

SYNTHESIS OF CHIRAL BINAPHTHYL CROWN ETHERS AND THEIR USE IN ANIONIC POLYMERIZATION OF METHYL METHACRYLATE AS INITIATOR LIGANDS*

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Abstract Some chiral binaphthyl crown ethers were synthesized. The anionic polymerization of methyl methacrylate (MMA) was carried out in the presence of *t*-BuOK, Ph₂CHK or Ph₂CHNa (RM), and RM coordination initiator by using chiral binaphthyl crown ethers as ligands, respectively. The results showed that in the former case the PMMA obtained has mainly isotactic structure but without optical activity, while in the later case the PMMA produced predominately has syndiotactic structure also without optical activity.

Key words Chiral binaphthyl crown ether, MMA, Anionic polymerization

INTRODUCTION

Anionic polymerization of MMA could be carried out with alkylolithium or Grignard reagent *etc.* in a non-polar solvent. However, this polymerization system often involves multiple active species and side reactions depending on initiator, counteraction, solvent and polymerization temperature *etc.* Therefore, the molecular weight distribution and stereomicrostructure of PMMA obtained would be very different^[1–4]. These differences would be mainly caused by the nucleophilic attack of the active species on the carbonyl group of the monomer and the polymer sub-unit chain. The reactivity of anionic species could be modulated by coordination of very active alkyl alkali metal with ligands to form ion pairs which might be very beneficial for the initiation of monomer and propagation of polymer chains^[5]. To date the efficient ligands discovered have been classified into three groups: (1) μ -coordinating ligands mainly alkali metal alkoxides *etc.*^[6], (2) σ -type ligands of the crown ether type^[7] and (3) μ/σ -type dual ligands as exemplified by polyether metal alkoxide^[8]. Numerous studies related to anionic polymerization of MMA have been done by some researchers using a series of ligands, even optically active ligands, to control the polymerization of PMMA having higher stereoregularity, narrow molecular weight distribution and optical activity^[9–11]. The present paper is directed towards these problems. The anionic polymerization of MMA was studied by using type 2 and type 3 ligands, *i.e.* optically active ligands with chiral host binaphthyl crown ethers and organometal compounds as initiators.

EXPERIMENTAL

The structure of several chiral binaphthyl crown ethers selected for this work is depicted in Fig. 1.

Materials

According to the method reported by Cai and co-worker^[12] (*S,R*)-($\pm$)-2,2'-Dihydroxy-1,1'-binaphthyl

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MS: (m/z) Fab 488 $[M]^+$, 511 $[M + Na]^+$; Elemental anal. of (*S*)-NE-6, Calcd. For $C_{30}H_{32}O_6$ (%): C 73.74, H 6.61. Found (%): C 73.48, H 6.67.

(*R*)-3,3'-Dimethyl-binaphthyl-20-crown-6 [(*R*)-MNE-6]^{16l}

(*R*)-2,2'-Di(methyletheroxy)-1,1'-binaphthalene (*R*-1)

NaH (2 g, 83 mmol) was added to a solution of (*R*)-BINOL (10 g, 35 mmol) in dried THF (200 mL) under nitrogen with stirring, and then refluxed for 0.5 h. After cooling to room temperature chloromethyl ether (18 g, 223 mmol) was added and stirred for 20 h, then filtered and concentrated under reduced pressure. The product was shaken with water and $CHCl_3$, respectively, several times and the organic layer was washed with brine, dried over anhydrous sodium sulfate and then concentrated under reduced pressure. The residue was purified by silica gel adsorption chromatograph with acetone-petroleum ether (b.p. range 60–90°C) (1:15, *V/V*) as elute to get (*R*)-2,2'-di-(methyletheroxy)-1,1'-binaphthalene (*R*-1) (8 g, 61%). ^1H -NMR (200 MHz, $CDCl_3$): δ 3.17 (s, 6H, $-OCH_3$), 4.96 (d, 2H, $-OCH_2$), 5.06 (d, 2H, $-OCH_2$), 7.12–7.38 (m, 6H, ArH), 7.54 (d, 2H, ArH) and 7.84–7.98 (d, 4H, ArH).

