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Nematogenic Polymers Having Rigid Chains. 1. Substituted Poly(*p*-phenylene terephthalates)

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Received September 13, 1984

ABSTRACT: We have investigated the effect of Cl, Br, C_6H_5, and C_6H_{13} substituents upon the transition temperatures of poly(*p*-phenylene terephthalate). The substituted polyesters are thermotropic nematogens. A single substituent lowers the crystal–nematic transition temperature, t_{KN}, from 600 °C to the range 290–405 °C, while substitution on both rings reduces t_{KN} to 205–235 °C. The polyester bearing a phenyl substituent on each ring is an amorphous glass. Disubstituted polymers crystallize more slowly and require annealing to exhibit a crystalline X-ray pattern. Substitution also reduces the degree of crystallinity, although most substituted polymers show Bragg spacings of 12 Å or greater, indicating regularity along the chain direction. The nematic–isotropic transition temperature, t_{NI}, is also lowered by substitution. A recent treatment which considers the temperature dependence of the unperturbed dimensions leads to the conclusion that all polymers which can be represented by the Kuhn chain model are in corresponding states at t_{NI}. This implies that a substituent which lowers t_{KN} also reduces the chain extension of the polymer.

Introduction

The possibility that thermotropic nematogens might be spun from the melt to obtain fiber properties similar to those of Kevlar at lower cost created special interest in this class of polymer. Segmented polyesters incorporating both a rigid and a flexible segment in the repeating unit have been extensively investigated in many laboratories. They have transition temperatures in a convenient range for experimental study and provide examples of nematic/cholesteric and several polymorphic smectic mesophases. However, Acierno et al.[1] found that fibers spun from the nematic phases of several of these polymers had poor mechanical properties. These authors offered as possible explanations the lower order parameter of semiflexible polymers, their shorter relaxation times (leading to loss of orientation past the spinneret, but prior to crystallization), and the relatively imperfect crystal structure which appears to be characteristic of this type of polymer.

One evident difference between these semiflexible polymers and poly(*p*-phenyleneterephthalamide) is the much higher chain extension of the latter. Arpin and Strazielle[2] reported a persistence length of 150–200 Å for that polymer, and about 500 Å for the related poly(*p*-benzamide). These values are much larger than the persistence lengths characteristic of typical nonmesogenic textile fibers, and they also exceed those of some other lyotropic polymers. Poly(*p*-phenylene terephthalate) and poly(*p*-hydroxybenzoic acid) are the analogues of poly(*p*-phenyleneterephthalamide) and poly(*p*-benzamide). According to the calculations of Erman, Flory, and Hummel,[3] these polyesters should have even larger persistence lengths than the corresponding polyamides, 784 and 740 Å, respectively.

High melting temperatures are expected[4] for rigid-chain nematogenic polymers due to the relatively small entropy change at the crystal–nematic transition. Frosini and co-workers[5] reported a melting temperature of 470 °C for poly(*p*-phenyleneterephthalamide). However, these workers did not indicate the DSC heating rate used in their studies. More recently Jackson,[6] using a fast heating rate of 80 °C/min, reported a melting temperature of 600 °C for this polymer, and 610 °C for poly(*p*-hydroxybenzoic acid). The latter values are probably the correct ones, and the lower melting temperature obtained by Frosini et al.[4] is most likely due to their use of a slower heating rate which led to thermal decomposition. Economy and co-workers[7] found that poly(*p*-hydroxybenzoic acid) could be compression molded at 440 °C and 4000 psi due to a crystal–crystal transition which occurs in the temperature range 325–360 °C. However, it is clear that the melting temperatures of these rigid-chain polyesters must be substantially reduced to permit fiber spinning.

There are several known ways to reduce the crystal melting temperature of a rigid-chain polymer, some of which are presumed to leave the chain highly extended. One involves the positional isomerism of a substituent on the aromatic ring. An early patent by Goodman, McIntyre, and Aldred[8] disclosed *p*-phenylene terephthalate polyesters bearing a methyl, methoxy, or halogen substiutent on one or both aromatic rings of the repeating unit. These polymers were reported to have melting temperatures in excess of 350 °C, which is still too high for melt spinning. One might have expected these polymers to be amorphous due to random variation along the chain of the position of the substituent; however, their X-ray patterns showed a number of sharp rings. Substituents having additional degrees of rotational or conformational freedom should provide larger reductions in the melting temperature,[4] as illustrated by the terephthalate polyesters involving phenylhydroquinone disclosed by Payet,[9] and those with hydroquinone and phenylterephthalic acid claimed by Harris.[10] Example IC of the latter patent gives melting temperatures of 335 and 300 °C for these two polymers.

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0024-9297/85/2218-0965$01.50/0

Majnusz, Catala, and Lenz[11] investigated poly(2-*n*-alkyl-1,4-phenylene terephthalates) in which the hydroquinone bore an alkyl substituent ranging from hexyl to dodecyl. They found that the melting and isotropization temperatures increase strongly with inherent viscosity, η_{inh}, reaching a plateau at approximately 1.5 dL/g for the decyl derivative. The melting temperatures, about 300 °C, were almost independent of the chain length of the alkyl substituent. Dicke and Lenz[12] investigated rigid-chain polyesters in which the hydroquinone was substituted with cyclic or branched alkyl groups. Most of these polymers had rather low inherent viscosities, but showed melting temperatures in the range 308–363 °C. Two equimolar copolyesters, again of rather low inherent viscosity, were crystalline and had melting temperatures almost as high as those of the homopolymers.

Despite the latter observation, the use of random copolymerization with rodlike units to lower the melting temperature has been disclosed in several patents.[13-17] The melting temperature may also be lowered by intentionally reducing the rodlike character of the chain, either through introduction of units having noncollinear bonds[6,18,19] or by copolymerization with more flexible units.[20] Both of the latter methods would be expected to reduce the tensile properties and, when the additive is used at higher levels, to eliminate the nematic phase. However, it is interesting to note that the homopolyester involving the bis diether of 4-benzoic acid was reported by Kleinschuster et al.[18] to give fibers having tenacity in the range 10–16 g/denier and modulus of 170–320 g/denier.

We here investigate the mono- and disubstituted poly(*p*-phenylene terephthalates) in order to obtain a set of transition temperatures measured under common experimental conditions. We have also studied mixtures of various compositions of the polyesters having a phenyl substituent on the hydroquinone or terephthalic acid moieties.

Experimental Section

Terephthalic acid of fiber-grade purity and 2-bromoterephthalic acid from Aldrich Chemical Co. were used without further purification. The 2-chloroterephthalic acid was synthesized by oxidation of 1-chloro-2,5-dimethylbenzene (Pfaltz and Bauer, Inc.) with aqueous $KMnO_4$ and purified by vacuum sublimation. Phenylterephthalic acid was prepared according to the procedure of Weissberger and Weissberger[21] and recrystallized twice from water (DSC mp 282 °C, lit. mp 280 °C).

