Polymer Bulletin 22, 497–504 (1989)

Polymer Bulletin

Liquid crystalline polyethers based on conformational isomerism

8. Synthesis and determination of the virtual mesomorphic phase transitions of polyethers and copolyethers based on 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl) ethane and 1,14-dibromotetradecane

V. Percec and Y. Tsuda

Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106, USA

SUMMARY

The synthesis and determination of virtual mesomorphic phase transitions of the polyether based on 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl) ethane (MBPE) and 1,14-dibromotetradecane (MBPE-14) and of the copolyethers based on MBPE and 1,14-dibromotetradecane with 1,5-dibromopentane (MBPE-5/14) , 1,8-dibromooctane (MBPE-8/14) and 1,9-dibromononane (MBPE-9/14) are presented. The homopolymer MBPE-14 is only crystalline, while the copolymers display a monotropic (MBPE-5/14 and MBPE-9/14) or even an enantiotropic (MBPE-8/14) nematic mesophase. The averaged virtual isotropic-nematic transition temperature of MBPE-14 determined from these copolymers is 87 ± 7 °C (ΔH = 2.77 ± 0.21 kcal/mru).

INTRODUCTION

Previous publications from this series have advanced the concept of flexible or rod-like mesogenic units based on conformational isomerism (1-7). This concept was used in the synthesis of liquid crystalline polyethers without flexible spacers (1), and of liquid crystalline polyethers with flexible spacers (2-8). The most thoroughly investigated series of polyethers with flexible spacers is based on the flexible mesogenic unit 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl) ethane (MBPE) (2-7). Presently we are investigating the influence of spacer length on the phase behavior of this series of polyethers (MBPE-n). Polyethers based on odd spacers display two nematic mesophases which are either virtual or monotropic. Polyethers based on even spacers display a virtual nematic mesophase. MBPE-8 shows a very narrow enantiotropic nematic mesophase. A combination of DSC and X-ray scattering experiments demonstrated that the nematic mesophase displayed by the odd polyethers and the one by the even polyethers is a classic Nu nematic (8, 9). No definitive assignment of the second nematic phase is yet available (8, 9). These virtual mesomorphic transition temperatures and their associated enthalpy changes were determined from copolymerization experiments (2-7).

The goal of this paper is to describe the synthesis of the polyether based on MBPE and 1,14-dibromotetradecane (MBPE-14) and determine its virtual phase transition temperature and enthalpy change from copolymerization experiments of MBPE and 1,14-dibromotetradecane with 1,5-dibromopentane, 1,9-dibromononane and 1,8-dibromooctane.

EXPERIMENTAL

Materials

1,5-Dibromopentane (97% from Aldrich) was fractionated by vacuum distillation. 1,7-dibromoheptane (97% from Aldrich), 1,9-dibromononane (97% from Aldrich) and 1,8-dibromooctane (98% from Aldrich) were used as received.

1,14-Tetradecanediol. A solution of 10.0 g (0.039 mol) of 1,14-tetradecanedioic acid (98% from Fluka) in 150 ml of $LiAlH_4$ dried THF, was added dropwise under nitrogen to 145 ml (0.145 mol) of BH_3-THF complex (1 M from Aldrich) at 0-5 °C. The temperature was raised to 50 °C and the reaction mixture was stirred overnight, after which it was poured into 2.5 l of water. The white precipitate was filtered and washed with water, $NaHCO_3$ and water. After drying the compound was recrystallized from benzene to yield 7.5g (84%) of white crystals. mp = 89 °C (ref 10, mp = 84.8 °C). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.26 (m, 20H, -($C\underline{H}_2$)$_{10}$-), 1.55 (m, 4H, $HOCH_2C\underline{H}_2$-), 3.64 (t, 4H, $HOCH_2C\underline{H}_2$-).

1,14-Dibromotetradecane. Bromine (10.5 g, 0.066 mol) was added dropwise under nitrogen to an ice cooled (0-10 °C) solution of 17.3 g (0.066 mol) of triphenylphosphine in 120 ml of dried DMF. To the resulting orange solution was added dropwise a solution of 7.2 g (0.031 mol) of 1,14-tetradecanediol in 120 ml of dried DMF, and the reaction mixture was stirred at 50 °C overnight. The reaction mixture was poured into 1 l of water and the white precipitate was filtered, washed with water and dried. Then it was extracted twice with 200 ml of hexane and the white insoluble solid (Ph_3PO) was filtered. Hexane was removed in a rotary evaporator and the residue was recrystallized from methanol to yield 9.8 g (88%) of white crystals. mp = 50 °C (lit 10, mp = 50.4 °C). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.26 (m, 20H, -($C\underline{H}_2$)$_{10}$-), 1.85 (quintet, 4H, $BrCH_2C\underline{H}_2$-), 3.41 (t, 4H, $BrC\underline{H}_2CH_2$-). -CH_2OH group could not be detected by NMR analysis.

