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Dedicated to Professor Bernhard Wunderlich on the occasion of his 65th birthday

PHASE BEHAVIOR IN HIQ40 LIQUID CRYSTALLINE POLYMERS

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Abstract

The thermotropic copolyester consisting of 40 mol% *p*-hydroxybenzoic acid and 30 mol% isophthalic acid/30 mol% hydroquinone (HIQ40), prepared by two different synthetic routes ("acidolysis" or "phenylester") was studied by differential scanning calorimetry and X-ray diffraction. All these samples show a glass transition temperature in the range of 125–141°C, dependent on the sample thermal history. A crystal to nematic transition is observed between 300 and 375°C. The samples prepared by the acidolysis route, when compared to those produced *via* the phenylester reaction, have higher crystallinity which is due to the formation of "IA/HQ" crystals. The crystallinity can be increased significantly (as much as twice) by annealing the polymers at 300°C. The heat of fusion (X → N,crystal to nematic) of the annealed acidolysis samples is also higher than that of the polymers prepared by the phenylester process. The nematic to isotropic (N → I) transitions are broad, exhibiting no definite clearing points. Several mesogenic transitions as suggested by X-ray studies and two crystallization peaks were found for all samples studied. This may be an indication that the samples consist of two, distinct polymeric compositions or that there are two crystal forms. Furthermore, since the intensity ratio of the two crystallization peaks changes as a function of annealing, it is clear that the chemical/physical state of the polymer depends on the thermal history of the samples. Attempts to prepare amorphous HIQ40 and nematic HIQ40 glass by quenching from the isotropic state (480°C and 400°C, respectively) were unsuccessful, however, it can be prepared by precipitation of the acidolysis polymer from solution.

Keywords: hydroquinone, isophthalic acid, *p*-hydroxybenzoic acid, thermotropic copolyester, X-ray and DSC

Introduction

The rich phase diagram [1] of the *p*-hydroxybenzoic acid/isophthalic acid-hydroquinone (HIQ) thermotropic copolyester system makes this an interesting system for studying the effects of phase on the processing and performance of polyesters. Previously published studies [3] show that the permeability of solvent cast HIQ40 films may be reduced by up to two orders of magnitude by

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annealing, and that this effect correlates with the solid state texture of the annealed samples. This study documents the changes noted in the DSC and WAXS behavior of HIQ40 (chosen because it exhibits the lowest melting point and highest solubility of the HIQ series), as a function of the effect of the method of synthesis and the thermal history of the sample.

The interpretation of the HIQ X-ray pattern has been discussed by Erdemir *et al.* [1]. Through molecular modeling, the equatorial diffraction pattern for HIQ fiber was generated and compared with the experiment. The X-ray diffraction of HIQ35 and the resolved components of the "para-crystalline" type A (PA's) diffraction and crystalline IA/HQ phases (C's) have been illustrated by Erdemir *et al.* [1] (other designations for structures of this type abound in the literature). For the sake of clarity, we will adopt the Erdemir language for these discussions. The crystalline phase can be indexed on an orthorhombic lattice with a =11.16 Å, b =7.84 Å and c =24.32 Å. Therefore, C1, C2 and C3, are measured to be 5.59 Å, 3.92 Å and 3.22 Å, corresponding to the (200), (020) and (220) reflections, respectively.

Several "para-crystalline" phases may exist, as evidenced by an increase in the intensity of the right shoulder of the main para-crystalline peak. These peaks may be resolved into two phases, type A para-crystalline (labeled as PA's) and type C para-crystalline (labeled as PC's). These "para-crystalline" phases are labeled as PA1 and PA2 and are identified by the (110) and (200) reflections, measured as 4.54 Å and 3.76 Å. Therefore, the unit cell parameters are a =7.52 Å, b =5.70 Å. These peaks appear to shift with monomer composition. The details of the molecular arrangement of the two para-crystalline phases are not well understood.

Experimental

Sample preparation

HIQ40 polymer was prepared by the acidolysis and phenylester methods (Fig. 1). C13 NMR indicated that both copolymers were random as prepared [2]. X-ray analysis indicated that the polymers produced *via* the phenylester route were semi-crystalline as-produced, whereas the polymers synthesized *via* the acidolysis method were mesogenic or amorphous.

Characterization

DSC measurements were performed with a TA Instruments 2100/910 DSC at 20°C min^{-1} heating and cooling rates. When necessary, the samples were annealed in the DSC sample holder. The following data were obtained from the DSC traces: T_g, the glass transition temperature, °C, which is the temperature

