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Registry No. 1, 114583-79-8; **2**, 36305-60-9; **3**, 7466-45-7; **4**, 114583-80-1; **5**, 124942-74-1; **6**, 117684-98-7; **7**, 124921-91-1; (**7**)(**9c**) (copolymer), 124921-96-6; (**7**)(**9c**) (SRU), 114633-53-3; 8, 124921-92-2; **10a** (copolymer), 124921-97-7; **10a** (SRU), 114633-54-4; **10b** (copolymer), 124921-98-8; **10b** (SRU), 118899-69-7; **10d** (copolymer), 124921-99-9; **10d** (SRU), 125048-58-0; **10e** (copolymer), 124922-00-5; **10e** (SRU), 118899-68-6; **10f** (copolymer), 124922-01-6; **10f** (SRU), 125048-56-8; **10g** (copolymer), 124922-02-7; **10g** (SRU), 125048-57-9; **10h** (copolymer), 124922-03-8; **10h** (SRU), 125048-61-5; **11a** (copolymer), 124922-04-9; **11a** (SRU), 125048-60-4; **11b** (copolymer), 124922-05-0; **11b** (SRU), 125048-62-6; **11c** (copolymer), 124922-06-1; **11c** (SRU), 125048-59-1; 1,2-diamino-4-fluorobenzene, 367-31-7; benzil, 134-81-6; 1,2-diamino-4-chlorobenzene, 95-83-0; 1,2-diamino-4-nitrobenzene, 99-56-9; toluene, 108-88-3; 4-*tert*-butylphenol, 98-54-4; 3-aminophenol, 591-27-5; 1,4-bis(phenylglyoxalyl)benzene, 3363-97-1; *m*-cresol, 108-39-4.

New Polymer Syntheses. 39. Thermotropic Copolyesters of 4-Hydroxybenzoic Acid and 3-Chloro-4-hydroxybenzoic Acid

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Received January 25, 1989; Revised Manuscript Received August 4, 1989

ABSTRACT: Numerous cocondensations of 3-chloro-4-acetoxybenzoic acid and 4-acetoxybenzoic acid were conducted at 320 °C in an inert reaction medium so that the molar ratio of the comonomers varied between 5:1 and 1:10. A second series of copolyesters with a molar composition near 1:1 was prepared under a variety of reaction conditions. All copolyesters prepared from acetoxybenzoic acids were crystalline, whereas those synthesized from (trimethylsiloxy)benzoyl chloride were mainly amorphous. DSC and WAXS measurements revealed that crystalline copolyesters rich in 4-hydroxybenzoic acid (4-Hybe) possess a first-order phase transition at temperatures between 200 and 340 °C, which represents a change from orthorhombic to pseudohexagonal chain packing. At compositions around 1:1, WAXS measurements conducted with synchrotron radiation indicate a melting process above 330 °C. Films can be pressed at 390 °C, and thermomechanical analyses yield heat distortion temperatures (HDT) in the range 290-320 °C for 1:1 copolyesters and HDTs around 390 °C for 1:4 copolyesters. The melting point rises with increasing fraction of 3-chloro-4-hydroxybenzoic acid (3-Cl-4-Hybe) up to temperatures above 400 °C. TGA measurements indicate thermostabilities (5% loss of weight measured in air) up to 500 °C.

Introduction

Poly(4-oxybenzoate), (4-Hybe)$_n$, is an interesting thermostable engineering plastic.[1-12] Unfortunately, it is difficult to process, because its high crystallinity and high melting point (T_m) require temperatures around or above 450 °C, where thermal degradation competes with processing.[5,6] Incorporation of a comonomer may reduce the melting point and ease mechanical processing. Incorporation of a comonomer also influences the crystallinity and the first-order solid-solid phase transition which is typical for pure (4-Hybe)$_n$. The present work, which is part of a systematic study of copolyesters of 4-Hybe, was aimed at studying the influence of 3-chloro-4-Hybe on the properties of 4-Hybe containing copolyesters. Chlorine is the smallest, thermostable and easily accessible substituent that may be introduced into poly(4-Hybe).

Experimental Section

Materials. 3-Chloro-4-hydroxybenzoic acid (Aldrich, St. Louis) and 4-hydroxybenzoic acid (gift of Bayer AG, D-4150 Krefeld) were acetylated with an excess of acetic anhydride in boiling toluene. They were recrystallized from toluene and dried over P_4O_{10}. The (trimethylsiloxy)benzoyl chlorides were prepared as described previously.[13] Marlotherm-S, a mixture of isomeric dibenzyl benzenes, was a gift of Chemische Werke Hüls (Marl, FRG).

