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SHORT COMMUNICATIONS

Synthesis of Model Compound for Maleimide Polymer

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The authors investigated asymmetric anionic polymerizations of *N*-substituted maleimide (RMI) with chiral ligand-organometal complexes. In the previous work,[1—6] optical activity of poly(RMI) was mainly attributed to asymmetric carbons on the polymer main chain, *i.e.*, configurational chirality. Main-chain carbons of poly(RMI) show chirality in the case of *trans* structures, *i.e.*, *threo-diisotactic* and *threo-disyndiotactic*. But the polymer consisting of *threo-disyndiotactic* structure as a whole cannot exhibit optical activity because (*S, S*)- and (*R, R*)-configurational pairs equivalently exist. Excess of (*S, S*)- or (*R, R*)-configuration for *threo-diisotactic* main chain leads to optical activity.

Previously, G. B. Butler *et al.* synthesized racemic *trans*-3,4-dimethyl-*N*-phenylsuccinimide (*trans*-DMPhSI) to establish the structure and stereochemistry of *N*-phenylmaleimide (PhMI) / vinyl ether alternating copolymer.[7] We prepared racemic *trans*-3,4-dimethyl-*N*-cyclohexylsuccinimide[3,8] (*trans*-DMCHSI) as model compound for optically active poly(*N*-cyclohexylmaleimide)[1,3—5] (CHMI) to clarify the main chain structure that would account for optical activity from ^{13}C NMR spectra. Optical activity, *i.e.*, specific optical rotation was not discussed because *trans*-DMPhSI was not resolved and it was difficult to resolve *trans*-DMCHSI. Therefore, specific optical rotation due to two asymmetric centers in monomeric unit was not clear. The relationship between *N*-substituent and specific optical rotation was unknown because other optically active model compounds were not prepared.

This work describes the synthesis of two *trans*-3, 4-dimethyl-*N*-substituted succinimide (*N*-substituent: 1-naphthyl, *trans*-DMNSI; phenyl, *trans*-DMPhSI) as model compounds of corresponding poly(RMI) such as poly(*N*-1-naphthylmaleimide)[9] (1-NMI) and poly(*N*-phenylmaleimide)[1—5] (PhMI). (—)-Isomers (*trans*-(—)-DMNSI and *trans*-(—)-DMPhSI) were successfully resolved to clarify configurational chirality of the corresponding polymer and relationship between specific optical rotation and *N*-substituent.

EXPERIMENTAL

Materials

Solvents for synthesis, measurement, and HPLC were purified in the usual manner. Commercially available L-(—)-sparteine (Sp, Aldrich) was used after distillation under reduced pressure.

Model Compounds

Model compounds were synthesized by method reported previously.[7] Synthetic path is shown in Scheme 1.

3,4-Dimethyl-N-1-naphthylmaleimide (DMNMI)

A solution of 1-naphthylamine (0.5 g, 3.5 mmol) in acetic acid (15 mL) was added slowly dropwise to a solution of excess 3, 4-dimethylmaleic anhydride (0.5 g, 4.0 mmol) in acetic acid (15 mL) at r.t. The solution was stirred overnight and poured into a large amount of water (300 mL). The precipitate was separated by filtration with a glass filter, and washed with water (20 mL) 3 times, followed by dried under vaccum at 25℃ to obtain DMNMI as a white powder (0.8 g, 3.2 mmol, 90%). mp 170—174℃. ^1H NMR (δ in ppm from tetramethylsilane (TMS) in $CDCl_3$) 2.13 (s, 6H,-CH_3), 7.32—7.95 (m, 7H, aromatic protons). ^{13}C NMR (δ in ppm from TMS in $CDCl_3$) 8.95 (-CH_3), 124.44, 125.30, 126.34, 126.70, 126.82, 128.34, 129.45, 130.44, 134.34 (aromatic carbons), 137.74 (C-3, 4), 171.39 (C-2, 5).

cis-3,4-Dimethyl-N-1-naphthylsuccinimide (cis-DMNSI)

