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Thermotropic Copolyesters Exhibiting a Cholesteric Phase. II

J. Watanabe [a] & W. R. Krigbaum [b]
[a] Department of Polymer Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo, 152, Japan
[b] Department of Chemistry, Duke University, Durham, N.C., 27706

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J. WATANABE

Department of Polymer Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo, 152 Japan

and

W. R. KRIGBAUM

Department of Chemistry, Duke University, Durham, N. C. 27706

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Copolyesters of 4,4′-dihydroxybiphenyl with HOOC—$(CH_2)_n$—COOH and chiral (+)-3-methyl adipic acid form thermotropic cholesteric phases. The cholesteric-isotropic transition temperature, and enthalpy and entropy changes, exhibit an even-odd effect in terms of the number, n, of methylene units in the aliphatic dibasic acid. The even members have larger values of all these quantities. The twist angle of the cholesteric phase also exhibits an even-odd effect, with the even members showing a smaller twist angle (larger pitch). The temperature dependence of the twist angle, or inverse optical pitch $1/\bar{n}P$ (where $\bar{n}$ is the refractive index of the copolymer), is approximately constant for $n \leqq 8$, but increases for still larger values of n. A theoretical treatment of the cholesteric twist angle given by Keating is used to deduce the structural features which might give rise to these observations concerning the pitch and its temperature dependence.

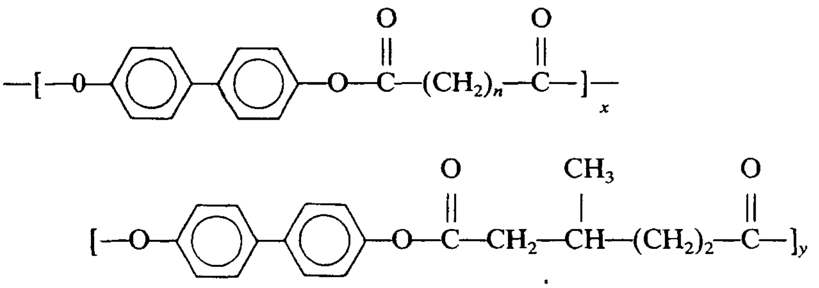
INTRODUCTION

The properties of polymeric cholesteric phases have been mainly investigated for the lyotropic mesophases of polypeptides[1,2] and cellulose derivatives.[3-5] In the early 1980's reports of thermotropic cholesteric polyesters were given by Van Luyen *et al.*,[6] Vilasagar and Blumstein,[7] and Krigbaum and coworkers.[8] More recently the thermotropic cholesteric polypeptides were investigated by Watanabe *et* *al.*[9,10] However, cholesteric behavior has not been as fully explored for thermotropic as for the lyotropic mesophases.

The homopolyesters formed from 4,4′-dihydroxybiphenyl and aliphatic dibasic acids, HOOC—$(CH_2)_n$—COOH, were earlier reported[11,12] to form a thermotropic nematic phase when n is odd and a highly ordered smectic S_H phase when n is even. Paper I[13] of this series investigated the thermotropic cholesteric phases formed by copolyesters of 4,4′-dihydroxybiphenyl with various ratios of azelaic acid, HOOC—$(CH_2)_7$—COOH and chiral (+)-3-methyladipic acid. The sense of the cholesteric helix was found to be left-handed, and the pitch, P, was in the visible range when the mole fraction of chiral units was between 0.3 and 0.5. The pitch decreased with increasing temperature with a coefficient $d(1/\bar{n}P)/dT = 7 \times 10^{-6}$ $\text{nm}^{-1}\text{K}^{-1}$, where $\bar{n}$ is the average refractive index of the cholesteric phase. This corresponds to $d \ln P/dT = -2.0 \times 10^{-3}/\text{K}$. The cholesteric structure could be preserved in the glassy polymer by fast cooling to avoid crystallization, and the perfection of its structure could be improved by annealing just below the crystal-cholesteric transition temperature. In the present paper we investigate other members of this series in which the dibasic acid has either an even or an odd number of methylene units.