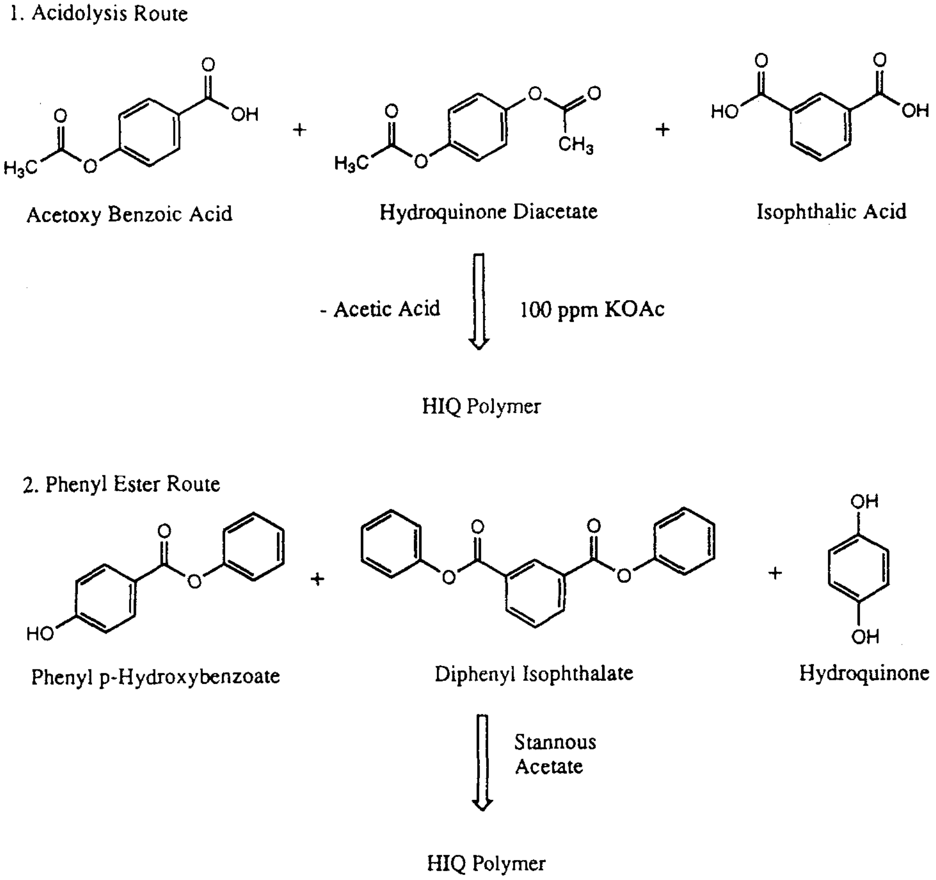

Fig. 1 Reaction scheme for the 'acidolysis' and 'phenylester' synthetic routes to HIQ polymer

at half of the heat capacity increase; T_{mp}, the peak temperature of melting, °C; T_m, the melting point, which is the highest temperature point of the melting endotherm, °C; ΔH_f, the heat of fusion, J g^{-1}; T_{co}, the starting temperature of crystallization during cooling, °C; T_{cp}, the peak temperature of crystallization during cooling, °C; ΔH_c, the heat of crystallization during cooling, J g^{-1}.

Wide angle X-ray diffraction measurements as a function of sample temperature were carried out using a curved position sensitive detector mounted on a PEI goniometer. The sample was loaded into an air tight furnace filled with inert helium mounted on the goniometer fitted with two thermocouples located in the sample approximately 1 cm apart to detect thermal gradients. The differences in temperature between the two thermocouples were less than 2°C. Monochromatic copper K_α radiation was utilized.

Results and discussion

DSC

All as-polymerized samples were subjected to the DSC analysis protocol as defined below:

1. The as-received samples were heated to 400°C (to erase the thermal history) at a rate of 20°C min^{-1}, cooled at 20°C min^{-1} to room temperature, and reheated at 20°C min^{-1} to 480°C (into the isotropic melt). The purpose of these experiments was to characterize the crystallization behavior of the samples, and also, to compare the thermal transitions of different HIQ40 polymers having similar thermal histories. These results are summarized in Table 1; a characteristic DSC trace is shown in Fig. 2.

In the tables, the acidolysis sample is designated as 1, the phenylester sample as 2, and the polymer obtained by methanol precipitation from N-methyl pyrrolidone (NMP) solution, as 3.

The first heating DSC traces of the as-received samples shows a glass transition in the range of 125–140°C (depending on thermal history) followed by a crystal to nematic transition at about 300 to 350°C. Only the methanol precipitated samples show "cold crystallization". It is especially interesting that the

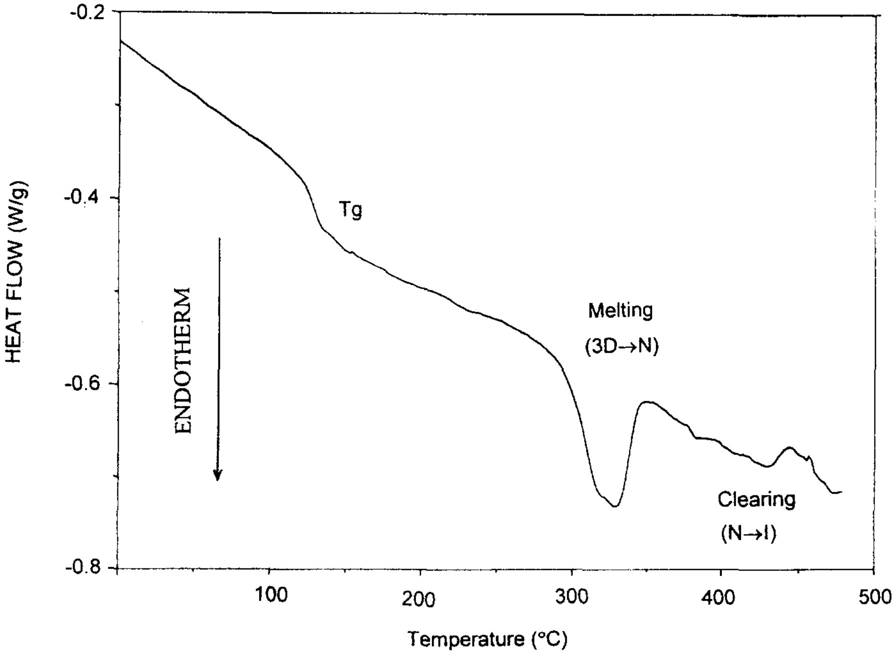

Fig. 2 DSC heating trace for a typical HIQ40 as-polymerized sample (heating rate 20°C min^{-1}). Second heating after cooling from 400°C at a rate of 20°C min^{-1}

Table 1 Melting and crystallization parameters of the as-received HIQ40 samples (first heating at 20°C min^{-1} to 400°C, cooling at 20°C min^{-1}, reheating at 20°C min^{-1} to 480°C)

Sample	1st heating				Cooling		2nd heating						
	T_g	T_{mp}^{*}	T_m^{*}	ΔH_f^{*}	T_{co}	T_{cp}	T_g	T_{mp}^{*}	T_m^{*}	ΔH_f^{*}	T_{mp}^{**}	T_m^{**}	ΔH_f^{**}
1	134.5	315.0	349.5	13.0	310.0	300.5	131.0	327.0	354.0	11.9	393.0	445.5	3.36
					268.0	261.0					432.5		
		380.0^{+}	390.0^{+}	0.79^{+}									
2	127.0	303.5	358.0	12.7	299.0	290.0	131.0	305.5	345.5	7.52	395.0	429.5	2.22
		330.0				277.5		325.5			408.0		
					253.5	247.5							
		375.5^{+}	389.0^{+}	0.16^{+}									
3	141.0	cold cryst. + melting			306.5	298.0	128.0	310.0	335.5	10.6	379.5	443.0	3.83
		(amorphous sample)				280.0					426.5		
					271.5	262.0							