Hydroquinone (Aldrich Chemical Co.) was purified by vacuum sublimation. The 2-chloro-, 2-bromo-, and 2-phenylhydroquinones were obtained from Eastman Kodak Co. The first two were recrystallized from chloroform, and the latter from *n*-hexane. The method of Love et al.[22] was used for the synthesis of 2-hexylhydroquinone (mp 85–86 °C, lit. mp 88[22] and 84–85.5 °C[23]).

Diacetates of the hydroquinones were prepared by heating the hydroquinone with an excess of acetic anhydride at 110 °C for 6 h. The remaining anhydride was distilled off under reduced pressure and the residue was crystallized from petroleum ether. The diacetate of 2-hexylhydroquinone was a liquid at room temperature.

Anal. Calcd. for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 68.95; H, 8.01.

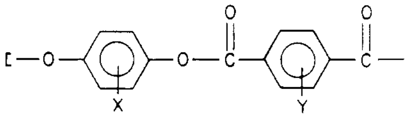
The purities of the other diacetates were checked by DSC melting temperature.

Polyesters were prepared by melt transesterification of the diacetate and aromatic diacid using 0.01% magnesium as a catalyst. Table I gives the polymerization conditions and inherent viscosities of the various polymers. The C_6H_5/H and H/C_6H_5 polyesters were soluble in a 25/40/35 wt % mixture of phenol/*p*-chlorophenol/tetrachloroethane. The disubstituted polymers were soluble in a 60/40 wt % mixture of phenol/tetrachloroethane. No suitable solvent was found for the monosubstituted halogenated polyesters. Inherent viscosities were generally determined at 25 °C by using 0.5 g/(100 mL) solutions; however, the inherent viscosity of Cl/Br was determined at 40 °C by using 0.1 g/(100 g) of solvent. The repeating unit of the polyester may be represented by the structural formula

Table I
Conditions of the Polyesterification Reactions

polyester	temp (°C)/ time (min)/ press. (mmHg)	η_{inh}, dL/g
	A. Monosubstituted Polymers	
Cl/H	285/30 340/180/0.2	*a*
Br/H	285/60 340/30 340/20/0.2	*a*
C_6H_5/H	285/50 340/30 340/15/0.2	1.70
C_6H_{13}/H	285/120 340/15 340/25/0.2	1.77
H/Cl	285/60 340/15 340/20/0.2	*a*
H/Br	285/35 340/15 340/60/0.2	*a*
H/C_6H_5	180–220/60 220–235/8 235–270/35 275/120/0.3	0.72
	B. Disubstituted Polymers	
Cl/Br	245/60 290/10 290/15/0.5	1.39
Cl/C_6H_5	207–240/30 240–260/50 260/30 275/70/0.3	0.47
C_6H_5/Br	245/120 285/60/0.2	0.85
C_6H_5/Cl	245/45 285/30 285/150/0.2	0.58
C_6H_5/C_6H_5	196–218/35 218–260/35 260–265/30 260/90/0.3	0.49
C_6H_{13}/Br	240/60 245/15/0.5 290/30/0.5	0.76

[a] No suitable solvent.



For brevity we designate these polyesters by the symbol X/Y, where X and Y are the substituents on the hydroquinone and terephthalic acid moieties, respectively. If the polymer is monosubstituted, then either X or Y will be H.

Microscopic observations were performed with a Model BH-2 Olympus polarizing microscope equipped with a Mettler FP5 hot stage. For temperatures between 300 and 360 °C a Koeffler hot stage was used. Polymer samples were held between a slide and cover slip, and photographs were taken by using a Nikon polaroid camera equipped with a PFM microscope cone attachment.

Transition temperatures and enthalpies were determined by using a Du Pont 1090/990 differential scanning calorimeter (DSC). Heating and cooling rates were generally 10 and 5 °C/min, respectively, but faster rates were used in special cases noted. Indium served as a reference for calibration of the temperature scale and enthalpies of transition. DSC thermograms were recorded on a 1091 disk memory device, and the standard data

Table II
Transition Temperatures (°C) of Substituted Poly(*p*-phenylene terephthalates)

substituent		heating (10 °C/min)					ΔH-(total), kJ/mol	cooling (5 °C/min)		
		t_G	t_{KK}	t_{KN}	t_{NI}[c]	$t_{NI} - t_{KN}$		t_{KK}	t_{NK}	ΔH-(total), kJ/mol
A. Monosubstituted Polymers										
Cl/H	*a*	220	300	372	510	138	10.1		337	6.3
Br/H	*a*		313	353	475	122	7.9		229	7.0
C_6H_5/H	*a*	170	320	346	475	129	5.3		305	4.5
	b			345			5.3		298	4.5
C_6H_{13}/H	*a*		311, 336	343	460	117	14.5	273	304	11.2
	b		270	330	462	132	9.7	270	298	8.1
H/Cl	*a*	220	208, 225, 296	402	490	88	7.1	291	326	3.8
H/Br	*a*		276	405	490	85	10.0		250	5.2
H/C_6H_5	*a*	130	210, 254	265	343	73	8.3		224	4.9
	b		264	287	369		7.5		227	5.2
B. Disubstituted Polymers										
Cl/Br	*a*	120	185	213	362	149	5.1		177	4.1
	b	120	181, 197	209			7.0		172	6.3
Cl/C_6H_5	*a*	113		233	360	127	1.9			
	b	113		225			2.4			
C_6H_5/Br	*a*	120	202	222	376	154	1.9			
	b	122	187, 198	224			2.4			
C_6H_5/Cl	*a*	108	190	206	368	162	6.3			
	b	108	191	206			6.1			
C_6H_5/C_6H_5	*a*	122			231		1.5			
	b	121			228		1.1			
C_6H_{13}/Br	*a*	121	152	208	365	157	4.6		158	4.0
	b	120	146, 173	208			4.5		157	4.1

[a] As-polymerized sample. [b] Sample annealed 15 h. [c] Heating rate 40 °C/min.

analysis programs were used to evaluate enthalpies and transition temperatures. X-ray flat plate photographs were recorded on Kodak SO-445 film using nickel-filtered Cu Kα radiation. The sample-to-film distance was calibrated by using silicon powder as a reference.

