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A DETAILED STUDY OF THE PHASE BEHAVIOR OF A SERIES OF THERMOTROPIC POLY(2-ALKYL-1,4-PHENYLENE TEREPHTHALATE)S

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Abstract—A series of thermotropic, rigid-rod polyesters was prepared from terephthalic acid and a series of alkylhydroquinone diacetates, which contained single n-alkyl substituent groups of increasing size from butyl, C_4, to dodecyl, C_{12}. The polyesters were synthesized in the melt and were investigated for their phase behavior by differential scanning calorimetry, DSC, by dynamic mechanical thermal analysis, DMTA and by visual observations of samples placed on a hot stage on a polarizing microscope. All members of the series showed multiphase behavior and all formed mesophases. The transition temperatures, including T_g for the amorphous glass, T_{gM} for the mesophase glass, T_m for the melting transition, and T_i for the nematic-to-isotropic transition, were all determined for most of the polymers. The melting behavior of each polymer in the series and the influence of the alkyl substituents in lowering the transition temperatures is discussed. The liquid crystalline textures observed at each stage are described, but an unequivocal nematic texture was observed for each polymer at a temperature approaching the nematic-to-isotropic transition.

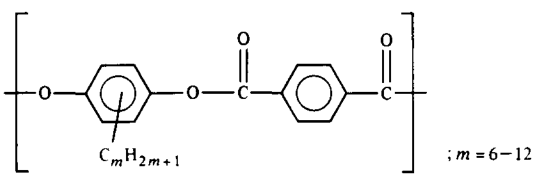
INTRODUCTION

Rigid-rod aromatic polyesters are a class of polymers which have useful thermal and mechanical properties [1, 2]. Some of them have been commercialized for their use in cases where outstanding thermal, mechanical and chemical properties are required [3]. The simplest representative of this class of polyesters are poly(1,4-phenylene terephthalate) (PPhT) and poly-4-hydroxybenzoate (PHBA) but these polymers have extremely high melting points, on the order of 600°C [4, 5], and cannot be processed without decomposition by conventional methods. However, a number of structural variations can lower the melting temperatures, T_m, of aromatic polyesters based on the principle of reducing chain symmetry and regularity.

The substitution of aromatic rings in aromatic polyesters in one of the possible ways to achieve a reduction of transition temperatures. This approach was first described in detail in the sixties [6, 7] and is still used in current patents. The most often ring substituents used are Cl, Br, CH_3, OCH_3, NO_2 and phenyl groups. Jackson [4, 8] and Krigbaum *et al.* [9], and more recently Jin *et al.* [10], described broadly the properties of aromatic polyesters containing such substituents.

We reported earlier on the results achieved by alkyl group substitution on the hydroquinone monomer in the synthesis of poly(2-alkyl-1,4-phenylene terephahalate)s (PAPhT) with normal, iso- and cycloalkyl substituents [11, 12], and we also described the influence of alkyl substituents (AS) on the properties of aromatic polyesters with flexible spacers in the main chain [13, 14]. Similarly, Ballauff [15–18] described the synthesis and properties of PPhT substituted with two alkoxy groups (AX) on the terephthalate residue. Markova *et al.* [19a] reported on a PPhT substituted with a carboxymethyl group on the hydroquinone ring.

In our earlier study, we described the synthesis and properties of a series of PAPhT of the following structure:



PAPhT

We concluded from visual observations of samples of these polymers, which were heated on a hot stage placed on a polarizing microscope, that the polymers in this series formed a smectic phase above their melting points, after which they appeared to undergo isotropization directly at a temperature of some 20–60°C higher. However, the polymers prepared for that study were of quite low molecular weight, M, with inherent viscosities, IV, well below 1.0 dl/g at a concentration of 0.2 g/dl.

EXPERIMENTAL PROCEDURES

Monomers

The AHQDA monomers were obtained as previously described [19b]. Fluka pure grade TA was used without further purification.

Polycondensation procedure

Equimolar amounts (0.01–0.03 mol) of the two monomers were weighed into a polycondensation tube, which was placed in a constant temperature bath. The tube was flushed with dry nitrogen then heated to 280°C. The polycondensation reaction began at approx. 270–275°C, as indicated by formation of acetic acid and its presence in the nitrogen stream leaving the tube. The polycondensation was carried out over the temperature range from 280 to 320°C at a heating rate of 10°C/hr, after which a vacuum was applied for 1 hr with an additional slow increase in temperature to 325°C. The tube was removed from the heating bath and cooled in air, while still under vacuum, to room temperature. The polymer was removed from the tube and ground with dry ice into a powder, which was extracted for 24 hr in a Soxhlet apparatus with acetone, then dried under vacuum to a constant weight.

