Structure and thermal transitions of poly(*p*-oxybenzoate-*co*-*m*-oxybenzoate)s

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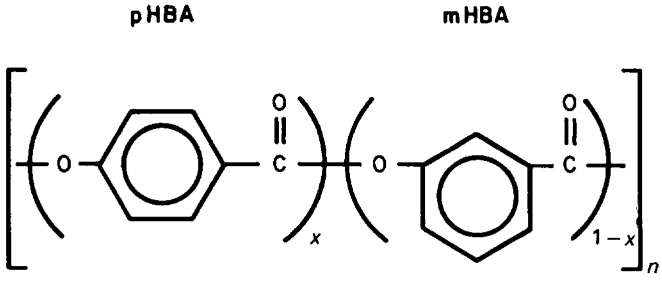
A series of copolyesters derived from *p*-hydroxybenzoic acid (pHBA) and *m*-hydroxybenzoic acid (mHBA) have been prepared via the corresponding (trimethylsilyloxy)benzoyl chlorides. It is shown that this method ('silyl method') leads to random copolyesters of good stability against thermal degradation and the formation of blocky structures. Materials with a low content of pHBA crystallize in the lattice of poly(mHBA). Copolyesters containing high amounts (50–100%) of pHBA have an increasing degree of crystallinity with increasing content of the linear *para* units. These materials crystallize within the unit cells of modifications I and II found for poly(pHBA). Polyesters having an intermediate range of compositions do not crystallize. The glass transition temperature is slightly lowered upon increasing the content of pHBA, and the range in which the transition takes place is broadened considerably. Polyesters with less than 50% pHBA units form only an isotropic melt. The semicrystalline copolyesters containing 50% and more pHBA exhibit a first-order transition to a mixture of the pseudo-hexagonal modification III of poly(pHBA) and an amorphous phase.

(Keywords: copolyester; structure; thermal stability)

INTRODUCTION

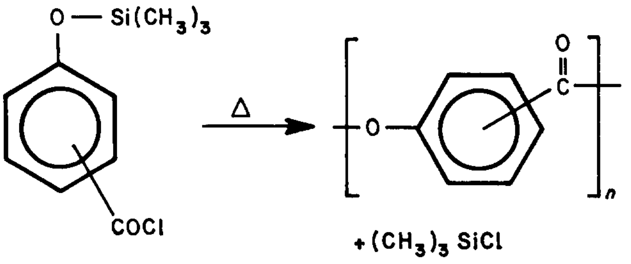
Stiff-chain polymers possessing the capability of forming a thermally stable mesophase have recently attracted considerable attention because of their potential application as high-performance plastics. Owing to the small gain in entropy when going from the crystalline state to the mesophase, these rod-like macromolecules often exhibit melting points at temperatures where thermal decomposition becomes a serious problem. However, if the regular chemical structure of the homopolymer is disrupted by side groups or non-linear links, the melting temperature may be reduced considerably[1]. Here we wish to present a systematic study of the alterations of the crystal structure of the rod-like poly(*p*-hydroxybenzoic acid) (poly(pHBA)) effected by the non-linear *m*-hydroxybenzoate (mHBA) units.



x, $1-x$ Mole fractions of the respective repeating units
n Degree of polymerization

The choice of this system derives mainly from the fact that the homopolymer of pHBA has been the subject of a number of exhaustive studies by Economy and coworkers[2,3], by Schwarz and Kricheldorf[4,5], and by Lieser[6]. Especially, using the technique of electron diffraction, Lieser[6] succeeded in demonstrating that poly(pHBA) exhibits two orthorhombic modifications I and II at room temperature (I: $a = 7.52$ Å, $b = 5.70$ Å, $c = 12.49$ Å; II: $a = 3.77$ Å, $b = 11.06$ Å, $c = 12.89$ Å). Heating above a first-order transition at 560 K for phase I and at 530 K for phase II leads to the observation of a pseudo-hexagonal phase III[6]. The respective homopolymer of mHBA, first prepared by Gilkey and Caldwell[7] in 1959, has been studied in greater detail by Kricheldorf *et al.*[8]

In this investigation, a number of copolymers have been prepared using the 'silyl method'[4,5,9]. Using the (trimethylsilyloxy)benzoyl chlorides[9]:



the co-condensation proceeds at moderate temperatures (~250°C) in the absence of any catalyst. Hence, the silyl method is expected to produce materials of greater stability against transesterification and the formation of block copolymers. In addition, the good thermal stability of the copolyesters allows a detailed study of the crystalline modifications up to temperatures of approximately 400°C. Together with the electron diffraction studies on two of the copolymers of the present series[10], the investigations by wide-angle X-ray scattering (WAXS) and thermal analysis (d.s.c.) reported herein give

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Table 1 Composition, polymerization temperatures and properties of the copolyesters

	Poly(mHBA)				Copolyester[a]									Poly-(pHBA)
					CO5	CO15	CO30	CO40	CO50	CO60	CO70	CO90	CO95	
Percentage of pHBA	0	0	0	0	5	15	30	40	50	60	70	90	95	100
Polymerization temp. (K)	403	438	473	523	523	523	523	523	523	523	543	573	553	563
Polymerization time (h)	6	6	3	3	3	3	3	3	3	3	3	3	3	3
Solubility[b]	s	s	s	s	s	s	s	s	i	i	i	i	i	i
Number-average degree of polymerization	16	16	35	70	100	70	120	120	44	45	45	47	46	21
Intrinsic viscosities	0.07	0.07	0.17	0.32	0.44	0.28	0.73	–	–	–	–	–	–	–

[a] Named according to their content of *para* units

[b] s = soluble, i = insoluble

a deeper insight into the phase behaviour of stiff-chain copolymers.