(*R*)-3,3'-Dimethyl-2,2'-dihydroxy-1,1'-binaphthalene (*R*-2)

A solution of *R*-1 (7.5 g, 20 mmol) in dried THF (130 mL) was cooled to 0°C in an ice-water bath under nitrogen. *n*-BuLi in hexane (2.3 mol/L, 30 mL) was added to the above solution by syringe and stirred for 1.5 h at 0°C. The reaction mixture was warmed to room temperature and dimethyl sulfate (10 mL) was added to the solution and stirred for 12 h. Then an aqueous solution of sodium hydrogen carbonate (1 mol/L, 5 mL) was added and the solvent evaporated off under reduced pressure. Dichloromethane (80 mL) was added to the residue which was washed with brine three times. Methanol (80 mL) and concentrated hydrochloric acid (6 mL) were added to the mixture and stirred for 3 h. After concentration under reduced pressure, the crude product was purified by silica gel adsorption chromatograph using a method similar to that in the preparation of *R*-1 to obtain (*R*)-3,3'-dimethyl-2,2'-dihydroxy-1,1'-binaphthalene (*R*-2) (4.5 g, 72%) with m.p. 205–206°C, $[\alpha]_D^{25} = +36.4^\circ$ (c, 1, $CHCl_3$). ^1H -NMR (200 MHz, $CDCl_3$): δ 2.51 (s, 6H, $-CH_3$), 5.12 (br, s, 2H, $-OH$), 7.04 (d, 2H, ArH), 7.18–7.38 (d, 6H, ArH) and 7.78 (d, 2H, ArH).

(*R*)-3,3'-Dimethyl-binaphthyl-20-crown-6 [(*R*)-MNE-6]

To a stirred mixture of *R*-2 (2.33 g, 7.42 mmol), dried THF (140 mL) and *t*-BuOK (1.7 g, 15.2 mmol) were added a solution of pentaethylene glycol di-*p*-toluene sulfonate (4.1 g, 75 mmol) in THF (10 mL) dropwise under nitrogen. After refluxing for 6h, it was treated similarly by the method used for preparing *R*-2. The product was purified by silica gel adsorption chromatography with acetone-petroleum ether (b.p. range 60–90°C) (1:10, *V/V*) as eluent to get (*R*)-3,3'-dimethyl-binaphthyl-20-crown-6 [(*R*)-MNE-6] (1.8 g, 47%). MALDI-TOF MS (m/z): Calcd. for $C_{32}H_{36}O_6$ (%); 516.63, Found (%). 516.32 $[M]^+$; 539.31 $[M + Na]^+$, 555.29 $[M + K]^+$.

(*S*)- and (*R*)-2,2'-Di-binaphthyl-28-crown-8 [(*S*)- and (*R*)-DNE-8]

(*S*)- and (*R*)-DNE-8 could be prepared from triethylene glycol ditoluene sulfonate according to the previous method used for the preparation of [(*S*)- and (*R*)-NE-6], respectively, and the yield of final products was 55% and 58%, respectively. ^1H -NMR (300 MHz, $CDCl_3$): δ 3.18–3.46 (m, 16H, $-OCH_2$), 3.99–4.16 (m, 8H, $-OCH_2$), 7.11–7.33 (m, 12H, ArH), 7.44 (d, 4H, ArH), 7.85 (d, 4H, ArH) and 7.92 (d, 4H, ArH); MALDI-TOF MS (m/z): Fab 800 $[M]^+$, 823 $[M + Na]^+$.