Polymer characterization

IV were measured at 25°C in a solution of 4-chlorophenol and 1,2-dichlorobenzene, 50:50 by weight, at a concentration of 0.25 g/dl using an Ubbelohde 150 type capillary viscometer. Polymer solutions were obtained by first swelling the polymer for about 20 hr in the solvent at room temperature, then heating the mixture for 5–10 min near the boiling point to dissolve the polymer. After cooling to room temperature, the solution was filtered through a 10–20 μm glass filter, and IV measurements were made on the newly prepared solutions. DSC thermograms were recorded on a Perkin–Elmer DSC-2 instrument equipped with a TADS device with samples of 5–10 mg at heating and cooling rates varying from 5 to 80° per min. Transition enthalpies were calculated with the TADS program with reference to the heat of fusion of indium, tin, lead and zinc. A Leitz Ortholux microscope or a Boetius melting apparatus, both equipped with crossed polarizes and hot stages were used for direct observations of the mesophases. Dynamic mechanical measurements were performed on a Polymer Laboratories dynamic mechanical thermal analyzer on molded samples at frequencies of 0.33, 1.0, 3.0 and 10 Hz, and heating and cooling rates of 5° per min.

RESULTS AND DISCUSSION

Because of the low M and the considerable uncertainty of the interpretations of the textures observed in the earlier work, an expanded series of polyesters with AS of $m = 4$–12 of much higher M was prepared in the present study from alkylhydroquinone diacetate monomers (AHQDA) and terephthalic acid (TA) as described earlier [11]. The IV of these polyesters were all closer to 1.5 dl/g at 0.25 g/dl as shown in Table 1. Of course, a polymer with an IV of 1.5 dl/g but substituted with a smaller AS group may not have a value of M which is exactly comparable with those of similar IV but substituted with larger AS groups. The differences in structure resulting from the variable lengths of the AS groups will most likely influence the hydrodynamic behavior of the PAPhT solutions, so similar inherent viscosities for the whole series are not necessarily an indication of equality in M. Absolute measurements of M are required, but have not as yet been made for the entire series because of solubility restrictions.

Table 1. Preparation and inherent viscosity of PAPhT samples

n-Alkyl group (AS)	Monomer amount (mol)	Yield[a] (%)	IV (dl/g)
Butyl, C_4	0.02	83.2	1.92
Pentyl, C_5	0.03	93.6	1.56
Hexyl, C_6	0.03	89.8	1.60
Heptyl, C_7	0.01	76.0	1.48[b]
Octyl, C_8	0.03	89.6	1.41
Nonyl, C_9	0.01	74.1	1.39
Decyl, C_{10}	0.03	92.1	1.62
Undecyl, C_{11}	0.02	90.0	1.36
Dodecyl, C_{12}	0.01	73.4	1.37

[a] After acetone extraction.
[b] After additional heating in the solid state.

From a previous report on the IV vs M relationship of poly(2-phenyl-1,4-phenylene terephthalate) [20] it may be estimated that, for an IV of 1.5 dl/g at comparable concentrations, the polyesters in Table 1 should have a number average molecular weight, $\bar{M}_n$, in the range of 10,000–20,000. Data obtained by vapor pressure osmometry of lower M samples in the present series of PAPhT suggest that the $\bar{M}_n$ of polymers described in this series are closer to 10,000. This M level is not sufficient for the samples to achieve their maximum melting, T_m, and isotropization, T_i, temperatures, but the differences in T_i and in T_m caused by the small variations of IV between the members of the series should be very small and can be neglected for the general comparison of the phase transition temperatures of the different PAPhTs.

The polymers in the present series were characterized for their phase behaviors by the use of a hot stage with a polarized light microscope, by DSC and by DMTA.

Glass transitions

There is a reasonable amount of data on the effect of substitution on the T_g of PPhT but some uncertainty on which glass transition is being observed. Frosini and coworkers [21] reported the T_g for unsubstituted PPhT to be 267°C, and T_g values reported for monosubstituted PPhT with the substituents on the hydroquinone residue ranged from 170°C for the Ph-substituted polymer [9] to 267°C for the norbornyl-substituted polymer [12]. For cycloalkyl-substituted PPhT a T_g value of about 210°C was observed, while for the 1-methylpentyl-substituted PPhT a value of 237°C was obtained [12]. In contrast, Berger and Ballauff, who investigated a similar series of PAPhTs [15] and Krigbaum *et al.* [9], who investigated the n-hexyl substituted PAPhT did not observe glass transitions for the samples in their investigations. Similarly, a T_g was not found in other monosubstituted PPhT samples [9, 10, 16, 19a], but T_g values were reported for almost all disubstituted samples of PPhT bearing one substituent on each phenylene ring [9, 10, 22].

In the present study we paid close attention to the possible formation of both amorphous and mesomorphous glassy phases in our series of PAPhTs by use of both DMTA and DSC measurements. DMTA studies were carried out over the temperature range

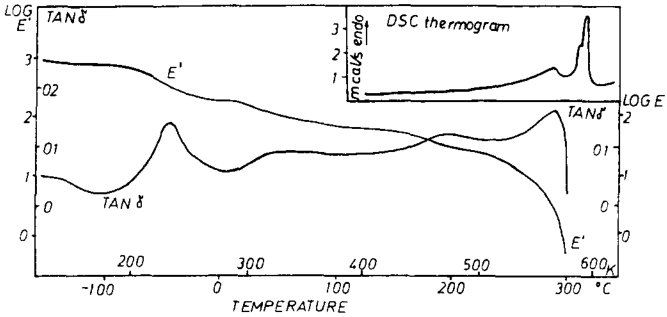


Fig. 1. Dynamic mechanical analysis at 1 Hz and the DSC thermogram for a quenched $PC_{10}PhT$ sample; the heating rates for both measurements was 5°C/min.

from −100° to 300°C, and the results for the PAPhT polymer with $m = 10$, which is selected as a typical processable member of the series, are shown in Fig. 1.