*X → N transition; **N → I transition; $^{+}$Unknown transition between X → N and N → I transition.
N is the nematic phase
I is the isotropic phase
X is the crystalline phase
T_g is the glass transition temperature, °C
T_{mp} is the peak transition temperature of melting, °C
T_m is the melting point, the highest temperature point of the melting endotherm, °C
ΔH_f is the heat of fusion, J g^{-1}
T_{co} is the starting temperature of crystallization, °C
T_{cp} is the peak temperature of crystallization, °C

methanol precipitated sample (apparently "amorphous") shows the highest glass transition temperature (141°C), implying that the glass transition associated with the amorphous phase of HIQ is higher than that of the semicrystalline nematogenic polymer. The crystallinity of all the samples is almost identical as judged from the heat of fusion. In most cases, the X → N (crystal to nematic) transition shows multiple endotherms, reflecting either the melting of two polymeric entities or the existence of several crystal modifications. There is a very small transition at ca. T=375–380°C with a heat of transition of 0.2–0.8 J g^{-1}. While not investigated directly, this is consistent with a N → I (nematic to isotropic) or a $LC_1 \rightarrow LC_2$ (liquid crystal to liquid crystal) transition.

When cooled from the nematic melt, two crystallization peaks were recorded for all samples (Fig. 3). As the relative size of these peaks varies with thermal history, it is likely that two crystalline phases are present in HIQ40 samples prepared by either the acidolysis or phenylester routes. The acidolysis sample crystallizes at a somewhat higher temperature than the phenylester sample.

Upon second heating, a glass transition is observed at 130–131°C for all samples, followed by a crystal to nematic transition between 270 and 350°C. The heat of fusion for the acidolysis sample is considerably higher than for the phenylester sample underlying the influence of the preparation method on the behavior of the sample. The nematic to isotropic transition takes place between

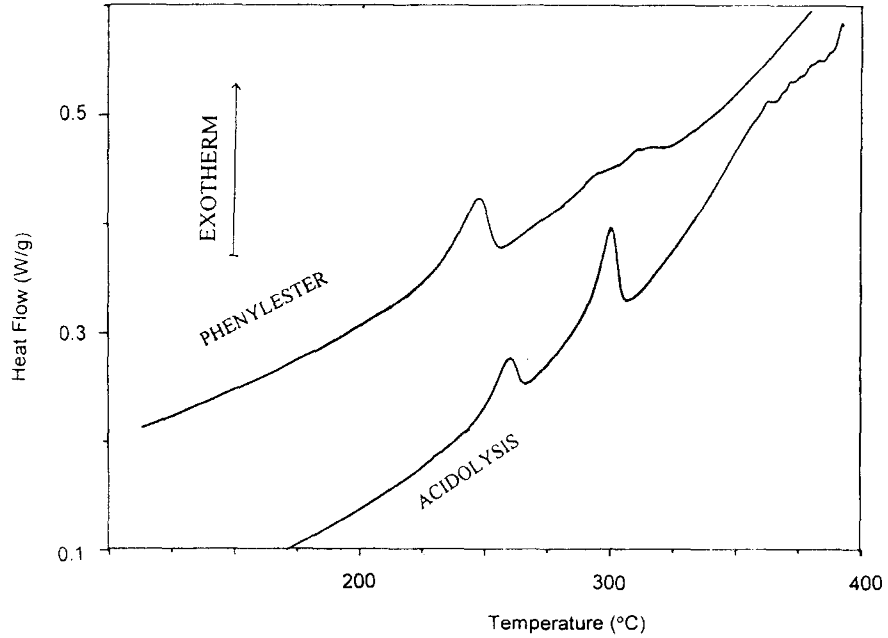

Fig. 3 DSC cooling trace for as-polymerized HIQ40, comparing the behavior of polymer prepared by the "acidolysis" and "phenylester" routes

370 and 460°C, it is very broad, and no definite clearing point is observed. This transition often manifests as a double peak, supporting the hypothesis that so-annealed HIQ40 may consist of two, chemically distinct species. The heat of this transition is 2–4 J g^{-1}, depending on the method of preparation and the thermal history.

2. The as-received samples were heated to 400°C (at 400°C the samples are nematic melts), and quenched by quickly immersing the DSC pans containing the samples into liquid nitrogen. The purpose of these experiments was to establish whether HIQ40 can be prepared as a pure nematic glass. The DSC parameters recorded during the subsequent heating of these quenched samples can be found in Table 2.

Table 2 Melting of HIQ40 samples quenched from 400°C

Sample	T_g	T_{mp}^{*}	T_m^{*}	ΔH_f^{*}	T_{mp}^{**}	T_m^{**}	ΔH_f^{**}
1	134.0	308.0 319.0	355.5	12.0	383.0 436.0	450.5	5.42
2	132.0	294.0 340.0	361.5	12.9	402.0 450.5	434.5 466.0	3.04 0.69
3	129.5	305.5	334.5	10.3	394.5 436.0	446.5	3.39

*X → N transition

**N → I transition

T_g is the glass transition temperature, °C; T_{mp} is the peak temperature of melting, °C; T_m is the melting point, °C; ΔH_f is the heat of fusion, J g^{-1}

As is shown in Table 2, all samples quenched from 400°C exhibit a crystal-to-nematic transition, therefore it is clear that HIQ40 cannot be quenched to the state of purely nematic glass. The glass transition of these samples is somewhat higher than those reported in Table 1, as are all the heats of transition. The higher glass transition temperatures and the higher heats of the nematic-to-isotropic transition imply that some molecular weight degradation takes place during the slow cooling of these samples.

3. The as-received samples were heated to 480°C (20°C min^{-1} into the isotropic melt, some decomposition noted by TGA), and immediately quenched with liquid nitrogen to ascertain whether isotropic, amorphous HIQ40 glasses can be prepared by quenching from the isotropic melt state. The results of these experiments are summarized in Table 3.

