The simplicity of the function (2) allows us to make an important mechanistic conclusion: For $p \gg 7$, the decay rate depends inversely on the degree of polymerization. For example, if we "cut" each macromolecule in half there is a twofold increase in the rate of decoloration. The explanation is easy if we assume that (a) only the edge merocyanine groups in a stack are converted into spiropyrans (i.e., the conversion occurs step-by-step from the ends of the stacks) and (b) each macromolecule forms only one stack, whose length is proportional to the degree of polymerization. The last assumption is inconsistent with a simple idea on the stack formation in the macromolecular loops. Indeed, it is hard to imagine that a macromolecule would form only one stack, irrespective of macromolecular length. Formation of loops in short macromolecules is in particular hindered by the stiffness of the polymethacrylate backbone bearing the bulky spiropyran or merocyanine groups. On the other hand, the formation of the *intra*molecular stacks can be explained if one assumes that the macromolecules have a regular configuration such as a helix, which would allow the possibility of the merocyanine molecules to form the stacks with a periodic structure.

The alternative explanation is based on the assumption that the merocyanine stacks are formed by *inter*molecular association of the macromolecules. Tazuke and co-workers found efficient association of macromolecules by donor–acceptor interactions of the side groups in an extremely dilute solution. Corresponding low molecular compounds do not associate in solution (see ref 11 and references therein). The second explanation could account for the fact that polydisperse polymer merocyanine–spiropyran conversion is described by the two-exponential function whereas the fractionated polymer decays with first-order kinetics. The association of macromolecules of different lengths leaves part of the merocyanine groups "unstacked". These "unstacked" groups are converted to the spiropyran groups faster than the "stacked" ones. The portion of the "unstacked" groups must be much less for the associated macromolecules of an equal length and the merocyanine–spiropyran conversion fits the first-order kinetics well.

Acknowledgment. We thank Dr. I. Khait for valuable discussions. Support from The U.S.–Israel Binational Science Foundation and the Minerva Foundation, Munich, FRG, is gratefully acknowledged.

Registry No. A (spiropyran) (R = $(CH_2)_2OCO(CH_3C{=}CH_2)$ (homopolymer), 99342-38-8.

References and Notes

(1) N. S. Kardash, V. A. Krongauz, E. L. Zaitseva, and A. V. Movshovitch, *Polym. Sci. USSR (Engl. Transl.)*, **16A**, 453 (1974).
(2) G. Smets, J. Breaken, and M. Irie, *Pure Appl. Chem.*, **50**, 845 (1978).
(3) J. Labsky, F. Mikes, and J. Kalal, *Polym. Bull.*, **2**, 785 (1980).
(4) J. Labsky, L. Koropecky, S. Nespurek, and J. Kalal, *Eur. Polym. J.*, **17**, 309 (1981).
(5) Y. Kalisky and D. J. Williams, *Macromolecules*, **17**, 292 (1984).
(6) V. A. Krongauz and E. S. Goldburt, *Macromolecules*, **14**, 1382 (1981).
(7) E. S. Goldburt, F. P. Shvartsman, S. N. Fishman, and V. A. Krongauz, *Macromolecules*, **17**, 1225 (1984).
(8) E. S. Goldburt, F. P. Shvartsman, and V. A. Krongauz, *Macromolecules*, **17**, 1876 (1984).
(9) T. Wismontski-Knittel and V. A. Krongauz, *Macromolecules*, in press.
(10) E. L. Zaitseva, A. L. Prohoda, L. N. Kurkovskaya, R. P. Shifrina, N. S. Kardash, N. A. Drapkina, and V. A. Krongauz, *Khim. Geterotsikl. Soedin.*, **10**, 1362 (1973).
(11) S. Tazuke, H. L. Yuan, *Macromolecules*, **17**, 1878 (1984).
(12) Present address: IBM T. J. Watson Research Center, Yorktown Heights, NY 10598.

