layers of these polymers. Rapid freeze-drying from dilute solution initially produces a randomly oriented material. The molecular migration necessary to form the long-range order of the cholesteric state must be a slow process, especially for high molar mass or unplasticized samples. Thus freeze-dried samples develop color very slowly. On the other hand, during slow evaporation of organic solvents or water, the polymer chains have greater freedom to migrate and form more rapidly the stable planar cholesteric arrangement. The stability of the cholesteric structure was observed with a number of unfractionated PPC samples of differing degrees of esterification that were prepared as thin layers between planar glass or plastic surfaces. The colors of these unsealed samples have remained unchanged for periods of up to 2 years.

PPC also forms lyotropic liquid crystalline phases in organic solvents. A series of solutions was prepared with concentrations ranging from 5% by weight to 95% by weight PPC in acetone. Dilute solutions were clear; concentrated solutions showed increasing turbidity, and at 90% PPC the solutions were iridescent. No distinct two-phase region was observed visually, even after prolonged standing. Visual observations with a polarizing microscope showed that the 30% solution was isotropic, and the 35% solution showed birefringence. The onset of birefringence was also detected by observations with an Abbé refractometer.

[(Propionyloxy)propyl]cellulose thus forms an ordered phase at concentrations between 30 and 35% by weight polymer in acetone. This is a somewhat lower concentration than required for (acetoxypropyl)cellulose in the same solvent[7] and for (hydroxypropyl)cellulose in a variety of solvents.[5,12] It is a much higher concentration than would be expected for a rodlike polymer of equivalent molecular weight[2] and, as suggested previously,[5] indicates that the cellulosic derivatives are not rigid in solution. The relationship between chain flexibility, critical concentration for mesophase formation, and side-chain structure is not yet quantitatively understood.

In summary, PPC forms lyotropic liquid crystalline phases in organic solvents, and the pure polymer forms a thermotropic liquid crystalline phase that shows cholesteric reflection at ambient temperatures. We suggest that the relatively stiff cellulose backbone forces a parallel orientation of the chains, the chirality of the cellulose chain imparts a twist to the parallel arrangement, and the flexible side chains allow the polymer molecules to migrate and form the equilibrium cholesteric arrangement. In the absence of solvent, the side chains control the average spacing between the almost-parallel cellulose backbones, and hence influence the pitch of the cholesteric helix.

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Odd–Even Effect in Thermotropic Liquid Crystalline 4,4′-Dihydroxy-2,2′-dimethylazoxybenzene–Alkanedioic Acid Polymers

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ABSTRACT: The thermal properties of a homologous series of mesogenic, thermotropic polyesters based on 4,4′-dihydroxy-2,2′-dimethylazoxybenzene and alkanedioic acids from $n = 2$ to $n = 14$ were studied. Because of moderate transition temperatures and molecular weights sufficiently high to minimize the dependence of thermal properties on molecular weight, a meaningful comparison of thermal properties could be obtained. The data indicate a remarkably regular odd–even effect for the transition temperatures, enthalpies, and entropies for the nematic (N) $\rightleftharpoons$ isotropic (I) transition. ΔH_{IN} and ΔS_{IN} are much higher than the corresponding values for low molecular weight analogues and increase continuously with the length of the flexible methylene sequence. The increase proceeds with approximately the same increment for the odd and even series of $[\Delta(\Delta H_{\mathrm{IN}})]_{\mathrm{av}} = 0.46$ kJ and $[\Delta(\Delta S_{\mathrm{IN}})]_{\mathrm{av}} = 1.52$ J/K per methylene group. This indicates that the flexible spacer takes part in the ordering process and that $\mathrm{N} \rightleftharpoons \mathrm{I}$ transition has a pronounced first-order character.

