Macromolecules **1990,** *23,* 1556–1558

On the Characterization of Main-Chain Liquid-Crystalline Oligomers Based on *trans*-1,4-Cyclohexylene Di-*p*-hydroxybenzoate

M. M. GAUTHIER,[†] XI-JUN HONG,[‡] J. A. RATTO, A. BLUMSTEIN, AND R. B. BLUMSTEIN*

Polymer Science Program, Department of Chemistry, University of Lowell, Lowell, Massachusetts 01854.

Received March 30, 1989;
Revised Manuscript Received August 28, 1989

Introduction

Since they were first described by Roviello and Sirigu,[1] thermotropic main-chain liquid-crystalline polymers (LCPs) formed by condensation between mesogens and flexible spacers have been extensively investigated. The mesogens studied to date are, for the most part, fully aromatic and will not be addressed here. In the present note we describe synthesis and preliminary characterization of oligomers based on the mesogen *trans*-1,4-cyclohexylene di-*p*-hydroxybenzoate (TCHB), as part of an investigation of main-chain LCPs incorporating cycloaliphatic moieties.

The following low molecular mass nematic derivatives of TCHB have been described in the literature: *trans*-1,4-cyclohexylene dialkoxybenzoates $C_nH_{2n+1}OC_6H_4CO$-$OC_6H_8OCOC_6H_4OC_nH_{2n+1}$ (n = 1, 4, and 6)[2,3] and *trans*-1,4-cyclohexylene bis[(*p*-ethoxycarbonyl)oxy]benzoate.[4] Polyesters $\{OC_6H_4COOC_6H_8OCOC_6H_4OCO(CH_2)_nCO\}$ with spacer length n = 4–8 and 10 have recently been prepared by Braun and Schulke,[4] but the nature of the mesophase was not reported. Herein, we describe the same structures, designated as P-n, with spacer length n = 7, 8, and 10, and a novel series $\{OC_6H_4COO$-$C_6H_8OCOC_6H_4O(CH_2)_n\}$ designated as PE-n, with n = 5 and 7–12. In the P-n and PE-n series the linking group between mesogen and spacer is an ester, –OCO–, and an ether, –O–, respectively.

Experimental Section

Synthesis of Monomers. *trans*-1,4-Dihydroxycyclohexane (I). Compound I was prepared from commercially available *cis*/*trans*-1,4-dihydroxycyclohexane with a yield of 84% following the procedure in ref 5. Trans content: >98%, based on a mp of 140 °C[5] and ^1H NMR peak at 3.6 ppm in D_2O.

[(*p*-Ethoxycarbonyl)oxy]benzoic acid (II) was prepared as in ref 6 and transformed into **[(*p*-ethoxycarbonyl)oxy]benzoyl chloride (III)** by reaction with thionyl chloride following standard procedures.

***trans*-1,4-Cyclohexylene bis[(*p*-ethoxycarbonyl)oxy]benzoate (V)** was prepared from III and I in a manner similar to that described in ref 4. Yield: 85%. Heating transitions: K158.6 N194I.

***trans*-1,4-Cyclohexylene Di-*p*-hydroxybenzoate (TCHB).** Hydrolysis of compound Vto give TCHB was carried out as in ref 4. Yield: 75%. Mp: 317.7 °C (followed by decomposition). ΔH_{KI}: 32.2 cal/g.

The potassium salt of TCHB used in the preparation of polyethers was prepared using standard methods.[7]

Synthesis of Polymers. Polyesters, P-*n*. Synthesis was carried out by room-temperature interfacial condensation between TCHB and the acid chloride of the appropriate alkanedioic acid prepared as described previously.[8] A typical example is given for P-10: 6.0 mmol (2.146 g) of TCHB was dissolved in 34.0 mL of 0.5 N NaOH, together with 1.2 mmol (1.6038 g) of benzyltriethylammonium chloride. The reaction was carried out in a Waring blender following addition of 6.0 mmol of freshly distilled diacid chloride dissolved in 36.0 mL of dry 1,2-dichloroethane. The product was precipitated in methanol, washed with hot water, methanol, and ether, dissolved in chloroform, and reprecipitated into ethanol. After Soxhlet extraction with ethanol, it was dried in vacuo. Yield: 56%. The NMR spectra were run in $CDCl_3$ at room temperature (^1H and ^{13}C). Structural assignments were in agreement with ref 4.