Efim Goldburt[12] and Valeri Krongauz*
Department of Structural Chemistry
The Weizmann Institute of Science, Rehovot, 76100, Israel

Received August 6, 1985

Transformation of a Monotropic Liquid Crystalline Polymer to an Enantiotropic One by Increasing Molecular Weight of the Polymer

There is an interesting phenomenon associated with liquid crystalline compounds: some are monotropic whereas most are enantiotropic. A compound is enantiotropic if it shows a stable liquid crystalline state both on heating to above its melting point (or, in certain instances, glass transition temperature) and on cooling from above its clearing temperature (i.e., isotropization temperature). It is monotropic, on the other hand, if it shows a liquid crystalline state only on cooling. It is believed that the monotropism is usually due to the extent of the crystalline order being great enough to preserve the true solid above the range of mesophase thermal stability,[1] and it is, therefore, possible to reveal the potential enantiotropic behavior of a monotropic compound by sufficiently depressing the melting point of the solid. For many low molecular weight systems various impurities have been used to achieve this objective.[2] A recent report from Lenz's group discussed the work of transforming an apparently non-liquid crystalline polymer to nematic by incorporating a small amount of a comonomer into the polymer chains.[3] Although copolymerization can depress a melting point and thus favor the formation of a liquid crystalline state, a polymeric system also can be changed significantly by the incorporation of comonomers. No matter how little the amount of added comonomer, the polymer behaves as a copolymer and not as a homopolymer. There are also monotropic systems of polymeric compounds. The transformation of a monotropic liquid crystalline compound to an enantiotropic one by increasing molecular weight was first observed by Blumstein and coworkers.[4] They synthesized model compounds of the nematic polyester poly(2,2′-dimethyl-4,4′-dioxyazoxybenzene-dodecanedioyl) and found that molecular weight and molecular weight distribution have a drastic influence on transition temperatures and mesophase stability. Their model compounds 9-DDA-9 and 9-DDA-9-DDA-9 are monotropic, and the lowest molecular weight to display an enantiotropic nematic phase is approximately 2800. Recently, we synthesized a monotropic liquid crystalline polyester of low molecular mass by polycondensation of 1,10-bis((chloroformyl)benzoyloxy)decane and 2-formyl-1,4-dihydroxybenzene.[5] In this communication we report the conversion of this monotropic polymer to an enantiotropic one by increasing polymer molecular weight.

Experimental Section. The polymer was synthesized by the solution polycondensation of the monomers 1,10-bis((chloroformyl)benzoyloxy)decane and 2-formyl-1,4-dihydroxybenzene:

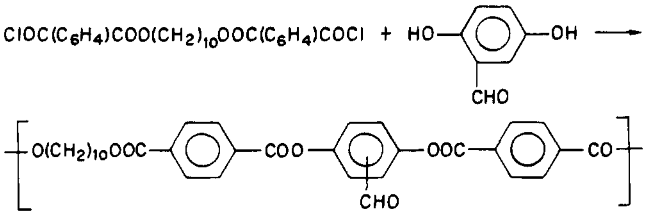

Table I
Physical Properties of the Polymer Fractions[a]

sample	inh viscosity	heating T_m	heating T_i	heating $T_i - T_m$	cooling T_{lc}	cooling T_c	cooling $T_{lc} - T_c$
1	0.140	144			139	107	32
2	0.150	139			122		
3	0.158	144			129	102	17
4	0.197	159	160[b]		160	112	48
5	0.198	158	161[b]		160	119	41
6	0.254	156	167	11	163	102	61
7	0.301	160	170	10	169	103	66
8	0.318	158	172	14	171	104	67
9	0.334	158	173	15	169	102	67
10	0.355	158	176	18	174	102	72
11	0.369	157	175	18	172	98	74
12	0.474	159	180	21	173	102	71
13	0.540	154	177	23	171	98	73
14	0.596	155	180	25	172	102	70
15	0.712	153	176	24	167	103	70

[a] The temperatures are all in °C; m = melting, i = isotropization, lc = liquid crystallization, and c = crystallization. [b] The sample was heated to 200 °C, cooled from 200 to 130 °C, and then heated again to find the temperature T_i.

