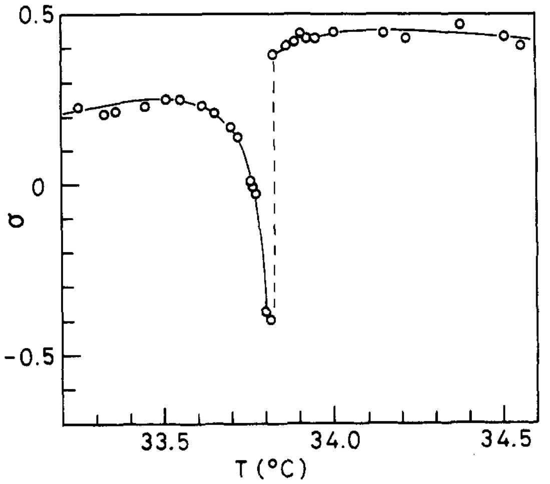


Figure 3. Poisson's ratio, σ as a function of temperature. Lines are guides for the eye.

of tension, the shift of transition temperature[8] was about 0.05 °C. A drastic softening of K toward T_0 both above and below T_0 is noted, though the softening is incomplete due to the first-order nature of the transition. On the contrary, μ shows only a small steplike anomaly at T_0.

The Poisson's ratio σ shows a very characteristic anomaly as shown in Figure 3. On approaching T_0 from below, σ decreases sharply and even becomes negative in the extreme vicinity of T_0. Negative Poisson's ratio demonstrates the fact that if we elongate the gel network in one direction, it elongates also in the perpendicular directions. Although the negative values of σ do not violate the stability condition, such values have not been found in any isotropic material so far.[10] (We should point out, however, that the equilibrium Poisson's ratio of gel network is somewhat different from the Poisson's ratio of conventional solids, because the amount of solvent contained in a gel is different before and after the deformation.)

In terms of K and μ, σ is expressed as

$$\sigma = (3K - 2\mu)/(6K + 2\mu) \qquad (1)$$

Thus we see that σ is negative when $\mu > 3K/2$. This condition is surely satisfied in the vicinity of the critical point of volume phase transition of gels, where K tends to zero while μ remains nearly constant.[11] The elastic stability condition limits σ to $-1 < \sigma < 0.5$.[10] We can see from eq 1 that $\sigma = -1$ corresponds to the volume instability ($K = 0$) and $\sigma = 0.5$ to the shear instability ($\mu = 0$). The drastic variation of σ around the volume transition will be more clearly seen if the gel undergoes a true critical transition. The measurement for this case is now in progress.

It has been demonstrated[8,12] that the anomalous swelling properties of NIPA/water gel can be explained fairly well within the Flory theory of gels provided that the empirically determined material parameters (the enthalpy and the entropy of solution) are used. We can indeed show that the free energy expression including the concentration-dependent polymer–solvent interaction parameter used in the previous studies[8,12] can reproduce quantitatively the present experimental results. The details will be reported elsewhere.

Acknowledgment. I am indebted to Professor A. Onuki and Dr. K. Sekimoto for fruitful conversations.

References and Notes

(1) Hirokawa, Y.; Tanaka, T. *J. Chem. Phys.* **1984,** *81,* 6379.
(2) Hirotsu, S. *J. Phys. Soc. Jpn.* **1987,** *56,* 233.
(3) Hirotsu, S. *J. Chem. Phys.* **1988,** *88,* 427.
(4) Tanaka, T.; Hocker, L. O.; Benedek, G. B. *J. Chem. Phys.* **1973,** *59,* 5151.
(5) Tanaka, T.; Sato, E.; Hirokawa, Y.; Hirotsu, S.; Peetermans, J. *Phys. Rev. Lett.* **1985,** *55,* 2455.
(6) For example: Horkay, F.; Zrinyi, M. *Macromolecules* **1982,** *15,* 1306. Geissler, E.; Hecht, A. M. *Macromolecules* **1981,** *14,* 185.
(7) Hirotsu, S., unpublished result.
(8) Hirotsu, S.; Onuki, A. *J. Phys. Soc. Jpn.* **1989,** *58,* 1508.
(9) The length L measured was not the whole length of the rod but the length between marks in the middle of the rod.
(10) Love, A. E. H. *A Treatise of the Mathematical Theory of Elasticity*; Dover: New York, 1944; Chapter III.
(11) In crystals also, if a structural phase transition is triggered by vanishing of bulk modulus (i.e., both phases belong to the same space group) and the transition is close enough to being continuous, negative Poisson's ratio will be observed. Though such a measurement has not been reported yet.
(12) Hirotsu, S.; Kaneki, A. *Dynamics of Ordering Processes in condensed Matter*; Komura, S., Furukawa, H., Eds; Plenum: New York, 1988; p 481.