EXPERIMENTAL

Methods and materials

The *m*- and *p*-hydroxybenzoic acids (mHBA and pHBA; Merck, zur Synthese) and chloroform (Merck, P.A.) were used without further purification. The respective monomers, *m*- and *p*-(trimethylsilyloxy)benzoyl chloride were prepared according to Schwarz *et al.*[9] and distilled prior to use.

Polycondensation in bulk was achieved by gradually heating the respective monomers or mixtures thereof. When the evolution of chlorotrimethylsilane became vigorous, the heating rate was slowed down and the chlorosilane was removed by a moderate stream of argon. The polycondensation was completed by raising the temperature for 3 h to the final value given in the second row of *Table 1*. In all cases reported herein the yields were practically quantitative. Materials containing less than 50% *p*-hydroxybenzoic acid units formed a yellowish viscous melt at the temperatures of polycondensation. These polyesters were soluble in chloroform and could be purified by precipitation into methanol. Higher amounts of the *para* component resulted in solidification before completion of the polycondensation. For purification these products were ground to a powder and washed with chloroform. In all cases the degree of polymerization was determined by end-group analysis using ^{1}H n.m.r. (Bruker AM 400) spectroscopy. Soluble polyesters could be analysed directly in deuterated chloroform; insoluble products were first hydrolysed in a mixture of $CD_3OD/D_2O/NaOD$ following the procedure devised by Schwarz and Kricheldorf[5]. The resulting degrees of polymerization are given in row 4 of *Table 1*. All materials are named according to their content of *para* units, i.e. copolyester CO30 is the polymer containing 30% *p*-hydroxybenzoic acid.

Intrinsic viscosities of the soluble products were determined at 25°C in chloroform using an Ubbelohde capillary viscometer. The respective data are gathered in row 5 of *Table 1*. Wide-angle X-ray scattering (WAXS) patterns were recorded with a powder diffractometer in reflection mode using Ni-filtered Cu Kα radiation. In all cases temperature control was better than ± 0.5 K. Thermal stabilities were assessed by thermogravimetric analysis (Netzsch STA 429) carried out under argon at a heating rate of 5 K min^{-1}. The temperature where 2% weight loss had occurred was taken as the limit of thermal stability. Differential scanning calorimetry (d.s.c.) measurements were performed using a Perkin–Elmer DSC-7. Optical microscopy was carried out with a Zeiss Photomikroskop equipped with cross-polarizers and a hot stage.

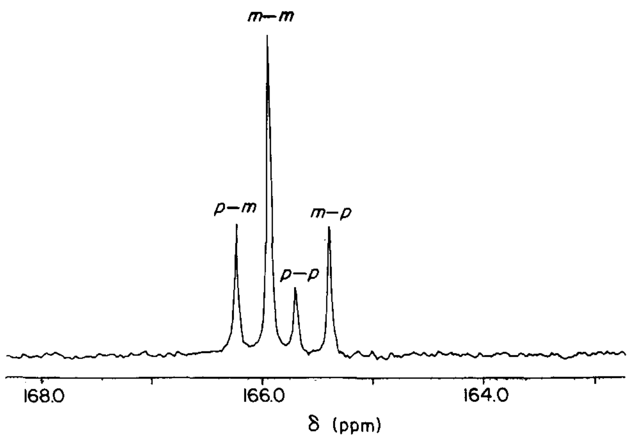

Figure 1 ^{13}C n.m.r. spectrum of copolyester CO30 showing the peaks originating from the carbon atoms of the ester groups. The assignment of the respective dyads has been made according to Schwarz[11]

The sequence distribution of the copolyesters of the soluble materials was studied by monitoring the splitting of the carbonyl carbon atoms of the ester groups in 400 MHz ^{13}C n.m.r. spectra. The peaks were assigned to the respective sequences according to Schwarz[11].

RESULTS AND DISCUSSION

Stability and sequence distribution

A careful study of the phase transition of copolyesters generally requires (i) good thermal stability and (ii) stability against extensive transesterification. As revealed by thermogravimetric analysis, the materials with up to 90% *meta* units are stable up to 700 K, whereas the thermal stabilities of copolyester CO95 and poly(pHBA) are restricted to approximately 600 K. The reason for this behaviour may be sought in the smaller degree of polymerization of the poly(pHBA) (see *Table 1*).

A second point of equal importance is the sequence distribution along the chain, which in most of the studies dealing with copolyesters is assumed to be random. *Figure 1* shows a ^{13}C n.m.r. spectrum for copolyester CO30 in $CDCl_3$, demonstrating that the different dyads can be resolved quantitatively.