The low temperature tan δ peak at approx. −40°C, which is associated with a step decrease in E′ in Fig. 1, is typical of that for a β-relaxation process for aromatic polyesters in general. The broad tan δ peak, and the associated small decrease in E′, which can be seen at approx. 50°C, is presently unassigned but may be related to the increase of mobility of the AS group in a manner similar to that found by Berger and Ballauff for a PAPhT containing long AS groups with $m = 17$ and 18 [15]. Their polymers showed T_m transitions by DSC measurements with peak temperatures of 19–28°C, which they described as a melting of the alkyl group substituents.

In Fig. 1 a small decrease of E′ is also seen close to 200°C. This decrease is associated with a small peak in tan δ, which suggests that a small amount of a glassy phase with a lower transition temperature may be present in the polymer. This assumption is also supported by results obtained by DSC measurements. On scanning samples which were untreated thermally very small discontinuities in the heat flow curves were observed close to 200°C. When the samples possessed a similar thermal history to that of the sample used for the DMTA measurement (in which the sample was rapidly preheated 15–20°C above the T_m and subsequently quenched on a copper plate at a cooling rate in the order of 10^3 per min), the first thermogram obtained after quenching for samples; with $m \geqslant 8$ showed a clear endothermic jump at that temperature. This and related results are collected in Table 2 and Fig. 2, and in Fig. 3 is shown a portion of the DSC thermogram for the quenched polymer with $m = 11$, $PC_{11}PhT$. The T_g values found for the different PAPhT samples by DSC fit well with the glass transition range of the other monosubstituted PPhTs described above [9, 10, 12].

The results of both the DMTA and the DSC studies seem to be evidence for the presence of a small amount of an amorphous glassy phase in the quenched PAPhT samples. This amorphous phase is apparently unstable and transforms quickly above the T_g to a more highly ordered phase, presumably a mesophase glass or possibly even a crystalline phase of very low perfection. For this reason the observation of a T_g by both DMTA and DSC is not always possible but depends instead on several factors including the quenching procedure, the state from which the polymer is quenched and the rate at which the sample is scanned in subsequent measurements. The most consistent DSC measurements were achieved for the PAPhT samples substituted with long AS groups, the C_{10} and C_{11} groups ($PC_{10}PhT$ and $PC_{11}PhT$), when the samples were first preheated for 10–20 sec above the T_m, quenched, and scanned at a heating rate of 20° per min.

As shown in Fig. 3, in some cases a cold crystallization-like exotherm was observed just above the glass transition in the DSC thermograms. Similar exotherms were found by Jackson [8] and by Menczel and Wunderlich [23]. They interpreted their results as indicative of a transformation from the amorphous to the mesophase state, not as crystallization.

Much stronger transitions for all polymers were observed in both the DMTA and the DSC measurements in the temperature range of 250–300°C. In the DMTA plot a clear tan δ peak and an abrupt E′

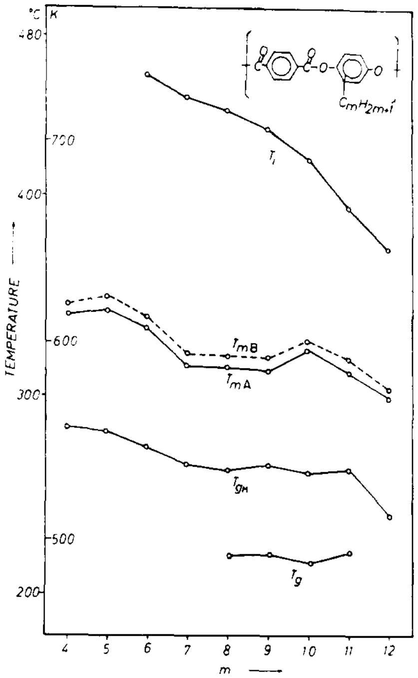


Fig. 2. Variations in T_g, T_{gM}, T_{mA}, T_{mB} and T_i, with size of the AS group in the PAPhT series, all having IV values of close to 1.5 dl/g.