Polycondensations. A. In Solution (Table I). A mixture of 3-chloro-4-acetoxybenzoic[14] acid and 4-acetoxybenzoic acid (100 mmol total) was suspended in 200 mL of Marlotherm-S and rapidly heated to 320 °C with stirring under a slow stream of nitrogen. When the elimination of acetic acid became vigorous (at ca. 240-260 °C), heating was stopped for approximately 15 min and then continued. After 16 h, the reaction miture was cooled and diluted with acetone. The crystallized polyester was isolated by filtration, extracted with hot acetone, and

Table I
Yields and Properties of Copolyesters Prepared by Cocondensation of 3-Chloro-4-acetoxybenzoic Acid (A) and 4-Acetoxybenzoic Acid (B) in Marlotherm-S

exp. no.	polymer	feed[a] ratio A/B	yield, %	Cl elemental anal., % calcd	Cl elemental anal., % found	composition[b] A′/B′	T_{m1},[c] °C	T_{m2},[c] °C	M_n[d]
1	**3a**	5/1	91	19.85	18.81	3.5/1		394	25 000
2	**3b**	2/1	89	16.52	15.41	1.7/1		357, 372	100 000
3	**3c**	1/1	98	12.91	11.60	1/1.2		300, 348	>100 000
4	**3c**	1/1	71	12.91	10.30	1/1.6		315, 366	>100 000
5	**3d**	1/2	78	8.98	8.01	1/2.4	170	360	>100 000
6	**3e**	1/3	92	6.89	6.03	1/3.7	175	373	55 000
7	**3f**	1/4	87	5.58	4.90	1/4.7	230	397	>100 000
8	**3g**	1/5	88	4.69	3.98	1/6.2	242		80 000
9	**3h**	1/7	89	3.56	2.73	1/9.5	278		30 000
10	**3i**	1/10	90	2.62	1.65	1/16	303		>100 000

[a] Initial molar units of monomers (B = 4-acetoxybenzoic acid). [b] Molar composition of the isolated copolyesters calculated from Cl analyses (A′ = 3-chloro-4-Hybe; B′ = 4-Hybe). [c] Endotherms as determined by DSC measurements with a heating rate of 20 °C/min. [d] Calculated from ^{1}H NMR spectroscopic end group analyses of hydrolyzed copolyesters.

Table II
Reaction Conditions and Results of Cocondensations of 3-Chloro-4-hydroxybenzoic Acid and 4-Hydroxybenzoic Acid[a]

exp. no.	monomers	condensation method	yield, %	Cl anal., %	composition[b]	M_n[b]
1	3-chloro-4-acetoxybenzoic acid, 4-acetoxybenzoic acid	bulk condens. 1 h/280 °C + 2 h/350 °C	84	12.70	1/1.1	>100 000
2	3-chloro-4-acetoxybenzoic acid, 4-acetoxybenzoic acid	bulk condens. 0.2 h/280 °C + 3 h/350 °C	70	12.40	1/1.1	35 000
3	3-chloro-4-hydroxybenzoic acid, 4-hydroxybenzoic acid	bulk condens. with acetic anhydride; 16 h/320 °C	65	10.95	1/1.4	45 000
4	3-chloro-4-(trimethylsiloxy)benzoyl chloride, 4-(trimethylsiloxy)benzoyl chloride	bulk condens. 16 h/320 °C	90	12.00	1/1.2	>100 000
5	3-chloro-4-(trimethylsiloxy)benzoyl chloride, 4-(trimethylsiloxy)benzoyl chloride	condens. in Marlotherm-S 16 h/320 °C	64	11.30	1/1.3	>100 000

[a] Molar ratios 1:1. [b] Molar composition of isolated copolyesters as determined from Cl elemental analyses (B′ = 4-Hybe units). [c] Calculated from ^{1}H-NMR spectroscopic endgroup analyses of hydrolyzed copolyesters.

Table III
Thermogravimetric Analysis[a] of Homo- and Copolyesters Containing 3-Chloro-4-hydroxybenzoic Acid

sample	temp (°C) at weight loss 1%	5%	10%	20%	50%
homopolyester 1		445	480	510	525
copolyester **3c** (Table I)		480	504	515	545
copolyester **3i** (Table I)		430	482	520	540
copolyester no. 3, Table II	(420)	490	500	510	520
copolyester no. 4, Table II	(370)	440	470	485	515
copolyester no. 5, Table II	(305)	370	435	485	510

[a] Measured with a heating rate of 10 °C/min in air.

dried at 60 °C/12 mbar. The cocondensation of 4-(trimethylsiloxy)benzoyl chlorides was conducted in the same way (nos. 4 and 5, Table II).