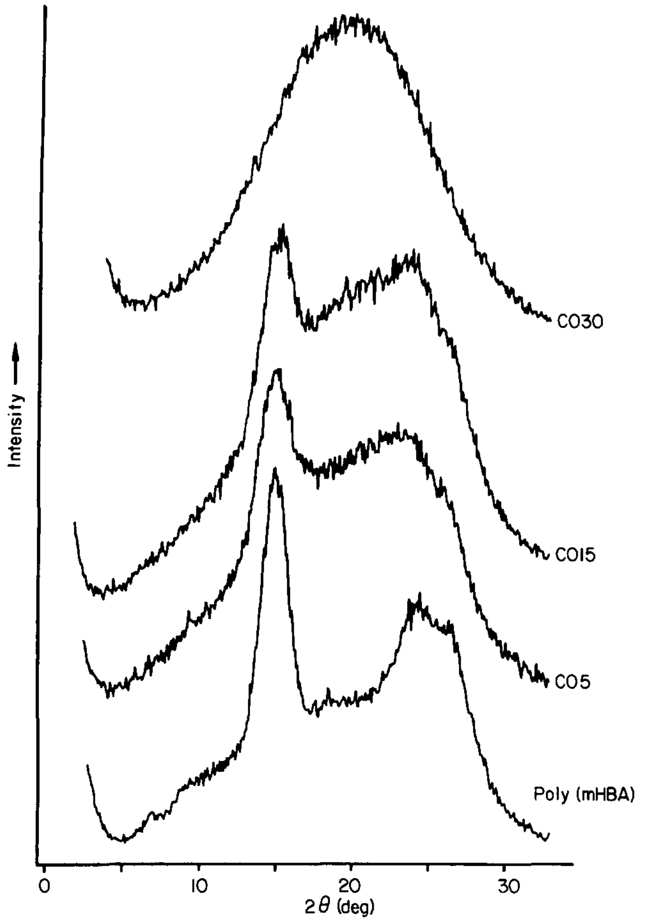

Figure 2 Wide-angle X-ray scattering patterns of the copolymers containing high amounts of mHBA; the numbers on the respective curves indicate the percentage of pHBA

Randomness of the sequence distribution requires that the ratio of the *meta–meta* dyads to the *meta–para* dyads is given by the monomer composition. Also, this ratio should be equal to the number of *meta–para* dyads divided by the number of *para–para* dyads. All spectra recorded on the soluble materials show that these conditions are met. To assess the influence of prolonged heating on the sequence distribution, the copolyester CO30 was kept for 3 h at 543 K. The ^{13}C n.m.r. spectrum recorded subsequently was found to be identical with the one obtained for the starting material. The reason for this stability against the formation of blocky structures may be the absence of any catalyst in the polycondensation process. Hence, the 'silyl method'[4,5,9] seems to be the most reliable synthetic route to copolyesters for structural and thermodynamic studies. Copolyesters containing more than 50% *para* units cannot be studied by n.m.r. spectroscopy, but the above findings suggest that transesterification will be of minor importance for these materials too.

Structure of the copolyesters at room temperature

As is revealed by WAXS, all soluble polymers having less than 50% *para* units are received as amorphous samples; a higher content of pHBA leads to semicrystalline materials. Crystallization of the amorphous polyesters containing up to 15% pHBA could be induced by stirring 1 g of material in 20 ml acetone for several days at room temperature. The poly(mHBA) could be crystallized too using a mixture of benzene and pyridine (50:50 vol %). This finding is in accordance with similar observations made by Kricheldorf *et al.*[8] Attempts to induce crystallization in these materials by annealing failed. The copolymers CO30 and CO40 crystallized neither from solution nor from the melt.

A comparison of the WAXS pattern of poly(mHBA) with those of copolymers CO5 and CO15 (both crystallized from acetone) can be seen in *Figure 2*. Most likely these copolymers crystallize in the lattice of poly(mHBA). If a two-phase model is assumed, which consists of crystallites dispersed in an amorphous phase, the WAXS diagrams displayed in *Figure 2* indicate that the degree of crystallinity (already low in the case of the homopolymer) seems to become even smaller when *para* units are built into the chain. Higher amounts of *meta* units (see upper part of *Figure 2*) finally lead to totally amorphous materials, a finding corroborated by d.s.c. analysis.

The WAXS analysis of copolymers with 40% and more *para* units is shown in *Figures 3a* and *3b*. For the sake of clarity, the diffractograms displayed in *Figures 3a* and *3b* only show the range from 1° to 34° in 2θ because all reflections above this range are very weak. The full analysis is found in *Table 2*. It is obvious from *Figure 3a* that the material containing 40% pHBA exhibits a very low degree of crystallinity, if any at all; the WAXS diagrams of copolyesters with higher amounts of pHBA reveal their crystal structure to be closely related to the structure of poly(pHBA). All X-ray reflections may be assigned to either form I or form II found by Lieser[6] when studying poly(pHBA). This finding is fully corroborated by a direct investigation of the crystal structure using electron diffraction on oriented samples[10]. *Table 2* summarizes the *d* values of the reflections following the analysis of Lieser[6] and of Li *et al.*[10]

An additional feature seen in *Figures 3a* and *3b* is the broadening of the peaks with increasing content of *meta* units ($\geq 40\%$). This fact may be ascribed to a decreasing size of the crystallites or more likely to the mismatch of chains and the disturbance of lateral packing in distinct directions effected by an increasing content of *meta* residues (cf. ref. 10).

Since some of the reflections seen in *Figure 3b* may be assigned solely to modification I or to modification II, the WAXS analysis demonstrates quantitatively that the amount of material crystallized in form II is decreasing with higher content of mHBA. Thus the strong reflections at 16° and 25° in 2θ of form II become much weaker when going from 100% pHBA to 90% pHBA; if the content of pHBA is below 70%, these reflections are very weak and the strongest peak at approximately 20° is solely due to form I.

