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Thermotropic Polyesters. 2. Investigation of the Mesophase Properties of Polymers Based on 4,4′-Dihydroxybiphenyl

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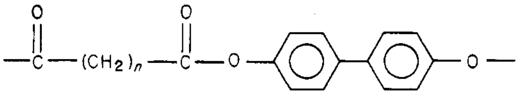
ABSTRACT: The thermotropic polyesters based upon 4,4′-dihydroxybiphenyl and aliphatic dibasic acids exhibit a unique odd–even effect. The polymers formed from dibasic acids having an odd number of methylene units exhibit a nematic phase, while those having an even number show a smectic mesophase. DSC heating curves of the odd-membered series exhibit an additional transition which is shown to be due to a smectic phase. The temperature range of stability of the nematic phase for the odd-membered series is rather narrow and decreases with increasing molecular weight, so that the nematic phase becomes monotropic for the polyester having η_{inh} = 1.90 dL/g. The smectic phase of the even-membered series is stable over a broader temperature range. Values are given for the enthalpy and entropy changes accompanying the transitions. Although the mutual miscibility method eliminated some possibilities, it failed to identify the type of smectic polymorph of the even-membered series. This is shown to be S_H by X-ray diffraction. The degree of crystallinity is higher for the even-membered series. Structural information concerning the crystalline and smectic phases of the even-membered series is deduced from X-ray diffraction data taken using unoriented samples.

I. Introduction

When a polymer molecule having mesogenic groups incorporated in the main chain enters a liquid crystalline phase, the molecule must adopt a conformation and packing compatible with the symmetry properties of that mesophase. This results in a coupling of the polymeric and mesogenic properties, so that the properties of the polymeric mesophase are not necessarily predictable from those of the analogous low molecular weight mesogen. Despite the widespread interest in polymers forming thermotropic mesophases, at present it is not possible to predict from the chemical structure of the repeating unit whether the temperature range of stability of the mesophase will be narrow or broad or whether the mesophase will be nematic or smectic. Information bearing on these questions must be collected by examining a variety of polymers exhibiting thermotropic mesomorphism. The first paper[1] of this series, hereafter referred to as paper I, reported the synthesis and properties of the homologous series of polyesters prepared from 4,4′-dihydroxybiphenyl and aliphatic dibasic acids containing 5–12 methylene units. The repeating unit of these polyesters can be represented



We designate these polymers by the letters PB followed by the number, *n*, of methylene units in the dibasic acid. This series exhibits a unique odd–even effect in that the mesophase is nematic for the polymers having an odd number of methylene units in the dibasic acid and smectic for the even-membered series. Differential scanning calorimetry (DSC) revealed an additional transition for the odd-membered series, which was not further characterized. Also, the smectic type of the even-membered series was not identified. In this paper we present a more detailed study of the identification and structure of these mesophases based upon more extensive DSC data, miscibility studies of binary mixtures with well-characterized low molecular weight mesogens, and X-ray diffraction.

It is often possible to distinguish between the nematic and smectic phases of low molecular weight compounds from the textures seen in the polarizing microscope. This procedure may fail for some polymeric mesophases due to their high viscosity. The identification of a particular smectic polymorph is a more difficult undertaking, even for small-molecule mesogens. The mutual miscibility, or contact method, developed for this purpose by Sackmann, Arnold, and Demus[2,3] involves construction of the phase diagrams of pairs of low molecular weight mesogens. Identification of the polymorphic modification rests upon the postulate that chemically dissimilar polymorphs of the *same* type will be mutually miscible in all proportions. According to this criterion there is only one type of nematic mesophase, and smectic polymorphs S_A through S_I were assigned in the chronological order of their identification. The preferred texture seen in the polarizing microscope and the sequential order of appearance of the mesophases with increasing temperature provide useful supplemental information. The binary phase diagrams may turn out to be simple, or quite complex. In the latter case, errors in the identification of small-molecule smectic polymorphs have occurred, even in the hands of experienced workers.[4] Turning to polymeric mesophases, there is no a priori reason to believe that the basic postulate of the mutual miscibility method will be applicable. Even if it is, the lower solubility and higher viscosity of binary systems involving a polymeric component may make determination of the phase diagram difficult. In view of these reservations, it is encouraging to note that the mutual miscibility method has been successfully applied to identify polymeric nematic and S_C phases by Fayolle, Noel, and Billard[5] and to identify polymeric nematic phases by Griffin and Havens.[6] However, the application of this procedure to more highly ordered polymeric smectic phases has yet to be demonstrated.

X-ray diffraction provides information concerning the arrangement and mode of packing of molecules and the types of order present in a mesophase. Important observations relating the diffraction pattern to the type of mesophase have been reported by Sachmann and coworkers,[7-9] by de Vries,[10,11] and by Azaroff.[12] The diffraction pattern of an unoriented sample can be divided into inner rings (indicative of longer layer spacings) and outer rings (representing shorter preferred spacings occurring in the lateral packing arrangement of the mole-

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Table I
Calorimetric Data

polymer	η_{inh}	ΔH_{total}	ΔH_1	ΔH_2	ΔH_i	ΔS_{total}	ΔS_1	ΔS_2	ΔS_i
A. Odd-Membered Series									
PB5	0.48	2.1	1.7		0.4	4.0	3.3		0.7
PB7-1	0.16	2.52	1.73		0.79	5.40	3.75		1.65
PB7-2	0.23	2.73	1.98		0.75	5.50	4.00		1.50
PB7-3	0.45	3.30	1.40	1.10	0.80	6.45	2.75	2.15	1.55
PB7-4	0.55	3.45	1.40	1.25	0.80	6.75	2.75	2.45	1.55
PB7-5	0.57	3.30	1.40	1.15	0.75	6.45	2.75	2.25	1.45
PB7-6	0.67	3.55	1.60	1.15	0.80	6.95	3.15	2.25	1.55
PB7-7	0.80	3.75	1.80	1.10	0.85	7.30	3.50	2.15	1.65
PB7-8	0.88	4.05	1.75	1.35	0.95	7.80	3.40	2.60	1.80
PB7-9	1.16	4.05	2.00	1.10	0.95	7.70	3.85	2.10	1.75
PB7-10	1.90	4.30	2.05		(2.25)	8.15	3.90		(4.25)
		3.65[a]	2.70[a]		0.95[a]	7.10[a]	5.30[a]		1.80[a]
average for PB7-1 to PB7-10		3.70	1.70	1.00	0.85	7.20	3.25	2.30	1.65
PB9	0.86	3.8				7.6			
PB11	0.60	4.5				9.2			
B. Even-Membered Series									
PB6	0.82	8.4	3.4		5.0	14.7	6.6		8.1
PB8-6	0.57	7.8	3.3		4.5	14.6	6.6		8.0
PB10	0.60	7.3	2.5		4.8	14.3	5.2		9.1
PB12	0.75	8.5	3.5		5.0	17.3	7.5		9.8

