Liquid Crystalline Behavior of Polymeric Glycols Terminated with Aromatic Diester and Diacid Mesogenic Groups

H. HOSHINO,* J.-I. JIN,† and R. W. LENZ, *Chemical Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003*

Synopsis

A series of bis(benzylterephthaloyl-*p*-oxybenzoyl)esters (mesogen I) and bis(*p*-carboxybenzoyl-*p*-oxybenzoyl)esters (mesogen II) of several different polymeric glycols was prepared, and their thermotropic liquid crystalline behavior was studied by differential scanning calorimetry and by visual observation on the hot stage of a polarizing microscope. The polymeric glycols used were poly(ethylene oxide) (A), poly(tetramethylene oxide) (B), polybutadiene (C), and the hydrogenated polybutadiene (D) glycols, with molecular weights between 650 and 6000. With one exception, the benzyl ester derivations were not thermotropic, but the corresponding carboxylic acid derivatives were, and the related model compound, the bis(*p*-carboxybenzoyl-*p*-oxybenzoyl)ester of 1,12-dodecanediol, was also found to be liquid crystalline. The nature of the mesophases formed by the diacids derived from the macroglycol derivatives could not be clearly identified by their optical textures. Several of the diacid derivatives formed elastomeric films, even though they were still of low molecular weight, presumably because of chain extension by dimerization and association of the terminal mesogenic groups.

INTRODUCTION

In previous investigations in this laboratory, the structure property relationships of many different liquid crystalline aromatic polyesters were investigated.[1-7] Included among these was a series of polymers containing a triad aromatic ester mesogenic group and a poly(ethylene oxide) flexible spacer of the following structure:

mesogenic group spacer

Here *n* is 1, 2, 3, 4, 4.1, 8.7, 13.2, and 22.3.[7] The latter four polymers were prepared from ethylene oxide oligomers terminated with hydroxyl groups and containing a distribution of oligomers of different lengths with a number average size as listed in the series. The first four polymers were prepared from individual poly(ethylene oxide) glycols of the exact size given. All of the polymers from

---

* Present Address: Sanyo Chemical Industries, Ltd., Kyoto, Japan.
† Present Address: Chemistry Department, Korea University, 1-Anam Dong, Seoul 132, Korea.

CCC 0021-8995/84/020547-08$04.00

$n = 1$ to $n = 8.7$ formed liquid crystalline mesophases, but the polymers with the longer flexible spacers, $n = 13.2$ and $n = 22.3$, did not. It was concluded that, for these polymers, the fraction of mesogenic units (the aromatic ester triads), which were responsible for inducing liquid crystallinity, had become too small in relation to the overall size of the units to maintain enough residual order in the system at temperatures above their melting points to be able to form a mesophase.

The behavior of the polymers in this series raised the question of whether liquid crystallinity could be obtained by placing the mesogenic groups on the ends of polymeric flexible spacers instead of within polymer chains containing alternating mesogenic groups and extended spacers. To investigate this possibility, several types of polymeric glycols with terminal mesogenic groups were prepared and characterized. The component glycols and mesogens had the following structures:

Mesogenic Groups R

I: —C(=O)—C₆H₄—OC(=O)—C₆H₄—COCH₂—C₆H₅

II: —C(=O)—C₆H₄—OC(=O)—C₆H₄—COH
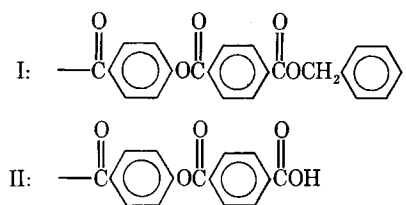
Polymeric Glycols X

A: poly(ethylene oxide): $-O(CH_2CH_2O)_n-$, $\bar{n} = 25, 40, 116$
B: poly(tetramethylene oxide): $-O(CH_2CH_2CH_2CH_2O)_n-$, $\bar{n} = 9, 23$
C: polybutadiene: $-O(C_4H_6)_n-O-$, $\bar{n} = 58$
D: hydrogenated polybutadiene: $-O(C_4H_8)_n-O-$, $\bar{n} = 58$