In this context it is instructive to note that Erdemir *et al.*[12] found a similar behaviour in the course of their study of a similar copolyester made from pHBA, hydroquinone and isophthalic acid. If the content of the latter, bent, moiety is high, the crystal structure of the poly(1,4-phenylene isophthalate) prevails and is only distorted by the linear units. However, if the number of linear moieties is high, the structure of the resulting copolymers is determined by pHBA, leading to the observation of modifications akin to forms I and III of poly(pHBA).

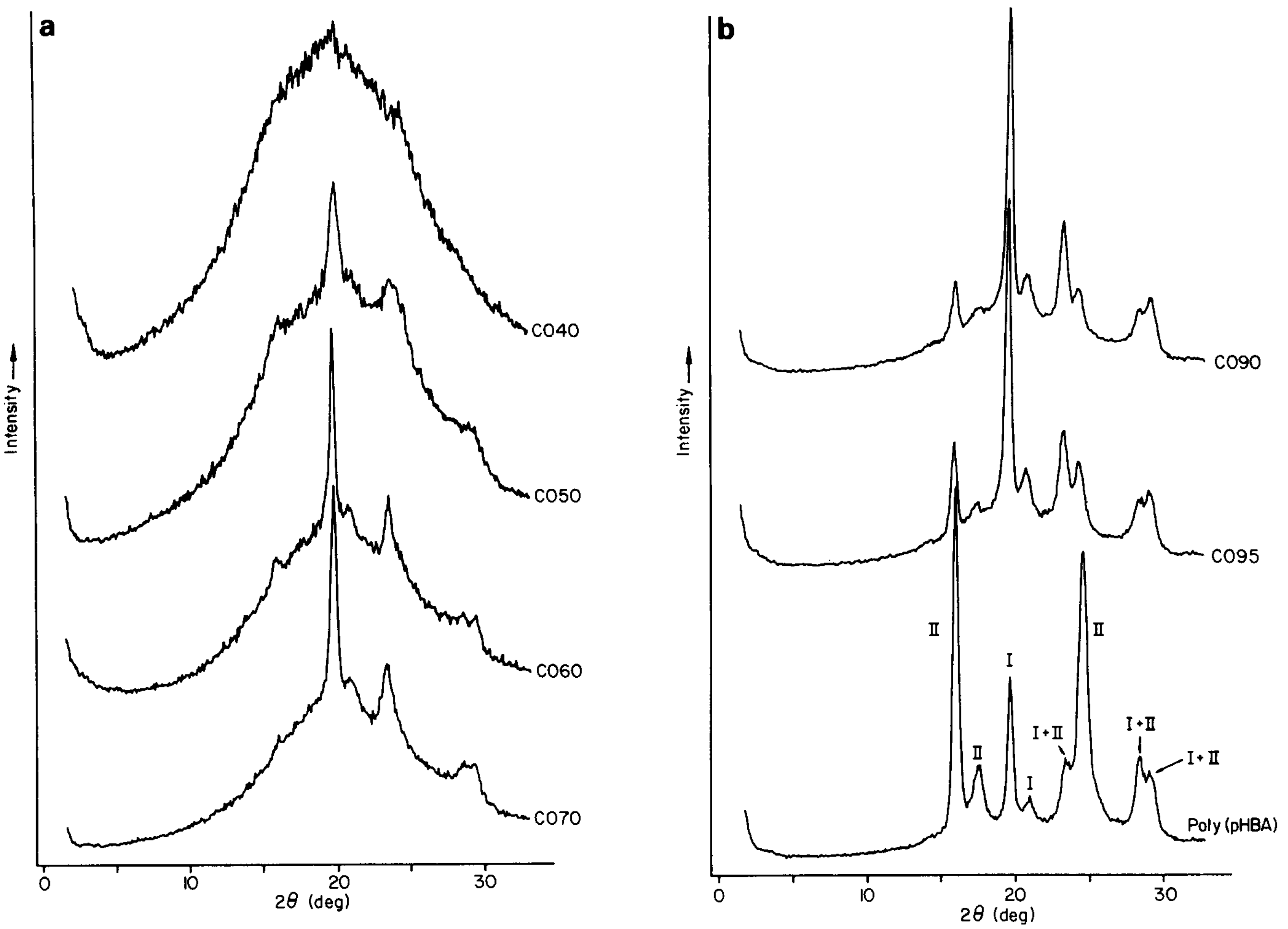

Figure 3 Wide-angle X-ray scattering patterns of the copolyesters CO40 to CO95 and of poly(pHBA). The numbers on the respective curves indicate the percentage of pHBA; in the case of poly(pHBA) the assignment of the reflections to modifications I and II has been made according to Lieser[6]

Table 2 X-ray reflections in copolyesters from pHBA and mHBA

WAXS peaks[a]						Assignment[6,10]			
						Form I		Form II	
CO50	CO60	CO70	CO90	CO95	Poly-(pHBA)	*hkl*	d_{calc}	*hkl*	d_{calc}
5.5 vw	5.55 vw	5.48 vw	5.45 w	5.48 m	5.48 s	–	–	020	5.53
–	–	–	4.92 vw	4.94 vw	5.03 w	–	–	021	5.08
4.48 s	4.5 s	4.48 s	4.43 s	4.45 s	4.5 m	110	4.54	–	–
4.22 vw	4.27 vw	4.21 vw	4.22 vw	4.22 vw	4.22 vw	111	4.27	–	–
3.75 m	3.79 m	3.77 m	3.76 m	3.77 m	3.76 vw	200	3.76	100	3.77
–	–	–	3.62 w	3.60 m	3.60 s	–	–	101/110	3.62/3.57
3.10 vw	3.12 vw	3.10 w	3.12 w	3.11 w	3.11 w	004/210	3.12/3.14	112/120	3.12/3.12
3.63 vw	3.05 vw	3.04 w	3.03 w	3.04 w	3.04 w	211	3.05	121	3.03
–	–	2.60 vw	2.60 vw	2.60 vw	2.60 vw	120/022	2.66/2.53	130/131	2.64/2.58
–	–	2.27 vw	2.25 vw	2.27 vw	2.27 vw	310/220	2.30/2.27	133/140	2.25/2.24
–	–	2.05 vw	2.08 vw	2.08 vw	2.08 vw	006	2.08	–	–