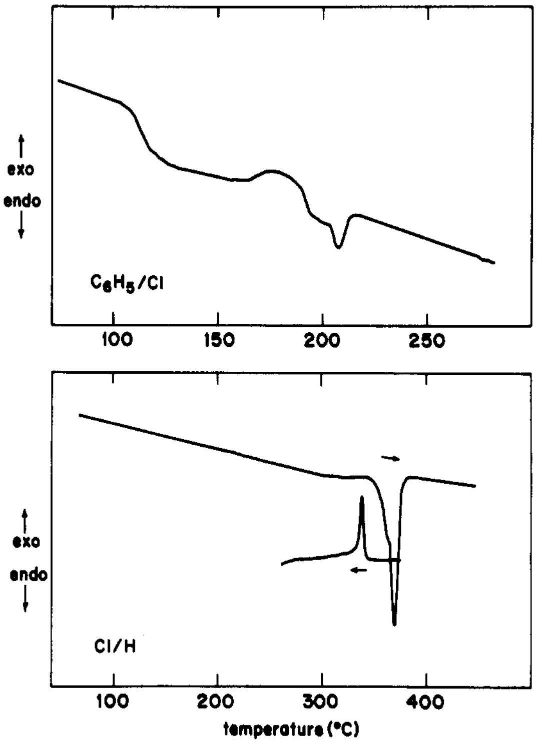


Figure 1. DSC heating curves (10 °C/min) of C_6H_5/Cl and Cl/H polyesters. Samples previously cooled at 5 °C/min.

Results

Glass Transition Temperatures. The glass transition was not prominent in the heating curve of any member of the monosubstituted series, and for some of these polymers it could not be detected by using a heating rate of 10 °C/min. Frosini et al.[5] reported a glass transition temperature, t_G, of 267 °C for poly(*p*-phenylene terephthalate), while Dicke and Lenz[12] found t_G values in the range 210–267 °C for polyesters in which hydroquinone was substituted with a cyclic or branched alkyl group. The t_G values of 220 °C given for Cl/H and H/Cl in column two of Table II are approximately in the same range. However, lower values are found when the substituent is phenyl, 170 °C for C_6H_5/H and only 130 °C for H/C_6H_5.

By contrast with the behavior of monosubstituted polyesters, the glass transitions were easily observable for all of the disubstituted polymers. This is illustrated in Figure 1, which compares the DSC heating curves (10 °C/min) of the C_6H_5/Cl (above) and Cl/H polyesters which had been previously cooled at 5 °C/min. The former exhibits a prominent glass transition at 108 °C and a crystallization exotherm prior to the crystal–nematic transition at 206 °C. The heating curve of the monosubstituted polymer shows a very weak glass transition at about 220 °C and no crystallization exotherm prior to melting. The t_G values of the disubstituted polymers are approximately 120 °C, except for Cl/C_6H_5 and C_6H_5/Cl, which were about 10 °C lower. These values were taken from heating curves using a rate of 10 °C/min. The dependence of the observed t_G upon heating rate for the C_6H_5/Cl, Cl/C_6H_5, and C_6H_5/C_6H_5 polyesters is illustrated in Figure 2. A linear dependence is found over the range 5–60 °C/min, but the t_G value observed for C_6H_5/Cl at 2 °C/min falls below the line representing values for that polymer at higher rates.

Transitions Involving the Crystalline State. Column three of Table II gives the transition temperatures, t_{KK}, involving different crystalline polymorphs. If we look first at samples which had not been annealed, comparison of the entries in columns three and eight suggests that, in several cases, the highest temperature polymorph is not the first to crystallize from the nematic phase on cooling. Thus, samples cooled at 5 °C/min probably consist of a

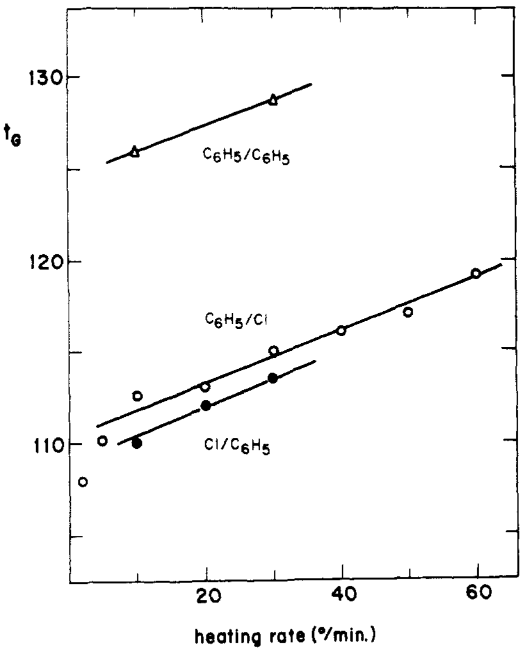


Figure 2. Glass transition temperatures of three disubstituted polymers shown as a function of heating rate.

mixture of crystalline forms. In selected cases DSC data were also collected for samples which had been annealed 15 h. If a crystallization exotherm appeared in the cooling curve, that temperature was adopted for annealing. If there was no crystallization exotherm, but t_{KN} could be located in the heating curve, annealing was performed somewhat below that temperature. Where no crystallization was observed on cooling and t_{KN} was not evident in the heating curve, annealing was performed some tens of degrees above t_G. In every case, annealing reduced the number of solid–solid transitions.

Crystal–nematic melting temperatures, t_{KN}, determined for the as-polymerized samples appear in column four of Table II. The heating rate was 10 °C/min, and subsequent cooling data (column nine) were run at 5 °C/min. Among the monosubstituted derivatives, H/C_6H_5 has the lowest t_{KN}. The preferred conformation of the carboxyl group is in the plane of the aromatic ring and trans, which results in a highly extended chain. A phenyl substituent on terephthalic acid may force the carboxyl group out of the plane of the ring, resulting in a less extended conformation. The much lower t_G of this polymer supports this conclusion. Examination of space-filling molecular models led us to expect a similar steric effect for bromoterephthalic acid, but the high t_{KN} and t_G of this polymer indicate this is not the case.

A monatomic substituent, such as Cl, can be attached to either ring in four positions. For a nonmesogen, this randomness would increase ΔS_f by $R \ln 4$ and produce a corresponding reduction of the melting temperature, t_M. A hexyl substituent would be expected to give a larger melting depression due to different conformations of the alkyl chain in the liquid state, and the same would be true of a phenyl substituent due to the additional rotational degrees of freedom. However, in the case of a nematogen we have two transitions, crystal–nematic and nematic–isotropic. While the entropy of positional isomerism should predominantly affect t_{KN}, it is not so evident how the additional configurational and rotational entropy will be partitioned between these phases.