1-(4-Hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (MBPE) (100% purity by HPLC) was synthesized as previously reported (2).

Techniques.

All analytical techniques used were described previously (2-6).

Synthesis of Polyethers and Copolyethers.

Both polyethers and copolyethers were synthesized and purified as described in previous publications (2-6).

The molecular weight of MBPE-8 synthesized previously (4, 5) was only Mn = 10,400. Mn increases (Mn ≈ 30,000) when a longer reaction time was used, i. e, 9 hrs instead of 6 hrs. Therefore, MBPE-8 used in all present calculations is based on the new sample described in Table II.

RESULTS AND DISCUSSION

Figure 1a and b presents the heating and cooling DSC scans for the copolymer system MBPE-8/14. MBPE-8 displays a very narrow enantiotropic nematic mesophase (4, 5). MBPE-14 is only crystalline. Upon copolymerization, the isotropic-nematic and nematic-crystalline transitions of MBPE-8 get well separated (Figure 1b). Copolymers MBPE-8/14 (90/10) to MBPE-8/14 (20/80) display well defined isotropization and crystallization peaks.

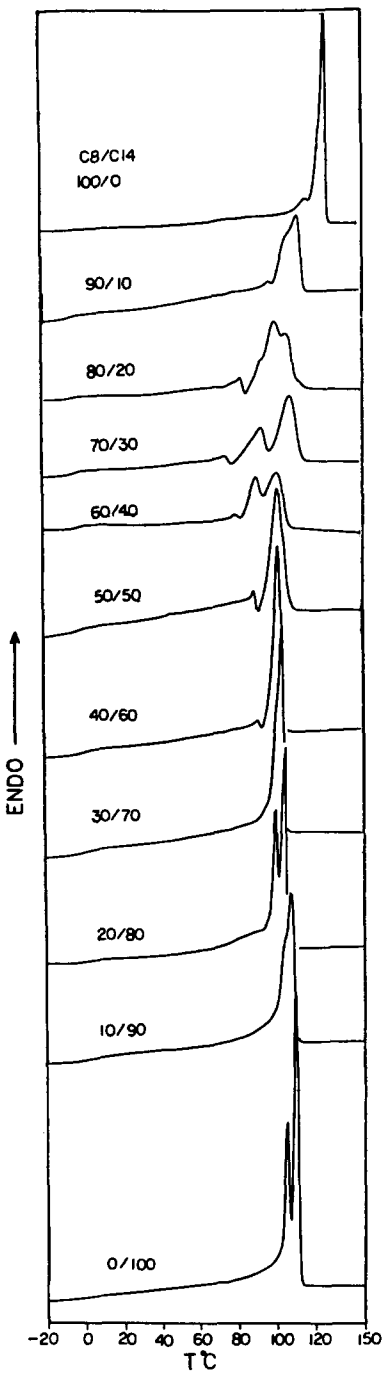

Figure 1a: Second heating DSC traces of MBPE-8/14 (20°C/min)