Shunsuke Hirotsu
Department of Biological Sciences, College of Science
Tokyo Institute of Technology, Ohokayama
Meguro-ku, Tokyo 152, Japan

Received September 8, 1989
Revised Manuscript Received November 28, 1989

Liquid-Crystalline Poly[oxybis(trimethylene) *p,p'*-bibenzoate]: Effect of the Central Ether Group

In recent years the interest in thermotropic mesogenic materials has grown extraordinarily. These compounds usually exhibit a mesophase at temperatures above the region of the crystalline solid and before the formation of an isotropic melt. Among them, aromatic polyesters constitute an important class of main-chain liquid-crystalline polymers but with the inconvenience of their very high melting points, sometimes not detected before the degradation of the sample.

One method of reducing the high melting points of all-aromatic, rodlike polyesters, so that the polymers will be sufficiently thermally stable to be injection molded or melt spun, is to introduce flexible aliphatic units into the polymer main chains. Poly(ether glycols) with an even number of carbons in the chain repeat segment, i.e., poly(oxyethylene glycol) or poly(oxytetramethylene glycol), have been widely used in the synthesis of polyesters. Less use has been done of the intermediate polyglycol, i.e., poly(oxytrimethylene glycol), which has an odd number of carbon atoms in the chain repeat unit.

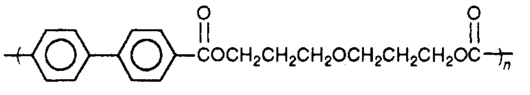
On the other hand, polyoxetanes with the structural unit $-OCH_2CR_1R_2CH_2-$ are an interesting class of polyethers where the properties can be easily modified by changing the nature of the substituents R_1 and R_2. The parent compound of this series, poly(trimethylene oxide) (PTO) (or polyoxetane), exhibits one of the lowest characteristic ratios in polymers and a great flexibility.[1] This property can be modified by substituting the two hydro-

0024-9297/90/2223-0905$02.50/0 © 1990 American Chemical Society

gens of the central CH_2 group in the repeat unit by two alkyl groups,[2] and a progressive change of flexibility may be obtained by a suitable choice of the substituents.

The preparation of several low molecular weight poly(oxytrimethylene glycols) has already been described,[3] starting from trimethylene oxide with boron trifluoride/ethyl ether as catalyst and 1,4-butanediol as coinitiator, and also from the ozonization of high molecular weight poly(trimethylene oxide). In this way, products of poorly defined molecular weight are obtained. However, during the last few years a new mechanism of cationic polymerization of oxyranes[4] has been developed. This mechanism assumes that, under certain conditions, propagation proceeds by addition of a protonated monomer molecule to the hydroxyl-terminated growing polymer. This method of synthesis leads to linear telechelics virtually free of undesirable cyclic oligomers. Therefore, it is possible to obtain dimers or higher oligomers derived from trimethylene glycol, with a high degree of structural regularity.

Thus, it seemed to be interesting to study the properties of the series of polyesters containing the bibenzoate unit as mesogen and the moiety $-CH_2CR_1R_2CH_2OCH_2CR_1R_2CH_2-$ as a flexible spacer in the main chain. This paper is concerned with the synthesis and properties of poly[oxybis(trimethylene) *p,p′*-bibenzoate] (PDTMB), the first member of the series, with structural formula:



PDTMB was obtained by melt transesterification of the diethyl ester of *p,p′*-bibenzoic acid (4,4′-biphenyldicarboxylic acid) and 3,3′-oxybis(propanol), the dimer of trimethylene glycol, using isopropyl titanate as catalyst. The preparation and characterization of the dimer has been previously described.[5] The polymer, in spite of the presence of the biphenyl group, is soluble in chloroform, and it was purified by solution in this solvent and precipitation with methanol. The intrinsic viscosity of the resulting polyester, determined in chloroform at 25 °C, was found to be 1.05 dL/g. The 200-MHz ^1H NMR spectrum of the PDTMB sample, acquired in solution of Cl_3CD, shows the AB spin system corresponding to the aromatic protons centered at 7.86 ppm, two triplets at 4.45 and 3.62 ppm, assigned to the methylene protons attached to the carbonyl and the ether group, respectively, and a multiplet at 2.07 ppm, corresponding to the central methylene protons in the structure above.

The calorimetric analysis of PDTMB was carried out using a Mettler TA3000 differential scanning calorimeter. Two thermal transitions were observed, as can be seen in Figure 1. Thus, after a first heating cycle from room temperature to 300 °C (not shown), the subsequent cooling led to an exothermic peak at 154 °C, followed by a second-order glass transition at 11 °C. A second heating cycle (lower curve in Figure 1) shows again the glass transition, now at 17 °C, plus a melting endotherm at 172 °C.