Table 2. Thermal transitions and thermodynamic data for PAPhT samples

AS group	Thermal transitions (°C)				ΔH_m,[b] (kJ/mol)	T_i,[c] (°C)	ΔH_i, (kJ/mol)	ΔS_i (J/mol.K)	$\Delta(T_i^c - T_{mA}^a)$, (°C)
	T_g	T_{gM}	T_{mA}	T_{mB}					
C_4	—	283	340	345	4.49	—	—	—	—
C_5	—	281	342	349	5.76	—	—	—	—
C_6	—	273	333	339	5.04	460[d]	—	—	127[c]
C_7	—	264	314	320	4.83	448	0.9	1.25	134
C_8	216	260	313	319	5.02	441	1.0	1.40	128
C_9	218	262	311	318	4.52	430	1.2	1.71	119
C_{10}	214	260	321	326	3.48	419	1.4	2.02	98
C_{11}	219	263	310	317	2.64	395	1.5	2.25	85
C_{12}	—	238	297	302	1.76	375	1.7	2.62	78

[a] From DSC thermograms obtained at a heating rate of 20°C/min.
[b] Calculated from the sum of the A + B endotherms.
[c] From DSC thermogram at a heating rate of 80°C/min.
[d] Taken from Ref. [9].
[c] Calculated using T_i from Ref. [9].

decrease at 280–290°C was observed for the $PC_{10}PhT$ sample, but these results could be indicative of either a glass or a melting transition. Nevertheless, this temperature range compares favorably with that of the transition recorded in the DSC thermograms as shown in Figs 1 and 4 and with changes in the state of the polymers observed for samples on a hot stage of a polarizing microscope. At that temperature, the polymer particles softened and coalesced.

The course of the transition which was recorded in the DSC measurements was strongly dependent on the prior heat treatment of the polymer, as shown in Fig. 4. A similar behavior was observed in the microscopy studies, and both observations strongly suggest that, in the temperature range of 250–300°C for the PAPhT series, a glass transition, T_{gM}, of a glassy mesophase occurs. It is possible that a simultaneous melting of low ordered crystalline regions may also occur in that temperature range as suggested by Berger and Ballauff [15]. The relation between T_{gM} and the value of m for the AS groups is presented in Fig. 2, and the data are collected in Table 2.

Melting transitions

At a temperature which was 50–60°C higher than the T_{gM} for each member of the series, strong endotherms were recorded for each polymer in the heating cycles of the DSC thermograms of the present PAPhT samples. Our observations suggest that the polymers melted at the first peak, peak A in the thermograms, as indicated by very careful observations of samples on the polarizing microscope. The shapes of the endotherms depended on the thermal histories of samples, including the polycondensation procedure, and also on the state from which the polymers were cooled.

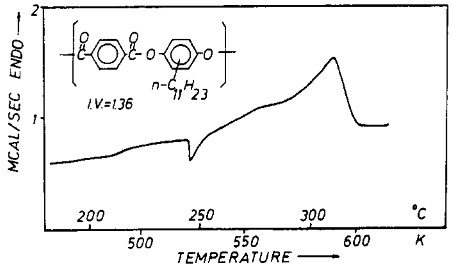


Fig. 3. DSC thermogram obtained at 20°C min for a quenched sample of the $PC_{11}PhT$ sample; quenching rate was approx. 10^{3}°C/min.

For the interpretation of the initial heating cycle thermograms of the nonheat treated samples shown in Figs 1A, B and 4, it should be noted that while identical conditions were used for the preparation of all of the polyesters in this series, the final states of the polymers in the reactor differed for the different members. That is, the polymers with $m \geqslant 7$ had T_m

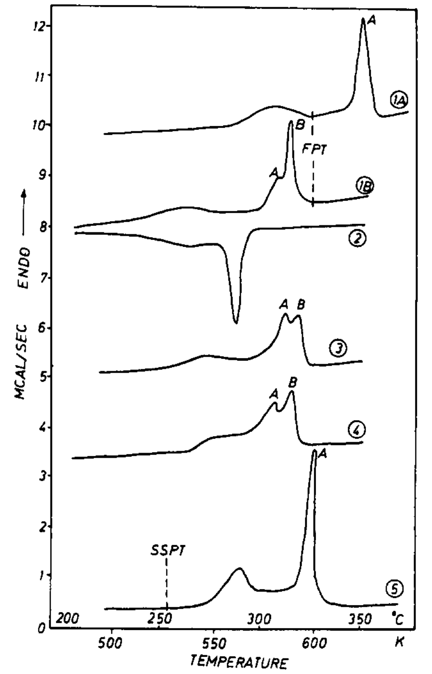


Fig. 4. DSC thermograms obtained at 20°C/min for the following PAPhT samples: 1A, PC_4PhT, first heating cycle after polymer isolation; 1B, PC_8PhT, first heating cycle after polymer isolation; 2, PC_8PhT, first cooling cycle from the mesomorphous melt; 3, PC_8PhT, second heating cycle after cooling the polymer from the mesomorphous melt at 20°C/min; 4, PC_8PhT, second heating cycle after quenching the polymer from the mesomorphous melt; 5, first heating cycle after cooling the sample below T_{gM} following both the solid state polycondensation reaction and annealing at 257°C for 12 hr; FPT, final polycondensation reaction temperature; and SSPT, solid state polycondensation reaction temperature.