Table I
Phase Transitions of P-*n* Polysters

n	η_{inh}[a]	$\bar{M}_n$[b]	$\bar{M}_w$[b]	transitions heating,[c] °C	 cooling,[d] °C	$-\Delta H_{IN}$, J/g
7	0.29	3000	3800	K222N249I K215N251I	I243N184K	7.3
8	0.25	2800	3400	K217N249I K219N260I	I242N185K	10.9
10	0.24	2500	3200	K205N223I	I220N186K	7.2

[a] Measured at 0.5 g/dL in 1,1,2,2-tetrachloroethane at 30 °C. [b] From GPC. [c] First and second heating scans. [d] First cooling scans.

Polyethers, PE-*n*. The syntheses were carried out by condensation of the potassium salt of TCBH with the appropriate α,ω-dibromoalkane. Literature procedures for polyetherification by phase-transfer catalysis[9,10] cannot be used, as TCBH hydrolyzes in the strongly alkaline medium required. A typical reaction was run as follows: 2.0 mmol (0.90 g) of the potassium salt of TCBH was suspended in 10 mL of dimethylformamide (DMF) and dissolved by raising the temperature to 70 °C. An excess (2.6 mmol) of 1,7-dibromoheptane was added and the contents of the flask stirred at 70 °C for 20 h. The product was precipitated into methanol, washed with hot water, methanol, and ether, extracted with ethanol for 24 h, dissolved in chloroform, and reprecipitated into methanol. Yield: 85%. The product was characterized by elemental analysis, IR, and ^1H and ^{13}C NMR. The chains were found to be end capped by bromoheptyl moieties, as expected.

Characterization of Polymers. The polymers were characterized by means of conventional approaches. Inherent viscosities were measured in 1,1,2,2-tetrachloroethane at 30 °C (0.5 g/dL). Gel permeation chromatography (GPC) was carried out in chloroform/ethanol (90/10, v/v), at a concentration of 0.25% (w/v), using Ultrastyragel columns of 5 × 10^2, 10^3, and 10^4 Å. A standard calibration curve of molecular weight versus elution volume was obtained with 17 well-characterized fractions of another main-chain polymer (poly(2,2′-dimethyl-4,4′-dioxyazoxybenzenedodecanedioyl), as described elsewhere.[11] Number average molecular weights of PE-*n* samples were also measured by end-group analysis of the bromoalkane chain ends using ^1H NMR in DMSO-d_6 and elemental analysis.

DSC scans were run using a Perkin-Elmer 2-C instrument with TADS-3600 microprocessor. Scanning rates were generally 20 K/min. Cooling scans were obtained following ca. 10 min of isothermal treatment some 15 °C above the isotropization temperature. TGA analysis and reproducibility of DSC scans suggest that samples remain thermally stable under these conditions. However, initial weight loss is detected in the vicinity of 280 °C. Thermogravimetric analysis (TGA) was performed using a Du Pont 951 thermogravimetric analyzer with a 1091 disk memory thermal analyzer (10 °/min under nitrogen). Polarizing microscopy was carried out on a Leitz Ortholux microscope with a Mettler FP-52 hot stage, and small-angle X-ray diffractograms were recorded as a function of temperature using a Rigaku diffractometer. WAX photographs were obtained at room temperature.

Results and Discussion

Properties of P-*n* polyesters are summarized in Table I, and a typical DSC scan is shown on Figure 1. Braun and Schulke reported somewhat higher transition temperatures, as expected from the slightly higher values of their inherent viscosities.[4] These authors did not disclose the nature of their mesophase nor the enthalpies of transitions. Optical microscopy performed on our samples indicates a nematic mesophase with a broad nem-

---

* To whom all correspondence should be addressed.

[†] Present address: Raytheon Company, Missile Systems Division, Tewksbury, MA 01876.

[‡] On leave from Institute of Organic Chemistry, Academia Sinica, Shanghai, People's Republic of China.

0024-9297/90/2223-1556$02.50/0

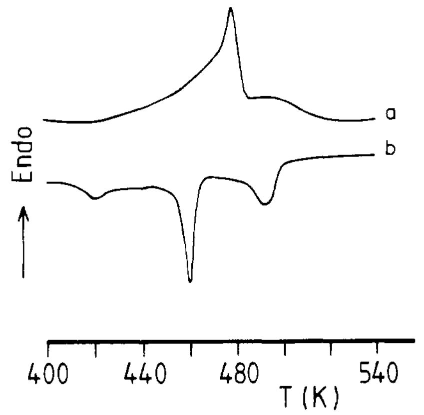

Figure 1. DSC scan of polyester P-10: (a) heating, (b) cooling.