The conclusion is, then, that only one kind of structure with a certain degree of order seems to be generated by the effect of temperature. Its nature was investigated by performing several X-ray diffraction experiments at variable temperature. The two representative diffractograms are shown in Figure 2. The lower one, obtained at 192 °C, represents the isotropic melt, with only a broad amorphous halo. The other diagram was obtained at 152 °C, where the sample begins to "crystallize" in a reasonable time. It shows now two sharp diffractions corresponding to spacings of 1.72 and 0.85 nm, besides the broad peak centered at 0.43 nm. The two sharp diffractions are assigned to the characteristic length of the smectic phase, in analogy with other similar systems,[6] and its second order, respectively. Similar diffractograms were obtained at lower temperatures and also after annealing the sample during 2 h at temperatures between 72 and 92 °C.

Two more attempts were done in order to obtain a possible more ordered structure. Thus, a DSC sample was

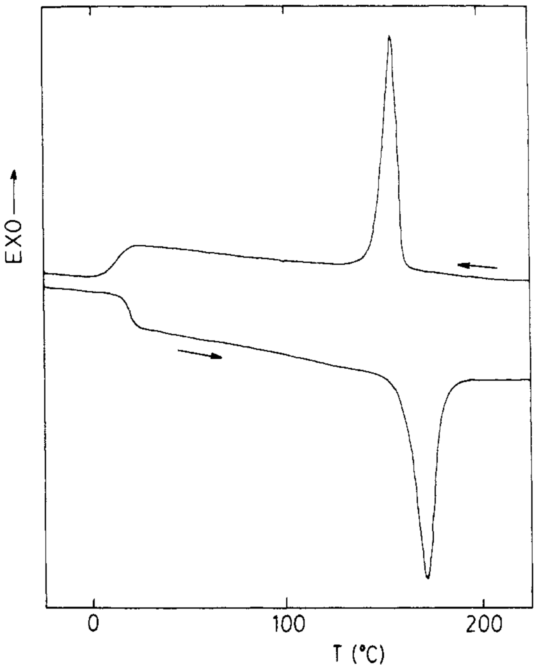


Figure 1. DSC curves of PDTMB representing a cooling cycle (upper) starting from the isotropic melt and the subsequent heating cycle (lower). Scanning rate 20 °C/min.

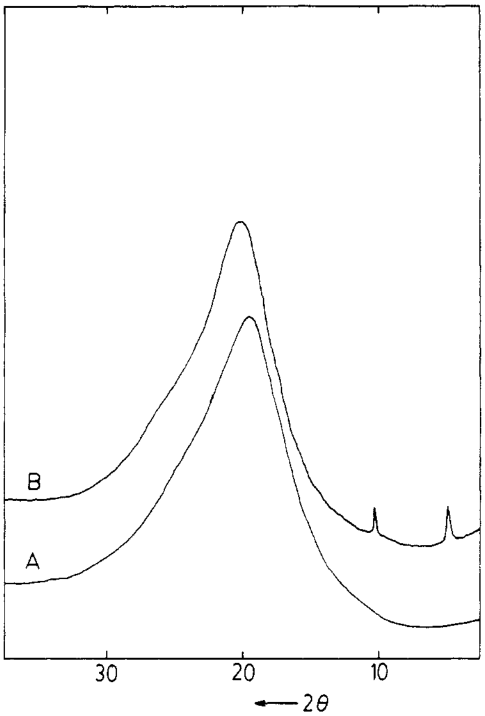


Figure 2. X-ray diffractograms obtained at different temperatures corresponding to PDTMB: (A) 192 °C; (B) 152 °C. Noise has been suppressed.

kept during 1000 min at 70 °C or 250 min at 110 °C. The subsequent heatings showed only the endothermic peak at 172 °C.

From these experiments and the kind of diffractograms, representative of a 2-dimensional state, it follows that the only structure obtained for PDTMB is probably a smectic liquid-crystalline phase, stable at any temperature below its isotropization point. We were unable to generate any other structure with a higher degree of order, although other similar systems[6-9] have been reported to be able to undergo a transformation from the mesophase to a more ordered crystal structure. The results from this work show, however, that the only transformations of the liquid-crystalline phase of PDTMB, at least in the time scale of our experiments, are either to the isotropic melt or to the glassy state.

The texture of PDTMB was analyzed by using a polarizing microscope. Only very small "spheres", although birefringent, were observed below the isotropization temperature. No other texture was detected even at the maximum resolution of the microscope (×400). More revealing textures have been reported, however, for other similar systems,[8] although there seems to be a tendency to observe them only for lower molecular weights.