Table III
Ratios of Transition Temperatures

substituent	ρ_X	ρ_Y	ρ_X/ρ_Y	ρ_X'	ρ_Y'	ρ_X'/ρ_Y'
H	1.00	1.00	1.00	1.00	1.00	1.00
Cl	0.76^5	0.77^5	0.99	0.84^5	0.84^5	1.00
Br	0.72	0.78	0.92	0.83	0.85	0.98
C_6H_5	0.74^5	0.76	1.10	0.83	0.70	1.18^5
C_6H_{13}	0.71			0.83^5		

In order to investigate the effect of individual substituents upon t_{KN}, we have calculated ratios, $\rho = T_{KN}'T_{KN}$, where T_{KN} is the transition temperature (K) of a reference polymer and T_{KN}' is that of the polymer having an additional substituent on one of the rings. Let ρ_X or ρ_Y designate the ratio when the additional substituent is on the hydroquinone or terephthalic acid ring. Thus, from the pairs Cl/Br and Cl/H, C_6H_5/Br and C_6H_5/H, and C_6H_{13}/Br and C_6H_{13}/H we obtain ratios 0.75, 0.80, and 0.78, which give an average $\rho_Y = 0.78$ for the bromo substituent on terephthalic acid. From the pairs Br/H and H/Br we find $\rho_X/\rho_Y = 0.92$, so that $\rho_Y = 0.72$ for the bromo substituent on hydroquinone. These ρ values are collected in Table III. A substituent having a smaller ρ value is more effective in lowering t_{KN}. Making use of the ρ values in Table III, and the melting temperatures listed in Table II for the seven mono- and five disubstituted polyesters, we calculate an average $t_{KN}° = 588 \pm 26$ °C for unsubstituted poly(p-phenylene terephthalate). Within the limits of uncertainty, this agrees with the DSC value of 600 °C reported by Jackson.[6] Another interesting prediction based on the ρ values in Table III concerns the C_6H_5/C_6H_5 polyester, which could not be crystallized by heat treatment. We calculate $t_{KN} = 158$ °C, which is only 35 °C above the glass transition for this polymer. Since the supercooling required to crystallize the other disubstituted polyesters is considerably larger than 35 °C, it is not surprising that the C_6H_5/C_6H_5 polymer could not be obtained in crystalline form.

Degree of Crystallinity. Although the densities of these polymers were not measured, we can draw some qualitative conclusions concerning the degree of crystallinity from the DSC and X-ray data. Values of ΔH_{total} given in column seven of Table II represent the sum of the enthalpy changes for the crystal–nematic and nematic–isotropic transitions. The latter is usually less than 2 kJ/mol, so the major contribution is from the crystal–nematic transition in most cases. The ΔH_{total} values are generally larger for the monosubstituted polymers, as compared to those bearing two substituents per repeating unit. It is interesting that the C_6H_{13}/H polyester, which has the lowest t_{KN} of the monosubstituted X/H polymers, appears by this criterion to be the most crystalline of this group.

Since only the amorphous phase undergoes a glass transition, polymers having lower degrees of crystallinity would be expected to show a more prominent glass transition. The glass transition could only be detected for some of the monosubstituted polyesters, whereas it was quite evident for all disubstituted polymers. This observation confirms that the monosubstituted polymers crystallize more readily. Annealing had little effect upon t_{KN} or ΔH_{total} of the monosubstituted polymers, while in most cases both were increased by annealing the disubstituted polyesters. Polymers involving phenylhydroquinone generally crystallize at a slow rate. Both C_6H_5/H and C_6H_5/Y polymers crystallize only partially when cooled at a rate of 5 °C/min, so the subsequent heating curves exhibit a crystallization exotherm prior to melting, as illustrated in Figure 1. This exotherm was still evident after the C_6H_5/Cl polymer has been annealed for 1 h, and only disappeared after 15 h of annealing. Fully amorphous samples of this polymer were prepared by quenching from

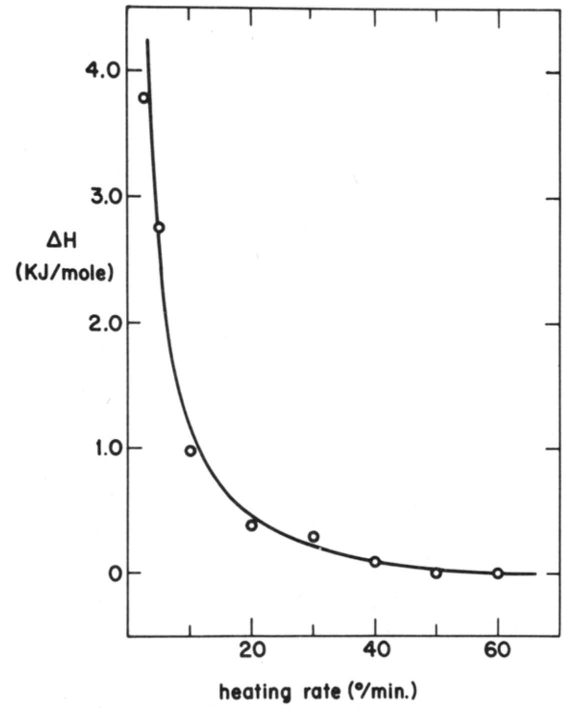


Figure 3. Total enthalpy change for a quenched sample of C_6H_5/Cl plotted as a function of heating rate.

the melt in liquid nitrogen, and DSC scans were taken of these samples at different heating rates. As shown in Figure 3, ΔH_{total} decreases in an approximately exponential manner as the heating rate is increased. The C_6H_5/C_6H_5 polymer could not be crystallized, and the degree of crystallinity of the Cl/C_6H_5 polymer was quite low. The fact that the calculated t_{KN} of C_6H_5/C_6H_5 is near t_G provides a reason for the former, but we can offer no explanation for the latter observation.

The monosubstituted polymers gave good X-ray patterns without annealing, while of the disubstituted polymers only C_6H_{13}/Br exhibited crystalline reflections prior to annealing. Thus, the crystalline contribution to ΔH_{total} in Table II for disubstituted polymers which had not been annealed must be due to crystallization during the DSC heating scan. Bragg spacings measured for the as-polymerized samples are collected in Table IV. Annealing the monosubstituted polymers had relatively little effect upon their X-ray diagrams. For example, annealing the H/Cl polymer only created very weak additional reflections at 3.84, 2.97, and 2.80 Å. The disubstituted polymers, with the one exception noted above, required annealing. The four rightmost columns of Table IV list the Bragg spacings of polymer samples which had been annealed for 15 h.

Spacing less than 5 Å arise mainly from preferred separations in the lateral packing of the macromolecules. A broad 4.6-Å spacing is found in the glassy sample of C_6H_5/C_6H_5. Spacings of 12 Å or more indicate regularity of packing along the chain direction. These are found for all but two of the polymers in this study, indicating that the lateral packing allows a regular arrangement of molecules along the chain direction in spite of the random sequence of the substituents on the rings.

