fairly good initiator for the asymmetric polymerization of TrMI in THF. The obtained polymers show negative optical activity which is opposite to the sign of the initiator.

Anionic copolymerizations of TrMI with N-benzylmaleimide(BzMI) and N-cyclohexylmaleimide(CHMI) are performed in THF at 0°C using Li-(+)-PMP as an initiator. The results of copolymerizations are summarized in Table 3. All copolymerizations proceed homogeneously. The copolymers show small negative optical activity which is also opposite to the sign of the initiator. Under the same polymerization condition, the obtained poly(N-benzylmaleimde)(Run 5 in Table 3) does not show optical activity, and the obtained poly(N-cyclohexylmaleimide)(Run 6 in Table 3) shows positive optical activity. It seems that the situation of configurational selectivity in copolymers might be more complicated.

Table 3 Copolymerization of TrMI with N-Benzylmaleimide and N-Cyclohexylmaleimide initiated by Li-(+)-PMP in THF at 0°C for 24h.$^{a)}$

Run	M_1:$M_2$$^{c)}$	M_2	Yield(%)	$F_T$$^{b)}$	$[\alpha]_D$$^{d)}$
1	1:1	BzMI	64.5	0.20	-3.5
2	1:2	BzMI	95	0.14	-2.5
3	1:1	CHMI	60	0.30	-3.0
4	1:2	CHMI	83	0.18	-1.0
5	$M_1 = 0$	BzMI	80	-	0
6	$M_1 = 0$	CHMI	94	-	+32

a). [M]/[Li]=20/1, [Sp]/[Li]=1.2/1, Monomer 1.0g, THF 20ml. b). F_T represent mole fractions of TrMI in copolymer and was determined by elemental analysis. c). M_1: TrMI. d).Specific rotation in units deg·dm^{-1}·g^{-1}·cm^{3}; Measured in THF (C=0,01 g·cm^{-3}).

UV spectrum for poly(TrMI) is measured in 1,4-dioxane solution and shown in Figure 2. The UV curve shows a broad absorption band from 240nm to 280nm which is due to the imide ring and phenyl groups.

CD spectrum for the (+)-poly(TrMI) obtained with Li-(-)-menthoxide is measured in 1,4-dioxane and a broad positive band is observed from 243nm to 273nm as shown in Fig. 2a. The absorption at 252nm might be mainly attributable to the $n \to \pi^*$ transition of two carbonyl groups in the imide ring. The absorptions at 256nm and at 261nm might be mainly ascribed to the π→π* transition of the phenyl groups. The CD spectrum for the (-) -poly(TrMI) obtained with Li-(+)-PMP exhibits a broad negative band from 243nm to 273nm which opposites to the band of (+)-poly(TrMI).

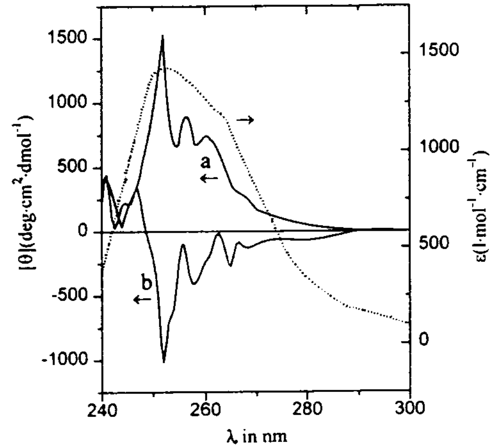


Figure 2. CD(continuous curve) spectra of (+)-poly(TrMI) obtained with Li-(-)-menthoxide (a, run 1 in Table 2) and (-)-poly(TrMI) obtained with Li-(+)-PMP(b, run 4 in Table 2) and UV(dashed curve) spectrum for the polymer (a) in 1,4-dioxane($C=0.20g\cdot L^{-1}$).

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