Thermal properties of linear, thermotropic polyesters have been recently an object of extensive investigations. An odd–even effect of the nematic to isotropic transition temperature was reported.[1-4] However, poor knowledge of molecular weights and molecular weight distributions (often in the oligomer range), high temperatures of isotropization impinging on decomposition, complex thermograms reflecting multiple melting, and the absence of

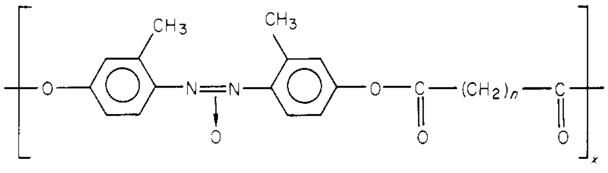
Table I
Transition Temperatures and Characteristics of 4,4′-Dihydroxy-2,2′-dimethylazoxybenzene–Alkanedioic Acid Polymers

n	transition to °C, heating	transition to °C, cooling	$[\eta]$, dL/g	$\overline{M}_n$ [a]
2	K234.8I[b]		0.32	
3	K185.8I(167.8N)	I134.8K	0.69	
4	K198.2N255I[b]		0.38	6 700
5	K135.8N173.8I	I168.8N[c]	0.63	13 300
6	K160.3N230.3I	I205.8N[c]	1.09	27 000
7	K98.3N164.6I	I156.8N[c]	1.35	36 000
8	K136.8N188.3I	I172.8N66.8K	1.36	36 400
9	K121N144I	I137N80K	0.79	17 800
10	K118.2N163.5I	I159.7N86.7K	0.80	18 000
11	K100.8N132.8I	I127.8N[c]	1.29	34 000
12	K110.8N143.8I	I135.8N75.8K	0.78	17 500
14	K121N134I	I122N95K	1.02	25 000

[a] Estimated from eq 1. [b] Partial decomposition. [c] Supercooling.

clear textures complicate the interpretation of the data reported.

In recent publications we have described the synthesis and properties of thermotropic polyesters with moderate transition temperatures.[5,6] These compounds are soluble in many solvents, and polymers with various molecular weights can be prepared easily, giving distinct, well-characterized sharp phase transitions. The study of thermal properties of such polyesters gives a clear picture of structure–property correlations in mesogenic polyesters and is therefore of obvious interest. In this paper we report a study performed on a homologous series of polyesters based on 4,4′-dihydroxy-2,2′-dimethylazoxybenzene and various alkanedioic acids (I), with n = 2–12 and 14.



I

Experimental Section

All polymers have been prepared according to a procedure described earlier.[5,6] Particular attention was paid to conditions (temperature, concentration of surfactant) that allowed the shift of the polycodensation toward relatively high molecular weights (see Table I). This is very important if a meaningful comparison is to be made of the extent of the mesophase interval and also of other thermodynamic properties such as transition temperatures, enthalpies, and entropies. Elemental analysis of C, H, and N for the synthesized materials was in good agreement with the calculated values. The polymers were studied by means of a Perkin-Elmer 2C differential scanning calorimeter. The values of transition temperatures T and transition enthalpies ΔH were determined from DSC traces after taking the polymer through at least one heating and cooling cycle (usually two) in order to ensure a constant thermal history. The heating and cooling rate was 20 °C/min. The cycling temperature was from 47 °C to a temperature of 15 °C above the nematic to isotropic transition. A typical DSC trace of the polyester with n = 12 is given in Figure 1. The positions of the peaks did not vary appreciably with the rate of heating or cooling. Microscopic observations of the transition temperatures were in agreement with the DSC thermograms and showed a very narrow biphasic (nematic and isotropic) region. The sharpness of the $N \rightleftharpoons I$ DSC peaks and of the transitions observed by microscopy point toward a polymer containing little low molecular weight contamination. The peak areas of the $K \rightleftharpoons N$ and $N \rightleftharpoons K$ transitions were dependent on the rate of cooling and in some cases the $N \rightarrow K$ peaks could be eliminated altogether by quenching of the nematic phase. In contrast the peak areas for $N \rightarrow I$ and $I \rightarrow N$ were much less rate dependent, indicating conditions closer to equilibrium. The values of ΔH were obtained from measured peak areas and the transition temperatures were obtained from the position of the peak maxima. Although values of ΔH on heating and cooling were not too different, it was found that the separation of peaks and the horizontality of base line were better during the cooling cycle. Consequently, the values of ΔH_{NI} and ΔS_{NI} plotted in Figure 2 are values determined from the $I \rightarrow N$ transition rather than the $N \rightarrow I$ transition. The relative error committed on ΔH was estimated to be less than ±5%. The polymers were characterized by intrinsic viscosity in 1,1,2,2-tetrachloroethane at 30 °C. For $n \geq 4$, molecular weights were estimated by means of the relationship