Many of the conclusions concerning the degree of crystallinity drawn from X-ray are in concordance with those deduced from the DSC data. However, we should note that there are cases in which this is not true. The X-ray pattern of the Br/H polymer gives no evidence of order along the chain direction, but ΔH_{total} for this polymer is relatively large, 7.9 kJ/mol. Also, the diffraction pattern of Cl/H is rather sparse, but its ΔH_{total} is 10.1 kJ/mol. Finally, the X-ray diagrams of C_6H_5/H and H/C_6H_5 are similar, but their ΔH_{total} values are rather different, 5.3 and 8.3 kJ/mol, respectively. We believe these disparities can be reconciled by the existence of crystalline polymorphism, as indicated by the solid–solid transition temperatures listed in Table II. As mentioned above, a lower temperature crystal polymorph is often the first to crystallize from the nematic phase, leading to a mixture of polymorphs in the samples prepared by cooling at 5 °C/min. Annealing may then transform one crystalline polymorph into another.

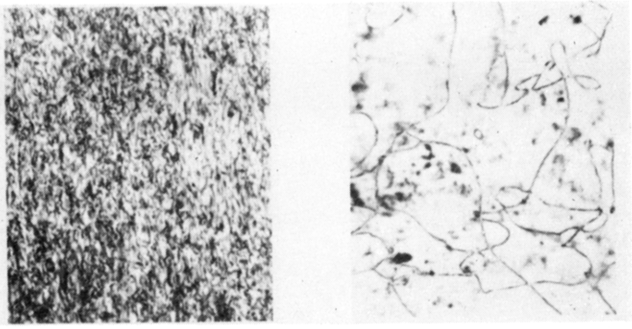


Figure 4. Textures observed for C_6H_5/Cl at 210 (left) and 290 (right) °C.

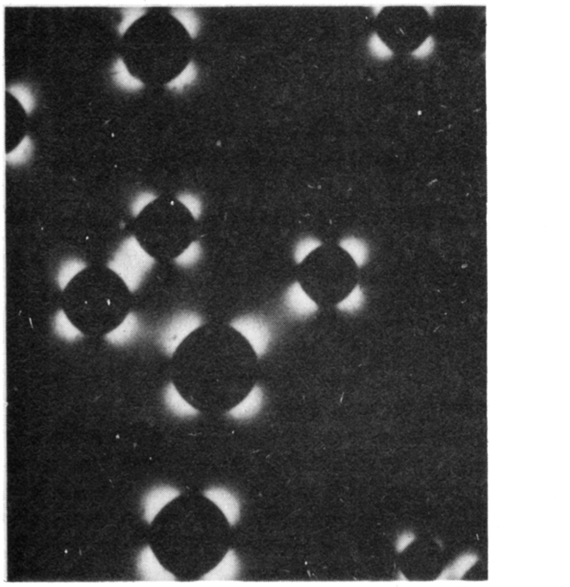


Figure 5. Photomicrograph of the quenched homeotropic texture of C_6H_5/C_6H_5 in the glassy state.

Mesophase Properties. All the mono- and disubstituted polyesters gave a nematic phase upon melting. At temperatures just within the nematic range, and for short heating times, the nematic texture is "entangled" with many disclinations, as illustrated for C_6H_5Cl on the left in Figure 4. The disubstituted polymers, due to their lower t_{KN}, could be heated further into the nematic range, or for longer times. In either case, this produced the "threaded" texture typical of low molecular weight nematics as illustrated on the right in Figure 4. The C_6H_5/C_6H_5 polyester exhibits a homeotropic texture which is dark under crossed polars. This texture could be quenched to a vitreous solid, as shown in Figure 5. The spherical inclusions in this photomicrograph are air bubbles in the glassy matrix.

Decomposition made microscopic examination difficult for those polymers having high melting temperatures. However, this problem could be partially overcome by

Table IV
Bragg Spacings (Å) of Crystalline Polymers at 25 °C

as-polymerized samples								samples annealed 15 h			
Cl/H	Br/H	C_6H_5/H	C_6H_{13}/H	H/Cl	H/Br	H/C_6H_5	C_6H_{13}/Br	Cl/Br	C_6H_5/Br	C_6H_5/Cl	C_6H_{13}/Br
			23.37 (vs)								
			17.92 (s)								
							16.07 (s)				16.30 (s)
						13.27 (s)				14.30 (s)	
		12.47 (vs)		12.66 (s)	12.45 (s)		12.24 (w)	12.66 (w)	12.18 (s)		12.14 (w)
						11.19 (w)					
									9.33 (w)		
							8.13 (w)				8.06 (w)
7.23 (vs)		7.82 (w)	7.79 (s)			7.29 (vw)				7.12 (w)	
		6.33 (w)		6.33 (vw)	6.34 (vw)	6.62 (w)			6.31 (vw)	6.18 (w)	
	5.54 (m)									5.46 (vw)	5.46 (vw)
			5.27 (vw)		5.27 (vw)			5.35 (w)	5.33 (vw)		
			5.00 (vw)	5.07 (vw)							4.96 (vw)
		4.87 (s)									
			4.53 (w)	4.62 (vs)		4.45 (s)			4.48 (vw)	4.57 (w)	
4.37 (w)											
		4.21 (s)	4.12 (s)	4.27 (s)	4.20 (w)		4.22 (vw)		4.21 (vvw)	4.19 (w)	4.19 (vw)
3.94 (s)					4.00 (vw)	3.93 (w)		4.05 (w)	3.82 (w)	3.97 (w)	
3.51 (w)	3.42 (w)					3.45 (vw)		3.41 (w)			
3.35 (vw)		3.34 (vw)		3.36 (vw)	3.34 (vw)					3.34 (vw)	
3.23 (vw)				3.27 (vw)					3.13 (vvw)		

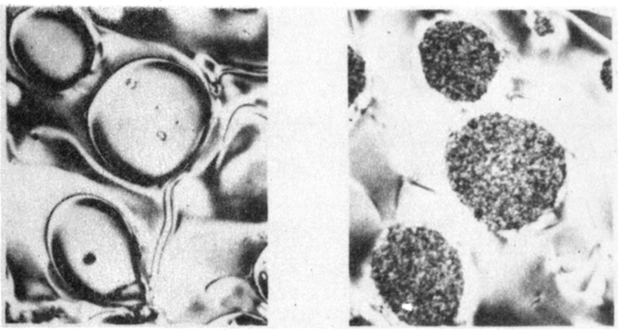


Figure 6. Coexistence of a low-viscosity nematic inclusion in a high-viscosity nematic phase of C_6H_5/Br at 280 °C (left) and the same sample cooled to 25 °C (right).

heating the hot stage to the test temperature and then depositing the sample on the heated slide. Majnusz, Catala, and Lenz[11] reported that the polyesters having hydroquinone substituents C_6H_{13} to $C_{12}H_{25}$ formed a smectic mesophase on melting. In the case of the C_6H_{13}/H polymer we suspect they may have only examined the entangled nematic texture, which they incorrectly identified as smectic.