[a] Key: s, strong; m, medium; w, weak; vw, very weak

Thermal analysis and phase behaviour at elevated temperatures

The objective of the next stage of this investigation was to establish the temperatures of the glass and melting transitions and to assess the nature of the resulting phases. Prior to calorimetric measurements, all received samples were heated up to 473 K and cooled down again at 20 K min^{-1} in order to set up a uniform thermal history. An exception was made for the crystalline poly(mHBA) and the crystallized copolymers CO5 and CO15, which were heated only up to 373 K and cooled down at 20 K min^{-1}. The thermogram registered on the following heating is called the first run. Glass transition temperatures T_g were taken as the temperature of half-devitrification of the sample and the temperatures of the first-order transitions were approximated by the respective peak positions. The resulting d.s.c. traces for the first and second runs (cooling rate after first run:

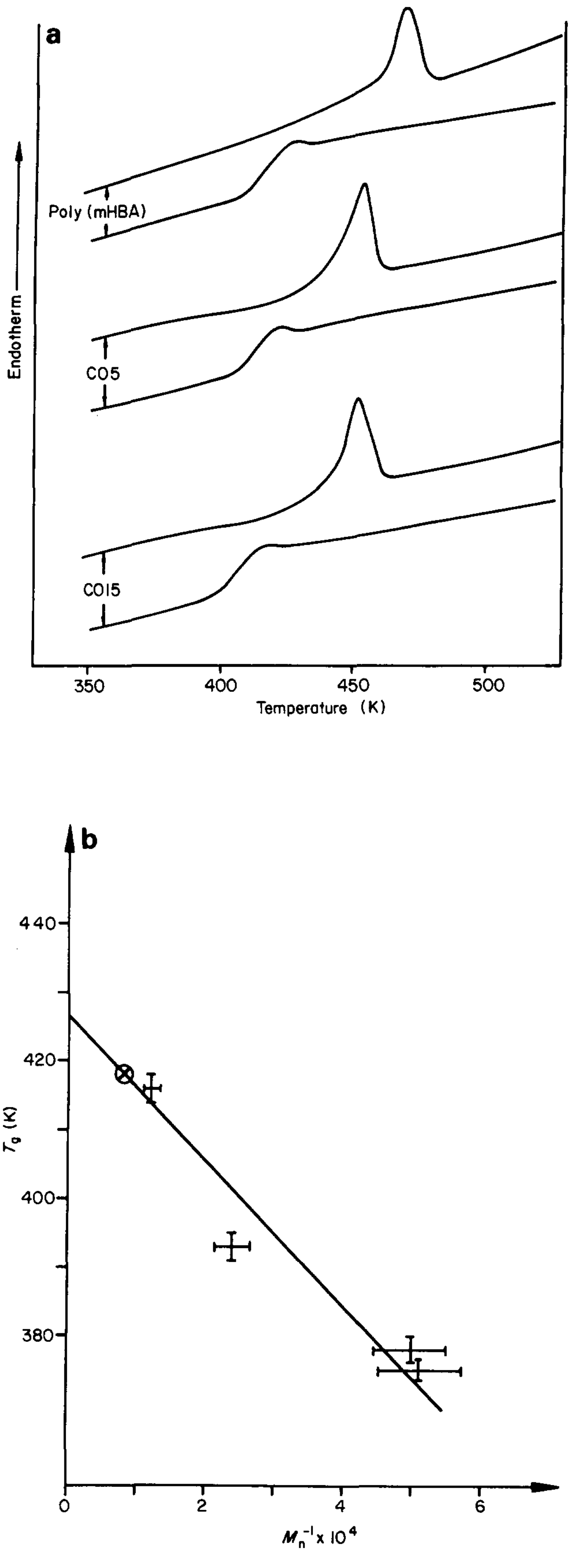

Figure 4 (a) D.s.c. analysis of the copolyesters containing high amounts of mHBA; the numbers on the respective curves indicate the percentage of pHBA. For each copolymer the upper curve displays the result for the first run of the crystallized material, and the lower curve shows the result for the second run performed after cooling the sample to room temperature. (b) Fox–Flory plot of the glass temperatures of poly(mHBA) *versus* the inverse number-average molecular weight. The circle denotes the value taken from the work of Kricheldorf *et al.*[8]

$20\,K\,min^{-1}$) of the poly(mHBA) with the highest molecular weight (see *Table 1*) and the copolymers CO5 and CO15 are displayed in *Figure 4a*.