DMNMI (0.10 g, 0.40 mmol), 10% palladium-activated carbon (0.03 g, 30 wt%) and ethyl acetate (20 mL) were put in a Schlenk reaction tube, and replaced by hydrogen atmosphere. The solution was vigorously stirred at r.t. for 12 h. The solution was filtered, and the filtrate was concentrated and recrystallized from hexane-ethyl acetate (1/1, v/v) to give *cis*-DMNSI as a white crystal (0.07 g, 0.29 mmol, 72 %). mp 144—145℃. ^1H NMR (δ in ppm from TMS in $CDCl_3$) 1.37—1.52 (m, 6H,-CH_3), 3.18—3.40 (m, 2H, H-3, 4), 7.27—7.98 (m, 7H, aromatic protons). ^{13}C NMR (δ in ppm from TMS in $CDCl_3$) 11.63, 11.97 (-CH_3), 38.80, 38.92 (C-3, 4), 121.38, 121.82, 125.23, 128.28, 126.13, 126.16, 126.38, 126.41, 126.99, 127.12, 128.55, 128.61, 129.78, 129.81, 134.27 (aromatic carbons), 179.75, 179.80 (C-2, 5).

trans-3,4-Dimethyl-N-1-naphthylsuccinimide (trans-DMNSI)

cis-DMNSI (0.15 g, 0.59 mmol) and three drops of Sp were dissolved in DMSO-d_6 (0.4 mL) into a NMR tube. The solution was heated at 60℃. The reaction was con-

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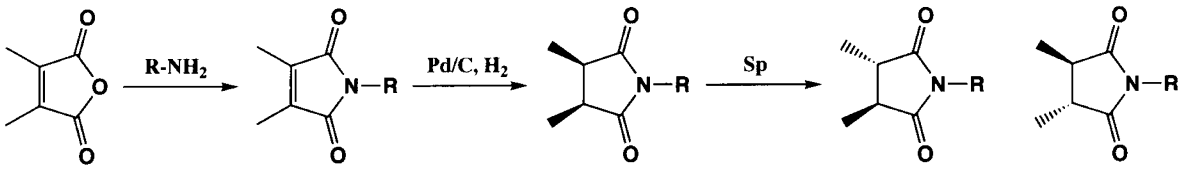

R = 1-naphthyl : DMNMI R = 1-naphthyl : *cis*-DMNSI R = 1-naphthyl : *trans*-DMNSI
phenyl : DMPhMI phenyl : *cis*-DMPhSI phenyl : *trans*-DMPhSI

Scheme 1.

Table I. Isomerizations of *cis*-DMNSI and *cis*-DMPhSI with Sp [a] in DMSO-d_6 [b] at 60℃

Run	Compound [c]	Reaction Time	Recovery	Conversion [d] of *trans*-isomer	$[\alpha]_{435}$ [e] of *trans*-isomer	e.e. [f]
		day	%	%	degree	%
1	*cis*-DMNSI	6	100	43	−9.9	17.4
2	*cis*-DMPhSI	12	75	67	−0.7	~0

[a] 3 drops. [b] 0.4 mL. [c] *cis*-DMNSI: 0.15 g, *cis*-DMPhSI: 0.20 g. [d] Determined by ^{1}H NMR spectra. [e] Based on *trans*-isomer, $c = 0.42$ g dL^{-1} (run 1), 0.74 g dL^{-1} (run 2), $l = 10$ cm, in THF. [f] Enantiomer excess. Determined by HPLC.

tinued until isomerization was complete judging from ^{1}H and ^{13}C NMR spectra (reaction time: 6 days). The solution was concentrated, and purified by column chromatography (hexane/ethyl acetate = 1/1, v/v) to remove small amount of DMSO-d_6. The obtained sample (white solid, recovery 100%) was mixture of *cis*- and *trans*-DMNSI (conversion 46.1%) from ^{1}H NMR spectrum. mp (mixture of *cis*- and *trans*-DMNSI) 133—146℃. ^{1}H NMR (δ in ppm from TMS in $CDCl_3$) 1.42—1.50 (m, 6H, $-CH_3$), 2.62—2.76 (m, 2H, H-3, 4), 7.24—7.88 (m, 7H, aromatic protons). ^{13}C NMR (δ in ppm from TMS in $CDCl_3$) 15.24, 15.74 ($-CH_3$), 43.58, 43.72 (C-3, 4), 121.69, 125.36, 125.50, 126.25, 126.51, 127.15, 128.23, 128.70, 129.29, 129.92, 134.41, 135.74 (aromatic carbons), 178.89 (C-2, 5).