[a] Determined from the areas of exotherms on cooling.

cules). The appearance of a broad halo or a sharp ring furnishes a qualitative indication of the degree of order. Comparison of the Bragg spacing corresponding to the inner ring with the length of the molecule allows one to distinguish between normal and tilted phases (i.e., whether the vector representing the average orientation of the long axes lies along the normal to the layers or makes some acute angle with it). If a sample can be obtained in the form of an oriented monodomain, it may be possible to extract more detailed structural information from its diffraction diagram.[12,13] Although it is not known what structural features play a role in determining the mutual miscibility of two chemically dissimilar mesophases, one would certainly expect that similarities and differences in the diffraction diagrams should correlate with the identification of these mesophases based upon the mutual miscibility method. Until very recently, this appeared not to be the case. Examples were reported of normal and tilted mesophases assigned to the same miscibility class, while in another case two smectic polymorphs giving very similar diffraction diagrams were assigned as different modifications by miscibility.

A number of these discrepancies were eliminated by a recent revision[8,14] of some of the earlier assignments based upon the mutual miscibility method. The newly recommended[15] assignments transfer a number of the mesogens previously assigned as S_B to the S_G class and interchange what had previously been the common S_G and S_H designations. Hence, one reading the literature must exercise special caution regarding statements involving these three smectic polymorphs. The revision eliminates the anomaly of both normal and tilted S_B phases. A different problem existed for the S_E polymorphs, which are generally regarded as normal phases. An earlier report suggested that the alkyl 4-[(*p*-phenylbenzylidene)amino]cinnamates might be examples of tilted S_E, since these mesophases gave a biaxial interference pattern.[16] However, subsequent X-ray investigations of these compounds by Doucet et al.[17] and by Leadbetter, Richardson, and Carlile[18] established that the molecules of these compounds are normal to the layers and the phase is biaxial due to an ordered lateral arrangement of the aromatic rings. Thus, there is currently reasonable accord between the diffraction results and the assignments based upon mutual miscibility.

II. Experimental Section

Enthalpy changes accompanying the phase transitions were measured for all polymers using a Perkin-Elmer DSC II differential scanning calorimeter. Samples of 5–10 mg were heated and cooled at a rate of 10 °C/min under a flow of dry nitrogen. In an effort to provide a common thermal prehistory, data were collected during the first cooling from the isotropic melt and during the second heating from ambient temperature. An additional set of data was collected using the DuPont 1090 DSC for all PB7 polymers. In this case the polymers had been previously cooled from the isotropic state at 2 °C/min. In both cases indium was used as a reference standard. The DSC II was also used to construct the binary phase diagrams for mutual miscibility studies. Supplemental information for the same purpose was obtained with an Olympus BH2 polarizing microscope equipped with a Mettler FP52 hot stage. Wide-angle X-ray photographs were recorded with a flat-plate camera using nickel-filtered Cu Kα radiation. The distance from sample to film was determined by using silicon powder. The polymer samples were heated during exposure with a modified Koeffler hot stage which could be maintained to within ±2 °C by a regulated heater. The sample temperature was monitored with a chromel–alumel thermocouple attached to a Fluke Model 801BR differential dc voltmeter. Densities of the semicrystalline polymers were determined by flotation in aqueous KBr solutions. Except for polymer PB7-10, the samples are the same as those investigated in part I.

III. Results

A. Enthalpies and Entropies of Transition. We label the crystal melting temperature t_1, the isotropization temperature t_i, and any intervening phase transition t_2. The same subscript notation is used to designate the corresponding enthalpy and entropy changes. The transition temperatures of these polymers, with the exception of PB7-10, were given in part I. Table I lists the measured enthalpy changes in kcal/mol and entropy changes in eu, or cal/(mol deg), where in both cases "mole" refers to a mole of repeating units. The transition temperatures were so closely spaced for PB9 and PB11 that only values for ΔH_{total} could be obtained. Also, for PB5 the sum of ΔH_1 and ΔH_2 was determined, but not the individual values.

Column 6 of Table I gives enthalpies of isotropization, ΔH_i, and the corresponding entropy changes appear in column 10. This is a nematic–isotropic transition for PB5 and PB7, and the ΔS_i values are 0.7 and 1.65 eu, respectively. For the even-membered series the transition is smectic– isotropic, and the average ΔS_i is 8.8 eu. This large value, coupled with the observation in part I of a very high viscosity for the mesophases of the even-membered series, suggests these smectic phases are highly ordered. For both the odd- and even-membered series, ΔS_i increases with the number, n, of methylene units in the dibasic acid. This probably reflects an increasing conformational entropy of the molecules in the isotropic phase as the length of the flexible segment is increased. For the PB7 polymers, the ΔH_1 values in column 4 increase with inherent viscosity, indicating the degree of crystallinity achieved under the specified cooling conditions increases with polymer molecular weight. The values of ΔH_{total} appearing in column 3 represent the transition from the partially crystalline to the isotropic phase. These increase with n for the odd-membered series but show no clear trend for the even-membered series. The latter values are significantly larger, and evidence will be given below indicating that the degree of crystallinity is substantially higher for the even-membered series. Blumstein and co-workers[19] have reported enthalpy changes measured by DSC for three samples of PB8. Two of these have very low inherent viscosities, but the third (having $\eta_{\text{inh}} = 0.67$ dL/g) should be comparable to our PB8-6. Their values for the annealed sample, $\Delta H_1 = 0.980$ and $\Delta H_i = 3.501$ kcal/mol are in rather poor agreement with the corresponding values in Table I, $\Delta H_1 = 3.3$ and $\Delta H_i = 4.5$ kcal/mol. We can offer no explanation for these differences.