Quenching from the melt is not an effective method to prepare either nematic or amorphous HIQ40 glasses. When the samples are quenched (at a cooling rate of 2 000–3 000°C min^{-1}) from the nematic or the isotropic state and reheated, all the transitions (i.e., glass transition, X → N, N → I) can be found

Table 3 Melting of HIQ40 samples quenched from 480°C

Sample	T_g	T_{mp}^*	T_m^*	ΔH_f^*	T_{mp}^{**}	T_m^{**}	ΔH_f^{**}
1	130.5	283.0 297.0	314.0	7.52	343.5 404.0	433.0	7.22
2	133.0	281.5	307.0	6.19	361.5 394.0	419.5	3.91
3	126.0	272.5	308.5	9.06	378.0 415.5	433.0	6.47

*X → N transitin

**N → I transition

T_g is the glass transition temperature, °C; T_{mp} is the peak temperature of melting, °C; T_m is the melting point, °C; ΔH_f is the heat of fusion, J g^{-1}

on the DSC traces. It is interesting to note that the heat of the N → I transition increases almost twofold as a consequence of quenching from 480°C, which can probably be attributed to increased mobility due to some molecular weight break-down caused by the high temperature exposure.

4. The as-received samples were heated to 480°C (into the isotropic melt) at 20°C $\min^{-1}$, cooled at 20°C $\min^{-1}$, and then reheated to 480°C at 20°C $\min^{-1}$. These experiments were carried out to determine the reversibility of the thermal

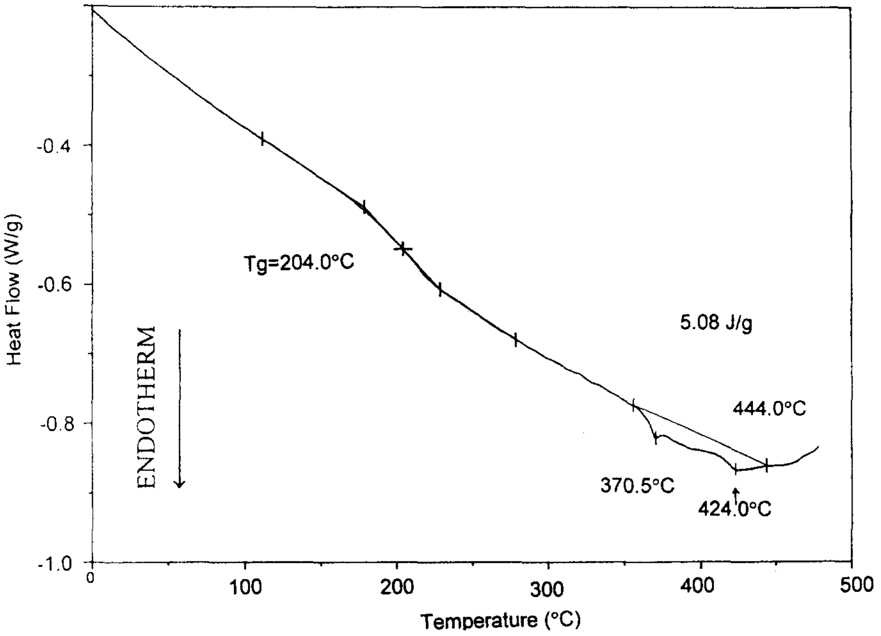

Fig. 4 DSC heating trace for HIQ40 previously heated to 480°C and quenched to room temperature

Table 4 Melting and crystallization parameters of the as-received HIQ40 samples
(first heating at 20°C min^{-1} to 400°C, cooling at 20°C min^{-1}, reheating at 20°C min^{-1} to 480°C)

	1st heating							Cooling		2nd heating						
Sample	T_g	T_{mp}^*	T_m^*	ΔH_f^*	T_{mp}^{**}	T_m^{**}	ΔH_f^{**}	T_{co}	T_{cp}	T_g	T_{mp}^*	T_m^*	ΔH_f^*	T_{mp}^{**}	T_m^{**}	ΔH_f^{**}
1	131.5	314.0	347.0	13.9	381.0 433.0	448.5	5.33	–	–	207.0	–	–	–	371.5 423.5	462.5	7.93
2	126.5	302.5 330.5	356.5	12.9	417.5	433.0	1.19	–	–	226.5	340.0 367.5	376.0	0.47	393.0 432.5	447.0	2.08
3	141.0	cold cryst. + melting (amorphous sample)		0.0^{***}	372.0 431.5	447.0	5.91	–	–	218.5	–	–	–	374.0 399.0	420.0	3.08

*X → N transition; **N → I transition; ***Amorphous sample
T_g is the glass transition temperature, °C
T_{mp} is the peak temperature of melting, °C
T_m is the melting point, °C
ΔH_f is the heat of fusion, J g^{-1}
T_{co} is the starting temperature of crystallization during cooling, °C
T_{cp} is the peak temperature of crystallization during cooling, °C

transitions of HIQ40. This series of experiments also gives insight into the thermal stability of the samples. These results are described in Table 4, and a characteristic DSC trace is shown in Fig. 4.

When the samples are cooled slowly (i.e., 20°C min^{-1}) from 480°C (from the isotropic melt), and reheated, no T_g is observed in the 130°C range, although a glass transition-like transition is observed at very high temperatures (200–220°C). It may be suggested that the samples prepared this way represent somewhat crosslinked, nematic glasses.

5. Samples were annealed at 300°C for 35 min in order to determine the effect of annealing close to T_m on crystallinity. These experiments were designed to answer the following questions:

a. The extent of the crystallinity increase during annealing. The comparison of the melting parameters of the annealed and as-received samples are shown in Table 5.

Table 5 Comparison of the melting parameters of HIQ40 polymers annealed at 300°C for 35 min and the as-received samples (first heating to 400°C, cooling at 20°C min^{-1}, reheating to 480°C)

Sample	Annealed sample				As-received sample			
	T_g	T_{mp}^*	T_m^*	ΔH_f^*	T_g	T_{mp}^*	T_m^*	ΔH_f^*
1	128.5	351.0 393.0	365.5 397.5	19.9 0.48	131.5	314.0	347.0	13.9
2	127.0	346.0	374.5	13.1	126.5	302.5 330.5	356.5	12.6
3	132.5	343.5 383.0	358.0 397.5	11.3 0.71	141.0	cold crystallization (amorphous sample)		

*X → N transition

T_g is the glass transition temperature, °C; T_{mp} is the peak temperature of melting, °C; T_m is the melting point, °C; ΔH_f is the heat of fusion, J g^{-1}

b. The extent, if any, of permanent changes in the samples caused by transesterification during the 300°C annealing, as manifest by changes in melting behavior. The second heating of the as-received samples after cooling from 400°C is compared to the second heating of the similarly cooled annealed samples. These results are summarized in Table 6.

c. The extent, if any, of permanent changes in the samples caused by transesterification during the 300°C annealing, as manifest by changes in crystallization behavior. The crystallization temperatures and heats of crystallization of the as-received and annealed samples are compared in Table 7.