Table II
Properties of PE-n Polyethers

		$\bar{M}_n$			
n	η_{inh}[a]	GPC	elem anal.[c]	$\bar{M}_w$: GPC	range of endotherm max, °C
5	0.09	1300	1800	1600	185–221
7	0.12	2400	3000	3100	137–209
8		*b*	1800	*b*	122–239
9	0.13	2400	1800	3000	143–202
10		*b*	1800	*b*	113–191
11	0.14	1700	2500	2600	141–188
12		*b*	2700	*b*	147–212

[a] In 1,1,2,2-tetrachloroethane at 30 °C and 0.5 g/dL. The n = even polyethers were insoluble. [b] n = even polyethers insoluble in chloroform. [c] End-group analysis by NMR generally agrees with elemental analysis.

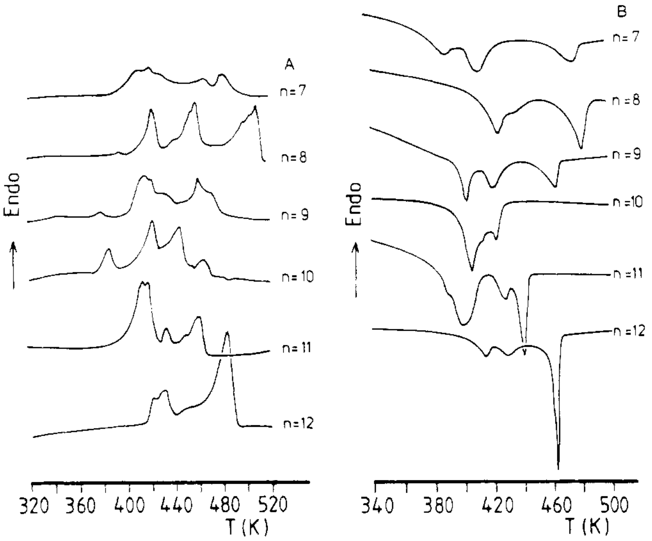

Figure 2. DSC scans of polyethers PE-n: (a) heating, (b) cooling.

atic–isotropic (N + I) biphase as expected for polydisperse samples of low molecular mass. Properties of PE-n polymers are summarized in Table II, and typical DSC scans on heating and cooling are illustrated in parts a and b of Figure 2. The samples are bromoalkoxy-terminated oligomers, $Br[(CH_2)_nOC_6H_4COOC_6H_8OCOC_6H_4O(CH_2)_n]_xBr$ with x of the order of 3–6. The GPC chromatograms do indeed show elution of discrete components.

In addition to the samples listed in Table II, a PE-7 polyether (sample PE-7A) was synthesized with equimolar amounts of bromoheptyloxy and TCHB end groups (M_n = 4300; range of endotherm maxima, 144–226 °C). Comparison of PE-7 and PE-7A shows a higher clearing temperature and lower heat of melting for the latter, in agreement with previous investigations of the influence of molecular mass and aromatic end groups.[12]

Except for PE-7, heating scans show a complex of melting endotherms. Cooling scans generally display three major peaks for n = odd. Sample PE-7 shows normal enantiotropic behavior, with a nematic mesophase that develops spontaneous homeotropic alignment on cooling. The value of ΔH_{NI} = 7.2 J/g is in line with literadture values for n = odd nematics of low molecular mass. For the remaining samples, combination of microscopy, WAX and SAX observation reveals a complex of K/K, K/N, N/I, I/N, K/I, and I/K transitions.

The data can be interpreted by analogy with observations made previously on model compounds and polymers based on mesogen 2,2′-dimethyl-4,4′-dioxyazoxybenzene.[12–14] Although the mesogen itself is nonmesomorphic, structures with aromatic end groups are nematic beginning with the twin model, which is monotropic. Chains with aliphatic end groups require 4–5 repeating units for appearance of mesophase. Moreover, the transition temperatures and mesophase stability are lower in the case of aliphatic end groups, at comparable chain length. Kinetics of crystallization is depressed by aromatic end groups.