All of the polymeric glycols used contained distributions of oligomers of different sizes with the number average length, $\bar{n}$, as indicated above. Each of the glycol oligomers, X, had two hydroxyl end groups which were reacted with the acid chloride of mesogen I to form the mesogen-terminated derivatives, $R_I–X–R_I$. These derivatives were converted to those containing mesogen II terminal groups, $R_{II}–X–R_{II}$, by hydrogenation to selectively convert the benzyl esters to carboxylic acids. Both types of derivatives were characterized by differential scanning calorimetry (DSC) and on a hot stage of a polarizing microscope.

RESULTS AND DISCUSSION

Polymeric Glycol Diesters of Mesogen I

The general properties of the polymeric glycol diesters of mesogen I are collected in Table I. As seen for the derivates of glycols A and B, the melting points of the compounds, as measured by DSC, were generally lowered by converting the glycols into aromatic diesters. Among the derivatives of this series, only A with $\bar{n} = 40$ showed liquid crystalline properties. This derivative showed a very weak stir-opalescence in the temperature range of 20–28°C. On analysis by DSC, the thermogram contained a pronounced melting endotherm, but the clearing temperature, for the transition from the mesophase to the isotropic phase, ap-

TABLE I
Properties of Initial Polymeric Glycols and Their Diester Derivatives of Mesogen I

Glycol type	$\bar{n}^a$	Form	T_m (°C)
A	25	Glycol	45
	25	Diester	10
	40	Diester	23[b]
	116	Glycol	68
	116	Diester	49
B	9	Glycol	20
	9	Diester	35
	23	Glycol	29
	23[c]	Diester	28
C	58[c]	Glycol/diester	—[d]
	58[c]	Glycol/diester	—[d]

[a] Calculated from value given by supplier (see Experimental) unless otherwise indicated.

[b] The only sample which retained birefringence above the melting points, having a clearing temperature at 28°C.

[c] Based upon molecular weight of diester determined by GPC relative to polystyrene standard; values of $\bar{M}_w/\bar{M}_n$ were 1.2 for B sample and 1.4 for C sample.

[d] Both the glycol and diester were liquid at room temperature.

peared only as a shoulder on the melting endothermic peak, which was centered at 23°C. An optical anisotropy was observed for the melt of this derivative on the polarizing microscope, but no specific features could be seen by which the type of mesophase could be judged. Neither the lower nor higher molecular weight diesters of A formed liquid crystalline melts.

Polymeric Glycol Diesters of Mesogen II

It has been reported that certain aromatic acids can form mesophases by forming stable dimers above their melting points through intermolecular hydrogen bonding.[8] If this principle is applied to the diacid derivatives of polymeric glycols terminated with mesogen II, such dicarboxylic acids would be expected to provide a sequence of hydrogen-bonded dimers connecting these oligomers that would enhance the rigidity and anisotropy of the molecules. That is, as a result of dimerization, the effective length of the mesogenic units would be doubled to form thermally reversible polymeric derivatives of the following general structure:

$$\text{---} \text{XR'C} \overset{\displaystyle O \text{---} HO}{\underset{\displaystyle OH \text{---} O}{\Big\langle}} \text{CR'} \text{---}$$
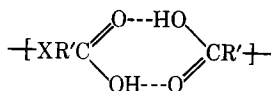
Indeed, all of the diacids, except that derived from the highest molecular weight polymeric glycol, A with $\bar{n} = 116$, showed liquid crystallinity above their melting points when observed on a polarizing microscope. The melting points and clearing temperatures of these derivatives are given in Table II. A model compound was also prepared and characterized for this behavior, that of the mesogen II derivative of 1,12-dodecanediol, and it showed a Schlieren texture, which is characteristic of nematic phase, as shown in Figure 1. However, the diacid derivatives of the polymeric glycols did not form intense optical textures,