3,4-Dimethyl-N-phenylmaleimide (DMPhMI)

DMPhMI was synthesized as reported previously.[7] mp 89—90℃ (lit.[7] mp 90—91℃). ^{1}H NMR (δ in ppm from TMS in $CDCl_3$) 2.06 (s, 6H, $-CH_3$), 7.30—7.47 (m, 5H, aromatic protons). ^{13}C NMR (δ in ppm from TMS in $CDCl_3$) 8.86 ($-CH_3$), 125.75, 127.39, 128.97, 131.95 (aromatic carbons), 137.41 (C-3, 4), 170.91 (C-2, 5).

cis-3,4-Dimethyl-N-phenylsuccinimide (cis-DMPhSI)

cis-DMPhSI was synthesized by the same method as *cis*-DMNSI. Yield 97% (white crystal). mp 127—128℃ (lit.[7] mp 128—129℃). ^{1}H NMR (δ in ppm from TMS in $CDCl_3$) 1.30—1.38 (q, 6H, $-CH_3$), 3.09—3.16 (m, 2H, H-3, 4), 7.27—7.50 (m, 5H, aromatic protons). ^{13}C NMR (δ in ppm from TMS in $CDCl_3$) 11.61 ($-CH_3$), 38.47 (C-3, 4), 126.33, 128.37, 128.84, 129.02, 131.93 (aromatic carbons), 179.37 (C-2, 5).

trans-3,4-Dimethyl-N-phenylsuccinimide (trans-DMPhSI)

trans-DMPhSI was synthesized by the same method for *trans*-DMNSI (reaction time: 12 days). Recovery 75% (white solid). Conversion of *trans*-DMPhSI 67%. mp (mixture of *cis*- and *trans*-DMPhSI) 133—146℃(lit.[7] mp 145—147℃). ^{1}H NMR (δ in ppm from TMS in $CDCl_3$) 1.18—1.34 (q, 6H, $-CH_3$), 2.43—2.54 (m, 2H, H-3, 4), 7.25—7.39 (m, 5H, aromatic protons). ^{13}C NMR (δ in ppm from TMS in $CDCl_3$) 14.86 ($-CH_3$), 43.02 (C-3, 4), 125.36, 126.22, 128.07, 128.25, 128.91, 131.97 (aromatic carbons), 178.27 (C-2, 5).

Resolution of Model Compounds

Enantiomers of *trans*-(−)-DMNSI and *trans*-(−)-DMPhSI were completely resolved by HPLC (e.e. almost 100%) under conditions at CHIRALPAK AD (Daicel Chemical IND., LTD., Tokyo, Japan) as column, hexane/2-propanol (9/1, v/v) as eluent, concentration 5.1 mg mL^{-1}, injected volume 0.5 mL, flow rate 0.5 mL min^{-1} (*trans*-DMPhSI), 1.0 mL min^{-1} (*trans*-DMNSI), temperature r.t. mp 178—179℃ (*trans*-(−)-DMNSI), 176—177℃ (*trans*-(−)-DMPhSI).

Measurements

Specific optical rotation ($[\alpha]_{435}$) was measured at 25℃ using a JASCO DIP-140. ^{1}H and ^{13}C NMR spectra were recorded with a JEOL EX-270 operating at 270 and 68 MHz, respectively. HPLC was monitored by a Shimadzu CHROMATOPAC C-R 7 Ae plus equipped with a Shimadzu SPD-10A UV detector (254 nm) and a JASCO-OR 990 polarimetric detector (350—900 nm). CD spectra were obtained by a JASCO J-20C. UV spectra were recorded by a Shimadzu UV-2200 apparatus.

RESULTS AND DISCUSSION

Table I summarizes the results of the isomerization of *cis*-DMNSI and *cis*-DMPhSI at 60℃ performed with chiral Sp to obtain predominant optical isomers and calculate specific optical rotations of pure optical isomers. *cis*-DMNSI (run 1) was converted to a *trans*-DMNSI mixture [(*S, S*) and (*R, R*)] in 43% yield. Specific optical rotation ($[\alpha]_{435}$) of the *trans*-DMNSI mixture was −9.9°, and (−)-isomer was excessively formed (e.e. = 17.4%). In the case of *cis*-DMPhSI (run 2), conversion and specific optical rotation of *trans*-DMPhSI mixture were 67% and −0.7°, respectively. Specific optical rotations of pure *trans* compounds could not be calculated because of low e.e.