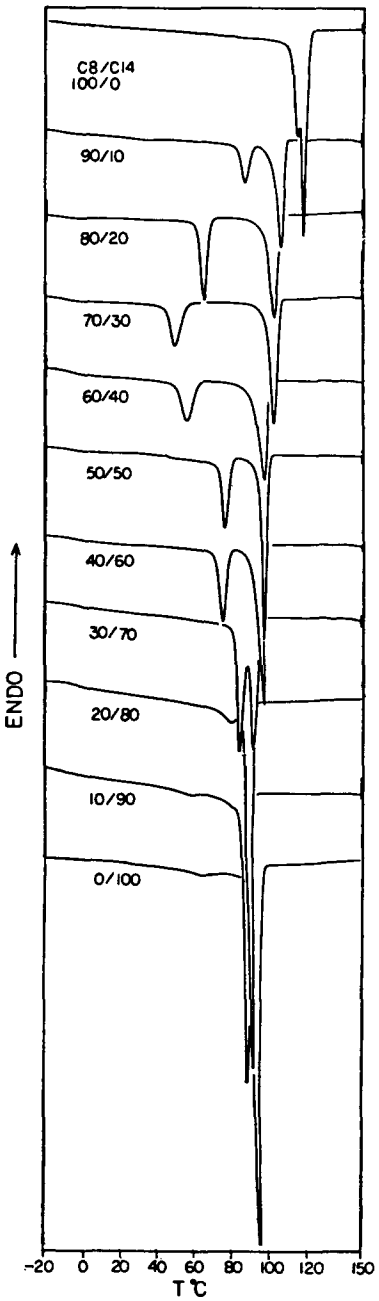

Figure 1b: Cooling DSC traces (20°C/min) of MBPE-8/14

On the heating DSC scans the nematic mesophase can be separated only for the polymers MBPE-8 to MBPE-8/14 (60/40) (Figure 1a). The assignment of all these phase transitions is summarized in Table I. The isotropic-nematic transition temperatures and their corresponding enthalpy changes are plotted in Figure 2. The virtual isotropic-nematic transition temperature and enthalpy change of MBPE-14 were determined by extrapolation.

Table I Characterization of Polyethers based on MBPE and 1,8-dibromooctane (MBPE-8), MBPE and 1,14-dibromotetradecane (MBPE-14) and of Corresponding Copolyethers [MBPE-8/14 (A/B)]

Copolymer MBPE-8/14 (A/B) 8/14 Mole Ratio	Mn GPC	Mw/Mn	Thermal transition (°C), and corresponding enthalpy changes (Kcal/mru) in parentheses Heating	Cooling
100/0	29,400	2.05	k 122 n 132(3.81*)i	i 119(3.53*) n 116 k
90/10	14,100	1.70	g -5 k 100(0.03) n 116 (2.56)i	i 107(2.18) n 87(1.08)k -8 g
80/20	14,000	2.03	g -5 k 85(0.29) k 104 n 111(4.01*)	i 102(2.25) n 65(1.25)k -8 g
70/30	21,200	1.92	g -4 k 77(0.17) k 96 n 112(3.84*) i	i 104(2.45) n 50(1.10) k -8 g
60/40	17,900	1.97	g -1 k 82 k93(0.05) n105(3.10*) i	i 97(2.44) n 56(1.12) k -2 g
50/50	19,700	1.90	g -2 k 91 (0.16) k 104(3.91) i	i 98(2.52) n 77(1.14) k -8 g
40/60	23,400	2.09	g 0 k 93(0.11) k 105(3.74) i	i 95(2.49) n 75(1.33) k -2 g
30/70	20,200	1.90	g 0 k 106(5.08) i	i 93(2.64*) n 85(2.45*) k -2 g
20/80	12,600	2.06	g 2 k 102 k 107(6.01*) i	i 89(4.85) k -5 g
10/90	32,900	1.89	g 3 k 110(5.96) i	i 89(5.13) k 0 g
0/100	17,900	1.66	g k 108* k 114(7.38*) i	i 96(6.59) k

* overlapping transition

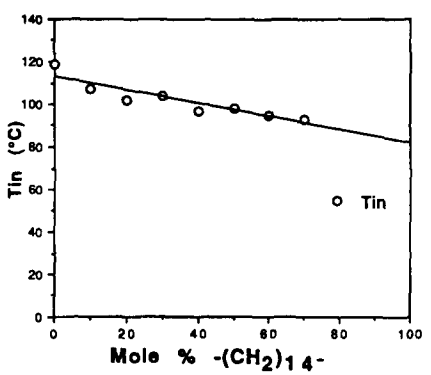

Figure 2a : Thermal transitions of MBPE-8/14

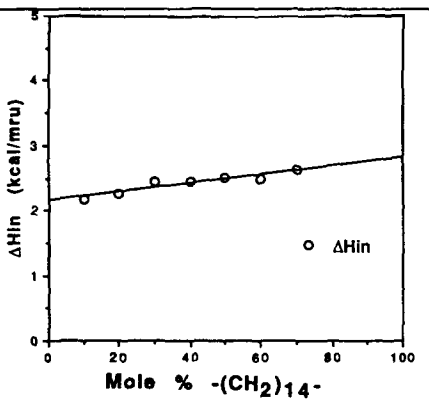

Figure 2b : Entalpy changes associated with phase transitions of MBPE-8/14

Figure 3a and b presents the DSC traces of the copolymer system MBPE-9/14. MBPE-9 displays a monotropic nematic mesophase at 69 °C, a second monotropic nematic mesophase at 58 °C and a crystallization peak at 48 °C (Figure 3b) (8, 9, 11). Upon copolymerization, the phase transition temperatures of MBPE-9 get first better separation, then the nematic-nematic peak disappears. The first nematic mesophase of these copolymers shows a linear dependence of composition, suggesting that the structural units of the copolymers are isomorphic in the first nematic phase but not in the second nematic or crystalline phases (Figure 3b). Table II summarizes all characterization data for MBPE-9/14 copolymers. The transition temperature and enthalpy change associated with the virtual nematic mesophase of MBPE-14 were determined by extrapolation.