EXPERIMENTAL

The copolymers may be represented schematically by the formula:



For brevity, this copolymer is denoted *PB-n*,4′(*x*,*y*), where x and y are the mole fractions of aliphatic dibasic acid and chiral (+)-3-methyladipic acid, respectively. These polymers were prepared by melt transesterification using equimolar quantities of diol and total dibasic acid. Inherent viscosities of the copolymers, which were determined using 0.5 g/dL solutions of a 60/40 mixture by weight of phenol and tetrachloroethane, were in the range 0.3 to 0.5 dL/g. The phase diagrams were constructed from DSC transition temperatures and hot stage polarizing microscope observations. The circular dichroism (CD) spectra were obtained using a Jasco model J-20 automatic recording spectropolarimeter.

RESULTS AND DISCUSSION

A. Cholesteric Phases of PB-7,4′ and PB-8,4′

In paper I[13] of this series we converted the nematogen PB-7 into one exhibiting a thermotropic cholesteric phase by the incorporation of chiral (+)-3-methyl adipate. The mesophase region was widened by copolymerization, and the conversion to a twisted nematic phase due to the addition of a chiral monomer is easily understood. On the other hand, the corresponding homopolyesters with an even number of methylene units in the flexible segment form a smectic S_H mesophase. Hence, the appearance of a cholesteric phase by copolymerization with a chiral monomer requires the conversion of the S_H phase into a nematic phase. In a previous paper[14] we investigated the properties of copolymers based on a single rigid segment and two flexible segments. It was demonstrated that the conversion of an S_H phase to a nematic phase occurs when $n = 6$ and 12, or when $n = 8$ and 7. In the former case the flexible segments differ substantially in length, and in the latter they differ in odd-even character.

Figure 1 shows the phase diagram of copolymers of (+)-3-methyl adipic acid (designated PB-4′) and the even membered PB-8. The crystal-smectic transition temperature is remarkably reduced by the first addition of chiral (+)-3-methyl adipate units, and disappears when the content of chiral units exceeds 30%. Moreover, a cholesteric phase appears upon the addition of PB-4′ units, which indicates the smectogenic character has been converted to a nematogenic character by the addition of this comonomer. A fairly broad temperature range of the cholesteric phase is found for the equimolar copolymer, and iridescent colors due to the selective reflection of visible light are seen in copolymers having chiral contents in the range 40% to 60%. The homopolyester PB-4′ was prepared, but it decomposed immediately after melting at 340°C, which prevented investigation of the thermotropic behavior of this polymer. Although this did not allow us to complete the phase diagram, we anticipate that it would be similar to the other copolymers investigated in the previous paper[13] which contained two flexible segments.

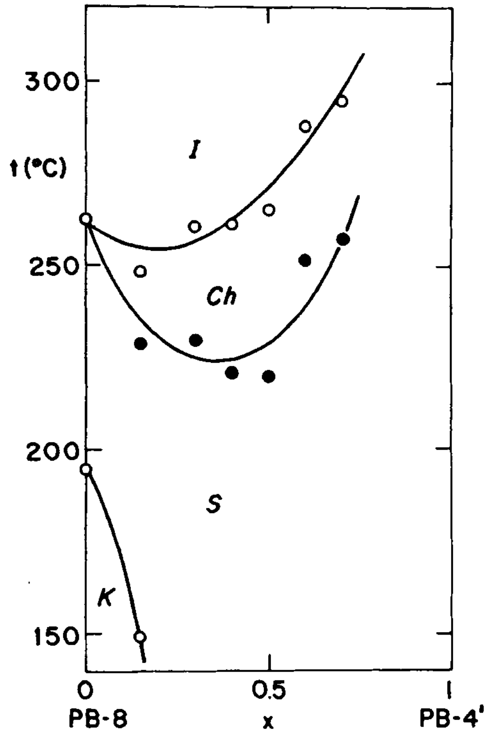


FIGURE 1 Phase diagram for PB-8,4′ copolymers constructed from DSC cooling data.

We designate the optical pitch by $\bar{n}P$. Figure 2 illustrates the temperature dependence of the inverse optical pitch, $1/\bar{n}P$, for three PB-8,4′ copolymers having different chiral contents. The inverse optical pitch (which is proportional to the twist angle) increases with chiral content, y, and with temperature, but its temperature dependence appears to be independent of y. Figure 3 compares the dependence upon chiral content of $1/\bar{n}P$, as measured at 220°C, for PB-7,4′ and PB-8,4′. For both copolymers $1/\bar{n}P$ varies linearly with chiral content over the rather limited range investigated; however, the slopes differ. A given mole fraction of chiral units is less effective in producing twist for PB-8,4′ as compared to PB-7,4′.