In the case of the homopolymer, crystallization has been induced by a mixture of benzene and pyridine; the copolymers have been treated with acetone. The first-order transitions are only seen in the first runs. Optical microscopy showed that the resulting melt is isotropic. The melting point for the poly(mHBA) of 470 K obtained here agrees very well with the value (471 K) given by Kricheldorf *et al.*[8] for a material treated similarly. There is no sign of a glass transition in the temperature range down to 220 K. Once molten, these materials easily supercool to amorphous glasses; the subsequent second runs shown in *Figure 4a* only reveal a glass transition. The Fox–Flory plot of the respective glass temperatures of the poly(mHBA) (cf. *Table 1*) displayed in *Figure 4b* shows that the molecular weights of the samples under consideration here are not high enough to render T_g independent of the degree of polymerization. Thus the value of T_g obtained from the poly(mHBA) having the highest degree of polymerization as well as the one given in the literature[8] (418 K, see circle in *Figure 4b*) are slightly lower than the value obtained by extrapolation (427 K).

The WAXS pattern of the polyesters containing a high amount of *meta* units (CO5 and CO15, see *Figure 2*) may be interpreted in terms of low crystallinity. Hence it is interesting to note that in these materials even a small percentage of crystallized material precludes the glass transition. An explanation may be given in terms of the great number of very small crystallites dispersed in the amorphous matrix. Thus the chains connecting these crystallites are rather short and do not have sufficient mobility to exhibit a glass transition. In the second run (see *Figure 4a*) these crystallites are not present, which leads to the observation of an ordinary glass transition in these materials. Further disturbance of the crystal structure of the poly(mHBA) by more *para* units in copolymers CO30 and CO40 leads to a negligible degree of crystallinity. Here the respective heating runs in the d.s.c. (upper part of *Figure 5a*) only indicate a glass transition.

If the amount of the *para* component is raised to 50% and more, the resulting material is semicrystalline. In contrast to the copolymers rich in mHBA, the glass transition and the solid–solid transition temperatures are now separated by ~ 150 K. The analyses of the high-temperature first-order transition for poly(pHBA) by Lieser[6] and for copolymers CO95 and CO50 by Li *et al.*[10] clearly demonstrate that two disordering processes lead to the explanation of the endotherms seen in *Figure 5a*. The orthorhombic modifications I and II transform into the pseudo-hexagonal modification III. In the case of the homopolymeric poly(pHBA), modification II disappears first on heating. At a slightly higher temperature, modification I transforms into modification III[6]. In contrast, the electron diffraction studies by Li *et al.*[10] revealed that modification I of copolymer CO95 is less stable than form II. In both cases it is obvious that the two disordering processes lead to the observation of a rather broad or even bimodal endotherm, as shown in *Figure 5a*. In addition, the polycondensation in bulk employed in this study will result in smaller crystallites than the polycondensation in solution used in previous

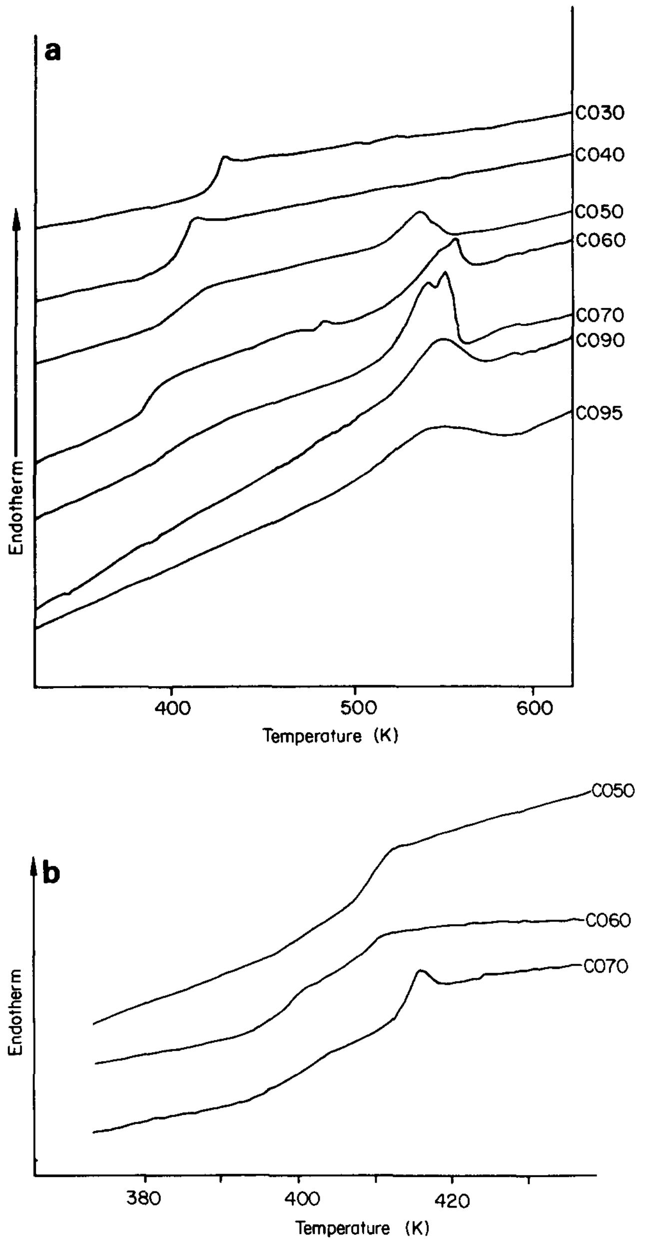

Figure 5 (a) D.s.c. analysis of the copolyesters CO30 to CO100. All curves shown refer to first runs (see text), and the numbers on the curves indicate the percentage of pHBA. (b) An enlarged view of the region of the glass transition

investigations[2,5]. This clearly is followed by a broadening of the endotherm seen in the d.s.c. analysis.