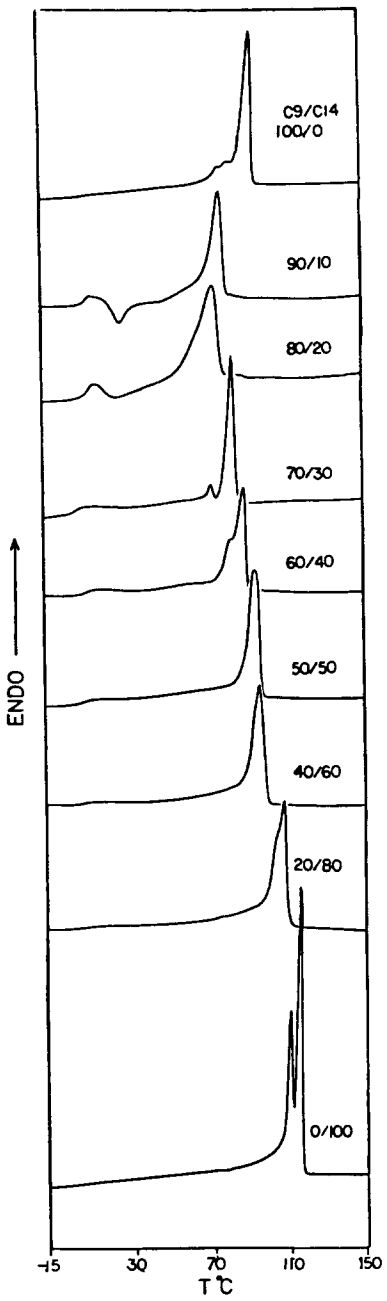

Figure 3a: Second heating DSC traces (20°C/min) of MBPE-9/14

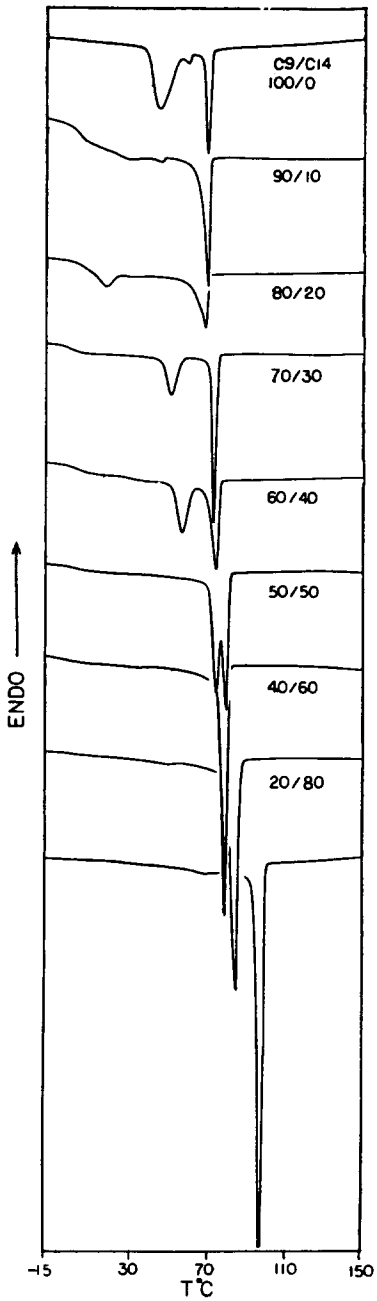

Figure 3b: Cooling DSC traces (20°C/min) of MBPE-9/14

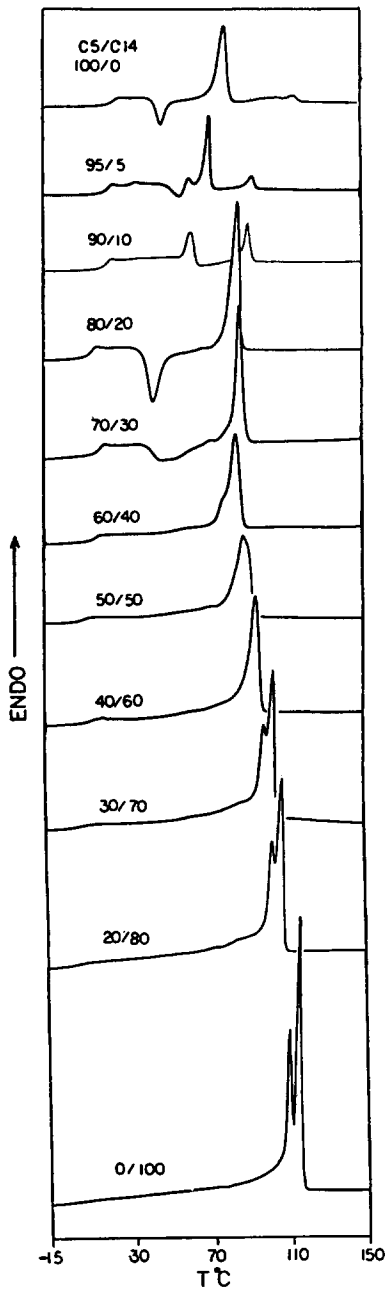

Figure 4a: Second heating DSC traces (20°C/min) of MBPE-5/14

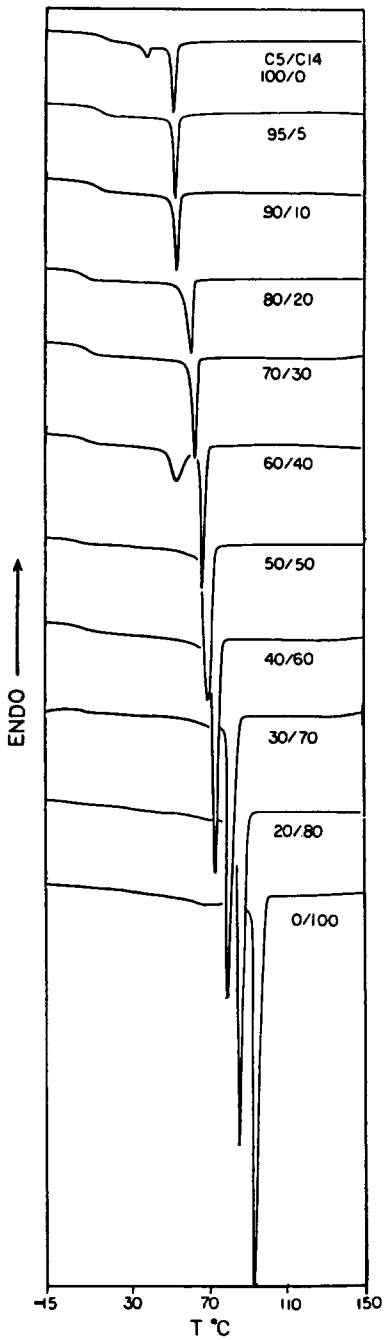

Figure 4b: Cooling DSC traces (20°C/min) of MBPE-5/14

Table II Characterization of Polyethers based on MBPE and 1,9-dibromononane (MBPE-9), MBPE and 1,14-dibromotetradecane (MBPE-14) and of Corresponding Copolyethers [MBPE-9/14 (A/B)]