In an earlier paper from this laboratory,[20] we attempted unsuccessfully to compare the entropy changes for the crystal–nematic and nematic–isotropic transitions of a thermotropic polymer. Data given in Table I for the PB7 polymers offer at least a qualitative answer to the question posed there. Evidence will be presented in the next section indicating that polymers of the odd-membered series exhibit a smectic mesophase between t_1 and t_2. Hence, the sum of ΔS_1 and ΔS_2 represents the entropy change for the transition from the partially crystalline polymer to the nematic phase, and ΔS_i represents the entropy change accompanying the nematic–isotropic transition. Evidence will also be given below indicating that the crystallinity of the odd-membered series is low (probably less than 25%). Nevertheless, accepting the latter value as an estimate, we obtain for PB7 $\Delta S_{\text{KN}} = 22$ eu and $\Delta S_{\text{NI}} = 1.65$ eu. We recognize that the former value should be corrected for the (unknown) volume change on fusion. However, it is unlikely this would alter the conclusion that ΔS_{NI} is small relative to ΔS_{KN} for PB7. If the molecules were rodlike in the nematic phase, we would expect ΔS_{NI} to be larger than ΔS_{KN}. We interpret this result as an experimental indication that a rod is not an appropriate model for this type of semiflexible polymer molecule in the nematic phase.

B. Identification of the Additional Phase in PB7. The DSC curves for semiflexible thermotropic polymers often provide evidence for one or more transitions in addition to the expected crystal–mesophase and mesophase–isotropic transitions. This is the case for the PB5 and PB7 polymers, which generally show three endotherms on heating and two exotherms on cooling. However, the cooling curves of the two PB7 polymers of lowest molecular weight, PB7-1 and PB7-2, have three exotherms. We have sought to identify the phase existing between t_1 and t_2 for the PB7 polymers. This is a difficult undertaking because the temperature span between t_1 and t_2 is generally only 3–5 °C, increasing to 12 °C for PB7-1.

Table II
Effect of Cooling Rate in PB7-5

cooling rate, °C/min	t_1, °C	t_2, °C	t_i, °C
none	231	235	243
100	231 (224)	235	243 (240)
50	232 (224)	237	244 (240)
20	233 (223)	237	244 (239)
10	232 (223)	237	243 (239)
5	233 (224)	237	244 (240)
2	238 (231)		244 (239)
1	240 (227)		249 (243)
a	239 (228)		249 (245)

[a] After four cycles between 210 and 230 °C.

The DuPont 1090 DSC was used to investigate the effect of cooling at different rates from the isotropic phase upon the subsequent heating curve. Table II gives the results of these thermal pretreatments upon a sample of intermediate molecular weight, PB7-5. The temperatures are those corresponding to the peaks of the endotherms, while values given in parentheses refer to the peak of the exotherm observed in the following cooling curve. Comparison of the 10 °C/min data with our previous results[1] obtained with a Perkin-Elmer DSC II indicates satisfactory agreement, except that the supercooling of the transition of t_1 is smaller according to the present data. Table II shows there is little dependence upon cooling rate in the range 100 to 5 °C/min. At 2 °C/min the endotherms previously observed at t_1 and t_2 are replaced by a single endotherm at a temperature somewhat higher than t_2. This slower cooling rate eliminated one endotherm for all PB7 polymers except the two of lowest molecular weight. Wide-angle X-ray photographs of PB7-5 samples cooled from the isotropic state at 10 and 2 °C/min were identical, which would appear to eliminate the possibility that a second crystal polymorph exists between t_1 and t_2. Since the interval between t_1 and t_2 is so narrow, a slower cooling rate is able to improve the crystal perfection and increase the melting temperature sufficiently to eliminate the intervening phase, which is most likely mesomorphic.

Returning to Table II, either cooling at a still slower rate of 1 °C/min or the temperature cycling pretreatment described in the footnote increases the temperatures of *both* the endotherm and exotherm at t_3. Evidently the longer exposure to high temperatures increases the molecular weight. Although this increase is rather modest for PB7-5 and polymers of higher inherent viscosity, it becomes more pronounced for polymers of lower inherent. A cooling rate of 2 °C/min increased the temperature observed, both during heating and during cooling, for the transition at t_i by 24 °C for PB7-1 and by 12 °C for PB7-2. It has been our experience that it is very difficult to obtain reliable DSC data for polymers having $\eta_{\text{inh}} < 0.3$ dL/g. The results of these thermal pretreatment experiments suggest that molecular weights in this range are easily altered by heating and that the molecular weight may even be changing during the DSC scan.

Figure 1 illustrates the DSC heating curves of a few selected polymers of the PB7 series. With increasing η_{inh}, the transition of t_2 appears to be moving toward t_i. We therefore prepared a polymer, PB7-10, of still higher η_{inh}, 1.90 dL/g, than those investigated in paper I. This polymer differed from all other PB7 polymers in exhibiting only two endotherms in its heating curve at 248.5 and 256.5 °C and two exotherms on cooling at 235 and 248.5 °C. Of

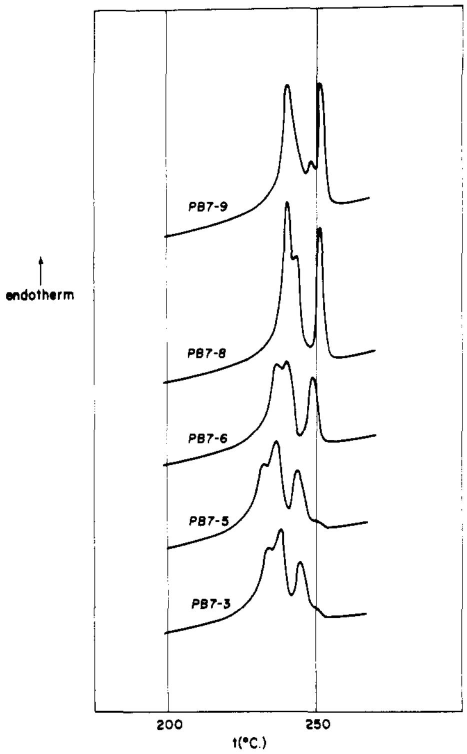


Figure 1. DSC heating curves for selected PB7 polymers.

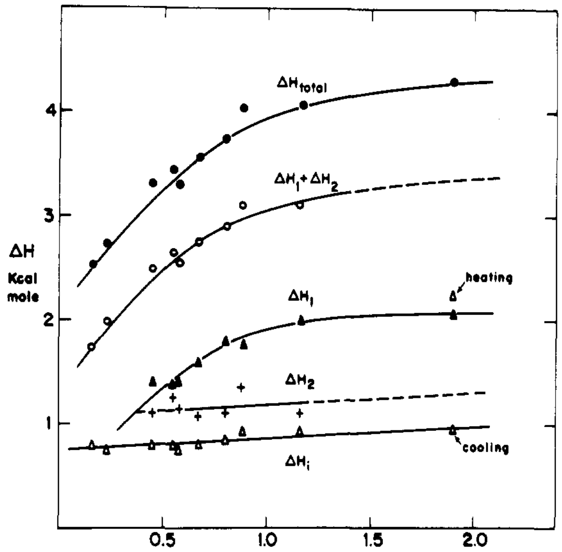


Figure 2. Dependence of the enthalpies of transition for the PB7 polymers upon inherent viscosity.

more interest, the enthalpy of isotropization measured from the heating curve is anomalously large, while the cooling curve gives the expected value.