A feature directly obvious from *Figure 5a* is the gradual increase of the temperature range in which the glass transition takes place when going to a higher content of the *para* component (cf. ref. 13). Therefore, for the present systems, T_g can be determined only up to a content of pHBA of 70%; the high crystallinity together with the broadening of the glass transition precludes the direct evaluation of T_g for CO90 and CO95. A further complication arises from the fact that in some cases the copolymers under consideration here even exhibit a double-step glass transition. This feature is clearly visible from enlarged portions of the respective d.s.c. traces shown in *Figure 5b*, and indicates the existence of regions of different mobility in the glassy state. Another feature important for the discussion of the glass transition is given by the dependence of T_g on molecular weight. The Fox–Flory plots for poly(mHBA) (see *Figure 4b*) demonstrate that T_g is still molecular-weight-dependent for this homopolymer. The copolymers will exhibit a similar dependence of T_g on the degree of polymerization. The double-step glass transitions shown in *Figure 5b* therefore may originate from fractionation during the polymerization process, which leads to regions where oligomers are enriched. The scattering of the data for the copolyesters covering the whole range of composition is certainly caused mainly by differences in the degree of polymerization (cf. *Table 1*). Despite these uncertainties the present data plotted in *Figure 6* unambiguously demonstrate that the mobility of the copolymers is increasing upon addition of pHBA, i.e. insertion of linear units into a flexible polymer chain is not necessarily followed by a decrease of the glass temperature. *Figure 6* furthermore suggests a value around 370 K for a hypothetical glass transition in poly(pHBA). Since this material is nearly fully crystalline at room temperature, experimental verification of this value is difficult to obtain.

The change of heat capacity ΔC_p at the glass transition amounts to $31\,\mathrm{J\,K^{-1}\,mol^{-1}}$ for poly(mHBA) and copolymers CO5–CO40. This is in accord with the empirical rule given by Wunderlich[14] that ΔC_p may be calculated to good approximation from the increments of the groups constituting the repeating unit. In the present case ΔC_p amounts to $33.6\,\mathrm{J\,K^{-1}\,mol^{-1}}$ due to the contributions of the phenyl group ($22.4\,\mathrm{J\,K^{-1}\,mol^{-1}}$) and of the ester group ($11.2\,\mathrm{J\,K^{-1}\,mol^{-1}}$), in good agreement with the value observed experimentally. Since the degree of crystallinity increases with increasing content of pHBA, the change of heat capacity at the glass transition found in the first heating runs is smaller than the above value (CO50, $21\,\mathrm{J\,K^{-1}\,mol^{-1}}$; CO60, $20\,\mathrm{J\,K^{-1}\,mol^{-1}}$; CO70, $11\,\mathrm{J\,K^{-1}\,mol^{-1}}$; CO90, CO95 and poly(pHBA), not measurable, see above).

The WAXS analysis of the transition of phases I and II to phase III is displayed in *Figure 7* for the copolyester CO90. The upper curve (A) refers to the starting material at room temperature (cf. *Figure 3b*). The diffractogram B taken at 603 K demonstrates, in accordance with the electron diffraction studies mentioned above[10], that the entire material is transformed into phase III. The strong reflection at 4.6 Å is the 100/010 reflection of the hexagonal packing of the chains[10]. The weak reflection at $2\theta = 27°$ cannot be indexed by the hexagonal unit cell but belongs to the off-meridional reflection, which may be

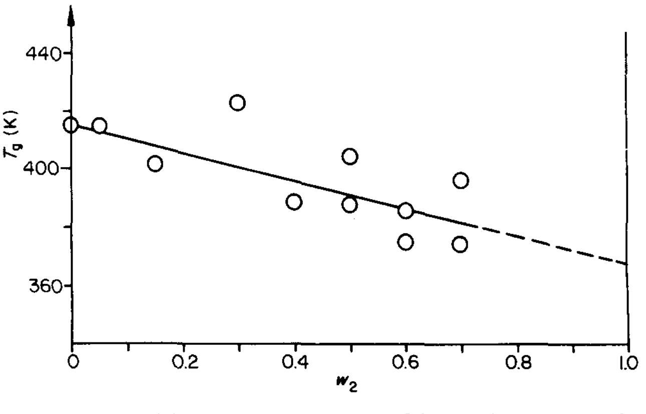

Figure 6 Plot of the glass temperatures T_g of the copolymers *versus* the weight fraction of the pHBA units