(*S*)- and (*R*)-2,2'-Di-binaphthyl-34-crown-10 [(*S*)- and (*R*)-DNE-10]

(*S*)- and (*R*)-DNE-10 could be prepared from tetraethylene glycol di-*p*-toluene sulfonate according to the previous method for preparing (*S*)- and (*R*)-NE-6 and the yield of the products was 45% and 50%, respectively. ^1H -NMR (300 MHz, $CDCl_3$): δ 3.18–3.51 (m, 24H, $-OCH_2$), 4.03–4.15 (m, 8H, $-OCH_2$), 7.12–7.33 (m, 12H, ArH), 7.42 (d, 4H, ArH), 7.83 (d, 4H, ArH) and 7.9 (d, 4H, ArH); MALDI-TOF (m/z): Fab 888 $[M]^+$, 911 $[M + Na]^+$; Elemental anal. for (*R*)-DNE-10: Calcd: for $C_{56}H_{56}O_{10}$ (%) : C 75.64, H 6.75. Found (%): C 75.34, H 6.24.

Polymerization

Representative procedure for the polymerization is exemplified as following: to an efficiently dried polymerization tube was added (*S*)-NE-6 (100 mg, 0.20 mmol), *t*-BuOK (22 mg, 0.20 mmol) and toluene (10 mL) under dried nitrogen. Then the solution was cooled to -78°C with stirring. To the above solution was added MMA (1.0 mL, 9.3 mmol) by syringe and polymerized under a positive pressure of nitrogen for 24 h. The polymerization was stopped by adding a small amount of methanol, then the mixture was poured into a large excess of methanol. The precipitate was filtered, dried in vacuum at 50°C and weighed.

RESULTS AND DISCUSSION

Optically Active Feature of PMMA

Cram and Sogah^[9] reported that high isotactic oligo- and poly(methyl methacrylate) with high optical rotation ($[\alpha]_{\text{D}}^{25} + 250^{\circ}$) could be obtained by asymmetric polymerization of MMA with *t*-BuOK chiral binaphthyl crown ethers or *n*-BuLi chiral diamine complexes as complexed initiator in a mixture of toluene and THF at -78°C and their optical activities were ascribed to the helical structure of the oligomers and polymers. Kanoh *et al.*^[17] have reported the polymerization of methyl methacrylate with complexes of *n*-BuLi and chiral diamine complexes as complexed initiator (similar to Cram's) and the results obtained are not in agreement with Cram's. In addition, a series of papers published by Okamoto *et al.* indicated that the ester group of methyl methacrylate is not bulky enough to maintain a helical structure to result in the optical activity of PMMA^[10, 18]. There is another example: the specific rotations of the random copolymers of triphenylmethyl methacrylate (TrMA) and methyl methacrylate obtained by chirally anionic complexes as initiator in toluene at -78°C are only dependent on the TrMA content of copolymers and showed an S-type curve change in which the TrMA fraction with helical chain played the crucial role and not the PMMA segment fraction^[19]. In general, the specific rotation of PTrMA stored in THF for 60 days could remain unchanged^[20]. But the specific rotations of two block copolymers [poly(TrMA-*b*-MMA)] stored in THF at room temperature would gradually decrease with time caused by the thermal movement of the MMA segment of two block copolymers in solution^[21], and resulted in uncoiling (mutarotation) of the TrMA helix. In fact, PMMA with high isotactic structure obtained by *n*-BuLi and FILi as initiator at low temperature in toluene did not show any optical activity^[11, 22, 23], as illustrated in Table 1.

Table 1 High isotactic triad of PMMA obtained from various initiators^a

Initiators	Solvents (V/V)	Temperature ($^{\circ}\text{C}$)	Tacticity (%) ^b			$[\alpha]_{\text{D}}^{25\text{c}}$	Refs.
			mm	mr	rr		
<i>n</i> -BuLi	Toluene	-78	72.0	17.0	11.0	0°	[11]
FILi ^d	Toluene	-78	86.0	6.0	8.0	0°	[22]
FILi ^d	Toluene	-60	Mainly isotactic			0°	[23]
<i>t</i> -BuOK ^e	Toluene/THF (9/1)	-78	67.7	20.8	11.5	0°	This paper
Ph ₂ CHNa ^e	Toluene/THF (9/1)	-78	66.6	27.3	7.1	0°	This paper