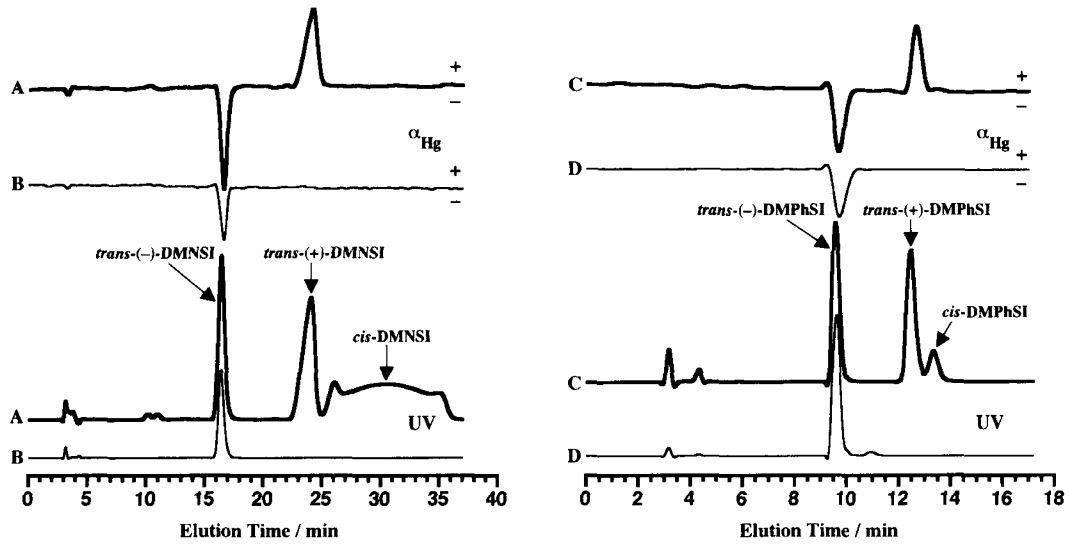

Figure 1. HPLC chromatograms of *trans*-DMNSI (left) and *trans*-DMPhSI (right) before (A, C) and after (B, D) resolution. Top and bottom curves were monitored by polarimetric and UV detectors, respectively.

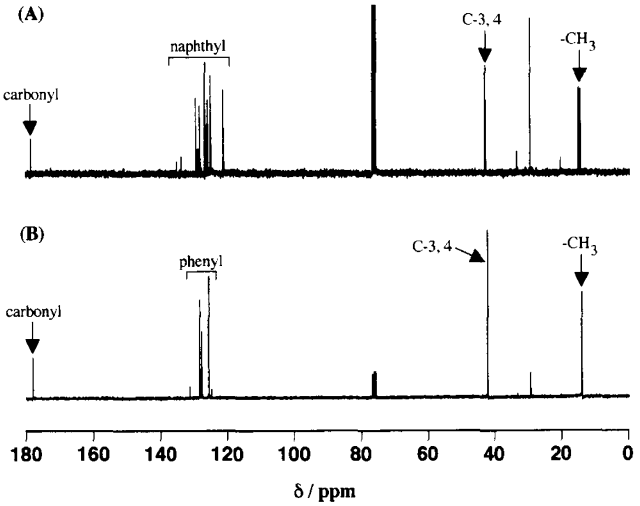

Figure 2. ^{13}C NMR spectra of resolved model compounds: (A) *trans*-(−)-DMNSI; (B) *trans*-(−)-DMPhSI in $CDCl_3$.

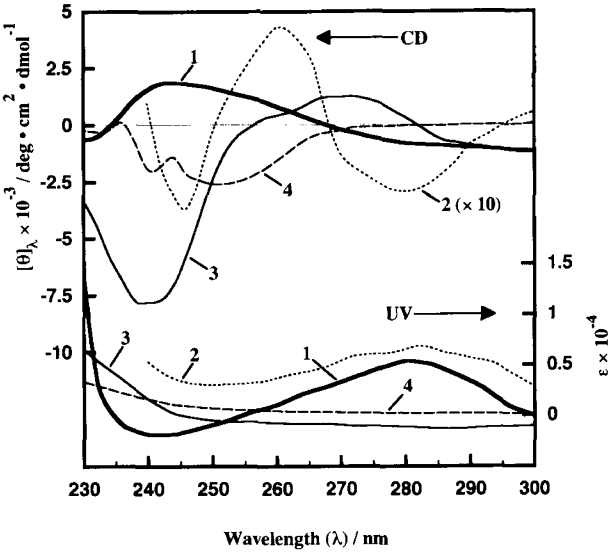

Figure 3. CD (top) and UV (bottom) spectra of *trans*-(−)-DMNSI (1), poly(1-NMI) (2, $[\alpha]_{435}$ −20.0°) *trans*-(−)-DMPhSI (3), and poly-(PhMI) (4, $[\alpha]_{435}$ −37.6°) in THF.