TABLE II
Thermal Properties of the Mesogen II Derivatives

Polymeric glycol	$\bar{n}$	T_m (°C)	T_i (°C)
A	116	60	—
A	25	19	35
B	23	11	57
B	9	90	—
D	58	—	97
1,12-Dodecanediol		259	277

but contained instead extensive dark isotropic regions, which suggest the coexistence of liquid crystalline domains and isotropic regions in these samples. The optical textures observed were unlike those of either nematic or smectic polymers, and the intensity of birefringence was rather weak for all of the liquid-crystal-forming compositions, presumably because of the dilution effect by the long segments of the polymeric glycol units in the central parts of molecules.

Of considerable interest is the observation that the diacid derivative of D was film forming at room temperature. That is, an elastomeric film was obtained by casting the polymer from a stationary THF solution in air on silicone-wax-coated glass. The occurrence of birefringence in these films greatly depended on the film preparation method used. The solution-cast film obtained by evaporation of THF, and one obtained by precipitation from a THF solution with water, were not birefringent as formed, but both of these samples became birefringent on heating to about 80°C.

On the other hand, a film sample obtained from a THF solution by drying with a rotary evaporator was birefringent even at room temperature. Possibly, because the samples dried from THF solution with the rotary evaporator experienced shearing forces during film formation, molecular orientation could have occurred to facilitate the formation of a mesophase which was retained at room temperature. The other samples had to be thermally annealed to form the
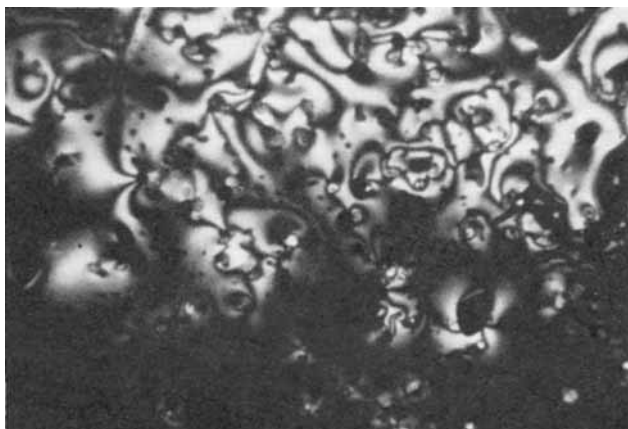

Fig. 1. Photomicrograph of Schlieren texture of the 1,12-dodecanediol diacid derivative (Mesogen II) on heating at 247°C (320× magnification).
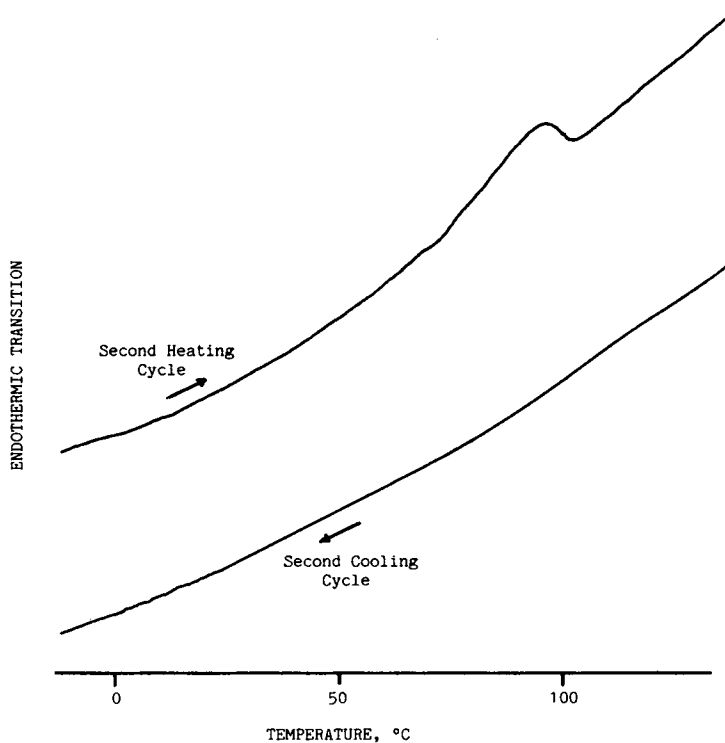
Fig. 2. DSC thermogram of the diacid derivative of D (Mesogen II) at a heating rate of 20°C/min and a cooling rate of 10°C/min.

mesophase. The mesogen II sample prepared from A with $\bar{n} = 25$ also formed a weakly elastic film.