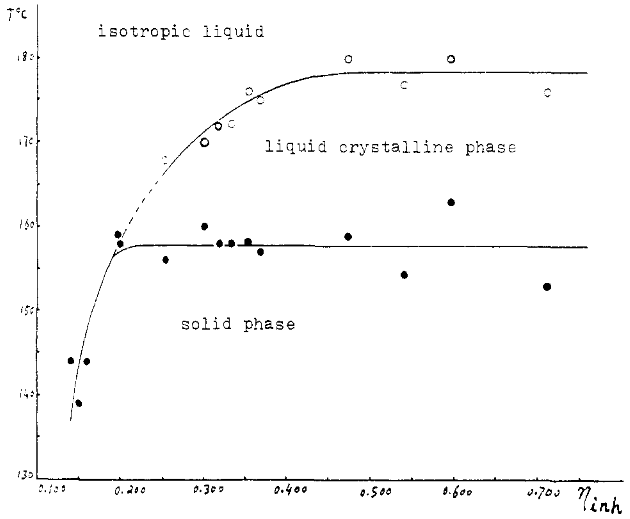

Figure 1. Phase diagram of the polymer constructed from the observed transition endothermic peak temperatures (Table I).

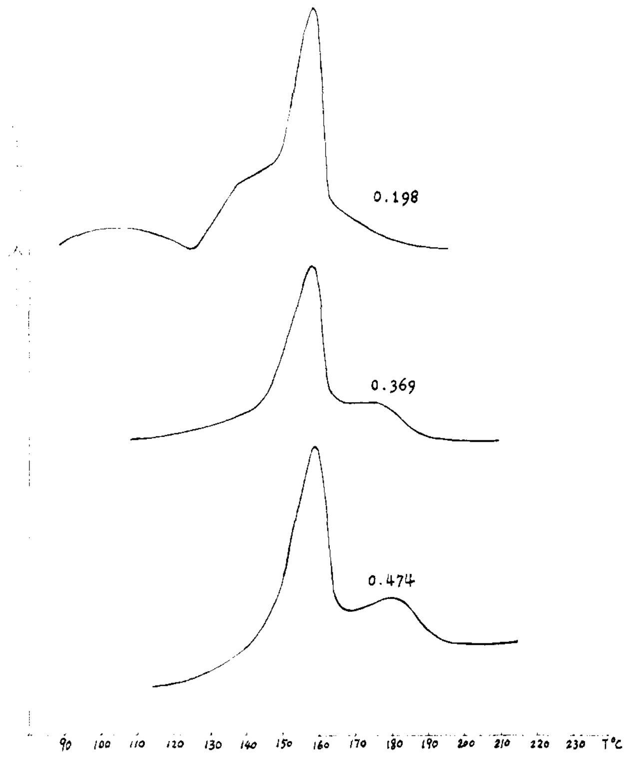

Figure 2. DSC thermograms of the samples with different inherent viscosities (in dL/g).

1,2-Dichloroethane and pyridine were used respectively as the solvent and HCl absorbent. The reaction was carried out at refluxing temperature under nitrogen for about 40 h, and the mixture was then poured into a large volume of methanol to precipitate the polymer. The precipitate was washed thoroughly with methanol and dried under vacuum at 40–50 °C.

Fractionation of the Polymer. Fractionation of the polymer was carried out by addition of ethanol (the precipitant) to a solution of the polymer in 1,1,2,2-tetrachloroethane. The polymer fractions thus obtained were dissolved in trifluoroacetic acid and then poured into a large volume of cold water, and the polymer fractions were recovered by filtration, washing with water, and drying. This procedure was designed to recover the formyl groups in the polymer, which may have been converted to acetals by reaction with alcohol during the fractionation.

Polymer Characterization. Solution viscosities of the polymer fractions were measured in a Ubbelohde viscometer at 40 °C at a solution concentration of 0.5 g/dL in tetrachloroethane. Thermal properties of the fractions were studied with a Shanghai CDR-1 DSC instrument under a nitrogen atmosphere with a heating rate of 10 °C/min. Phase transitions of the polymers were also examined on a heating stage (Leitz, 350) of a polarizing microscope (Leitz, SM-LUX-POL).

Results and Discussion. Inherent viscosities of the polymers in the range 0.140–0.712 dL/g are shown in Table I. Molecular weights of the fractions have not been obtained as yet. Table I also contains thermal properties of the fractions. The peak temperature of the DSC melting endotherm of each sample is represented by T_m, and T_i is the isotropization peak point. Transition temperatures vs. viscosities are plotted in Figure 1. As shown, both T_m and T_i are molecular weight dependent; both increase with molecular weight in the lower molecular weight range and then reach a plateau. The same observation has been made with the tempertature range (ΔT) of the stable liquid crystalline phase. These results are similar to those reported by Blumstein[4] and Lenz.[6] In addition, in our polymer system it is likely to have a triple point at an *inherent viscosity of approximately* 0.2 dL/g and a temperature ~158 °C, where T_m and T_i meet.