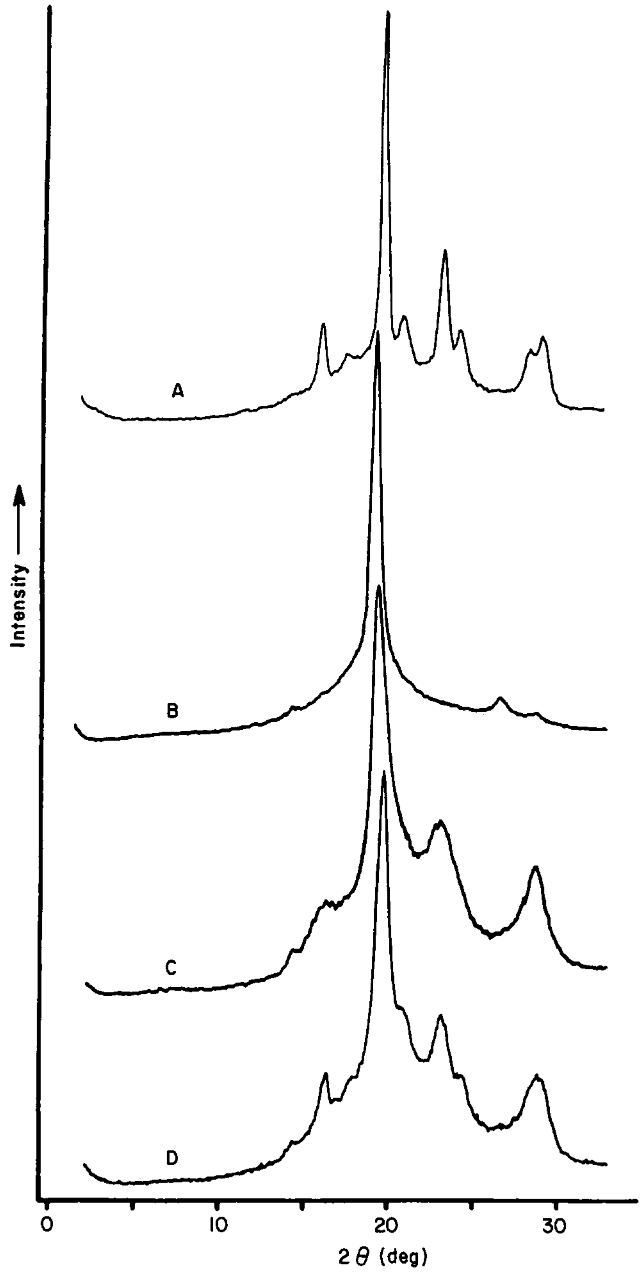

Figure 7 Wide-angle X-ray scattering patterns of the copolymer CO90 containing 90% pHBA units: A refers to the starting material at room temperature; B displays the results for the high-temperature phase III at 603 K; C shows the diffractogram monitored after cooling down to room temperature at ~20 K min^{-1}; and D displays the result after annealing the material for 3 h at the temperature of polymerization (530 K)

related to the structure factor of the isolated chains[10]. The occurrence of hexagonal packing suggests that the rotational disorder of the chains has increased strongly. The X-ray investigation of the high-temperature phase of CO70 shows this material to consist of phase III and an amorphous phase that may exhibit nematic ordering. Since the diffractograms were taken from unoriented samples, no further conclusion can be drawn from the present data.

The comparison of curve C in *Figure 7* monitored after cooling down to room temperature (at ~20 K min^{-1}) with the result obtained from the starting material (curve A) reveals that only a part of the copolyester is retransformed into phases I and II. Additional experiments with CO70 demonstrated that the entire material may be supercooled to room temperature if the material is quenched (200–20 K min^{-1}). D.s.c. heating runs taken subsequently from these samples indicate a glass transition but do not exhibit any sign of a first-order transition. The respective changes of the heat capacity ΔC_p of copolyesters CO50–CO70 are therefore considerably higher (CO50, 27 J K^{-1} mol^{-1}; CO60, 24 J K^{-1} mol^{-1}; CO70, 17 J K^{-1} mol^{-1}; see above). If the content of *para* units exceeds 70%, even high cooling rates (up to 200 K min^{-1}) cannot prevent the conversion of part of the material to forms I and II. But the present results demonstrate that in all cases a part of the disorder effected by the transition into phase III is frozen in when cooling down to room temperature. This can be seen too from the smaller enthalpies of transition and by a shift of the d.s.c. endotherm to lower temperatures in the second runs.

The change of the structure effected by heating beyond the transition to phase III cannot be reversed entirely by annealing of the material below this transition. Curve D of *Figure 7* displays the diffractogram that results after annealing of the copolyester CO90 exactly at the temperature of polycondensation for 3 h (cf. *Table 2*). Only a minor improvement of crystallinity has taken place, as can be seen from a comparison of curves A and D in *Figure 7*. A part of the order built up during polycondensation in phases I and II is evidently lost irreversibly when going to phase III. This finding can be explained by the following arguments. During polycondensation in phases I and II, the setting up of growing polymer chains is achieved to comply with the requirements of the orthogonal lattices. In the high-temperature phase III, rotational disorder of the chains predominates and will destroy the order set up in the low-temperature modifications. The transition from III to II requires the glide of a lattice plane; the respective transition from III to I requires a corresponding change of the lattice parameters[6]. The rotational disorder effected by phase III will certainly disturb the transformation back to the forms I and II because of the mismatch of the chains. The strain thus effected may cause an irreversible breaking of the crystals followed by a broadening of the X-ray reflections. The rotational disorder frozen in will be followed by an additional broadening of the reflections. Since in copolymers CO50 to CO70 phase III can be supercooled to room temperature, it is evident that an increasing content of *meta* units incorporated into the crystals of I and II[10] puts an even more severe constraint on the transformation of III into I and II. Here it may be conceivable that laterally matched sequences of the random copolymer are formed during polycondensation below the transition into III. Such 'non-periodic layer crystallites'[15] would certainly be disassembled when going to phase III. In this case the re-formation of the initial structure requires the reassessment not only of the orientational correlation of the chains but also of the respective longitudinal ordering. From these considerations it is evident that an increasing content of *meta* units will help to stabilize phase III.

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