Another interesting feature of sample D with mesogen II diacid terminal groups was that it did not develop a strong birefringence on cooling from the isotropic melt. The optical texture was a uniform dark gray without any pattern. Only when it was cooled to −25°C, on a cold stage of a polarizing microscope, did it develop a bright birefringence pattern. This behavior could be an example of "inverse monotropism," as observed by Iimura and co-workers for polyurethanes prepared from the reaction of 3,3'-dimethyl-4,4'-biphenyldiyldiisocyanate with diols.[9] This type of irreversibility was observed in the DSC thermogram of this sample. As shown in Figure 2, even though this sample showed a definite clearing endotherm at about 100°C in the heating cycle, no corresponding exotherm was observed in the cooling cycle.

The diacid derivative from A with $\bar{n} = 116$ did not form a mesophase above the melting point, but it had a typical crystalline morphology with very sharp melting endotherms. It became spherulitic on cooling from the isotropic melt.

The diacid derivative of B, $\bar{n} = 9$, was powdery solid, and B, $\bar{n} = 23$, was a viscous liquid at room temperature, while their initial polymeric glycols were both waxy solid. None of these samples formed films by solution casting.
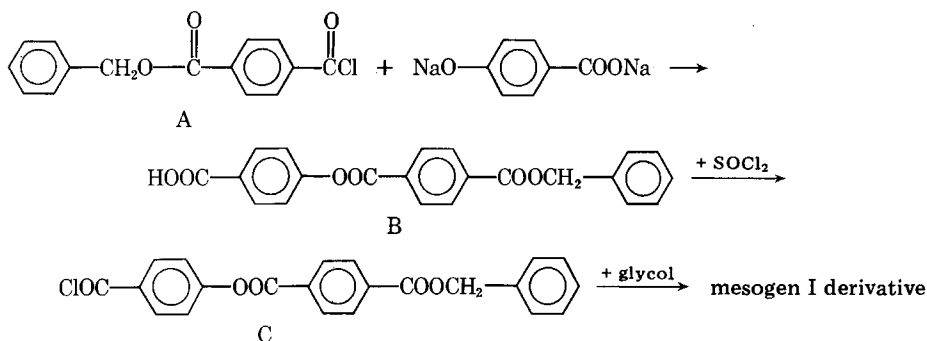
Except for the model compound, the diacid derivative of 1,12-dodecanediol,

the nature of the mesophases formed by the polymeric glycol derivative was not clear. In every case, the optical textures observed on the polarizing microscope revealed the presence of dark regions, indicating the coexistence of liquid crystal phases and isotropic regions. In all cases also, the intensities of birefringence of the liquid crystal melts were very weak, presumably because of the dilution effect of the nonmesogenic polymeric glycol units present in the molecules.

EXPERIMENTAL

Synthesis of Mesogen I Derivatives

The derivatives of mesogen I were prepared by the following route:

$$\text{Ph}-CH_2O-\underset{O}{\overset{O}{C}}-\text{C}_6H_4-\underset{O}{\overset{O}{C}}Cl \;(\mathbf{A}) \;+\; NaO-\text{C}_6H_4-COONa \;\longrightarrow$$

$$HOOC-\text{C}_6H_4-OOC-\text{C}_6H_4-COOCH_2-\text{Ph} \;(\mathbf{B}) \;\xrightarrow{+\;SOCl_2}$$

$$ClOC-\text{C}_6H_4-OOC-\text{C}_6H_4-COOCH_2-\text{Ph} \;(\mathbf{C}) \;\xrightarrow{+\;glycol}\; \text{mesogen I derivative}$$