$$[\eta] = 4.65 \times 10^{-4} M^{0.76} \quad \text{(ref 6)} \qquad (1)$$

Although this relation was obtained by us for a homopolyester of 4,4′-dihydroxy-2,2′-dimethylazoxybenzene and dodecanedioic acid (DDA-9), it was also shown to hold for a statistical copolymer of DDA-9 and 4,4′-oxy-2,2′-dimethylazoxybenzene–methyl 3-adipate) (MAA-9)[6] and not to be overly dependent on the length of the flexible methylene sequence for $n > 3$.

Results and Discussion

Table I gives the transition temperatures on heating and on cooling for the polyester series together with their in-

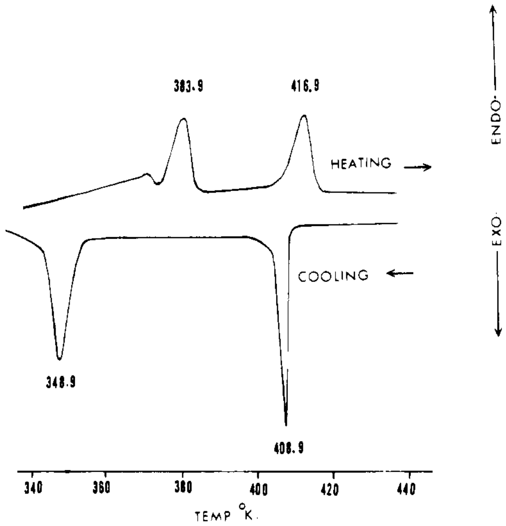


Figure 1. Typical DSC thermograms of the n = 12 polyester. Heating and cooling rate: 20 °C/min.

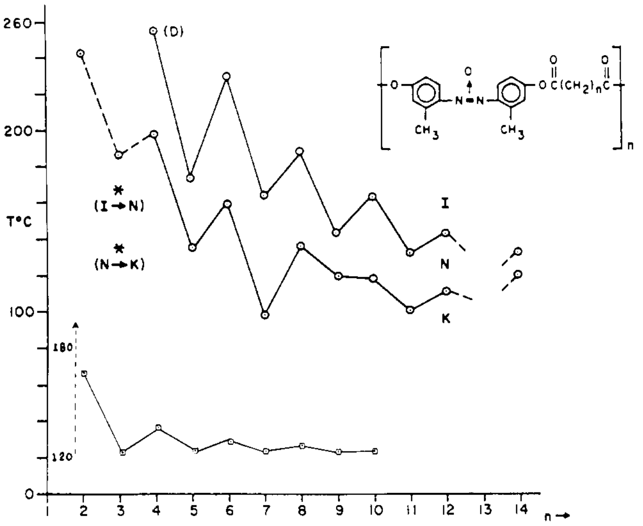


Figure 2. Transition temperature as a function of the number n of methylene units in the flexible spacer: (D) points impinging on decomposition; (*) monotropic phase transition.