A similar influence of end groups on phase behavior was pointed out by Percec and Shaffer,[15,16] and a similar transition from monotropic to enantiotropic behavior was reported for other polyethers[17] and polyesters.[18] The DSC scans reported by Percec et al. for α,ω-dibromoalkyl polyethers based on α-methylstilbene and n = odd spacers are very similar to that shown here.[16,17]

Of the samples listed in Table II, only PE-7 appears to have a molecular mass high enough to display unambiguous enantiotropic behavior, similar to that of P-n polyesters. The remaining samples seem to show separate melting of individual oligomers and molecular nucleation of cooling transitions; i.e., I/K transitions may occur at temperatures above I/N transitions. This appears to be especially pronounced in the case of n = even chains in agreement with odd/even alternation of the extent of molecular segregation previously investigated by us for another system.[19] Since the N phase may be supercooled to room temperature, N/I transitions may appear on heating below K/I transitions. This behavior was indeed observed previously for the twin model of 2,2′-dimethyl-4,4′-dihydroxyazoxybenzene.[14]

Thermal cis/trans isomerization in 1,4-cyclohexane derivatives is well documented,[20–23] especially for derivatives of 1,4-cyclohexanedicarboxylic acid. However, Osman[24] reports that solution esterification of *trans*-1,4-cyclohexanediol with aliphatic or aromatic chlorides leads to the pure trans esters. Hence, TCHB as well as polymers P-n and PE-n is expected to remain in the trans configuration. Indeed, only methine and methylene peaks corresponding to the trans configuration of cyclohexane are observed in the ^{13}C spectra, as illustrated in Table III. The peak assignments were made following Polk et al.[22] who have studied isomerization in block copolyesters containing cyclohexane rings.

The spectrum of P-7 was run following annealing in the isotropic phase and was found identical with that of the untreated sample. This suggests the absence of thermal isomerization under the DSC cycling conditions employed in this study in agreement with the reproducibility of transition temperatures. However, the sam-

Table III
^{13}C Chemical Shifts (ppm) in Chloroform

compd	methine	methylene
trans-1,4-diacetoxycyclohexane	71.04	28.17[a]
	71.7	28.20[b]
TCHB	71.4	27.8
PE-10	71.01	27.90
P-7[c]	71.5	27.8

[a] This work. [b] From ref 22. [c] Before and after annealing in the isotropic phase.

ples are subject to thermal degradation in the vicinity of 275-280 °C, as mentioned in the Experimental Section.

Acknowledgment. Support by the National Science Foundation (Grant DMR 8600029) and U.S. Army Natick Research and Development Program is acknowledged.

References and Notes

(1) Roviello, A.; Sirigu, A. *J. Polym. Sci., Polym. Lett Ed.* **1975**, *13*, 455.
(2) Dewar, M. J. S.; Goldberg, R. S. *J. Am. Chem. Soc.* **1970**, *92*, 1582.
(3) Karamysheva, L. A.; Koushev, E. I.; Titov, V. V. *Zh. Org. Khim.* **1976**, *12*, 1508.
(4) Braun, D.; Schulke, U. *Makromol. Chem., Rapid Commun.* **1986**, *187* (5), 1145.
(5) Olberg, R. C.; Pines, H.; Ipatieff, V. N. *J. Am. Chem. Soc.* **1944**, *66*, 1096.
(6) Ober, C.; Jin, J. I.; Lenz, R. W. *Polym. J.* **1982**, *14* (1), 9.
(7) Vogel, A. *Textbook of Practical Organic Chemistry*, 3rd ed.; Longman's: London, 1962.
(8) Blumstein, A.; Thomas, O. *Macromolecules* **1982**, *15*, 1264.
(9) N'Guyen, T. D.; Boileau, S. *Polym. Bull.* **1979**, *1* (12), 817.
(10) Schaffer, T.; Percec, V. *Makromol. Chem. Rapid Commun.* **1985**, *6*, 97.
(11) Blumstein, R. B.; Thomas, O.; Gauthier, M. M.; Asrar, J.; Blumstein, A. *Polymeric Liquid Crystals*; Blumstein, A., Ed.; Plenum Press: New York, 1985; p 239.
(12) Blumstein, R. B.; Stickles, E. M.; Gauthier, M. M.; Blumstein, A.; Volino, F. *Macromolecules* **1984**, *17* (2), 177.
(13) Blumstein, R. B.; Stickles, E. M. *Mol. Cryst. Liq. Cryst., Lett. Sect.* **1982**, *82*, 151.
(14) Blumstein, R. B.; Poliks, M. D.; Stickles, E. M.; Blumstein, A.; Volino, F. *Mol. Cryst. Liq. Cryst.* **1985**, *129*, 375.
(15) Shaffer, T. D.; Percec, V. *Makromol. Chem., Rapid* Commun. **1985**, *6*, 97.
(16) Percec, V.; Shaffer, T. D. *Advances in Polymer Synthesis*; Culbertson, B., McGrath, J. E., Eds.; Plenum Press: New York, 1985; p 133.
(17) Percec, V.; Nava, H. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 405.
(18) Zhou, G. F.; Duon, X. G.; Liu, Y. L. *Macromolecules* **1986**, *19*, 247.
(19) D'Allest, J. F.; Sixou, P.; Blumstein, A.; Blumstein, R. B. *Mol. Cryst. Liq. Cryst.* **1988**, *157*, 229.
(20) Griz, V. E.; Levin, S. Z. *Zh. Org. Khim.* **1972**, *8*, 1638.
(21) Kricheldorf, H. R.; Schwartz, G. *Makromol. Chem.* **1987**, *188*, 1281.
(22) Polk, M.; Bota, K.; Nandu, M.; Phingboedhipakkiys, M.; Edeogu, C. *Macromolecules* **1984**, *17*, 129.
(23) Jackson, W. J., Jr.; Darnell, W. R. U.S. Patent 4321206 and 4342862, 1982.
(24) Osman, M. A. *Macromolecules* **1986**, *19*, 1824.