^a Polymerization conditions: [MMA]/[Li] = 20 mol/mol, Solvent/monomer = 20 mL/g

^b Determined by ¹H-NMR methyl chemical shifts in polymer backbone: mm, isotactic δ 1.20; mr, heterotactic δ 1.02; rr, syndiotactic δ 0.83

^c $[\alpha]_{\text{D}}^{25}$: specific rotation

^d FILi: 9-fluorenyllithium

^e Polymerization conditions: [MMA]/[M] = 46 mol/mol; solvent/monomer = 10 mL/g

Here is another example: a highly isotactic PMMA was derived from the original polymer, PTrMA with high isotacticity and optical rotation $[\alpha]_{\text{D}}^{25}$ 350° (c 0.5, THF), by hydrolysis with CH₃OH-H₂SO₄ followed by methylation with CH₂N₂. The polymer (PMMA) thus obtained has an isotactic structure with triad distribution of mm/mr/rr = 84/10/6 but with no optical activity^[24]. Therefore, it was confirmed further that PMMA with high isotacticity will not show optical activity.

Stereo-Microstructure of PMMA

Anionic polymerizations of methyl methacrylate have been reported in many references. To improve this polymerization system, crown ether macrocyclic compounds have been used as efficient ligands for preparing stable alkali metal solution in low dielectric constant solvents. Kaempf *et al.*^[25] studied the effect of dicyclohexyl-18-crown-6 (DCHE) on the solubility of alkali metals Na⁺, K⁺, Rb⁺ and Cs⁺ in benzene as DCHE/M⁺ initiating polymerization of MMA. The PMMAs obtained have mainly syndiotactic structure (48%–62%). Boileau *et al.*^[25] also reported that the PMMA obtained by the coordination of lithium naphthalene (N-Li), sodium naphthalene (N-Na) and potassium naphthalene (N-K) with macroheterobicycles (Cryptates), respectively, would have mainly syndiotactic structure also. However, Cram's results indicated that the complexes with chiral host of the crown ethers containing one or two binaphthyl units with alkali metal as an anionic initiators would produce highly isotactic PMMA. In order to verify directly the previous results we carried out the anionic polymerization of MMA in the presence of *t*-BuOK, Ph₂CHK and chiral binaphthyl crown ethers, (*S*)-NE-6, (*R*)-MNE-6, (*S*)-DNE-8, (*S*)-DNE-10 and (*R*)-DNE-10 (Fig. 1) as a pairing coordination initiators, respectively. These results are shown in Table 2.

Table 2. Anionic polymerization of MMA at –78 °C for 18 h in some solvents^a

Run	C.I (M.R) ^b	[C.I] (mmol)	[M]/[C.I] ^c (%) ^d	Yield (%)	<i>M_w</i> (10 ⁴) (g/mol)	<i>M_n</i> (10 ⁴) (g/mol)	<i>M_w</i> / <i>M_n</i>	Tacticity		
								mm	mr	rr
1	<i>t</i> -BuOK(0/1)	7.7	46.0	10	16.0	12.0	1.35	67.7	20.8	11.5
2	(<i>S</i>)-NE-6/ <i>t</i> -BuOK(1/1)	7.7	94.0	96	9.5	8.6	1.10	6.3	34.9	58.8
3	(<i>R</i>)-MNE-6/ <i>t</i> -BuOK(1/1)	15.4	47.0	~100	5.4	4.4	1.22	4.8	27.8	67.4
4	(<i>S</i>)-DNE-8/ <i>t</i> -BuOK(1/1)	7.7	94.0	~99	6.1	5.3	1.15	7.9	30.4	61.7
5	(<i>S</i>)-DNE-10/ <i>t</i> -BuOK(1/1)	7.7	94.0	~100	4.3	2.6	1.64	7.7	30.9	61.4
6	Ph ₂ CHK (0/1)	7.6	98.0	~100	12.1	9.0	1.34	–	–	–
7	(<i>R</i>)-NE-6/ Ph ₂ CHK(1/1)	6.0	62.0	~100	6.9	4.6	1.48	9.5	30.3	60.2
8	(<i>R</i>)-MNE-6/ Ph ₂ CHK(1/1)	7.6	49.0	~100	4.5	3.4	1.31	5.2	26.2	68.6
9	(<i>R</i>)-DNE-10/ Ph ₂ CHK(1/1)	6.0	62.0	~100	4.8	3.9	1.22	9.5	31.2	59.