B. Even-odd effects

A series of equimolar chiral copolymers was next prepared in which the number, n, of methylene units ranged from 5 to 12. All of these

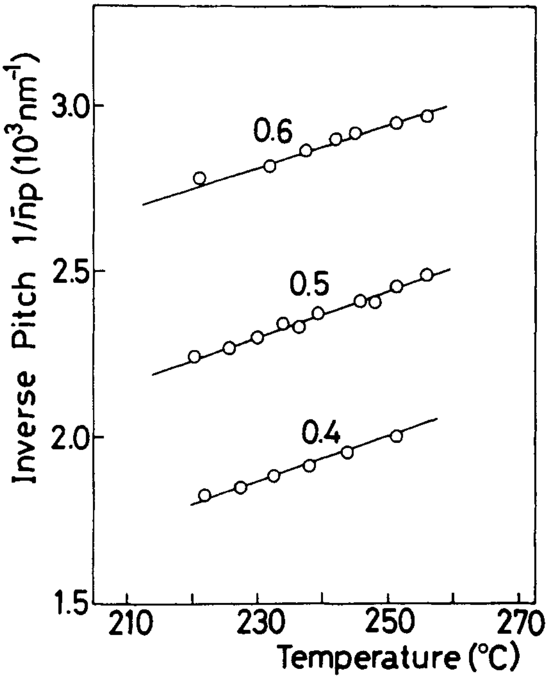


FIGURE 2 Temperature dependence of the inverse optical pitch for three PB-8,4′ copolymers having mole fraction of chiral units y = 0.4, 0.5 and 0.6.

copolymers exhibited two endotherms in the differential scanning calorimeter heating curves. The endotherm at lower temperature corresponds to the crystal-cholesteric transition for n odd, and to the smectic-cholesteric transition when n is even. The higher temperature endotherm marks the cholesteric-isotropic transition. Some of the polymers exhibited other transitions, but these will not be discussed further. Data obtained from the cooling curves concerning the temperature range of the cholesteric phase and the enthalpy and entropy changes upon isotropization are collected in Table I. The final column gives the temperature dependence of the inverse optical pitch for these equimolar copolymers.

In Figure 4 is shown the behavior of the two transition temperatures as a function of the number, n, of methylene units in the dibasic acid. Both temperatures exhibit the usual even-odd oscillation, and the temperature range over which the cholesteric phase is stable becomes more narrow as n increases. Similarly, an even-odd oscillation is found in the isotropization entropies, ΔS_i, as shown in Figure 5, and for the isotropization enthalpies. ΔS_i for the even members is approximately

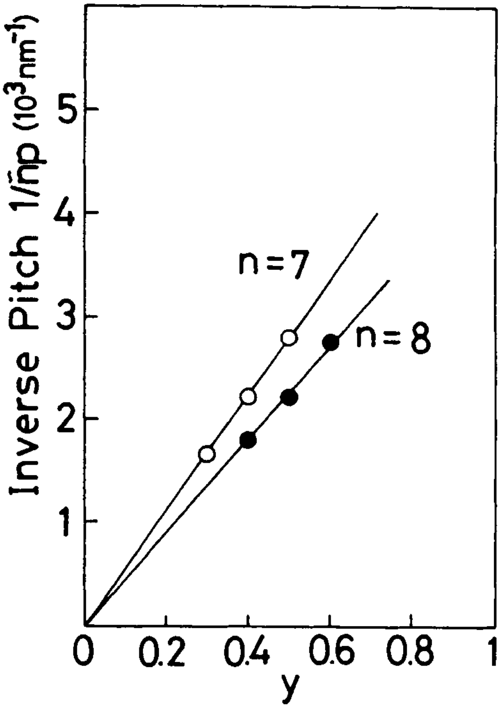


FIGURE 3 Comparison of the dependence of the inverse optical pitch at 220°C upon chiral content, *y*, for PB-7,4′ and PB-8,4′ copolymers.

twice that of the odd members. It seems unlikely that the entropies of the isotropic phases of the even and odd members would differ by this magnitude, leading to the conclusion that the cholesteric phase of the even-membered series is more highly ordered.