Table II
Transition Enthalpies and Entropies of Homologous 4,4′-Dihydroxy-2,2′-dimethylazoxybenzene–Alkanedioic Acid Polymers[a]

n (CH$_2$)	ΔH_{KN}	ΔH_{NI}	ΔH_{IN}	ΔH_{NK}	ΔS_{KN}	ΔS_{NI}	ΔS_{IN}	ΔS_{NK}
2	9.03	*d*	*d*	*d*	17.47	*d*	*d*	*d*
3	7.94 (KI)		1.42[c]	6.02	17.31		3.22	14.76
4	7.86	*d*	*d*	*d*	16.88	*d*	*d*	*d*
5	1.00	1.80	1.84	*d*	2.47	4.01	4.14	*d*
6	4.77	5.85	6.06	2.93	10.99	11.62	12.67	8.44
7	2.72	2.30	2.30	*d*	7.32	5.27	5.35	*d*
8	3.26	5.89	6.48	2.30	7.94	12.79	14.55	6.77
9	8.23	2.51	2.63	7.23	20.90	6.02	6.44	20.48
10	8.78	6.27	7.02	8.86	22.45	14.38	16.22	24.62
11	9.61	3.14	3.09	*d*	25.71	7.73	7.73	*d*
12	7.69	6.69	7.40	8.61	19.73	16.05	18.10	24.66
14[e]	9.20	7.11	7.73	9.57	23.32	17.47	19.56	26.00

[a] ΔH given in kJ/mru and ΔS given in J/K mru. [b] Decomposition. [c] Monotropic transition. [d] Supercooling of the nematic phase. [e] Values obtained for a rate of heating and cooling of 10 °C/min (due to small mesophase interval).

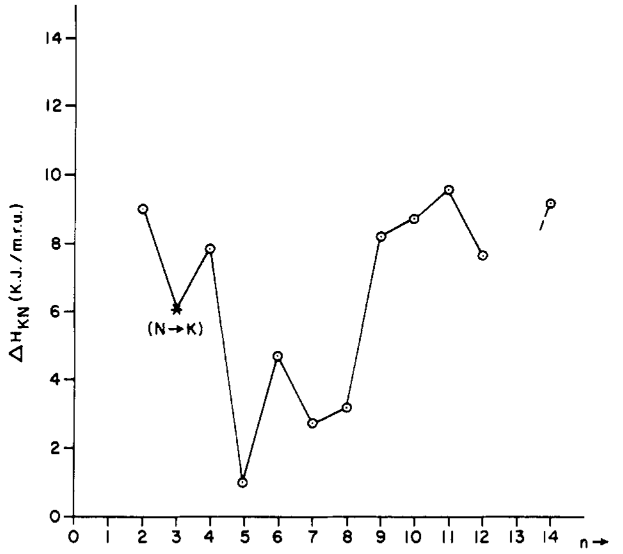


Figure 3. Transition enthalpy for crystalline to nematic transition, ΔH_{KN}, as a function of n (for n = 3 the value for ΔH_{NK} was used).

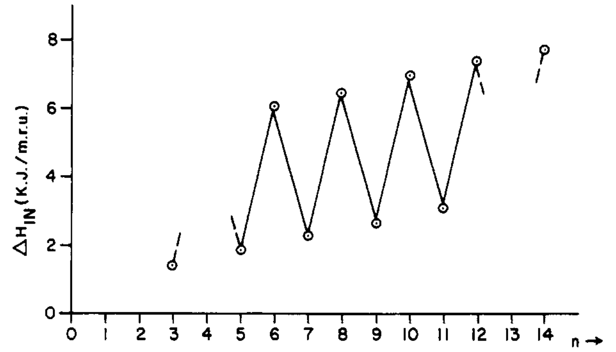


Figure 4. Transition enthalpy for the isotropic to nematic transition, ΔH_{IN}, as a function of n. The value of ΔH_{IN} for n = 4 is absent because of partial decomposition.