^a Run. 1 and 6: Toluene/THF(9/1); Run. 2, 3, 4, 5, 7, 8, and 9: Toluene

^b [C.I]: Complexed Initiator; M.R.: Molar ratio

^c [M]/[C.I.]: Molar concentration ratio between monomer and initiator

^d Determined from ¹H-NMR methyl chemical shifts in polymer backbone: mm, isotactic δ 1.20; mr, heterotactic δ 1.02; rr, syndiotactic δ 0.83

It can be seen from Table 2 that the molecular weight of PMMA obtained by using *t*-BuOK and Ph₂CHK as anionic initiators is higher than that of other PMMAs obtained by anionic initiators having as chiral host the crown ethers containing one or two binaphthyl units complexed with alkali metals, but their molecular weight distributions (MWD) are somewhat broader. It could be caused by higher initiating activity of *t*-BuOK and Ph₂CHK. In addition, it can also be seen from Table 2 that the PMMAs obtained in the presence of anionic initiators with chiral host crown ethers containing one or two binaphthyl units complexed with alkali metal have predominantly syndiotactic structure. Hence, Cram's conclusions might be premature. Vigmer *et al.*^[26] also reported that in the presence crown ether group with chirality or nonchirality as chelating agents the microstructure of PMMA prepared by the complexed alkoxides was predominantly syndiotactic which is consistent with the reactivity of the complexed ion pairs observed in the propagation step. It is caused by the formation of crown-separated ion pairs in equilibrium with free ions. Because the encircled M⁺ (such as K, Na and Li) is the cation captured by the crown ether, the “naked anions” are expected to exert higher reactivity in the

nucleophilic addition to vinyl monomer than the RM initiator. The carboanion end group of the growing polymer chain is assumed to have a conformation, which may expose the carbocation to attack. This conformation is selected to permits that lowest degree of steric strain leading to the formation of a syndiotactic placement^[28–31]. Although Yasuda^[32] has described the mechanism of producing isotactic and syndiotactic PMMA by organo transition metal as initiator, the mechanism of forming isotactic or syndiotactic PMMA obtained from RM and RM/chiral binaphthyl crown ethers as coordinated initiators is still unclear.