TABLE I

Characterization of copolyesters

Polymer	Temperature range°C of liquid crystal[a]	ΔH_i[a] (kcal/mole)	ΔS_i[a] (cal/mole K)	$10^5 \times d(1/\bar{n}P)/dT$ (nm^{-1} K^{-1})
PB-5,4′	239–280	0.77	1.40	0.70
PB-7,4′	188–244	0.83	1.60	0.70
PB-8,4′	214–265	1.43	2.65	0.71
PB-9,4′	181–233	0.88	1.75	0.97
PB-10,4′	216–252	1.48	2.80	1.15
PB-11,4′	195–221	1.05	2.12	1.39
PB-12,4′	210–239	1.50	2.93	1.51

[a] Based on DSC cooling data.

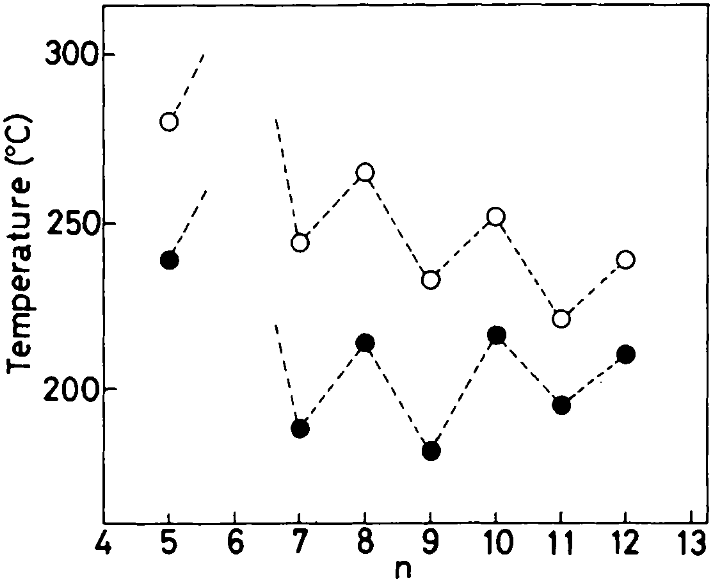


FIGURE 4 Dependence upon the number, *n*, of methylene units in the aliphatic dibasic acid of the crystal-cholesteric (odd) or smectic-cholesteric (even) transition temperature (filled circles) and cholesteric-isotropic temperatures (open circles).

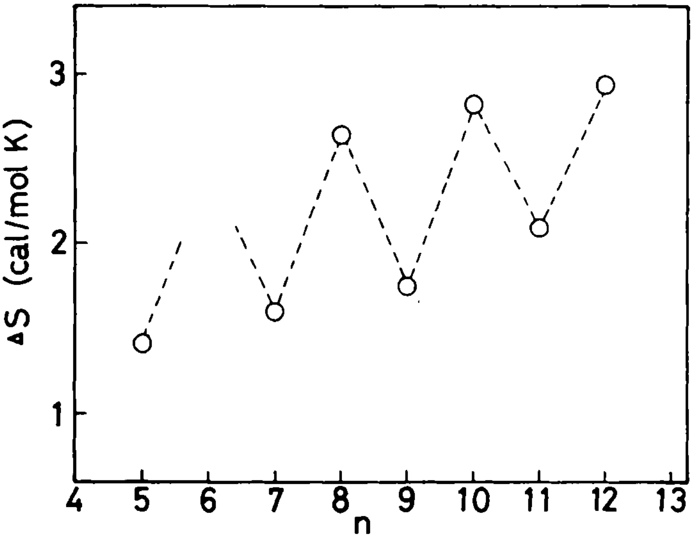


FIGURE 5 The entropy of isotropization plotted against the number, *n*, of methylene units in the aliphatic dibasic acid.

The temperature dependence of the inverse optical pitch, $1/\bar{n}P$, is shown in Figure 6. Each polymer is identified in this figure by its number, *n*, of methylene units. Apart from the smaller magnitude of the inverse pitch for the even members, one notes that the slope increases with *n*. Figure 7 illustrates values of $1/\bar{n}P$ at 220°C plotted against the number, *n*, of methylene units in the aliphatic dibasic acid. For PB-9,4′ and PB-11,4′ the values of $1/\bar{n}P$ at 220°C were obtained by extrapolation. An even-odd oscillation is apparent, with the even members exhibiting a larger cholesteric pitch (smaller $1/\bar{n}P$) for a fixed chiral composition, *y*. Even-odd effects have been reported for the homologous series of cholesteryl ω-phenylalkanoates by Ennulat and Brown,[15] but so far as we are aware, the present work provides the first experimental evidence for an even-odd oscillation of the pitch of cholesteric polymers. The slopes, $d(1/\bar{n}P)/dT$, taken from Figure 6 appear plotted against *n* in Figure 8. The temperature dependence of the inverse optical pitch is nearly constant for $n \leqq 8$, but it becomes progressively larger with further increase in *n*. There may be a slight even-odd oscillation in the upper branch, but this effect is small compared to the increase in temperature dependence with *n*.