A second set of DSC data was collected with the DuPont 1090 for PB7 samples that had been cooled from the isotropic state at 2 °C/min. Values shown in Table I represent averages of the two sets of data. Thus, ΔH_1 and ΔH_2 were measured only one time from the Perkin-Elmer heating curves, the sum $\Delta H_1 + \Delta H_2$ was evaluated from two heating curves, and ΔH_i is the average of four values from two heating curves and two cooling curves. The dependence upon η_{inh} of these enthalpy changes for the PB7 polymers is shown in Figure 2. ΔH_1 increases significantly with η_{inh}, whereas ΔH_2 and ΔH_i are nearly independent of η_{inh}. If ΔH_i for PB7-10 is taken as 0.95 kcal/mol, as determined from the cooling curve, than subtraction of this value from ΔH_{total} yields 3.25 kcal/mol as the hypothetical $\Delta H_1 + \Delta H_2$ for this polymer. Reference to Figure 2 shows that this is a very reasonable value for a polymer having η_{inh} = 1.90 dL/g. Furthermore, when the measured ΔH_1 = 2.05 kcal/mol is subtracted from 3.25 kcal/mol, the 1.30 kcal/mol difference happens to coincide precisely with the difference in ΔH_i values determined from the heating and cooling curves. Hence, we conclude that PB7-10 exhibits crystal–smectic and smectic–isotropic transitions on heating and isotropic–nematic and nematic–crystal transitions on cooling. Thus 2.05 kcal/mol is the enthalpy change for the transition from partially crystalline PB7-10 to the smectic phase. Figure 2 indicates that this value, as well as the hypothetical ΔH_2 = 1.30 kcal/mol cited above, stand in reasonable accord with the trends in these two quantities for the other PB7 polymers. We conclude that the PB7 polymers exhibit both a smectic and a nematic mesophase and that the extra transition observed in paper I is a smectic–nematic transition. The smectic phase is monotropic for all PB7 polymers except the two of lowest inherent viscosity.

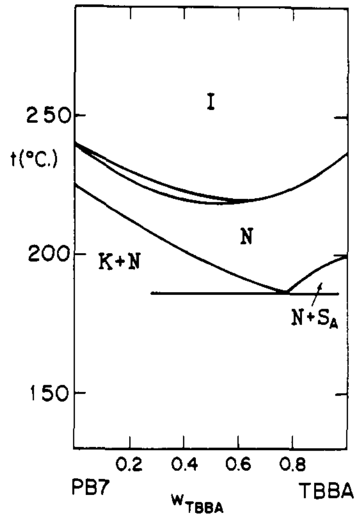


Figure 3. Phase diagram for the binary system PB7-8 and TBBA.

C. Smectic Polymorph of the Even-Membered Series. Paper I reported that polyesters of the even-membered series exhibit a smectic mesophase of high viscosity. The calorimetric data presented above indicate that ΔH_i is quite large for these polymers. Both of these observations suggest that the smectic mesophase is highly ordered.

In an attempt to identify the type of mesophase of the even-membered polymers, we applied the mutual miscibility method by preparing binary mixtures of known composition with two standard low molecular weight compounds. Information from the DSC heating and cooling curves, as well as observations using the polarizing microscope, was used to determine the binary phase diagrams. One small-molecule reference substance, terephthalidenebis(4-*n*-butylaniline) (TBBA) exhibits the mesophases N, S_A, S_C, S_G, and S_H.[13] As a test of the procedure, a binary phase diagram was determined for mixtures of TBBA and PB7-8. As shown in Figure 3, a nematic phase exists across and entire composition range, indicating this polymer has a nematic mesophase. This conclusion is in agreement with the identification given in paper I (which was based upon the observation of a schlieren texture in the microscope). A similar miscibility diagram was obtained for mixtures of PB11 and TBBA, again confirming the conclusion reached in paper I. However, we were unable to obtain a unique identification of the smectic polymorph of PB8 using the mutual miscibility method. The binary phase diagram (not shown) for PB8-5 with ethyl *p*-azoxycinnamate indicated an in-

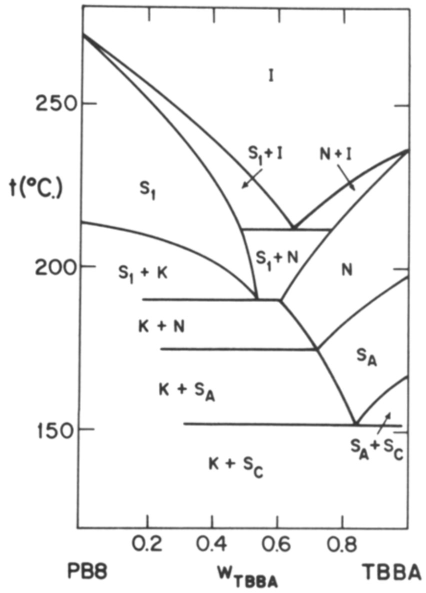
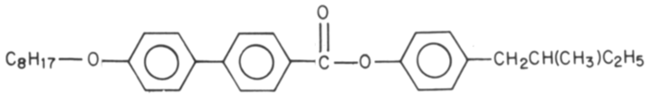


Figure 4. Phase diagram for binary mixtures of PB8-5 and TBBA.

terrupted S_A phase. The phase diagram shown in Figure 4 for mixtures of PB8-5 with TBBA indicates incomplete miscibility with the N, S_A, and S_C phases of the latter compound. Lack of other small-molecule reference materials prevented our continuation of this study. However, Professor G. W. Gray was kind enough to examine mixtures of PB8 with 8OSI, a compound having the formula



and exhibiting the mesophases N, S_A, S_C, S_I, S_G', and S_H'. His results eliminated N, S_A, S_C, and S_I as possibilities. In conclusion, the mutual miscibility method indicates the smectic phase of PB8 may be one of the normal phases S_B or S_E or one of the tilted phases S_F, S_G, or S_H.