REFERENCES

- 1 Allen, P.E.M., Fisher, M.C., Mair, C. and Williams, E.H., "Anionic Polymerization: Kinetics Mechanism Synthesis" ACS Symp. Ser., New York, N.Y., 1984, p.166
- 2 Hatada, K., Kitayama, T., Okahata, S. and Yuki, H., *Polymer J.* 1982, 14: 971
- 3 Matzuzaki, K., Tanaka, H. and Kanai, T., *Makromol. Chem.*, 1981, 182: 2905
- 4 Hatada, K., Ute, K., Tanaka, K., Okamoto, Y. and Kitayama, T., *Polymer J.* 1986, 18:103
- 5 Zundel, D.T., Teyssie, P. and Terome, R., *Macromolecules* 1998, 31: 2433
- 6 Dvoranek, L. and Vlcek, P., *Polym. Bull.*, 1993, 31: 393
- 7 Varshney, S.K., Jerome, R., Bayard, Ph., Jacobs, C., Fayt, R. and Teyssie, Ph., *Macromolecules*, 1992, 20: 1442
- 8 Nugay, N., Nugay, T., Jerome, R. and Teyssie, Ph., *J. Polym. Sci. Polym. Chem.*, 1997, 35, 361: 1543
- 9 Cram, D.J. and Sogah, D.Y., *J. Am. Chem. Soc.*, 1985, 107: 8301
- 10 Okamoto, Y., Suzuki, K., Ohta, K., Hatada, K. and Yuki, H., *J. Am. Chem. Soc.*, 1979, 101: 4763
- 11 Chen, C.F., Ren, C.Y. and Xi, F., *Chin. J. Polym. Sci.*, 1995, 13: 91
- 12 Cai, D.W., Hughes, D.L., Verhoeven, T.R. and Reider, P.J., *Tetrahedron Lett.*, 1995, 36: 7991
- 13 Dale, J. and Kristiansen, P.O., *Acta Chim. Scand.*, 1972, 26: 1471
- 14 Newcomb, M., Moore, S.S. and Cram, D.J., *J. Am. Chem. Soc.*, 1977, 99: 6405
- 15 Kyba, E.P., Helgeson, R.C., Madan, K., Gokel, G.W., Tarnowski, T.L., Moore, S.S. and Cram, D.J., *J. Am. Chem. Soc.*, 1977, 99: 2564
- 16 Peacock, S.S., Walba, D.M., Gaeta, F.C.A., Helgeson, R.C. and Cram, D.J., *J. Am. Chem. Soc.*, 1980, 102: 2043
- 17 Kanoh, S., Kawaguchi, N., Sumino, T., Hongo, Y. and Suda, H., *J. Polym. Sci., Polym. Chem.*, 1987, 25: 1603
- 18 Okamoto, Y., Yashima, E., Nakano, T. and Hatada, K., *Chem. Lett.*, 1987, 759
- 19 Chen, C.F., Ren, C.Y. and Xi, F., *Acta Polymerica Sinica (in Chinese)*, 1995, 3: 337
- 20 Wang, Y.C., Ding, M.X., Luo, Y.X. and Wang, F.S., *J. Polym. Sci., Polym. Lett.*, 1989, 27: 475
- 21 Chen, C.F., Lui, W.H., Chen, Y.M., Ren, C.Y. and Xi, F., *Acta Polymerica Sinica (in Chinese)*, 1996, 1: 126
- 22 Yuki, H., Hatada, K. and Ohta, K., *Macromol. Sci.- Chem.*, 1975, A9 (6): 983
- 23 Nagai, H., *J. Appl. Polym. Sci.*, 1963, 7: 1697
- 24 Okamoto, Y., Mohri, H., Nakano, T. and Hatada, K., *Chirality*, 1991, 3: 277
- 25 Kaempt, B., Raynal, S., Collet, A., Schue, F., Boileau, S. and Lehn, J.M., *Angew. Chem.*, 1974, 13: 611
- 26 Boileau, S., Kaempt, B., Lehn, J.M. and Schue, F., *Polym. Lett. Ed.*, 1974, 12:203
- 27 Vigmer, M., Collet, A., Schue, F. and Mula, B., "Recent adv. anionic polymerization" in: "Proc. Int. Symp. 1986" ed. by Hogen-Esch, T.E. and Smid, J., New York, N.Y., Elsevier, 1987, p.249
- 28 Boilson, S., Kaempt, B., Lehu, J.M. and Schue, F., *J. Polym. Sci., Polym Lett.*, 1974, 12: 203
- 29 Kopolov, S., Hogen-Esch, T.E. and Smid, J., *Macromolecules*, 1973, 66: 133
- 30 Zundel, D.T., Teyssie, P. and Terome, R., *Macromolecules*, 1998, 31: 2433
- 31 Hatada, K., *J. Polym. Sci., Polym. Chem.*, 1999, 37: 245
- 32 Yasuda, H., *Catalysts and Catalysis*, 1999, 41(3): 178