The twist angle, ⟨θ⟩, between adjacent pseudonematic layers sep-

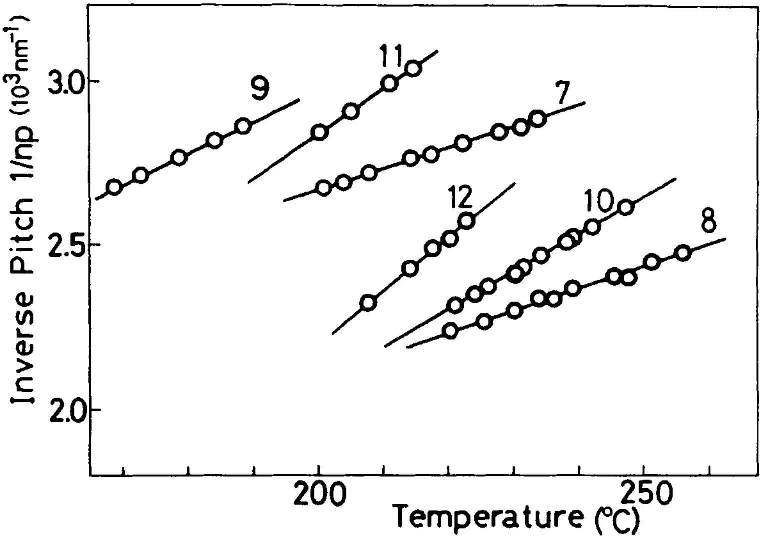


FIGURE 6 Temperature dependence of the inverse optical pitch for copolymers identified by the number, *n*, of methylene units.

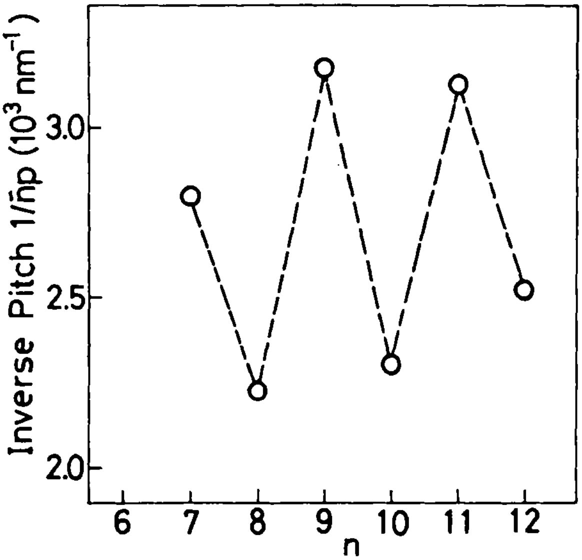


FIGURE 7 Dependence upon *n* of the inverse optical pitch, $1/\bar{n}P$, at 220°C.

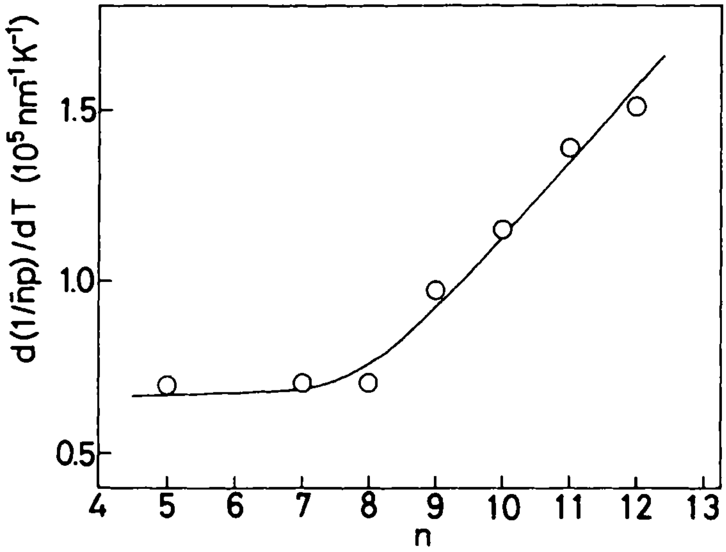


FIGURE 8 Variation of the temperature dependence of the inverse optical pitch with *n*.