We therefore turned to X-ray diffraction in a further effort to identify the smectic type of the mesophase given by the even-membered polymers. The optically isotropic S_D phase can be eliminated from further consideration. The order of appearance of the remaining smectic polymorphs with *decreasing* temperature is

$$S_A\ S_C\ S_B\ S_I\ S_F\ S_G\ S_H$$

$$S_A\ S_B\ S_E$$

S_A, S_B, and S_E are normal phases, while the remainder are tilted. In each series, the degree of order of the smectic phase increases from left to right. The lateral packing within the layers is disordered for S_A and S_C, and the remaining smectic types are ordered to some degree. The outer ring of the x-ray diagram is diffuse for S_A, S_C, and S_F, while S_B shows a single sharp ring and S_E, S_I, S_G, and S_H exhibit several sharp outer rings. Among the ordered normal phases, the lateral packing is hexagonal in S_B but not in S_E. The ordered tilted phases S_I and S_G have pseudohexagonal symmetry in the plane perpendicular to the molecules, while S_H does not. Thus S_B and S_G, and S_E and S_H, appear to be normal and tilted phase counterparts.

Figure 5 shows the diffraction diagram of the smectic phase of PB8-9 taken at 216 °C. It has one sharp inner ring and two sharp outer rings, which eliminates S_F (diffuse outer ring) and S_B (one sharp outer ring). The Bragg spacing corresponding to the inner ring, 16.5 Å, is significantly shorter than the length of the molecule, 22.0 Å, indicating a tilted phase. This observation, in conjunction with the miscibility studies, indicates the smectic phase is either S_G or S_H. As will be shown below, the lateral packing in the plane perpendicular to the molecules is represented by an oblique lattice having $a' = 9.0$ Å, $b' = 6.15$ Å, and $\gamma' = 92°$. Since this is not hexagonal, S_I and S_G are eliminated, and the X-ray results are sufficient, standing alone, to determine that the smectic phase of the even-membered series is S_H.

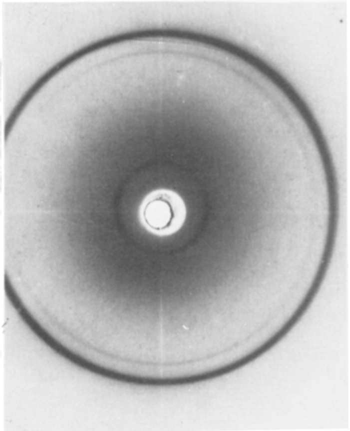


Figure 5. Diffraction diagram of the smectic phase of PB8-9 taken at 216 °C.

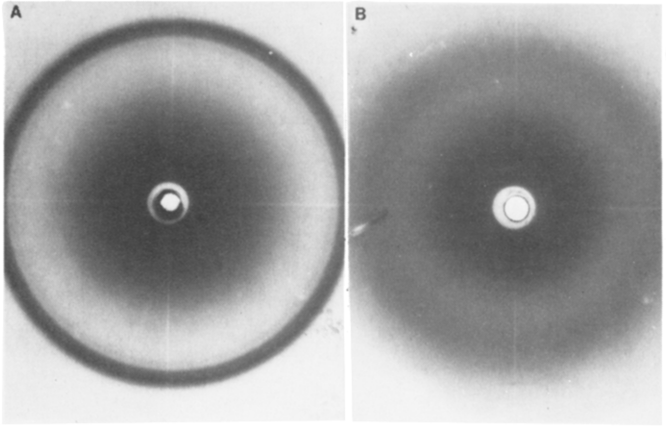


Figure 6. Diffraction photographs of PB7-5: (A) in the crystalline state at 25 °C; (B) the nematic phase at 240 °C.

D. Structural Aspects of the Crystalline and Mesomorphic Phases. Although we were not able to prepare monodomain samples of any of these polymers, the X-ray data obtained with randomly oriented samples nevertheless do furnish some additional information for both the odd- and even-membered series. Figure 6A shows a flat-plate diffraction photograph of crystalline PB7-5 taken at 25 °C. There are only five reflections, corresponding to Bragg spacings of 18.4, 4.67, 4.41, 4.22, and 3.73 Å. A small number of reflections was found for the other polymers of the odd-membered series, suggesting that the degree of crystallinity of all polymers of the odd-membered series is fairly low at room temperature. These five reflections disappear in the vicinity of the DSC transition temperature t_2 and are replaced by two diffuse halos corresponding to spacings of approximately 15 and 5 Å, as illustrated in Figure 6B for PB7-5 at 240 °C. Similar results were obtained for the mesophase of PB5, but the narrow temperature range of the nematic phases of PB9 and PB11 prevented our obtaining diffraction photographs of the nematic phases of these polymers.

Figures 7 and 5 represent the diffraction photographs of PB8-9 taken at 25 and 216 °C, respectively. These are

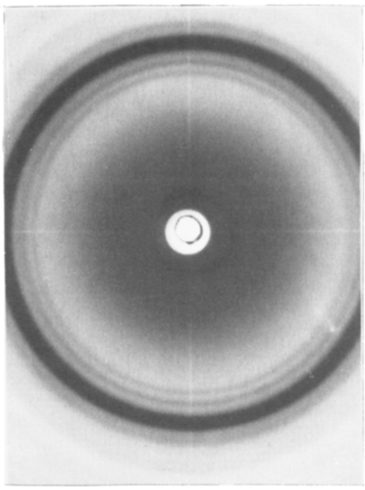


Figure 7. X-ray diffraction pattern of crystalline PB8-9 at 25 °C.

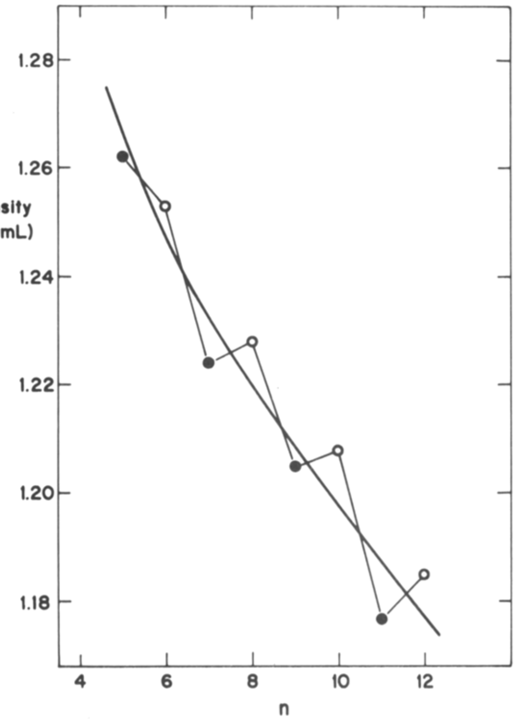


Figure 8. Density of semicrystalline polymers at 25 °C shown as a function of the number, *n*, of methylene units in the dibasic acid.

typical of polymers of the even-membered series. Ten sharp rings are found in the diffraction diagram of PB8 at room temperature, indicating a higher degree of crystallinity in comparison to the odd-membered series. The densities of the semicrystalline polymers measured at 25 °C provide further evidence for this conclusion. As shown in Figure 8, the density of the semicrystalline samples shows an odd–even alternation, with the even-membered series having a relatively higher density.