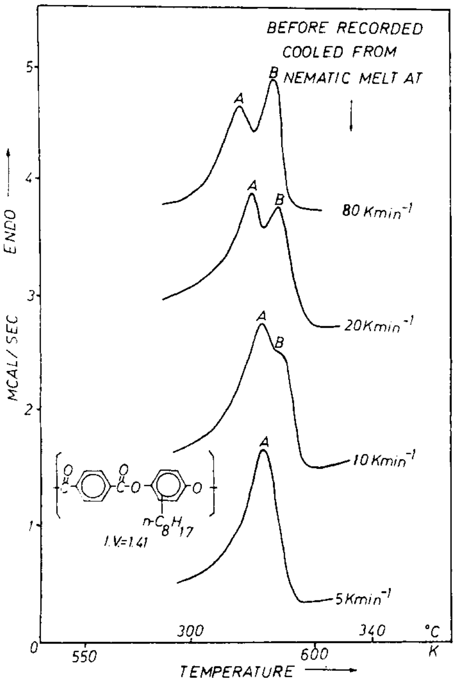


Fig. 5. DSC melting peaks at a heating rate of 20°C/min for the PC$_8$PhT polymer cooled at different rates from the LC melt before the heating cycle; cooling rates are indicated.

values below the final polymerization temperature of 320–325°C, while the polymers with $m < 7$ had T_m values above that temperature. Hence, for the latter samples, the polymerization reaction was completed in the solid state under conditions which favored crystallization, while for the former the polymers were still molten. These differences are apparently reflected in the types of endotherms obtained for the first DSC heating cycles, and reproducible thermograms were obtained only after the samples in the DSC pans were cooled from the mesomorphous melt and reheated.

For polymers in which the polycondensation reaction was completed below T_m only a single peak was observed in the first heating cycle as shown in Fig. 4, 1A, while those in which the samples remained molten in the polymerization had two peaks. In either case, however, after the first heating and cooling cycles at rates of 20° per min all samples, which were cooled at 20° per min, showed two endothermic peaks, T_{mA} and T_{mB} in the second heating cycle as seen in Figs 4 and 6 and reported in Table 2. The temperature difference between the two peaks was only a few degrees and the dependence of these peak temperatures on m is shown in Fig. 2. The melting temperatures and the sum of the enthalpies of the two transitions, ΔH_m, are collected in Table 2.

The positions of the two peaks recorded in the DSC thermograms were influenced by the rate at which the polymers were cooled from the melt before the DSC thermograms were obtained. After moderate cooling rates, two peaks were clearly recorded in thermograms of the following heating cycle, while when slow or very fast cooling rates were applied before the first heating cycle only a single peak was present. The portion of the thermograms containing the melting endotherms for the PC$_8$PhT sample which had been cooled at different rates from the melt prior to the heating cycle are presented in Fig. 5. The relationship between the two peaks was also influenced by the type of AS group in the polymer. Figure 6 contains the portion of thermograms containing the melting endotherms for the different PAPhTs which were cooled from the melt prior to the heating scan at a standardized rate of 20° per min.

The total disappearance of the lower temperature peak, A, in the thermogram of the PC$_{11}$PhT sample was observed when the sample was quenched, as shown in Fig. 3. On the other hand, for the PC$_8$PhT sample the higher temperature peak, **B**, was absent in the thermograms of samples cooled from the melt at 5° per min before the scan.

Multiple endotherms have been observed for melting transitions of several aromatic polyesters and polyethers, including PET, PEEK and the poly(ethylene terephthalate-co-4-oxybenzoate) [24–26]. Most often it is concluded that this behavior is caused by a continuous melting and recrystallization process during the DSC scan [25, 27–32], although alternative explanations are also proposed [33–37]. Melting–recrystallization was suggested by Ballauff *et al.* [15, 16] as an explanation for the behavior of PAPhT and of poly(1,4-phenylene-2,5-dialkoxyterephthalates), while Krigbaum *et al.* [9] and Jin *et al.* [10] attributed the multiple melting peaks they observed in substituted PPhT to crystalline polymorphism. Noel [38] suggested that multiple first order transitions could also be characteristic of the transition from the solid to the nematic phase and gave different reasons for the behavior observed including poly-

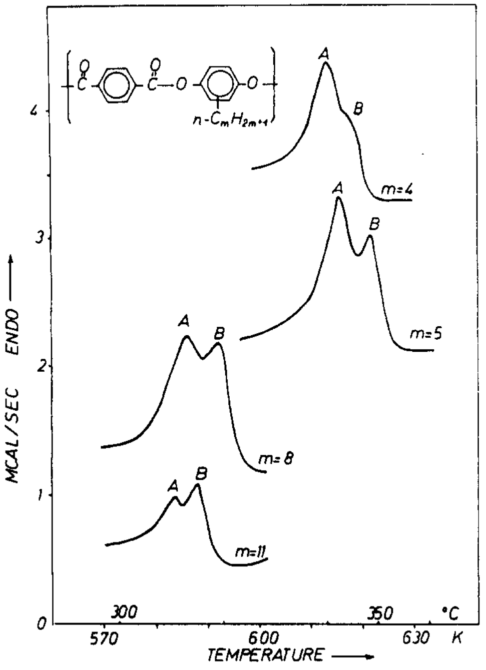


Fig. 6. DSC melting peaks obtained at heating rate of 20°C/min for the different PAPhT polymers cooled from the LC melt at 20°C/min before the heating cycle; m is the number of carbon atoms in the AS group.

morphism and also both solid-to-mesophase and mesophase-to-mesophase transitions. Other explanations given for double endotherms observed in thermograms of polymeric liquid crystals were that given by Kricheldorf [39], who suggested the formation of a thermodynamically less stable high temperature phase at a solid–solid transition in PHBA, and that given by Wendorff, Zimmermann and coworkers [40–42], who explained the presence of such peaks in rigid aromatic copolyesters as a consequence of different kinetics of phase ordering processes.