arated by a distance a is given by:

$$\langle\theta\rangle = \frac{2\pi a}{P} \tag{1}$$

The observed values of $\langle\theta\rangle$ are quite small, on the order of 10^{-2} radian, so that on a local molecular scale the cholesteric structure is indistinguishable from that of a nematic. The treatment of Flory and Ronca[16] gives for the enthalphy of isotropization of a thermotropic nematic phase:

$$\Delta H_i = RT^*s(1 - s/2) \tag{2}$$

Here T^* is a measure of the strength of the orientation-dependent interactions and s is the nematic order parameter. This relation indicates that the larger ΔH_i values seen for the even-membered copolymers could arise from stronger orientation-dependent interactions, from a larger order parameter, or from a combination of these factors. These differences are consistent with our earlier speculation[12] concerning the molecular structures of the even and odd members, since the former were predicted to be more lath-like.

Turning to the observations concerning the cholesteric pitch, we find a number of theoretical treatments. De Gennes[17,18] presented an early phenomonological theory of the helical pitch, and this was followed by molecular theories due to Keating,[19] Goossens,[20] and Boettcher.[21] Russian workers[22,23] subsequently produced a modified Keating-Boettcher treatment. These developments have been reviewed by Schroeder,[24] and by Chilaya and Lisetskii.[25] In the present copolymer system the pitch decreases monotonically with temperature, so we might hope to gain some qualitative insights concerning the pitch and its temperature dependence from the treatment of Keating.[19] He considers the thermally excited libration of a molecule about an axis parallel with the cholesteric helix axis. Due to the chirality of the cholesteric molecules, the average twist angle $\langle\theta\rangle$, does not vanish, but is given by:

$$\langle\theta\rangle = \frac{A\theta_o^2}{4\omega_o^2} \tag{3}$$

where θ_o is the amplitude of the libration and ω_o is its angular frequency. From the equipartition principle, $(1/2)I\omega_o^2\theta_o^2 = kT$, where I

is the moment of inertia of the molecule, so that equation (3) may be written:

$$\langle\theta\rangle = \frac{AkT}{2I\omega_o^4} \tag{4}$$

As mentioned above, the larger ΔH_i values of the even members indicate that these have a larger order parameter, or stronger orientation-dependent interactions. In either event, we can expect the copolymers with even n to have a smaller amplitude of libration, θ_o, and thus a smaller twist angle, $\langle\theta\rangle$. This prediction is in accord with the data shown in Figure 7. If we assume that I and ω_o in equation (4) are independent of temperature, then $d\langle\theta\rangle/dT$ is predicted to be a constant, in agreement with the observations collected in Figure 6:

$$\frac{d\langle\theta\rangle}{dT} = \frac{Ak}{2I\omega_o^4} \tag{5}$$

We may expect that the methylene chain does not maintain the all-*trans* conformation as the number of methylene units is increased. If copolymers with $n > 8$ have some *gauche* conformations, this would reduce the moment of inertia, I, and increase the temperature dependence of the average twist angle, $\langle\theta\rangle$. This provides an explanation for the increasing branch of $d(1/\bar{n}P)/dT$ found in Figure 8. While the treatment of Keating[19] provides some qualitative insights, the actual situation is clearly more complicated than we have pictured. For example, we have assumed that I and ω_o are independent of temperature. In this case, equation (5) predicts that $d \ln \langle\theta\rangle/d \ln T = 1$. A plot of $\ln (1/P)$ *vs*. $\ln T$ for the present copolymers yields larger slopes, even for the lower members of the series. This may indicate that the assumption that I and ω_o are independent of temperature is incorrect, or it may point to other factors affecting the twist angle which are not considered in this simple treatment. Also, equation (5) would predict that the even members having $n \leqq 8$, which have smaller $\langle\theta\rangle$ values, should also exhibit smaller $d(1/\bar{n}P)/dT$ values. Figure 8 indicates this is not the case.

Acknowledgment

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