Table 6 Comparison of the melting parameters of HIQ40 polymers on the second heating: reheating after annealing at 300°C for 35 min and cooling at 20°C min^{-1}; and reheating after heating the as-received samples to 400°C and cooling at 20°C min^{-1}

Sample	Annealed sample							As-received sample						
	T_g	T_{mp}^{*}	T_m^{*}	ΔH_f^{*}	T_{mp}^{**}	T_m^{**}	ΔH_f^{**}	T_g	T_{mp}^{*}	T_m^{*}	ΔH_f^{*}	T_{mp}^{**}	T_m^{**}	ΔH_f^{**}
1	132.0	326.0	348.5	10.2	410.5 458.5	447.5	3.50	131.0	328.0	349.5	11.3	397.5 427.5	449.0	4.26
2	132.0	311.5	344.5	7.52	412.0 464.0	434.0 476.0	3.13 0.73	131.0	303.5 325.0	345.0	11.0	408.5	433.0	1.49
3	130.0	319.5	340.5	9.92	393.0 429.5	443.0	5.40	126.0	310.0	337.0	9.52	424.5	443.0	4.09

*X → N transition; **N → I transition

T_g is the glass transition temperature, °C

T_{mp} is the peak temperature of melting, °C

T_m is the melting point, °C

ΔH_f is the heat of fusion, J g^{-1}

Table 7 Influence of annealing (at 300°C for 35 min) of the HIQ40 samples on the crystallization temperature during reheating and subsequent cooling

Sample	Cooling after annealing			Cooling from 400°C		
	T_{co}	T_{cp}	ΔH_c	T_{co}	T_{cp}	ΔH_c
1	311.5	304.5	4.66	307.0	300.5	3.27
	265.0	250.5	0.70	267.5	260.0	1.81
2	296.5	289.0	1.63	297.5	290.5	0.76
	252.5	245.0	1.80	255.0	248.0	2.83
3	305.5	300.5	2.96	306.5	298.5	1.77
	268.0	261.0	1.21	269.0	262.0	2.81

T_{co} is the starting temperature of crystallization, °C; T_{cp} is the peak temperature of crystallization, °C; ΔH_c is the heat of crystallization, J g^{-1}

When these polymers are annealed at 300°C, i.e., close to the X → N transition, the temperature of this transition and the degree of crystallinity increases substantially (as indicated by the increased heat of fusion from about 11 to about 22 J g^{-1}). After cooling a previously annealed sample from the nematic state, the temperature range and the heat of transition of the higher temperature crystallization peak increases, while the temperature of the lower the temperature peak and its heat decreases (Fig. 5), indicating that the ratio of the two

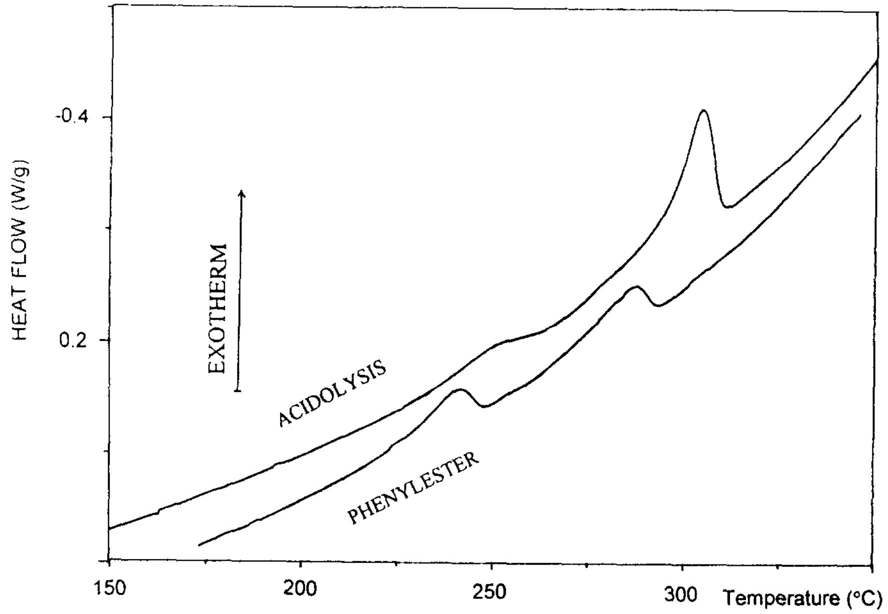

Fig. 5 DSC cooling trace of 300°C annealed HIQ40, comparing the crystallization behavior of polymer produced by the "acidolysis" and "phenylester" routes