The Bragg spacings observed for the crystalline and smectic phases of these polymers, along with a visual indication of their intensities, are listed in Table III. Interpretation of these results tests upon the following assumptions:

(i) The molecule, including the hydrocarbon portion of the dibasic acid residue, is in its most highly extended form.

(ii) In such a homologous series, the outer reflections with spacings that are independent of the number of methylene units in the diacid can be attributed to the lateral packing in the plane perpendicular to the molecular axis.

Table III
Bragg Spacings for Even-Membered Series

A. Crystalline Phase

PB6	PB8-10	PB10	PB12
	19.30 s	21.0 s	23.0 s
13.85 s	14.16 w		
12.12 vvw			
9.97 w			
7.42 m	7.70 vw		
6.83 vvvw			
5.40 vvvw			
4.98 w	4.97 m	4.98 vw	4.99 w
4.67 m	4.69 m	4.64 m	4.53 m
4.23 vs	4.24 vs	4.24 s	4.35 s
4.00 m	4.02 m	3.96 vw	4.10 vs
	3.88 vvvw	3.86 vvw	3.79 m
	3.59 vvvw		3.67 vvw
3.50 m	3.48 w		3.46 w
			3.18 vw
			2.95 vvw

B. Smectic Phase[a]

PB6 (276 °C) (19.4 Å, 42.5°)	PB8-10 (216 °C) (22.0 Å, 41.4°)	PB10 (228 °C) (24.4 Å, 39.7°)	PB12 (220 °C) (26.9 Å, 39.7°)
14.3 s	16.5 s	18.8 s	20.7 s
12.32 vw			
7.19 w			
6.20 vvw			
5.34 vw	5.16 vvw		
5.02 m	4.99 w	5.05 w	5.06 m
4.53 s	4.50 vs	4.54 vs	4.54 vs
3.83 vvw			
3.56 vvw			

[a] The length of the extended molecule and the tilting angle of the molecule relative to normal are given in parentheses.

(iii) For the smectic phase, the spacing corresponding to the innermost ring can be assigned as the thickness of the smectic layer.

Let us begin with the crystalline state. The spacings of five of the outer reflections are common to most of the polymers (the 3.50 Å spacing was not observed for PB10). These can be accounted for by an oblique lattice with $a' = 8.59$ Å, $b' = 5.06$ Å, and $\gamma' = 100°$ containing two molecules. This is somewhat similar to crystalline biphenyl, for which the corresponding lattice perpendicular to the molecules is rectangular with $a' = 7.7$ Å and $b' = 5.6$ Å.[21] All crystal structures containing the biphenyl moiety, and in which the interaction between the aromatic rings is predominant, are characterized by a herringbone arrangement of the rings viewed end-on.[21–23] We will assume that the polymers of the even-membered series have a similar lateral packing. The smectic phases generally exhibit only two outer rings with spacings of 5.0 and 4.5 Å; however, the smectic phase of PB6 shows several additional reflections. In the latter case an oblique lattice containing two chains is indicated, with $a' = 9.1$ Å, $b' = 6.3$ Å, and $\gamma' = 93.7°$. By analogy with this result, the following can be suggested for the smectic phases of the other polymers: $a' = 9.0$ Å, $b' = 6.15$ Å, $\gamma' = 92°$ for PB8 at 216 °C and $a' = 9.1$ Å, $b' = 6.1$ Å, and $\gamma' = 90°$ for PB10 at 228 °C and PB12 at 220 °C.

Spacings corresponding to the inner rings observed in the crystalline polymers and in the smectic phases of the even-membered series appear plotted in Figure 9 against

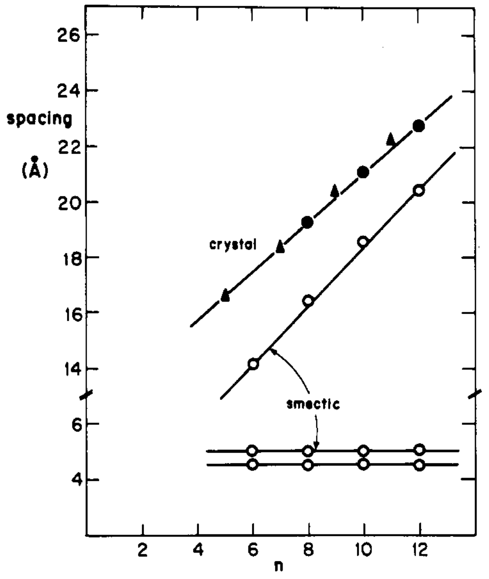


Figure 9. Dependence upon the number of methylene units of the X-ray spacings measured for crystalline PB7 (▲), crystalline PB8 (●), and smectic PB8 (○).

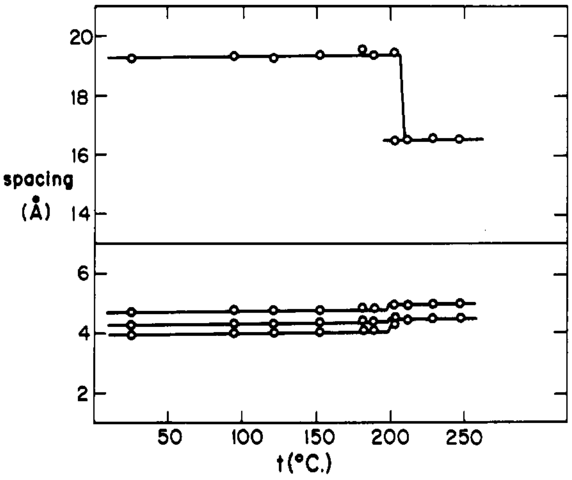


Figure 10. Temperature dependence of some selected spacings for PB8-4.