In the present study, it was observed by WAXD that all of the PAPhT samples were crystalline after removal from the polymerization reactor. That is, all of the polymers synthesized crystallized to some extent, but the polymers with $m \geqslant 7$ crystallized only during cooling after the polycondensation, while the polymers with $m \leqslant 6$ crystallized, and may have even been annealed, during the final stage of polycondensation under almost isothermal conditions. Ordering processes also apparently occurred during the acetone wash of the polymers after the polycondensation, and the PAPhT samples with the larger AS groups probably increased in crystallinity while the other polymers, which crystallized during the final stage of polycondensation, did not. In Fig. 7 the thermograms of the PC_5PhT and of the $PC_{11}PhT$ samples, before and after the acetone wash, are presented. The changes recorded in the DSC thermograms of the $PC_{11}PhT$ sample can be interpreted to be the result of solvent-induced crystallization in the swollen state, which does not occur in the PC_5PhT sample, presumably because the latter, after the polycondensation reaction, already has a higher crystalline order and because of the higher resistance of this polymer to swelling by acetone.

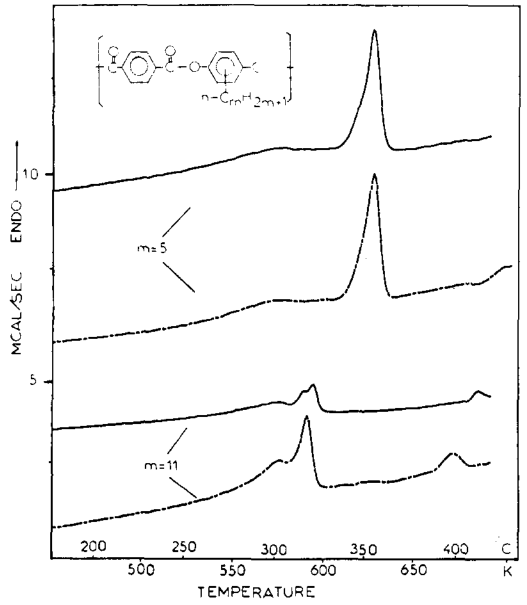


Fig. 7. DSC thermograms obtained at 20°C/min for untreated samples (——) and for samples extracted with acetone for 24 hr at ambient temperature (—·—) m in AS group is indicated.

Hence, based on the results of the thermal analysis and on the behavior of the polymers during the acetone treatment, it seems most probable that the lower temperature endotherm, A, is strongly dependent on the crystallization conditions and is representative for the crystalline structures present in the as-polymerized polymers before the first DSC scan. The higher temperature peak B, however, represents the final stage of melting and includes any recrystallization processes which occur during the DSC scan. For the latter, the portion of the sample for all polymers, on cooling from the mesophase melt, which does not crystallize well can form either a mesophase glass or a low ordered crystalline phase. The presence of both of these phases was found in all PAPhTs in increasing amounts as the size of the AS group increased and when faster rates of cooling of the polymer melts was applied. That is, with increasing size of the AS group, the degree of crystallization decreased as shwon in Fig. 6 by the decrease of peak A as m increased. This conclusion is also confirmed by the thermodynamic data obtained.

The A and B endotherms for the different PAPhT samples showed the highest ΔH_m values, in the range of 6–8 kJ/mol for the polymers that completed their formation in the solid state ($m \leqslant 6$), which resulted in crystallization under almost isothermal conditions, while the ΔH_m values were lower for polymers that were formed entirely in the melt state ($m \geqslant 7$), which crystallized under nonisothermal conditions. The ΔH_m values under the latter conditions varied from 4.6 kJ/mol to 1.9 kJ/mol for the PC_8PhT and the $PC_{12}PhT$ samples, respectively. A comparison of the ΔH_m values for the samples of the PAPhTs having similar thermal histories (that is, when all polymers were cooled at standard conditions from their melts) showed also a clear decrease in the ΔH_m values, as seen in Table 2 when $m \geqslant 8$. Similar tendencies were found for ΔH_c values obtained in the DSC cooling cycles under standardized cooling conditions of 20° per min.

The entropies of melting, ΔS_m, calculated from the DSC data obtained under standardized conditions are plotted in Fig. 8. It is seen from these data that the highest ordered structures were present in the PAPhT samples with AS having $m = 5$–8, while in the PC_4PhT, and in the polymers with AS of $m > 8$, lower ordered phases were formed at comparable cooling conditions as indicated by their ΔS_m values. The lower values of ΔS_m found for the PAPhT polymers with $m > 8$ are probably indicative of kinetically limited processes under the cooling conditions applied. For example, a virgin $PC_{11}PhT$ sample, which had been solid state crystallized isothermally for 7 hr at 277°C, gave the following melting data: $T_m = 345°C$, $\Delta H_m = 12$ kJ/mol, $\Delta S_m = 19.4$ J/mol K. Hence, this data shows clearly that even the PAPhT samples substituted with larger AS groups can form highly ordered structures, but it should also be noted that these values were achieved along with a simultaneous increase in M during the isothermal crystallization process in which the IV increased from 1.36 to about 5 dl/g.