Significantly we have been able to observe monotropic behavior in polymer fractions with inherent viscosities lower than 0.19 dL/g. As seen in Table I, samples 1–3 show only one melting endotherm peak on heating but two exotherms on cooling. The latter, liquid crystallization and crystallization, were also observed in a hot-stage polarizing microscope. A critical molecular weight may be necessary for a mesogenic polymer to show a mesophase on heating, below which the mesophase cannot exist at a temperature above T_m, but a stable mesophase may be obtained during cooling from the isotropic melt if there is a significant temperature difference between the supercoolings of the two transitions. In the polymer system reported here the liquid crystallization temperature, T_{lc}, of the isotropic melt is only a few degrees below the isotropization temperature, T_i, of the mesophase, while the crystallization temperature, T_c, is lower than the initial melting point, T_m, by as many as 40–60 °C.

The enantiotropic behavior begins when the polymer reaches an inherent viscosity of about 0.2 dL/g. Samples 4 and 5 have one sharp melting endotherm each on heating (Figure 2). However, as the figure shows, the curve for viscosity 0.198 dL/g may have hinted a transition following the melting. In addition, on cooling from about 200 °C to room temperature the sample showed two far-separated exotherms, one peaked at 160 °C, the other at 119 °C. The former is higher than the melting point (158 °C) and is proved (with a polarizing microscope) to be the transition temperature from isotropic liquid to liquid crystalline, T_{lc}. The latter is of crystallization, T_c. Furthermore, if the sample is cooled to ~130 °C (above T_c, in order to avoid crystallization) and then heated again, it shows a transition at 161 °C. This isotropization temperature is so close to the melting peak point that the two endotherms, T_m and T_i, would overlap if the sample is heated from its crystalline state, making T_i almost impossible to be distinguished. Figure 2 shows that T_i is more distinguishable if the molecular weight is higher. Both T_i and ΔH_i increase with increasing molecular weight.

Interestingly, Figure 2 is very similar to that of Bassett and Turner,[7] who found a critical pressure for polyethylene to form a smectic B phase. What this similarity means has still to be discovered.

Acknowledgment. The financial support of this work by the Science Academy of China is gratefully acknowledged.

Registry No. (1,10-Bis((chloroformyl)benzoyloxy)decane)·(2-formyl-1,4-dihydroxybenzene) (copolymer), 99328-36-6; (1,10-bis((chloroformyl)benzoyloxy)decane)·(2-formyl-1,4-dihydroxybenzene) (SRU), 99397-51-0.

References and Notes

(1) Barrall, E. M., II In "Liquid Crystals, The Fourth State Of Matter"; Saeva, F. D., Ed.; Marcel Dekker: New York, 1979; p 345.

(2) Vogel, M.; Barrall, E. M.; Mignosa, C. P. *Mol. Cryst. Liq. Cryst.* **1971**, *15*, 49.

(3) Zhou, Q.-F.; Jin, J.-I.; Lenz, R. W. *Can. J. Chem.* **1985**, *63*, 181.

(4) Blumstein, R. B.; Stickles, E. M.; Gauthier, M. M.; Blumstein, A.; Volino, F. *Macromolecules* **1984**, *17*, 177. Blumstein, R. B.; Stickles, E. M. *Mol. Cryst. Liq. Cryst. Lett.* **1982**, *82*, 151. Blumstein, R. B.; Stickles, E. M.; Blumstein, A. *Ibid.* **1982**, *82*, 205.

(5) Zhou, Q.-F.; Zhang, B.-J., unpublished work.

(6) Majnusz, J.; Catala, J. M.; Lenz, R. W. *Eur. Polym. J.* **1983**, *19*, 1043.

(7) Bassett, D. C.; Turner, B. *Philos. Mag.* **1974**, *29*, 925.

Qi-Feng Zhou,* Xiao-Qing Duan, and Ya-Lei Liu

Chemistry Department, Peking University
Beijing, China

Received August 5, 1985