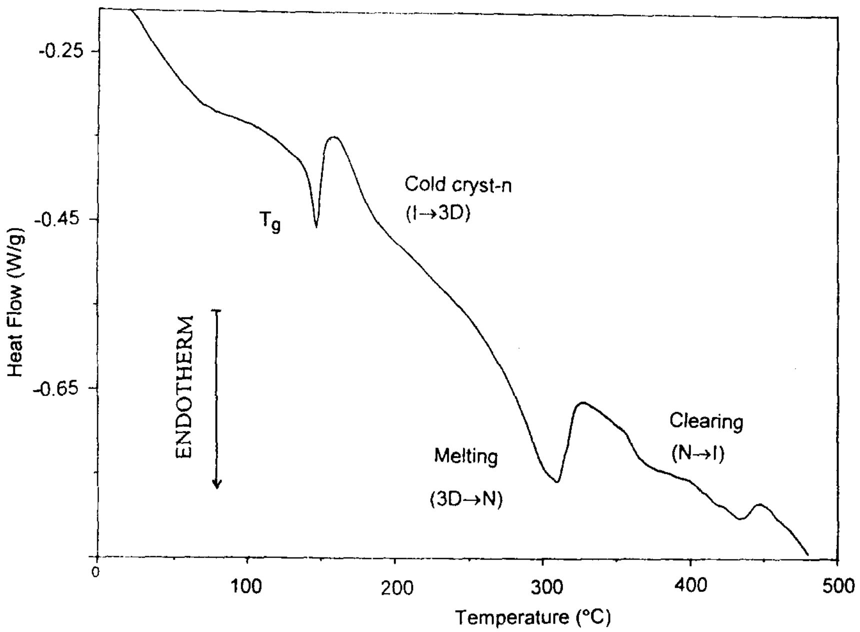

Fig. 6 DSC heating trace of HIQ40 polymer precipitated from NMP

crystallizable components of HIQ40 changes during annealing. When the samples are annealed in the nematic state (400°C), cooled at 20°C to room temperature and reheated, no glass transition in the 130°C range is observed but a glass-like transition appears at high temperature (Table 1), suggestive of chemical changes, i.e., crosslinking or transesterification, in the system.

Samples of HIQ40 prepared *via* the acidolysis route may be dissolved in NMP (% by wt.) and precipitated with methanol to produce apparently amorphous samples. Optical microscopy shows no resolvable textures for these samples, consistent with the hypothesized amorphous nature of the sample. The DSC trace shown in Fig. 6 and WAXS diffraction data (Fig. 7) also support the conclusion that the polymer so-produced is amorphous. In the DSC, a cold crystallization is recorded after a very shallow glass transition, followed by the crystal-to-nematic transition. In most cases, the total heat of the runs is close to zero, consistent with these samples being in the isotropic amorphous state. As previously stated, the glass transition temperature of these samples (ca. 136–140°C) is higher than that of the semicrystalline nematic HIQ40 samples (ca. 130°C). Other studies have shown that the permeability of HIQ40 quenched from dilute solution is similar to that of other amorphous glassy polyesters [3]. The T_g of the amorphous polymer is higher than that measured for the semicrystalline nematic polymers (136–141°C *vs.* 131°C) produced from the melt. It is unclear whether the cold crystallization peak is noted in the DSC trace (Fig. 6)

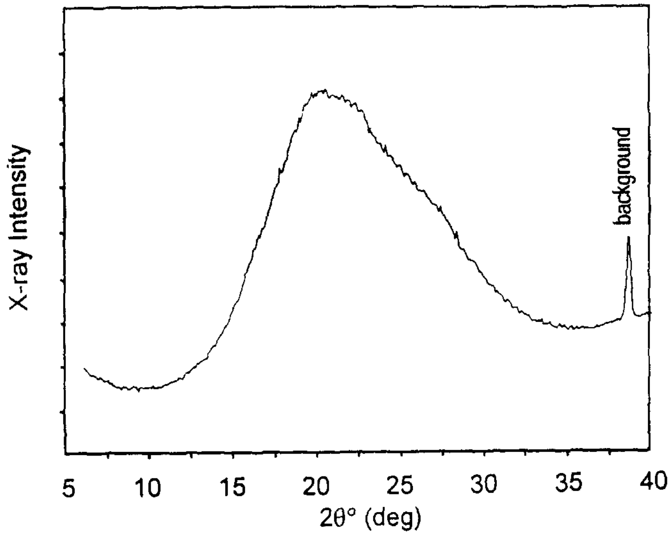

Fig. 7 Wide angle X-ray diffraction pattern of HIQ40 precipitated from solution

represents an I → N → X or I → X transition, but polymers heated through the T_g and T_{xcold} (cold crystallization) range show a fine nematogenic texture between crossed polars.

X-ray diffraction

The X-ray diffraction patterns for HIQ40 powders prepared by the acidolysis and phenyl ester routes are shown in Fig. 8. Both samples show a very strong broad peak at about d=4.5Å. In the phenylester sample, however, three small crystalline peaks can be observed on the shoulder of the strong broad peak, indicating that the sample prepared *via* the phenylester route develops some crystalline order during synthesis. The d-spacings measured from these peaks are 5.50 Å, 3.96 Å and 3.25 Å. The polymer may be described as bi-phasic with the ordered lines originating from the IA/HQ rich regions and the broad amorphous peak emanating from the HBA rich regions.

Diffraction experiments as a function of temperature were performed on the HIQ40 powders utilized above. Both samples were predominately liquid crystalline (para-crystalline) at room temperature. Judging by the shape and the width of the para-crystalline peaks of the two samples, it can be concluded that the phenylester sample is predominately type A, while the acidolysis sample contains both the A and C type structures. In addition, the phenylester sample has a crystalline component due to crystalline IA/HQ as stated above.

During heating, both samples showed a transition in the shifting of the major broad peak to lower 2θ angle at about 270–290°C which can be interpreted as

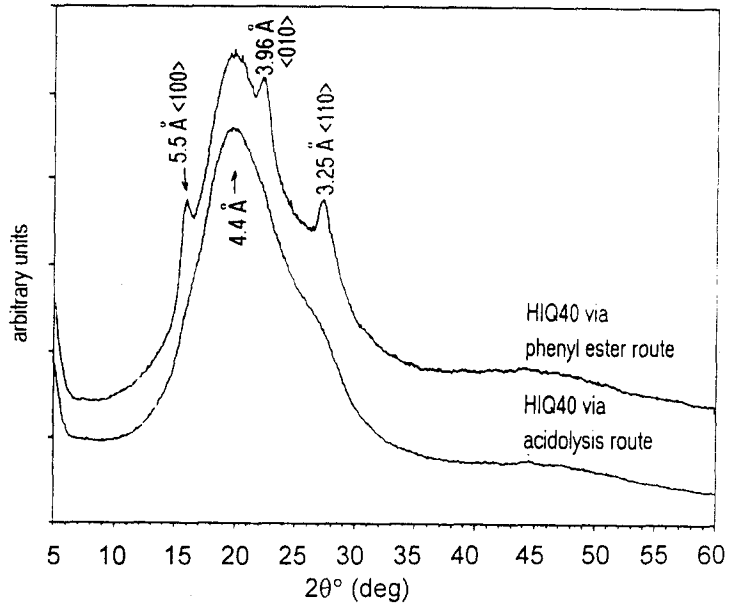

Fig. 8 Wide angle X-ray diffraction patterns of HIQ40 polymer produced by the "acidolysis" and "phenylester" methods

an expansion of the average intermolecular distances between chains as well as an improvement in the molecular ordering of the predominant liquid crystalline phase. During the cooling cycle, this average intermolecular distance contracts, to form the type A para-crystalline phase. At about 230°C, a crystalline phase corresponding to the apparent segregation of the IA/HQ component (it has been shown that some level of HBA can be accommodated in this structure, although in a relatively high energy conformation) appears and continues to develop on cooling in both samples. From the change in the width of the para-crystalline peak, it can be concluded that the resulting para-crystalline phase, after the heating and cooling cycle, is predominately of the type A in both the acidolysis and phenylester synthesized HIQ40.