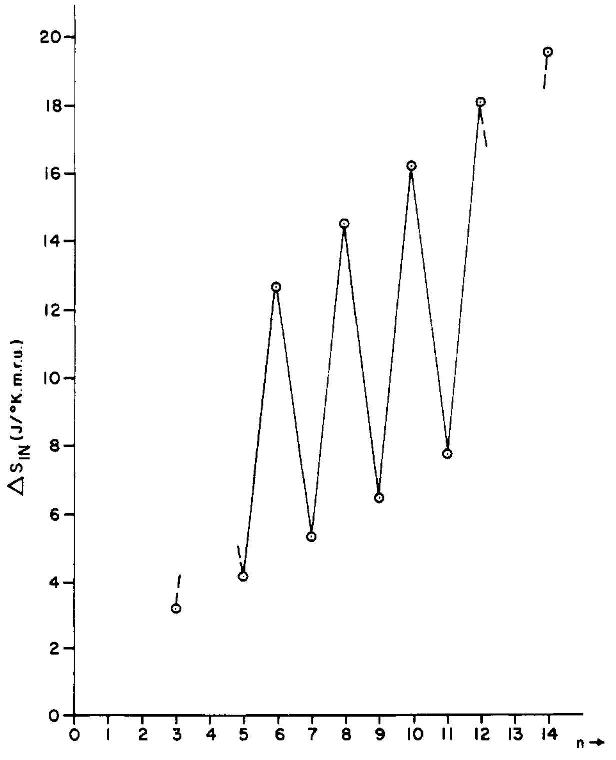


Figure 5. Transition entropy for the isotropic to nematic transition, ΔS_{IN}, as a function of n.

trinsic viscosities and their estimated $\bar{M}_n$. Figure 2 gives the transition temperatures as a function of the number of methylene units in the spacer for the K → N and N → I transitions. One may note the progressive decrease of both transition temperatures with n. The first member of the series (n = 2) does not have a nematic phase, presumably because of the high transition temperature. The second homologue (n = 3) displays a monotropic nematic phase and gives one of the few examples of a monotropic nematic phase reported for polymers. One can also note the narrowing of the nematic mesophase interval with n (for n = 6, ΔT = 70 °C; for n = 14, ΔT = 13 °C), and this occurring without the appearance of a smectic phase.

The values of ΔH and ΔS on heating and cooling are listed in Table II. ΔH_{KN}, ΔH_{IN}, and ΔS_{IN} are plotted in Figures 3–5, respectively. We can see for both parameters for the N $\rightleftharpoons$ I transition a clear and regular odd–even effect. In contrast the K $\rightleftharpoons$ N transition does not display a clear odd–even effect. This is related to the more pronounced off-equilibrium nature of the K $\rightleftharpoons$ N transition as can be seen from Tables I and II, in which the data for n = 5–7 indicate a variable degree of supercooling of the N → K transition and consequently a variable degree of crystallinity in the supercooled sample in spite of our efforts to keep constant its thermal history.

It is obvious from Figures 4 and 5 that ΔH_{IN} and ΔS_{IN} steadily increase for the odd and the even series. For ΔH_{IN} the increase is from 1.42 kJ/mru for n = 3 to 7.73 kJ/mru for n = 14 (mru = mole of repeat unit). For ΔS_{IN} the increase is from 3.22 J/(K mru) for n = 3 to 19.6 J/(K mru) for n = 14. The increase for both odd and even series proceeds with an average increment $[\Delta(\Delta H_{IN})]_{av}$ of 0.46 kJ and $[\Delta(\Delta S_{IN})]_{av}$ of 1.52 J/K per methylene unit. This confirms our previous conclusions[5,6] based on DSC data for the copolyester obtained from the 4,4′-dihydroxy-2,2′-dimethylazoxybenzene and methyl(+3)adipic and dodecanedioic acids (DDA/MAA*-9) as to the extended nature of the aliphatic spacer in the nematic state. The polymer appears to be in the random coiled conformation in the isotropic melt.[7] If we assume that the entropy increment per CH_2 $[\Delta(\Delta S)]_{av}$ is due to conformational entropy, it becomes possible to roughly estimate the extent of this phenomenon; taking from the literature the value for the gauche → trans energy per CH_2, estimated to be 2–3 kJ/mol,[8] the experimental $[\Delta(\Delta H_{IN})]_{av}$ per CH_2 of 0.46 kJ represents an increase of the population of trans conformers between 15 and 23% at the isotropic → nematic transition. This should lead to a significant extension of the flexible spacer. The value of this extension is uncertain, because of the lack of knowledge about the respective populations of trans/gauche conformers in the pretransitional state. It is, however, likely that in the pretransitional state, this ratio exceeds 0.5. This would suggest that in the nematic state the population of trans conformers could well exceed 75%.