The thermodynamic data for the melting and crystallization of PAPhT samples are comparable to those of similar rigid-rod polyesters, including substi-

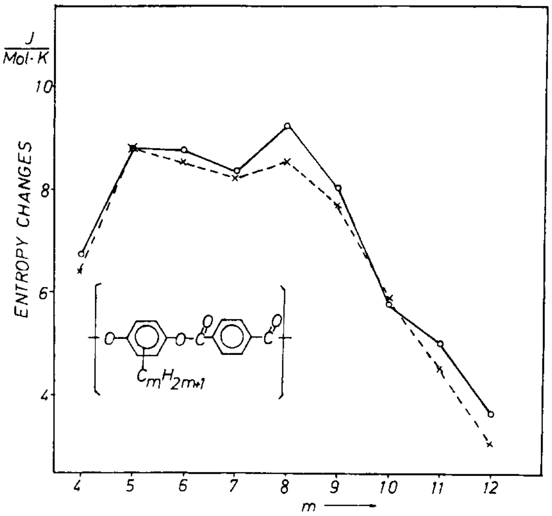


Fig. 8. Variations of entropy values for crystallization from the melt, ΔS_c (——) and for subsequent melting, ΔS_m (– – – –) with size of the AS group in the PAPhT; all samples had IV values close to 1.5 dl/g.

tuted poly(1,4-phenylene-trans-hexahydroterephthalates), for which ΔH_m values of 1–11 kJ/mol were found [9, 10, 43, 44], and comparable ΔH_m data were also found for nonsubstituted fully aromatic polyesters and copolyesters, including values of 5.9 kJ/mol for PHBA [45] and 2.25 kJ/mol for the less symmetric copolymer HBA–HNA [46].

Isotropization transitions

In our earlier studies [11] we described an apparent isotropization of our PAPhT polymers, but we subsequently found that we had mistaken a homeotropization for an isotropization. We had not studied sufficiently carefully the behavior of the PAPhT samples at temperatures close to or above 400°C, partly because we had observed that at that temperature strong decomposition effects occurred. Krigbaum *et al.* [9] later described an isotropization temperature for PC_6PhT with a T_i of 460°C for a sample with an IV of 1.77 dl/g, and similar T_i values were found for other substituted PPhT. Ballauff [15] also gave data for the T_i of the PAPhT with $m \geqslant 10$. Based on these reports, we undertook a more careful study of the series described in this report.

Because of the rapid decomposition above 420°C, the DSC thermograms were recorded at much higher heating rates, but the evaluation creates difficulties because above 420°C the isotropization endotherm must be detected in thermograms of an unstable character. As a result, the reliability and reproducibility of the DSC data obtained above 420°C was poor. We did not give any consideration to endothermic events which appeared above 450°C, but below 420°C we could obtain meaningful data, although it was apparent that the thermal history and the nature of the solid state influenced the temperature as well as the broadness and the enthalpy of the isotropization peaks recorded.

For the present series, as seen in Fig. 2 and in Table 2, an increase in the size of the AS group had a greater effect on decreasing T_i than T_m, so the temperature range for LC behavior decreased from approx. 130°C to approx. 80°C with increasing size of the AS from $m = 7$ to 12. Furthermore, unlike the other transitions, T_i decreased continuously with increasing m as shown in Fig. 2. On the other hand, ΔH_i increased from 0.9 to 1.7 kJ/mol on increasing m from PC_7PhT to $PC_{12}PhT$, while ΔS_i increased from 1.42 to 2.78 J/mol °K. Both of these observations suggest the existence of increasing order in the nematic phase with increasing m.

X-ray investigations, which will be published elsewhere, showed evidence for formation of a biaxial nematic phase as discussed below. Berger and Ballauff [15], on the basis of X-ray investigations, proposed a layered structure for the mesomorphous phase of their PAPhTs with AS of $m \geqslant 14$. In the present case, after the acetone extraction of the $PC_{11}PhT$ sample, the T_i decreased by 18°C indicating that a structural change may have occurred in the mesomorphous glass phase. Furthermore, two separate endotherms were occasionally observed at temperatures at which isotropization would be expected. These results indicate quite strongly that differences in the morphologies or organizations of the LC mesophases of the different PAPhT samples were possible. However, for the members of the series containing smaller AS group, which showed a T_i above 420°C, the isotropization data was probably influenced by the occurrence of thermal degradation, so the interpretation of those results is more questionable.

The present results compare favorably with those published by Krigbaum *et al.* for PC_6PhT [9], but the disagreement between our results and those of Berger and Ballauff [15] for PAPhTs with $m \geqslant 10$ may be explained by differences in the IV values and/or by the different thermal histories of our samples. Berger and Ballauff used a slower heating rate in their DSC measurements.