Each *trans* compound mixture was resolved by HPLC with CHIRALPAK AD to evaluate the properties of pure *trans* compound. Figure 1 shows HPLC chromatograms before (A, C) and after (B, D) resolution for *trans*-DMNSI and *trans*-DMPhSI recorded by UV and polarimetric (α_{Hg}) detector. Chromatogram of *cis*-DMNSI exhibited broad peaks because of conformers. For both model compounds, only *trans*-(−)-isomers could be isolated in pure form. Specific optical rotations ($[\alpha]_{435}$) of the resolved *trans*-(−)-DMNSI and *trans*-(−)-DMPhSI were −126.7° and −127.6° (c = 0.7 g dL^{-1}, l = 10 cm, THF), respectively. These values were almost the same in spite of different structures of *N*-substituent, suggesting that magnitude of specific optical rotation for optically active poly-(RMI) is not affected by species of *N*-substituent.

Figure 2 shows ^{13}C NMR spectra of resolved-model compounds (A: *trans*-(−)-DMNSI, B: *trans*-(−)-DMPh SI) in $CDCl_3$. The peaks of carbons on 3- and 4-positions for model compounds were assigned to main-chain carbons for corresponding poly(RMI) having *threo-diisotactic* or *threo-disyndiotactic* structure. Two peaks due to methyl groups and two peaks due to 3- and 4-position carbons of *trans*-(−)-DMNSI appeared at 15.24, 15.74 ppm and 43.58, 43.72 ppm, respectively, because of conformational change induced by rotation of naphthyl groups. Signals due to naphthyl groups were more complicated. Judging from these results, peak positions of corresponding signals for poly(1-NMI) may depend not only on the main chain structure but conformation of naphthyl group as well. In the case of *trans*-(−)-DMPhSI, signals of methyl groups and 3- or 4-position carbons were observed as one peak at 14.86 ppm and 43.02 ppm, respectively. In an earlier work on *trans*-DMCHSI,[3,8] each signal was recognized as one peak (methyl: 15.04 ppm, C-3 and C-4: 42.70). This indicates that these signal patterns are not influenced by the rota-

tion of phenyl and cyclohexyl groups. That is, main chain signals for poly-(PhMI) and poly(CHMI) may be little affected by conformation of the *N*-substituent.

Figure 3 displays CD and UV spectra of resolved-model compounds (1: *trans*-(−)-DMNSI, 3: *trans*-(−)-DMPhSI) and corresponding polymers (2: poly(1-NMI), $[\alpha]_{435} = -20.0^\circ$, 4: poly(PhMI), $[\alpha]_{435} = -37.6^\circ$) in THF. In all spectra, CD peaks appeared at the range of UV absorption band due to π-π^* and n-π^* transitions. Compared with the model compound and corresponding polymer, UV curves were similar, but CD curves were extremely different in spite of the same sign of specific optical rotation, suggesting that chirality of the model compounds was affected by substituents bonding to asymmetric carbons of 3- and 4-positions of imide ring. That is, to clarify the optical property of poly(RMI) in detail, model compounds having more suitable structure are desired. Further studies on this point are in progress.

REFERENCES

1. T. Oishi, H. Yamasaki, and M. Fujimoto, *Polym. J.*, **23**, 795 (1991).
2. Y. Okamoto, T. Nakano, H. Kobayashi, and K. Hatada, *Polym. Bull.*, **25**, 5 (1991).
3. K. Onimura, H. Tsutsumi, and T. Oishi, *Polym. Bull.*, **39**, 437 (1997).
4. K. Onimura, H. Tsutsumi, and T. Oishi, *Macromolecules*, **31**, 5971 (1998).
5. K. Onimura, H. Tsutsumi, and T. Oishi, *Chem. Lett.*, 791 (1998).
6. T. Oishi, K. Onimura, Y. Isobe, H. Yanagihara, and H. Tsutsumi, *J. Polym. Sci., Part A: Polym. Chem.*, **38**, 310 (2000).
7. K. G. Olson and G. B. Butler, *Macromolecules*, **17**, 2480 (1984).
8. T. Oishi, K. Fujii, K. Onimura, and H. Tsutsumi, *Kobunshi Ronbunshu*, **54**, 914 (1997).
9. T. Oishi, K. Onimura, Y. Isobe, and H. Tsutsumi, *Chem. Lett.*, 673 (1999).