Preparation of B. Into the acid chloride of monobenzyl terephthalate, which was prepared by the literature method,[4,10] was placed 200 mL dry ether in a dropping funnel. Into a three-necked flask was placed 172 mL of $1N$ aqueous solution of sodium hydroxide (172 mmol), and 11.9 g of p-hydroxybenzoic acid (87 mmol) was added. Both solutions were cooled for 1 h in the refrigerator before their reaction. With vigorous stirring, the acid chloride solution was added to the latter solution; the resulting precipitate was filtered, dried, and ground well in a mortar, and the salt was neutralized with dilute HCl with a crude yield of 83%. Recrystallization of B was carried out from a solution in n-butyl alcohol, mp 184–190°C.

Preparation of C. A 50-mL three-necked round flask equipped with a dropping funnel and a stopcock was degassed under vacuum and purged with dry nitrogen. The reaction was carried out under a dry nitrogen atmosphere. To the flask was added 2.6 g of recrystallized thionyl chloride (0.65 mmol) and 5 mL of N-methylpyrrolidone (NMP). The flask was warmed and stirred to dissolve the acid chloride and fitted with a dropping funnel, which contained the polymeric glycol (0.25 mmol), triethylamine (0.75 mmol), dried with CaH_2, and NMP (2 ml). The glycol solution was added dropwise to the acid chloride solution for 10 min and stirred at room temperature for 1 h. The temperature was raised to 80°C, and the reaction mixture was allowed to stir overnight. The product was diluted with acetone and precipitated in 500 mL of water under vigorous agitation. The crude product was separated by decantation, dried in air overnight, reprecipitated in an appropriate organic solvent, and finally dried in the vacuum oven for many hours. For the synthesis of the diester of D, NMP was not compatible with D and so tetrachloroethane was used instead.

TABLE III
Yields and Analysis of Polymeric Glycol Diesters (Mesogen I)

Polymeric glycol	$\bar{n}$	Yield (%)	Analysis			
			C		H	
			Calcd	Found	Calcd	Found
A	25	41	62.56	62.49	7.06	7.26
A	40	14	60.62	60.98	7.57	7.25
A	116	73	56.56	56.15	8.55	8.91
B	9	72	70.30	69.73	7.47	7.42
B	23	19	68.47	68.46	9.33	9.75
C	58	93	84.14	85.31	9.36	9.99
D	58	50	81.86	80.87	11.81	11.56

Synthesis of Mesogen II Derivatives

The diacid derivatives of mesogen II were prepared by the hydrogenolysis of the diesters of series I. In a typical reaction, 1.3 g of the mesogen I glycol diester was dissolved in 33 mL THF, and 0.33 g of 5% Pd on $CaCO_3$ was added. A hydrogen pressure of 300 psi was maintained in the reactor, and the reaction was run at room temperature for about 5 h. The product solution was dried with Drierite overnight before filtration with the aid of Celite. THF solvent was removed on a rotary evaporator.

Polymeric Glycols, X

The polybutadiene glycol, C, was obtained from Japan Synthetic Rubber Company, which specified its analysis as follows: 10% *cis*-1,4, 35% *trans*-1,4, 55% 1,2-polybutadiene; $\overline{M}_n$ = 2120; average functionality of 1.97 (hydroxyl number of 0.91 meq/g). The other polymeric glycols were purchased from Polysciences Inc. under the following designations: A, $\bar{n}$ = 25, PEG-1000; A, $\bar{n}$ = 40, PEG-1540; A, $\bar{n}$ = 116, PEG-6000; B, $\bar{n}$ = 9, PTMG-650; B, $\bar{n}$ = 23, PTMG-2000.