One of the C_6H_5/Br samples exhibited two coexisting nematic phases. This may have been due to some dibromoterephthalic acid present as an impurity in the diacid monomer, which led to the formation of a mixture of the polymer and nematogenic oligomers. The left-hand photograph in Figure 6 shows the texture of the two nematic phases. The low molecular weight nematogen clearly exists as a separate phase, because it only partially adopts the homeotropic texture of the polymer. On cooling, the oligomer crystallizes while the polymer forms a glass, as seen in the right-hand photo in Figure 6. Immiscible nematic phases of polymers bearing nematogenic side chains and a low molecular weight nematogen have been reported by Ringsdorf et al.[24] and by Finkelmann and co-workers.[25] So far as we are aware, ours is the first example of coexisting nematic phases in a system involving a polymer having nematogenic groups in the main chain. The miscibility criterion developed for the identification of mesophases by Sackmann and Demus[26,27] does not require complete miscibility of like mesophases in *every* binary system, so these observations are not in violation of that principle.

Table V
Transitions of Copolymers of Terephthalic Acid with Phenyl- and Chlorohydroquinones

$x_{C_6H_5}$[a]	t_{KK}[b]	t_{KN}[b,c]	ΔH_{total},[a] kJ/mol
1.00	320	346 (305)	5.30 (4.55)
0.72	321	332 (293)	6.47 (4.25)
0.46	270, 312	322 (284)	5.82 (4.07)
0.22		326 (292)	5.48 (3.51)
0.00	300	372	10.1 (6.3)

[a] Mole fraction of phenylhydroquinone. [b] Transition temperature in °C. [c] Values in parentheses from cooling curves taken at 10 °C/min.

The nematic–isotropic transition temperatures, t_{NI}, appearing in column five of Table II were determined by DSC using a faster heating rate of 40 °C/min. Comparison of the $t_{NI} - t_{KN}$ differences in column six for the first and last three monosubstituted polymers show that the nematic range is reduced when the substituent is on terephthalic acid rather than hydroquinone. Also, in general the nematic range is somewhat broader for the disubstituted derivatives than for those bearing one substituent. To investigate the effect of the different substituents upon t_{NI}, ratios of temperatures were taken as described above. A prime is appended to ρ_X and ρ_Y to indicate ratios of t_{NI} values. Our analysis suggests that t_{NI} for Cl/C_6H_5 is too high compared to the other isotropization temperatures, so that value was discounted in calculating the ρ' values listed in Table III, and in the subsequent calculations. From the t_{NI} values for the other 12 polymers, and the ρ' values in Table III, we estimate $t_{NI}^0 = 627 \pm 12.3$ °C for unsubstituted poly(*p*-phenylene terephthalate). According to these estimated t_{KN}^0 and t_{NI}^0 values, the parent polymer has a relatively restricted nematic temperature range of only 40 °C. Evidently substitution reduces t_{KN} more than t_{NI}, resulting in a wider nematic temperature range for the substituted polymers. The ρ'_X/ρ_Y' ratio is near unity for all substituents except phenyl, where a larger depression of the isotropization temperature is indicated when that substituent is on the terephthalic acid moiety.

Copolyesters and Mixtures of Homopolymers. Three copolyesters of phenyl- and chlorohydroquinone were synthesized and their crystal–crystal and crystal–nematic transition temperatures determined by DSC using a heating rate of 10 °C/min. Cooling curves were also collected at 10 °C/min. Column one of Table V gives the

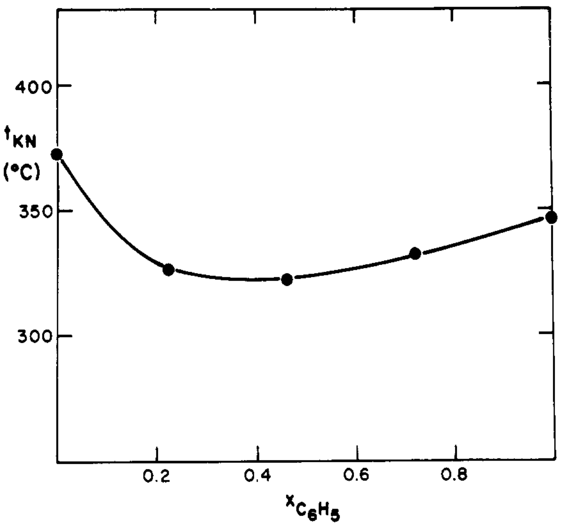


Figure 7. Crystal-nematic transition temperatures of phenyl- and chlorohydroquinone terephthalate copolyesters shown as a function of the mole fraction of phenylhydroquinone.

Table VI
Bragg Spacings (Å) of Phenyl- and Chlorohydroquinone Terephthalate Copolyesters

$x_{C_6H_5}$[a] 0.00	0.25	0.50	0.75	1.00
			13.39 (s)	
		12.81 (s)		12.47 (s)
				7.82 (w)
7.23 (s)				
	6.75 (w)		6.68 (w)	6.33 (w)
		6.08 (w)	6.13 (vw)	
	5.89 (w)		5.58 (w)	
4.37 (w)	4.40 (s)	4.50 (s)	4.53 (s)	4.87 (s)
3.94 (s)				4.21 (s)
3.51 (w)	3.72 (vw)			
3.35 (vw)				3.34 (vw)
3.23 (vw)				

[a] Mole fraction of phenylhydroquinone.

mole fraction of phenylhydroquinone, while columns two and three list the transition temperatures (°C). The t_{KN} values appear plotted against the mole fraction of phenylhydroquinone in Figure 7. We note that the melting temperature of the Cl/H homopolymer can be reduced by 50 °C through copolymerization with 35 mol % of phenylhydroquinone. The shape of the melting curve suggests that the copolyesters form a mixed crystal rather than a eutectic. This type of behavior has been observed for semiflexible copolyesters based upon 4,4′-dihydroxybiphenyl and saturated dibasic acids.[28] The Bragg spacings listed for the copolymers in Table VI indicate that, although there are significant differences, their crystal structures resemble that of C_6H_5/H more than Cl/H. It is noteworthy that a longer spacing in the range 11.9–13.4 Å appears in the diffraction pattern of the copolymers, but not in the Cl/H homopolymer. The ΔH_{total} values in column six of Table V indicate that the copolymers have about the same degree of crystallinity as the C_6H_5/H homopolymer. This is an interesting comparison of the effect of two different types of randomness upon the melting temperature.