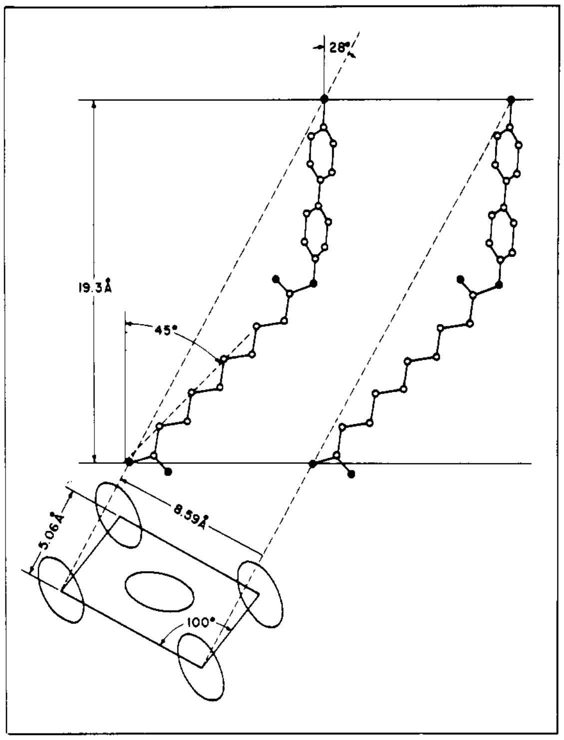


Figure 11. Approximate arrangement of molecules in crystalline PB8.

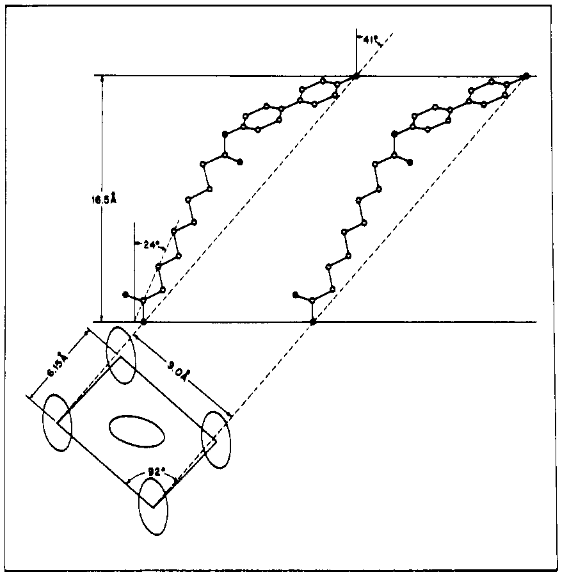


Figure 12. Deduced molecular arrangement of PB8 molecules in the smectic phase.

the number, *n*, of methylene units in the dibasic acid. Here, the filled and open circles refer to the crystalline and smectic phases of the even-membered series, and the filled triangles represent inner ring spacings of the crystalline phases of the odd-membered series. For the smectic phases the inner-ring spacings increase from 14 to 20 Å as the number of methylene units ranges from 6 to 12, while the spacings of the two outer rings are essentially constant. These are precisely the observations that would be anticipated for a smectic phase having a thickness that increases with the length of the molecule but a lateral packing common to all members.

The inner-ring spacings of the smectic phase are not strongly dependent upon temperature, as illustrated for PB8-4 in Figure 10. Hence, these can be compared with the extended lengths of the molecules. The latter, as calculated from known bond distances and angles,[24] appear near the top of Table III. From these two values one can determine the angle between the molecule and the layer normal to be about 28° for PB8 in the crystalline phase and 41° in the smectic phase. Large tilt angles have previously been reported for the smectic phases of low molecular weight compounds.[25,26] From Figure 9 the incremental increase in the inner-ring spacing per methylene unit is 0.88 Å for the crystal and 1.07 Å for the smectic phase. Both values are smaller than the projected length of a methylene unit along the chain direction, 1.26 Å, indicating the methylene chain of the dibasic acid makes an angle with respect to the layer normal. This angle is approximately 45° in the crystal and 30° in the smectic phase. Figures 11 and 12 illustrate the approximate molecular arrangements of PB8 in the crystal and smectic phase, respectively. The biphenyl moieties are nearly parallel to the 19.3 Å spacing of the crystal, giving a large area of contact of the aromatic rings and indicating strong aromatic interactions.[26,27] The corresponding angle is approximately 65° to the normal in the smectic phase. This suggests weak interactions between the aromatic rings, which would permit easier translation and rotation of the molecules in the mesophase. Densities can be calculated from the cross-sectional areas perpendicular to the molecules and the length of the fully extended molecule. These will, of course, be lower limits. For PB8 these are 1.24 g/mL in the crystal at 25 °C and 0.97 g/mL in the smectic phase at 216 °C. These values would be approximately equal at the higher temperature if the volume expansion per degree is 1.4×10^{-3} for the crystal. This is the order of magnitude calculated from the temperature coefficients of the spacings shown in Figure 10. However, the theoretical density for the crystal appears to be somewhat low in comparison to the 1.23 g/mL given for semicrystalline PB8 in Figure 8. The molecular length could be shortened, and the theoretical densities increased, by the presence of *gauche* bonds in the hydrocarbon chain of the diacid residue; however, the alternating tendencies exhibited by these polyesters appear to require the hydrocarbon chain to be predominantly in the all-trans conformation.

IV. Discussion

We have used X-ray diffraction to determine that polymers of the even-membered series form the highly ordered S_H smectic phase. Our attempts to identify this smectic polymorph by the mutual miscibility method were unsuccessful, despite the fact that one of the low molecular weight reference compounds, TBBA, forms an S_H phase. Two reasons can be cited for this failure. For mesogens exhibiting several polymorphic smectic phases, the highly ordered ones will appear at the low end of the liquid crystal temperature range. Hence the temperature interval of the S_H phase in small-molecule systems is likely to be far below that of the polymeric smectogen. Secondly, in the binary phase diagram the S_H phase is bounded both above and below by phases in which there is very limited miscibility of the two components. This makes it difficult to obtain mixing of the two components on any reasonable time scale. Both of these conditions are likely to apply to other highly ordered polymeric smectic phases. Thus, it appears that X-ray diffraction will be the method of choice for the identification of polymeric smectic phases that are highly ordered.

The polymers based upon 4,4′-dihydroxybiphenyl are of particular interest because many of their properties exhibit odd-even effects. Polymers of the even-membered series have higher degrees of crystallinity and melt to a highly ordered smectic S_H phase that is stable over a wider temperature range. The degree of crystallinity of the odd-membered series increases with molecular weight but is always less than that of the even-membered series. The nematic phase of the odd-membered series is only observed over a restricted temperature interval. The fully extended conformations of PB7 and PB8 are compared in Figure 13. The even-membered series has a transoid arrangement of the biphenyl rings, which leads to a shorter crystallographic repeat length. This should stabilize the crystalline state and may also favor the formation of a smectic mesophase. Also, the trans arrangement of the carbonyl dipoles would be expected to contribute to the stability of the crystalline phase of the even-membered series. It seems likely that dipole–dipole interactions are also largely responsible for the formation of a highly ordered smectic phase, since the arrangement of the biphenyl rings in PB8 indicates less interaction of the aromatic rings in the smectic phase as compared to the crystal. Finally, the smaller width about the chain axis should stabilize the mesophase. This may offer a partial explanation for the broader temperature interval of stability of the mesophases of the even-membered series. It should be noted that several of the structural features that stabilize the crystalline phase also increase the temperature range of stability of the mesophase, and some of them favor the formation of a smectic phase.