Figure 9 shows the acidolysis HIQ40 powder diffraction patterns during the heating cycle. Each pattern was acquired for a period of 3 minutes with 20°C temperature steps up to 310°C. At room temperature, the sample exhibits a liquid crystalline phase. This is indicated by one large peak, centered at about 4.5 Å and having a slight shoulder on the right. The right shoulder does not appear to change in position or intensity until 290°C. At about 290°C, the broad liquid crystalline peak sharpens and there is also a slight peak shift toward lower angles. The nature of this transition is not understood at present but the sharpening of this peak can be probably interpreted as an improvement in molecular ordering of the para-crystalline phase.

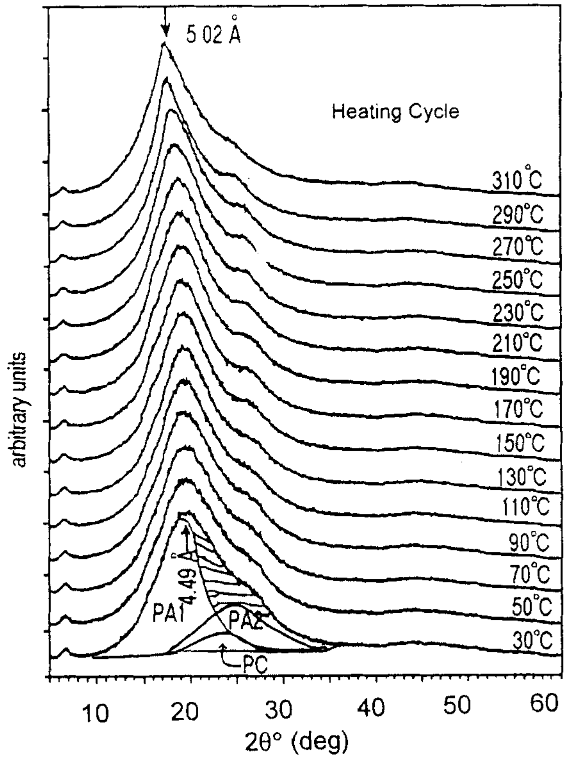

Fig. 9 Wide angle X-ray diffraction patterns of HIQ40 polymer produced by the "acidolysis" process as function of increasing measurement temperature from room temperature to 310°C

The diffraction pattern during the cooling cycle for the acidolysis sample is shown in Fig. 10. At 270°C the PA1 peak becomes less sharp and shifts back to its original 2θ angle position, suggesting the reappearance of the para-crystalline phase. At 250°C, there is the appearance of the three crystalline peaks which continue to grow stronger in intensity upon continued cooling. These *d*-spacings, 5.50 Å, 3.96 Å and 3.22 Å, are attributed to the IA/HQ crystalline phase. It can also be observed that the C3 peak is shifting to a stable 2θ value, at ~130°C, during cooling to room temperature.

The diffraction patterns for the phenylester sample during the heating cycles are shown in Fig. 11. At room temperature, the sample has two phases, namely, the para-crystalline phase and the IA/HQ crystalline component. At about 270°C, the para-crystalline peak PA1 sharpens and shifts towards lower (2θ) angle. This is also observed in the acidolysis sample.

Figure 12 shows the X-ray diffraction pattern of the phenyl ester sample during the cooling cycle. While abbreviated in temperature, it is clear that the cool-

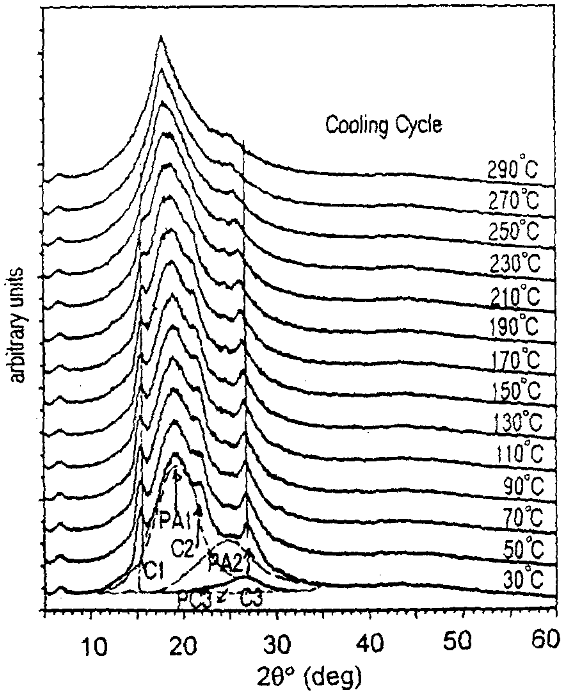

Fig. 10 Wide angle X-ray diffraction patterns of HIQ40 polymer produced by the "acidolysis" process as a function of decreasing measurement temperature from 290°C to room temperature

ing behavior of the phenyl ester sample is similar to those of the acidolysis sample.

The results described above are consistent with the DSC results. The transition at 312°C corresponds to the sharpening and shifting of the para-crystalline peak on heating and, on cooling, the peak at 297°C is the reappearance of the para-crystalline phase. At approximately 260°C, the crystallization of the IA/HQ component begins.