The isotropization transitions could be observed directly by polarized light microscopy for the $PC_{11}PhT$ and $PC_{12}PhT$ samples. Rapid heating and cooling permitted the visual observation of the reversible texture changes at T_i, and that T_i values observed were closely comparable to those obtained from DSC measurements by taking into account the effects of slight overheating on the DSC thermograms at the very fast scan rates applied. For the members of the series substituted with smaller AS groups, because of thermal degradation, no reproducible isotropization could be visually observed by microscopy, but for the PC_8PhT melt, loss of birefringence was observed at about 380°C. On comparing this observation with the DSC data, it may be concluded that homeotropization may be responsible for this effect, as was observed earlier for the lower *M* PAPhT samples.

Textures of mesophases

In our earlier report [11], we suggested that the LC textures observed for the PAPhT samples were more characteristic of a smectic than a nematic phase. Krigbaum *et al.* [9] describe the textures they observed for similar polymers as being "entangled nematic" textures, while Berger and Ballauff [15] describe those for the PAPhTs they studied as being of the nematic type. For the present series of polymers, the LC phases could be observed with the polarizing light microscope only on samples which were rapidly preheated above the T_m to form a continuous liquid layer between the glass slides. The premelted samples became discolored only on the edge of the melt region so observations of the center of the melt could be made. This procedure gave good correlations between the melting and the crystallization temperatures recorded in the DSC thermograms and those observed in the microscopy studies. Under these conditions, the polymer melts showed undefined textures just above T_m, but usually within 10–30 min on cyclic cooling and heating in the region above T_m the melt changed in appearance to a threaded nematic texture. At rates of temperature change on the order of 10°C/min, the temperature changes required for an observable change in texture on heating and cooling was 32°C for PC_5PhT and 14°C for PC_8PhT but only 2–3°C for $PC_{10}PhT$.

The texture change observed on cooling the PC_5PhT melt, however, was different of that observed on cooling the $PC_{10}PhT$ melt. In both cases the melts were cooled from a state characterized by the threaded nematic textures. The PC_5PhT melt required an undercooling of 32°C below T_m in order to develop a texture change, which took more than 10 sec to occur, during which the texture changed to an undefined turbid appearance. The $PC_{10}PhT$ melt, however, needed an undercooling of only 3°C to develop a complete texture change, which occurred within 1–2 sec. In that case, an increae in the number of disclinations was observed in the texture, but the sample was still highly birefringent. These effects were reversible and reproducible.

The texture changes observed for the PC_5PhT melt on cooling are assigned to the occurrence of crystallization, but those observed for the $PC_{10}PhT$ melt on cooling suggest a process close to an equilibrium for a transition between two different types of mesophases, possibly between the uniaxial and the biaxial nematic phase. In most cases, the quenched nematic melts showed multiphase textures, including threaded nematic texture.

Thermal stability

DSC and DTA studies as well as microscopy observations indicated that the polyesters of this series are thermally stable up to 350°C in an inert atmosphere, and their decomposition begins between 350° and 420°C, depending on the heating conditions. Therefore, by choosing appropriate heating rates the thermal analysis of PAPhT samples could be carried out up to 420°C. Above 420°C rapid decomposition strongly affected the DSC thermograms, and the polymers changed in their properties very quickly at that temperature. Furthermore, at temperatures above 250°C, and notably above 270°C in either an inert atmosphere or in vacuum, the M of the samples increased with time as indicated by IV measurements. The increase in IV was accompanied by an increase in the thermodynamic data, and the temperature, enthalpy and entropy values of the phase transitions all increased significantly. On exposure to air all samples darkened rapidly, even at 250°C, and became increasingly insoluble with time. Apparently, crosslinking occurs under these conditions, most likely by oxidative reactions of the pendant AS groups.

Jackson [8] found a similar behaviour for poly(1,4-phenylene terephthalate)s substituted on the hydroquinone ring with CH_3, Cl and Ph substituents. Polymers containing the CH_3 and the Cl substituents appeared to crosslink on heating to 300°C in air, while the polymer substituted with the Ph group remained soluble after being heated to 300°C in air.

CONCLUSION

The polymers described in this study may be divided into three classes according to the size of the AS group present: (1) The PAPhT samples with small AS groups, those with $m = 4$–6, showed the highest degrees of crystallinity, so much so that it was difficult to detect their T_g. (2) With $m = 7$–9 the polymers behaved almost identically to each other so that their properties, except for T_i, did not differ, including their T_{gM}, T_m, crystalline and LC properties. (3) On increasing m in AS from 10 to 12, a continuous decrease in all of the transition temperatures, except the T_g, was observed, and the decrease in T_i was great enough to permit the observation of their isotropic melts. In the three PAPhT samples, after quenching, large amounts of a glass mesophase were detected, but while these samples had lower degrees of crystallinity than the other members of the series, higher entropy changes were observed for their nematic-to-isotropic transition than for the PAPhT samples with smaller AS groups, indicating a better organization of the mesophases for the polymers in this group.

The X-ray diffraction studies now in progress on the crystalline and the LC phases will be published separately [47], but preliminary results are comparable with those published by Berger and Ballauff [15, 18], by Hermann-Schönherr *et al.* [48] and by Watanabe *et al.* [49] for rigid-rod polymers with flexible side chains.

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