Hydrogenation of C.[11] The hydrogenation of C was carried out at 70°C in a Parr 0.5-L high pressure reactor. 10 g of C (185 mmol of double bonds) was dissolved in 200 mL of THF in a 0.5-L glass reaction sleeve. A catalyst composed of 5% palladium of calcium carbonate was added, and the sleeve was placed in the bomb chamber, which was equipped with a mechanical stirrer and gas inlet and outlet valves and connected to a nitrogen cylinder. The reaction sleeve was flushed for 15 min with a slow flow of N_2 gas, the bomb was then pressurized with H_2 to a pressure of 480 psi, the stirrer was engaged, and the reaction was allowed to run for about 5 h. Stirring was stopped, and the remaining gas was vented out of the reactor. The suspension was filtered by suction through Celite filter aid, to remove the catalyst, and dried with Drierite overnight. The solvent was removed with the rotary evaporator, and the hydrogenated product was noticeably more viscous than the starting material. The infrared absorption bands at 910 cm^{-1} (vinyl), 965 cm^{-1} (*trans*-vinylene), 990 cm^{-1} (vinyl), 1640 cm^{-1} (vinyl, vinylene), 3080 cm^{-1} (vinyl, vinylene), which were found in the starting PB, had disappeared completely. The NMR spectrum of the product also verified that complete hydrogenation had occurred.

TABLE IV
Yields and Analysis of Polymeric Glycol Diacids (Mesogen II)

Polymeric glycol	$\bar{n}$	Yield (%)	Analysis			
			C		H	
			Calcd	Found	Calcd	Found
A	25	81	57.70	57.71	6.96	7.20
A	116	59	55.55	55.12	8.68	8.93
B	9	74	66.76	65.88	7.59	7.73
B	23	85	66.69	65.40	9.52	7.87
D	58	99	81.14	80.77	12.14	12.58
1,12-Dodecanediol		80	68.28	67.30	5.73	5.52

ANAL. Calcd: C 84.37%; H 14.25%. Found: C 83.74%; H 14.60%.

The yields and elemental analysis of all of the mesogen I diester derivatives prepared by these procedures are collected in Table III and those of the Mesogen II diester derivatives in Table IV.

The optical textures and the thermal transitions of the derivatives were determined by observation of the samples placed on the hot stage or the cold stage attached to a Leitz Ortholox polarizing microscope. Thermal transitions were also determined by DSC analysis under a nitrogen atmosphere with a Perkin-Elmer DSC-2 instrument using indium as the standard.

References

1. J.-I. Jin, S. Antoun, C. Ober, and R. W. Lenz, *Br. Polym. J.*, **12**, 132 (1980).
2. R. W. Lenz and J.-I. Jin, *Macromolecules*, **14**, 1405 (1981).
3. S. Antoun, R. W. Lenz, and J.-I. Jin, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 1901 (1981).
4. C. Ober, J.-I. Jin, and R. W. Lenz, *Polym. J (Jpn)*, **14**, 9 (1982).
5. B.-W. Jo, R. W. Lenz, and J.-I. Jin, *Eur. Polym. J.*, **18(3)**, 233 (1982).
6. C. Ober, R. W. Lenz, J.-I. Jin, and E. Chiellini, "Thermotropic Polyesters Based on p-Hydroxybenzoic Acid," presented at the 65th Canadian Chemical Conference, May 30–June 2, 1982, Toronto, Canada.
7. G. Galli, E. Chiellini, C. K. Ober, and R. W. Lenz, *Makromol. Chem.*, **183**, 2693 (1982).
8. G. W. Gray and P. A. Winsor, Eds., *Liquid Crystals and Plastics Crystals*, Ellis-Horwood, New York, 1974, Vol. 1, Chap. 4.
9. K. Iimura, N. Koide, H. Tanabe, and M. Takeda, *Makromol. Chem.*, **182**, 2569 (1981).
10. M. Zahn and B. Seidel, *Makromol. Chem.*, **29**, 70 (1959).
11. M. Rachapady, G. G. Smith, V. R. Rain, and W. W. Grassley, to appear.