Conclusions

A. DSC

1. The glass transition of HIQ40 occurs over a broad temperature range, 126–141°C, depending on the thermal history and the phase nature of the samples. T_g of the isotropic amorphous polymer is 141°C while T_g of the semicrystalline nematic glass is 130–133°C. Quenched samples have somewhat higher glass transition temperatures than the slowly cooled samples.

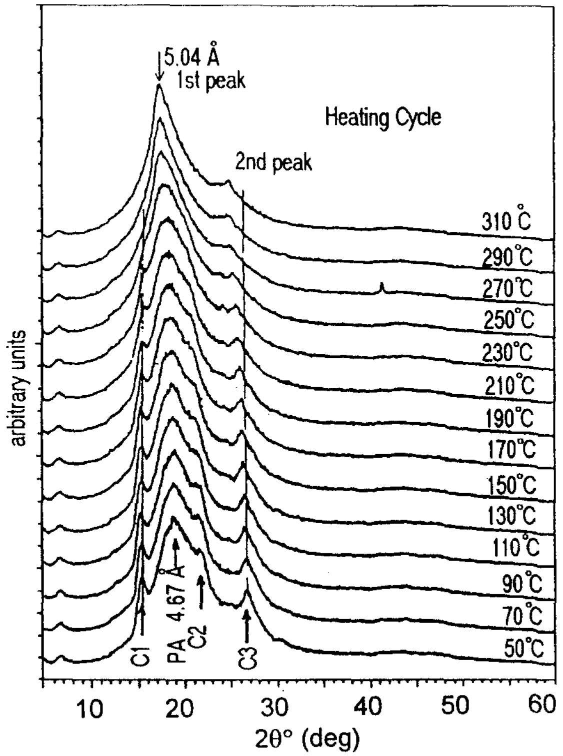

Fig. 11 Wide angle X-ray diffraction patterns of HIQ40 polymer produced by the "phenylester" process as function of increasing measurement temperature from 50°C to 310°C

2. The crystal-to-nematic transition of HIQ40 takes place between 300 and 375°C depending on the method of sample preparation and the thermal history of the sample. The heat of this transition is 7–25 J g^{-1}. Annealing at 300°C increases the three-dimensional crystallinity of the samples. In all cases, HIQ produced *via* the phenylester route shows higher crystallinity than HIQ produced *via* acidolysis.

3. The endothermic peak corresponding to the nematic-to-isotropic transition in most cases is a double peak indicating the presence of two mesogenic phases. There seems to be a correlation between the end-point of the nematic-to-isotropic transition and the heat of this transition: the higher the end-point of the transition, the higher its heat. As expected, there is a linear relationship between the heats of the crystal-to-nematic and nematic-to-isotropic transitions: the ratio of these two heats is 3.4–3.5.

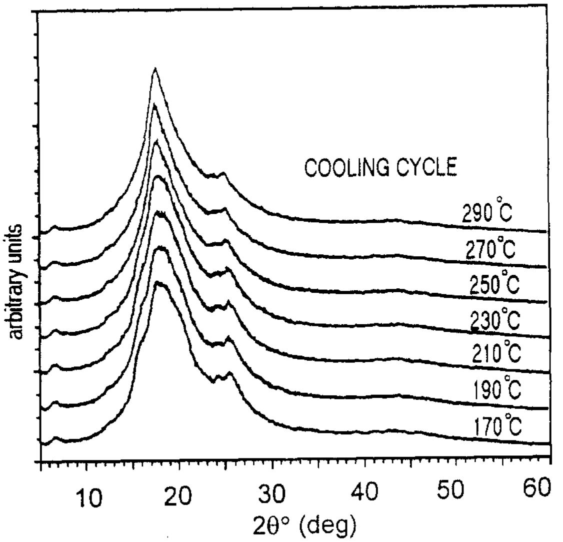

Fig. 12 Wide angle X-ray diffraction patterns of HIQ40 polymer produced by the "phenylester" process as a function of decreasing measurement temperature from 290°C to 170°C

4. Two crystallization peaks corresponding to the nematic-to-crystal transition are always recorded. This indicates that two crystalline moieties are present in the samples. Therefore, the HIQ40 samples should be considered as two-component polymeric systems. Since the ratio of the heats of crystallization for these two peaks changes with annealing at 300°C, it can be suggested that significant physical or chemical changes take place under these conditions. The heat of the crystallization (nematic-to-crystal) processes seem to be the most sensitive to changes in the sample composition.

5. Nematic glasses cannot be prepared by quenching the nematic melt, the samples crystallize during quenching. Similarly, isotropic amorphous samples cannot be prepared by quenching the polymers from the isotropic melt: the isotropic-to-nematic and the nematic-to-crystal transitions do take place even at extremely fast quenching conditions.

6. The DSC-results indicate that apparently crosslinked nematic glasses, having zero three-dimensional crystallinity can be prepared when the samples are cooled to room temperature at 20°C min^{-1} from the isotropic melt (from 480°C). These sample have extremely high glass transition temperatures (ca. 200–220°C), no crystal-to-nematic transitions, but they do have nematic-to-isotropic transitions.

7. Isotropic amorphous HIQ40 samples can be prepared by precipitation from solution.

B. X-ray diffraction

The high temperature X-ray diffraction experiments carried out on HIQ40 powders prepared *via* the phenylester and acidolysis routes indicated that at room temperature, the acidolysis sample exhibits only the liquid crystalline phase while the phenylester prepared samples possess a biphasic crystalline/nematic structure. The present interpretation based on the calculations of Erdemir *et al.* [1], suggests that the para-crystalline (liquid crystalline) phase is of two types, namely, type A and type B. Both types of para-crystalline phases can be observed in the two as-prepared samples. The phenylester sample, however, shows the presence of predominately A type para-crystallinity, along with a small amount of crystallinity, the crystalline phase corresponding to the apparent segregation of IA/HQ. During the heating cycle, there is a transition at ~270–290°C in both samples and there is a shift of the peaks of the liquid crystalline (para-crystalline) structure. At ~250°C, the IA/HQ component, present only in the phenylester sample melts. Upon cooling, both samples behave in a similar fashion. At about 240–250°C the development of the crystalline IA/H-like phase can be observed which persists down to the room temperature. The emergence of the liquid crystalline structure emerges at about 130°C and is similar, independent of the chemical origin of the powders.

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