Copolymer MBPE-9/14 (A/B) 9/14 Mole Ratio	Mn GPC	Mw/Mn	Thermal transition (°C), and corresponding enthalpy changes (Kcal/mru) in parentheses Heating	Cooling
100/0	20,600	1.38	g 6 k 75 k 80 k 91(2.67) i	i 69(1.05) n_1 58(0.06) n_2 48(2.13) k 0 g
90/10	17,900	1.70	g 6 k 75(3.32) i	i 68(1.19) n_1 0 g
80/20	18,800	1.93	g -1 k (2.66)71 i	i 67(1.24) n_1 16(0.33) k -2 g
70/30	27,600	1.89	g 2 k 71(0.12) k 82(2.48) i	i 72(1.70) n_1 50(0.81) k -2 g
60/40	14,900	2.32	g 6 k 78 k 86(2.97*) i	i 73(1.83) n_1 55(1.34) k 3 g
50/50	17,500	1.96	g 3 k 92(3.38) i	i 78(1.87) n_1 73(2.39) k 1 g
40/60	19,400	2.75	g 3 k 95(4.06) i	i 77(3.65) k 3 g
20/80	17,600	2.78	g 4 k 106(3.94) i	i 83(4.26) k -1 g
0/100	17,900	1.66	k 108 k 114(7.38*) i	i 96(6.59) k