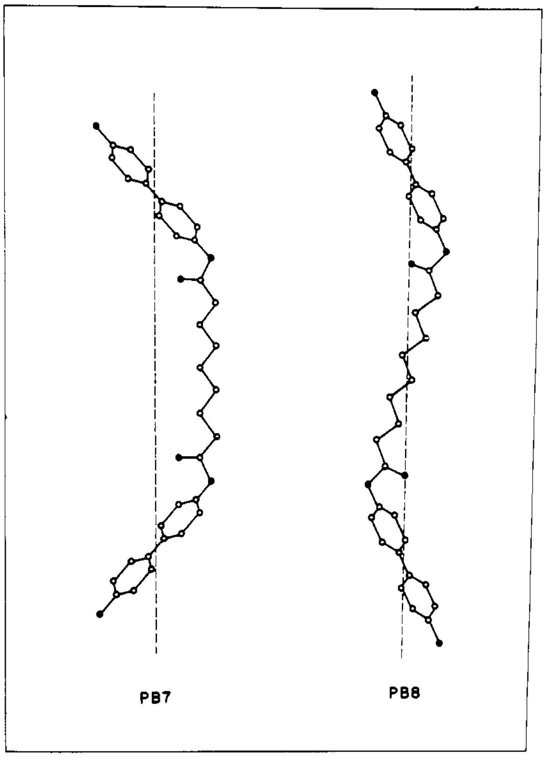


Figure 13. Comparison of the extended-chain structures of PB7 and PB8.

The fully extended structure shown for PB7 in Figure 13 requires two chemical repeating units per crystallographic repeat. This would entail a very large repeat distance in both the crystalline and smectic phases. As shown in Figure 9, the longest spacings measured for the crystalline phases of the odd-membered series are about the same as those of the even series. This suggests that the molecules of the odd-membered series adopt a higher energy twisted conformation in order to reduce the repeat length. This may lead to a less favorable packing arrangement in the crystalline state. As noted above, $\Delta S_{\mathrm{total}}$ is smaller for the odd-membered series. For example, $\Delta S_{\mathrm{total}} = 7.2$ eu for PB7, as compared with about 14.5 eu for PB6, PB8, and PB10. Part of this difference can be ascribed to the lower crystallinity of the odd-membered series. However, the difference of ΔS_1 values is only about 3 eu, leaving a 4-eu difference in $\Delta S_{\mathrm{total}}$ unaccounted for. This may indicate that the crystalline phase of the odd-membered series is partially disordered and has a higher entropy. The other possible explanation—that the isotropic phase of the odd-membered series has a lower entropy—seems less likely.

The calorimetric data for the PB7 polymers also provide some insight into how the stabilities of the nematic and smectic phases of this polymer vary with molecular weight. The temperature interval of the nematic phase decreases with molecular weight, and for PB7-10 the nematic phase is only observed on cooling from the isotropic state. The PB5 and PB7 polymers also exhibit a monotropic smectic phase over a very short temperature interval. This smectic phase is probably less highly ordered, since $\Delta S_2 + \Delta S_i$ averages only 4.0 eu for PB7, as compared with 8.8 eu for the S_H phase of the even-membered series. If the melting temperature of the crystalline phase is increased by annealing, the smectic phase is no longer found. The degree of crystallinity and the melting temperature both increase with polymer molecular weight; however, for the polymer of highest molcular weight, PB7-10, the semicrystalline polymer melts to a smectic phase. Hence, for the PB7 polymers the stability of the nematic phase decreases, and that of the smectic phase increases, as the polymer molecular weight is increased.

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Registry No. $HO_2C(CH_2)_5CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 copolymer, 86129-23-9; $HO_2C(CH_2)_5CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 (SRU), 74790-60-6; $HO_2C(CH_2)_6CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 copolymer, 86129-24-0; $HO_2C(CH_2)_6CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 (SRU), 74790-61-7; $HO_2C(CH_2)_7CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 copolymer, 86129-25-1; $HO_2C(CH_2)_7CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 (SRU), 86129-19-3; $HO_2C(CH_2)_8CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 copolymer, 70788-15-7; $HO_2C(CH_2)_8CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 (SRU), 70800-12-3; $HO_2C(CH_2)_9CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 copolymer, 86129-26-2; $HO_2C(CH_2)_9CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 (SRU), 86129-20-6; $HO_2C(CH_2)_{10}CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 copolymer, 86129-27-3; $HO_2C(CH_2)_{10}CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 (SRU), 86129-21-7; $HO_2C(CH_2)_{11}CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 copolymer, 86129-28-4; $HO_2C(CH_2)_{11}CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 (SRU), 86129-22-8; $HO_2C(CH_2)_{12}CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 copolymer, 86129-29-5; $HO_2C(CH_2)_{12}CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 (SRU), 74790-62-8; TBBA, 85628-40-6.

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Proton Tunneling within the Hydration Structure of OH^--Containing Perfluorosulfonate Ionomer Membranes

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ABSTRACT: Structural and dynamic aspects of the ionic-hydrate associations within Nafion (du Pont) sulfonate films that were equilibrated in alkali hydroxide solutions were studied by noting infrared spectral behavior mainly in the region of the O–H stretching vibration. It was seen that a continuous absorption that begins in this region and extends to lower wavenumbers is a characteristic function of the external caustic strength. This phenomenon is attributed to the tunneling of protons across hydrogen bonds. The state of hydrogen bonding, as suggested by the infrared spectra, may be reasonably interpreted within the framework of the accepted cluster morphology.

Introduction

Past infrared and nuclear magnetic resonance spectroscopic investigations of Nafion[1] perfluorosulfonate membranes, in the monovalent cationic salt forms, have yielded much useful information regarding side-chain–counterion interactions and the nature of hydration as a function of water content.[2-4] A knowledge of the nature of molecular interactions within the ionic clusters of membranes containing co-ions, in this case, OH^- (e.g., separators in chlor-alkali cells), is necessary for a rational understanding of OH^- conductivity in this medium.

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