Communications to the Editor

Polymerization of Styrene with $Mg(OH)_xCl_{2-x}$-Supported (x = 0-2) $Ti(O^nBu)_4$ Catalysts Combined with Methylaluminoxane

Introduction. It is well-known that syndiotactic polystyrene is obtained by using a kind of homogeneous Kaminsky-Sinn type catalyst composed of some titanium or zirconium compounds in combination with methylaluminoxane (MAO).[1-7] Afterward, we found that a heterogeneous, SiO_2-supported $Ti(O^nBu)_4$ catalyst also gives syndiotactic polystyrene when MAO is used as cocatalyst.[8] More recently, we have carried out styrene polymerization by using similar supported catalysts prepared from $Ti(O^nBu)_4$ and $Mg(OH)_xCl_{2-x}$ (x = 0-2) and found that the tacticity of polystyrene is markedly affected by the presence of Cl in the carrier. This paper reports brief results on the polymerization.

Experimental Section. Materials. Styrene (Kanto Chemical Co., Inc.) was washed with an aqueous solution of sodium hydroxide, dried over calcium hydride for 12 h, and distilled under a reduced pressure. Toluene used as solvent was purified by refluxing over calcium hydride for 24 h, followed by fractional distillation. $Ti(O^nBu)_4$ (Tokyo Kasei Kogyo Co., Ltd.), $Mg(OH)_2$ (Kanto Chemical Co., Inc.), $MgCl_2$ (Toho Titanium Co.), $MgCl_2 \cdot 6H_2O$ (Wako Pure Chemical Industries, Ltd.), and MAO (Toso-Akzo Co., 2.4 mol/L in toluene) were used without further treatment.

Preparation of Catalysts. Mg(OH)Cl was prepared from $MgCl_2 \cdot 6H_2O$ according to the procedures reported previously.[9]

$Ti(O^nBu)_4/MgCl_2$ Catalyst (Cat-1). In a 100-cm^3 glass reactor were added 500 mg of $MgCl_2$, 0.1 mmol of $Ti(O^nBu)_4$, and 28 cm^3 of toluene under nitrogen, and the mixture was refluxed at its boiling point for 4 h. This mixture was used as catalyst.

$Ti(O^nBu)_4$/Mg(OH)Cl Catalyst (Cat-2). In a 100-cm^3 glass reactor were added 6.79 g of Mg(OH)Cl, 44.2 mmol of $Ti(O^nBu)_4$, and 50 cm^3 of heptane under nitrogen. After raising the temperature to its boiling point, the mixture was kept standing for 5 h with stirring. Then the precipitate was filtered under nitrogen, washed 10 times with plenty of heptane and dried under a reduced pressure at 40 °C for 1 h.

$Ti(O^nBu)_4/Mg(OH)_2$ Catalyst (Cat-3). In a 100-cm^3 glass reactor were added 7.39 g of $Mg(OH)_2$, 63.4 mmol of $Ti(O^nBu)_4$, and 50 cm^3 of toluene under nitro-

0024-9297/90/2223-1558$02.50/0