Table VII
Transition Temperatures (°C) of Mixtures of C_6H_5/H and H/C_6H_5 Homopolyesters

$w_{C_6H_5/H}$[a]	t_{KK}	t_{KN}	t_{NI}	$t_{KN} - t_{NI}$
0.00	225	285	360	75
0.10	228	250	388	138
0.25		232	406	174
0.50		230	(368)	(138)
0.75	231	272	458	186
0.90	234, 276	312		
1.00	323	348	475	127

[a] Weight fraction of C_6H_5/H homopolyester.

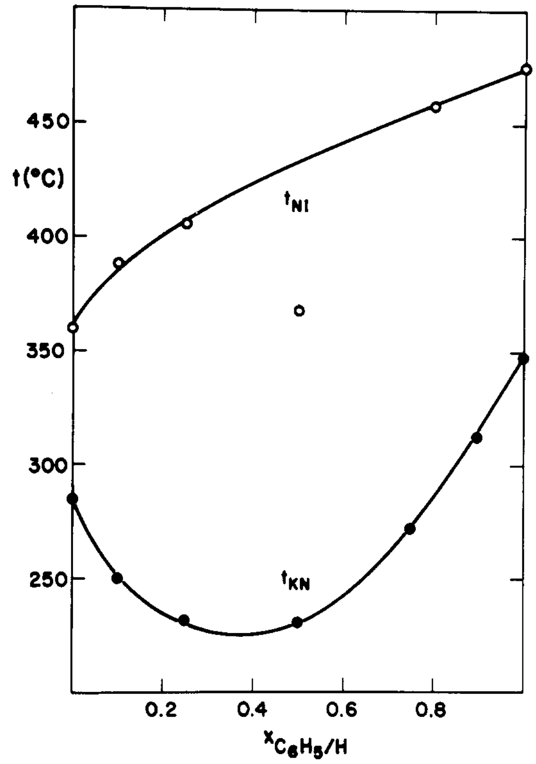


Figure 8. Nematic–isotropic and crystal–nematic transition temperatures of mixtures of C_6H_5/H and H/C_6H_5 homopolymers plotted as a function of the mole fraction of C_6H_5/H homopolyester.

The mesophase properties were also examined for five mixtures of the C_6H_5/H and H/C_6H_5 homopolymers. These mixtures were prepared in two ways. In the first method, weighed amounts of the two homopolyesters were sealed in a DSC pan and heating and cooling, cycles were repeated until the transition temperatures became reproducible in successive heating curves. This generally required three or four cycles. The second method involved solution of the known weights of the polymers in a solvent composed of equal weights of $CHCl_3$ and hexafluoro-2-propanol. The polymer was precipitated in methanol, filtered, and dried overnight in a vacuum oven at 80 °C. The first and second heatings gave concordant results using this method, indicating complete mixing.

The DSC heating curves for these mixtures were measured at a rate of 30 °C/min. The crystal–nematic and nematic–isotropic transition temperatures, t_{KN} and t_{NI}, are listed in °C in Table VII and appear plotted against the mole fraction of C_6H_5/H homopolyester in Figure 8. We note that t_{KN} shows negative deviations from a linear relation between the homopolymer melting temperatures, while t_{NI} shows positive deviations from additivity. Thus, the mixtures have a significantly wider nematic range than the homopolyesters. The mixture having mole fraction C_6H_5/H equal to 0.375 has a melting point 40 °C lower than that of the H/C_6H_5 homopolymer. Also, the nematic range of the latter is increased from 78 to 197 °C. The composition dependence of t_{KN} indicates the mixtures form a mixed crystal, just as was the case for the copolymers. This result differs from that reported previously for mix-

Table VIII
Bragg Spacings (Å) of Mixtures of H/C_6H_5 and C_6H_5/H Homopolymers

$w_{C_6H_5/H}$[a]						
0.00	0.10	0.25	0.50	0.75	0.90	1.00
13.27 (vs)						
	12.92 (vs)	12.49 (vs)	12.36 (vs)	12.44 (vs)	12.59 (vs)	12.47 (vs)
7.20 (vw)	7.35 (vw)	7.70 (w)	7.60 (w)	7.60 (w)	7.60 (w)	7.82 (w)
6.62 (m)	6.68 (w)	6.18 (w)	6.18 (w)	6.40 (m)	6.29 (w)	6.33 (w)
		4.77 (s)	4.78 (s)	4.96 (s)	4.78 (s)	4.87 (s)
4.45 (s)	4.48 (s)					
	4.16 (w)	4.16 (s)	4.13 (s)	4.31 (s)	4.23 (s)	4.21 (s)
3.93 (w)						
3.45 (vw)	3.30 (vw)	3.30 (w)	3.29 (vw)	3.25 (vw)	3.30 (vw)	3.34 (vw)

[a] Weight fraction of C_6H_5/H homopolymer.

tures of polyesters prepared from 4,4′-dihydroxybiphenyl with pimelic and azealic acids.[28] In that case the crystal melting exhibited eutectic behavior. The Bragg spacings listed in Table VIII were measured for samples which had been heated into the nematic range, held for 1 h at t_{KN}, and were then cooled at 10 °C/min. The spacings indicate that the crystal structure of the mixtures resembles that of C_6H_5/H for compositions having a weight fraction of that polymer 0.25 or greater.

Discussion

We have compared the effectiveness of different substituents in lowering the crystal–nematic melting temperature of poly(*p*-phenylene terephthalate). With one exception, a single substituent reduces t_{KN} from 600 °C for the parent polymer into the range 340–405 °C. Any substituent lowers t_{KN} due to positional isomerism. C_6H_{13} and C_6H_5 have additional conformational or rotational degrees of freedom per repeating unit and are therefore more effective than Cl or Br in lowering t_{KN}. The exception mentioned above is H/C_6H_5, which has a t_{KN} of approximately 290 °C. This is substantially lower than the t_{KN} value of C_6H_5/H, 345 °C. The glass transition temperatures of H/C_6H_5 and C_6H_5/H, 130 and 170 °C, appear to support the conjecture that H/C_6H_5 has a less extended chain than C_6H_5/H. Substitution of both rings, again with one exception, reduces t_{KN} into the range 205–235 °C. The exception is C_6H_5/C_6H_5, which remains noncrystalline after long heating. As indicated above, we believe the failure of this polymer to crystallize is due to reduction of t_{KN} to the vicinity of t_G for this polymer.