The participation of the flexible spacer in the ordering process is also reflected in the unusually high value of ΔS_{NI}. Taking into account the degree of crystallinity of the DDA-9 as determined by measurements of heat capacity,[9] $W_c \sim 0.5$, we find $\Delta S_{NI}/\Delta S_{KN} \sim 0.2$–$0.3$. Since the typical $\Delta S_{NI}/\Delta S_{KN}$ ratio for low molecular liquid crystals is 0.02–0.03,[11] our values indicate a considerable degree of order in the nematic phase of the azoxy polyesters.[6,10] Similar results were also reported by several authors[1-3] for a variety of thermotropic liquid crystalline polyesters. It is implicitly assumed that the nematic phase is continuous throughout the polymer, i.e., that the "degree of liquid crystallinity" is 1. This assumption is justified by the following facts: ΔH_{NI} is not affected significantly by supercooling (in contrast to ΔH_{Kn}), and ΔH_{NI} increases regularly with *n*.

It is remarkable that T_{NI}, ΔH_{IN}, and ΔS_{IN} oscillate with a persistence and regularity, the extent of which is not found in low molecular liquid crystals. Superimposed in Figure 2 are the data of Arnold[11] for the symmetrical 4,4′-alkoxyazoxybenzene series; T_{NI} oscillations damp very rapidly in the 4,4′-alkoxyazoxybenzene series for $n > 4$ while in the high molecular weight series a persistent oscillation of T_{NI} exists for all values of *n* explored in this work.

For low molecular weight nematogens deJeu et al.[12] proposed a qualitative explanation of the odd–even effect based on two opposing trends. One trend is due to alternation of increments of polarizabilities (small and large) along the molecular axis of the mesogenic molecule for odd and even numbers of aliphatic backbone atoms all in a trans conformation. The other trend, in opposition to the first, is the increased tendency for gauche conformations (increased flexibility) with the increase of *n* and of the temperature T_{NI}. The combination of both factors explains qualitatively the alternation of thermodynamic parameters such as T_{NI} and ΔS_{NI} and the rapid damping of this alternation. It explains also the ascending trend of $T_{NI}(n)$ for low values of T_{NI} (prevalent trans conformers) and the descencing trend of $T_{NI}(n)$ for high values of T_{NI} (increased flexibility). One cannot easily see how this explanation can account for the simultaneous persistence of strong alternations in the whole interval of *n* and a rather large descending trend of $T_{NI}(n)$, such as found here.

Before an explanation is advanced, one has to remember the fact that the aliphatic chain in polymeric polyesters such as the one here is attached on both ends to the mesogenic moiety. Also one has to bear in mind the strongly first-order character of the $N \rightleftarrows I$ transition in high molecular weight mesogens such as described here when compared to their low molecular weight analogues. This character is evident from the large values of ΔH_{NI} ascending monotonously and confirms similar conclusions reached from the study of the pretransitional magnetic birefringence Δn of melts of DDA-9 of $\bar{M}_n \sim 4000$ in which a $T_{IN} - T^*$ of some 27 °C was found, contrasting with $T_{IN} - T^*$ of 3.4 °C found for *p*-azoxyanisole,[13] where T^* is the second-order transition temperature[14] obtained by extrapolation of $\Delta n^{-1}(T)$ to 0.

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