* overlapping transition

Finally, DSC traces of the copolymer MBPE-5/14 are presented in Figure 4a and b. Their interpretation is summarized in Table III . MBPE-5 displays a first monotropic nematic transition at 51 °C (2-4, 9) and a second monotropic nematic-nematic transition at 37 °C (Figure 4b). Copolymers MBPE-5/14 from MBPE-5 to MBPE-5/14 (60/40) display only the first monotropic nematic mesophase. The transition temperatures of this monotropic nematic phase and its associated enthalpy change were used to determine the transition temperature of the first virtual mesophase and enthalpy change of MBPE-14.

Table IV summarizes the virtual isotropic-nematic phase transition temperature and its associated enthalpy change of MBPE-14 determined from these copolymerization experiments as well as the averaged values.

Table III Characterization of Polyethers based on MBPE and 1,5-dibromopentane (MBPE-5), MBPE and 1,14-dibromotetradecane (MBPE-14) and of Corresponding Copolyethers [MBPE-5/14 (A/B)]

Copolymer MBPE-5/14 (A/B) 5/14 Mole Ratio	Mn GPC	Mw/Mn	Thermal transition (° C), and corresponding enthalpy changes (Kcal/mru) in parentheses Heating	Cooling
100/0	19,000	1.90	g 20 k 79(1.44) k 115(0.33) i	i 51(0.57) n_1 37(0.10) n_2 13 g
95/5	16,500	1.86	g 18 k 60(0.12) k 70(0.70) k 93(0.15) i	i 53(0.69) n_1 13 g
90/10	16,500	1.79	g 17 k 61(0.45) k 90(0.48) i	i 53(0.70) n_1 10 g
80/20	17,200	1.69	g 9 k 85(2.74) i	i 60(0.94) n_1 4 g
70/30	22,800	1.86	g 13 k 87(2.15)i	i 63(1.05) n_1 6 g
60/40	22,000	1.78	g 10 k 85(2.35) i	i 68(1.44) n_1 53(0.93) k 5 g
50/50	17,700	1.71	g 4 k 88(2.53) i	i 69(2.87) k 1 g
40/60	23,000	2.13	g 8 k 94(3.13) i	i 73(3.06) k 4 g
30/70	16,100	1.91	g 6 k 92 k 102(4.78*) i	i 82(3.85) k 2 g
20/80	23,400	1.58	g 0 k 100 k 105(5.11*) i	i 86(4.56) k
0/100	17,900	1.66	k 108 k 114(7.38*) i	i 96(6.59) k

* overlapping transition

Table IV Virtual Phase Transition Temperatures and Thermodynamic Parameters[ ] of MBPE-14

MBPE-14	Thermal transitions(°C), and the corresponding enthalpy changes(kcal/mru) in parentheses cooling
determined from	
MBPE-5/14	i 96(6.59) k [94(2.56)] n
MBPE-8/14	i 96(6.59) k [82(2.83)] n
MBPE-9/14	i 96(6.59) k [85(2.92)] n
MBPE-14 (averaged)	i 96(6.59) k [87±7(0.21)] n

ACKNOWLEDGEMENTS

Financial support of this work by the National Science Foundation, Polymer Program (DMR-86-19724), is gratefully acknowledged.

REFERENCES

1) V. Percec and R. Yourd, Macromolecules, 21, 3379 (1988)
2) V. Percec and R. Yourd, Macromolecules, 22, 524 (1989)
3) V. Percec and R. Yourd, Macromolecules, 22, 3229 (1989)
4) V. Percec and R. Yourd, Makromol. Chem., in press
5) V. Percec and R. Yourd, Makromol. Chem., in press
6) V. Percec and Y. Tsuda, Macromolecules, in press
7) V. Percec and Y. Tsuda, Polym. Bull., submitted
8) G. Ungar, J. L. Feijoo, A. Keller, R. Yourd and V. Percec, Macromolecules, submitted
9) S. Z. D. Cheng, M. A. Yandrasits and V. Percec, Polymer, submitted
10) P. Chuit, Helv. Chim. Acta., 9, 271 (1929)
11) J. L. Feijoo, G. Ungar, A. J. Owen, A. Keller and V. Percec, Mol. Cryst. Liq. Cryst., 155, 487 (1988)

Accepted November 20, 1989 C