As expected, the degree of crystallinity is less for disubstituted polymers than for those bearing a single substituent. Nevertheless, all the polyesters in this study except Cl/H and Br/H showed a Bragg spacing of 12 Å or greater, indicating regular packing along the chain direction. Disubstituted polyesters crystallize more slowly. In fact, all disubstituted polymers except C_6H_{13}/Br require annealing to exhibit a crystalline diffraction pattern. Also, polyesters incorporating phenylhydroquinone crystallize at slower rates.

Crystalline polymorphism is common for low molecular weight mesogens, and it is prevalent among the semiflexible, segmented polyesters. It also occurs for the rigid-chain substituted poly(*p*-phenylene terephthalates). On cooling from the nematic phase, the first crystals to appear are often not the highest temperature modification. Hence, a slowly cooled sample may contain several crystalline polymorphs. Poor mechanical properties might be expected for such a sample due to a high concentration of defects in the crystalline phase. Annealing favors the growth of a particular crystalline polymorph, so the DSC heating curves of annealed samples generally exhibit fewer crystal–crystal transformations. Heat treatment of fibers spun from rigid-chain polyesters significantly improves their mechanical properties, as disclosed in the Luise patent.[29] The fibers are heated in a stepwise manner, and under a flow of nitrogen. This increases the molecular weight and degree of crystallinity. It may also transform the mixture of crystalline polymorphs into a single solid modification. For example, Kyotani and Kanetsuna,[30] in their study of the rigid-chain poly(chloro-1,4-phenylene *trans*-1,4-cyclohexanedicarboxylate), observed a change in the diffraction pattern beginning about 170 °C, a crystal–crystal transformation in the range 190–220 °C, and the appearance of a new reflection at 5.2 Å (perhaps presaging the onset of melting) just above 290 °C. The heat treatment of this fiber, described in the patent of Kleinschuster, Pletcher, and Schaefgen,[18] involved the temperatures 170, 230, 260, and 290 °C. Comparison with the observations of Kyotani and Kanetsuna indicates this treatment should transform the crystalline regions of the fiber to the high-temperature modification.

It is not possible to predict how any substitutent will affect t_{KN} or t_{NI}. We might anticipate a larger reduction of t_{KN} since positional isomerism (and presumably also the additional degrees of freedom imparted by substituents such as C_6H_5 and C_6H_{13}) should primarily affect the crystal–nematic transition. In fact, a larger reduction does occur for t_{KN}, so that substitution broadens the nematic temperature range. For the parent poly(*p*-phenylene terephthalate) the nematic range is predicted to be about 40 °C. The nematic range of the monosubstituted X/H polymers varies from 119 to 138 °C, averaging 127 °C. However, a given substituent on hydroquinone or terephthalic acid produces different results. The nematic ranges of the three monosubstituted H/Y polyesters are 88, 85, and 73 °C, for an average of only 82 °C. Thus, substitution on terephthalic acid appears to destablilize the nematic phase. This general behavior of the H/Y polyesters may require a different explanation than that of greater flexibility given for the particular case of H/C_6H_5, since the glass transition temperatures of both Cl/H and H/Cl are 220 °C.

The observation of a thermotropic nematic–isotropic transition in rigid-chain polyesters can only be explained by taking into account the temperature dependence of the unperturbed molecular dimensions.[31] We have recently modified Flory's treatment[32] of Kuhn chain polymers to allow the axial ratio of the Kuhn link to be temperature dependent.[33] An interesting prediction arising from this modification is that all polymers which can be represented by the Kuhn chain model are in corresponding states at their nematic–isotropic transition temperatures. Specifically, the axial ratio of the Kuhn link should have its critical value, 6.7018, at t_{NI}^0. It seems unlikely that substitution would significantly alter the absolute magnitude of $d \ln \overline{r_0^2}/dT$; hence, this prediction implies that those

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substituted polyesters having lower t_{KN} values must have smaller chain extensions at ambient temperatures. The poor mechanical properties reported by Acierno et al.[4] for fibers spun from the nematic phases of semiflexible polyesters would lead us to expect, therefore, that the more flexible H/C_6H_5 would have poorer fiber properties than C_6H_5/H. This does appear to be the case. The Harris patent[10] cites for heat-treated fibers of H/C_6H_5 the following values for the tenacity, (g/denier), elongation (%), and modulus (g/denier): 10.0/3.14/352. Jackson[6] gave for a heat-treated fiber of C_6H_5/H the values 32/4.3/910.

Acknowledgment. This work was supported by the U.S. Army Research Office on Contract DAAG29-84-0033.

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Comparison of the Phase Behavior of Binary Systems Involving Low and High Molecular Weight Thermotropic Nematogens

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Received August 30, 1984

ABSTRACT: Binary phase diagrams were determined for the low molecular weight nematogen *p*-azoxyanisole with diluents *N,N*-diphenylacetamide and acetanilide. Comparison with the Warner–Flory theory indicates the width of the biphasic region is correctly estimated, but the predicted depression of T_{NI} is too large. Moreover, the two diluents give different depressions, suggesting a dependence of the nematic order upon the shape of the diluent molecule. The observed depressions of T_{KN} are also compared with prediction. The isotropization temperatures were determined for poly(*n*-hexyl isocyanate) (PHIC) in toluene, and the temperature dependence of the persistence length of PHIC was determined from viscosity data in toluene and tetrahydrofuran (THF). The nematic range of PHIC extends over a very broad composition range, which cannot be accounted for in terms of hard and soft interactions. Flory's treatment of Kuhn chain polymers is modified to account for the temperature dependence of the unperturbed dimensions. For PHIC, extrapolation of the axial ratio of the Kuhn link to T_{NI}° follows expectation. For other polymers, such as (hydroxypropyl)cellulose, a small contribution from soft interactions may be necessary. We suggest that a negative temperature coefficient plays an important role in the mesophase behavior of rigid-chain polymers, and perhaps even of low molecular weight nematogens.

Introduction

Early statistical mechanical treatments of nematic phenomena stressed the effect of the asymmetric shape of the nematogen upon the entropy of the system. Both the virial aproach of Onsager[1] and Ishihara[2] and the lattice model treatment of Flory[3] demonstrated that a solution of rodlike particles will transform to an anisotropic nematic phase when the concentration of rods exceeds a critical value which is dependent upon the axial ratio of the rod. By contrast, the theory of Maier and Saupe[4] postulated that the nematic phase is stabilized solely by energy difference arising from orientation-dependent interactions. Their treatment was concerned with thermotropic mesomorphism in one-component systems. It is now recognized that the nematic phase may be stabilized by both energy and entropy differences between the nematic and isotropic phases. Both effects were incorporated in a treatment of

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0024-9297/85/2218-0973$01.50/0