The type of mesophase of PDTMB can be inferred from the comparison with other poly(bibenzoates), particularly poly(heptamethylene *p,p'*-bibenzoate) (P7MB) with a structure very similar to PDTMB: the only difference is the change of the central methylene of that polymer by an ether group. P7MB has been reported to give rise to a smectic mesophase with a characteristic length[6,9] of 1.74–1.72 nm, showing an X-ray diffractogram for the mesophase almost identical with PDTMB. In fact, the change of a methylene by an oxygen is expected to produce minor differences in the length of the repeating unit and hence the smectic layer spacing. Curiously, the clearing temperature of the mesophase of P7MB[9] is about 10 deg lower than that for PDTMB, when one might expect a lowering of that temperature by the effect of the oxygen. However, there may be differences in the molecular weight, having the opposite influence (although the intrinsic viscosity of the PDTMB sample studied here is very similar to the value of 1.03 dL/g found for P7MB[9]).

The really important effect of the ether group, compared to the all-methylene spacer is the suppression of the crystalline state, and its seems that the flexibility introduced by the ether group does not affect the formation and characteristics of the mesophase, considering the similarities of the X-ray diffractograms. That the mesophase of PDTMB is not very different from the one of P7MB is also confirmed by the similarities of the enthalpies of isotropization (19 J g^{-1} for the former polymer and 18.5 J g^{-1} for the latter one[9]), and by the corresponding entropies, even closer (0.043 J g^{-1} K^{-1} for both polymers).

In conclusion, the substitution of the central methylene of poly(heptamethylene *p,p'*-bibenzoate) by an ether group leads to a polymer, PDTMB, with similar characteristics concerning the liquid-crystalline state of the two polymers. However, the presence of the oxygen atom precludes the formation of a 3-dimensional crystal structure in PDTMB, presumably as a consequence of the increase in flexibility introduced by the ether group. Thus, the properties of the liquid-crystalline phase of PDTMB can be studied at room temperature. Experiments are now in progress in order to study the mechanical properties and the kinetics of the formation of the mesophase of this polymer, as well as to synthesize new poly(bibenzoates) derived from the dimers of other substituted trimethylene glycols and to investigate the effect of different substituents on the properties of the resulting polyesters.

Acknowledgment. We acknowledge the financial support of the Comisión Interministerial de Ciencia y Tecnolgía, Project No. MAT88-0220.

References and Notes

(1) Mark, J. E. *J. Chem. Phys.* **1977**, *67*, 3300.
(2) Saiz, E.; Riande, E.; Guzmán, J.; de Abajo, J. *J. Chem. Phys.* **1980**, *73*, 958.
(3) Conjeevaram, S. V.; Benson, R. S.; Lyman, D. J. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 429.
(4) Wojtania, M.; Kubisa, P.; Penczek, S. *Makromol. Chem., Macromol. Symp.* **1986**, *6*, 201.
(5) González, C. C.; Bello, A.; Pereña, J. M. *Makromol. Chem.* **1989**, *190*, 1217.
(6) Watanabe, J.; Hayashi, M. *Macromolecules* **1988**, *21*, 278.
(7) Meurisse, P.; Noel, C.; Monnerie, L.; Fayolle, B. *Br. Polym. J.* **1981**, *13*, 55.
(8) Krigbaum, W. R.; Watanabe, J. *Polymer* **1983**, *24*, 1299.
(9) Pérez, E.; Bello, A.; Marugán, M. M.; Pereña, J. M., submitted for publication.

A. Bello, E. Pérez,* M. M. Marugán, and J. M. Pereña

Instituto de Ciencia y Tecnología de Polímeros
Juan de la Cierva 3, 28006-Madrid, Spain

Received August 2, 1989
Revised Manuscript Received November 7, 1989

Registry No. PDTMB, 124399-69-5; PDTMB (copolymer), 124399-68-4.

Copolymerization of Alkenes with Sulfur Dioxide: A Semiempirical Molecular Orbital Study

Alkane- and arenesulfonyl radicals ($RSO_2^{\bullet}$) are reactive electrophilic intermediates that have been detected in a number of chemical reactions,[1] e.g., during the addition of alkane- and arenesulfonyl halides to unsaturated C–C bonds[2] and the alternating copolymerization of alkenes with liquid SO_2.[3] Because of the strongly electrophilic character of sulfonyl radicals, structural factors that affect the electron density distribution in the double bond manifest themselves in the relative reactivities of unsaturated compounds toward these radicals.[2g] Also, the alkene/SO_2 copolymerization systems exhibit low ceiling temperatures, T_c, reflecting the importance of depropagation reactions in such systems and the relative weakness of the C–S bond.[3]

Computational studies of reactions involving sulfonyl radicals should help to identify the various electronic and steric factors responsible for the observed reactivity order of alkenes and the observed low T_c values, but no such studies have been reported. Surveys of the literature indicate that computational studies of SO_2-containing compounds by both ab initio[5] and semiempirical[6] molecular

0024-9297/90/2223-0907$02.50/0