B. Cocondensation with Acetic Anhydride (no. 3, Table II). A mixture of 50 mmol of 3-chloro-4-hydroxybenzoic acid, 50 mmol of 4-hydroxybenzoic acid, 110 mmol of acetic anhydride, and 10 mg of magnesium oxide was heated to 200 °C. Most of the eliminated acetic acid was removed over a period of 30 min with a slow stream of nitrogen under stirring. The temperature was then raised to 320 °C for 16 h and the product worked up as described.

C. Bulk Condensations (no. 2, Table II). A mixture of 50 mmol of 3-chloro-4-acetoxybenzoic acid, 50 mmol of 4-acetoxybenzoic acid, and 10 mg of magnesium oxide was heated in a round-bottomed cylindrical glass reactor under stirring to 260 °C. The eliminated acetic acid was removed with a slow stream of nitrogen over a period of 10 min. The temperature was then raised to 320 °C and maintained for 16 h. After the mixture cooled, the copolyester was powdered, extracted with boiling acetone, and dried at 60 °C/12 mbar.

Measurements. The DSC measurements were conducted with a Perkin Elmer DSC-4 in aluminum pans under nitrogen at a heating rate of 20 °C/min. The thermomechanical measurements were conducted with a Perkin Elmer TGS-2 at a heating rate of 10 °C/min under a load of 1 kg/mm^2. The films used for these measurements were pressed at 390 °C and 200 atm in vacuo for periods of 10 or 30 s.

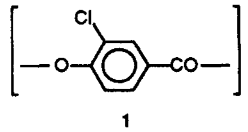
The ^{1}H NMR spectra were measured with a Bruker AM 360 FT spectrometer in 5-mm-o.d. sample tubes. Fifty milligrams of a copolyester was hydrolyzed in a mixture of 0.7 mL of CD_3OD and 0.3 mL of 40% $NaOD/D_2O$. TMS served as internal standard.

The WAXS powder patterns were measured on a Siemens D-500 diffractometer at room temperature with Cu Kα radiation using a Ni filter. For the set of slits between the radiation source and scintillation detector, angles of 10°, 1°, 0.1°, and 0.05° were chosen. The patterns were recorded in steps of ϑ = 0.1° with a radiation time of 20 s/data point.

The time-resolved WAXS measurements at elevated temperatures were conducted with a synchrotron radiation beam line (λ = 1.50 Å) at HASYLAB, DESY Hamburg, by means of a vacuum furnace and a one-dimensional, position-sensitive detector. The heating rate was 20 °C/min, and the accumulation time for one spectrum was 10 s.

Results and Discussion

Syntheses. In addition to the homopolyesters 1 and 2, two series of copolyesters were prepared starting from commercial 4-Hybe and 3-chloro-4-Hybe. First, the acetylated hydroxybenzoic acids were condensed in an inert reaction medium (Marlotherm-S) at 320 °C (eq 1). This temperature was chosen because it is close to the phase transition of poly(4-Hybe), so the chain growth of the oligomers precipitated from solution can easily proceed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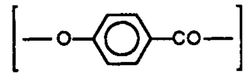
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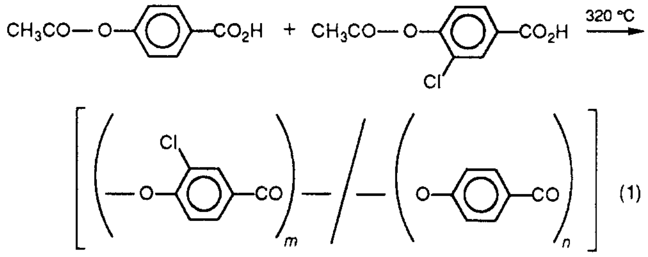
in the mobile pseudohexagonal chain packing.[8,10] Higher temperatures do not significantly improve the chain growth process but may favor side reaction (decarboxylation, Fries rearrangement, etc.). The molar ratios of the monomers were varied between 5:1 and 1:10 as indicated in eq 1 and Table I. For the discussion below, these copolyesters (**3a–i**) will be named according to the composition of the monomer mixture, which is not exactly identical with the composition of the isolated copolyesters (Table I).



(1)

3a–i

m/*n*: **a**, 5/1 **f**, 1/4
b, 2/1 **g**, 1/5
c, 1/1 **h**, 1/7
d, 1/2 **i**, 1/10
e, 1/3

A second series of copolyesters was prepared from monomer mixtures with a molar ratio of 1:1. The activation of the hydroxybenzoic acid and the reaction conditions were varied. Two polycondensations (nos. 1 and 2, Table II) were again conducted with 4-acetoxybenzoic acids in the absence of solvent. In this case, details of the procedure have a strong influence on the properties of the resulting copolyester. When the polycondensation is mainly conducted at 280 °C (no. 1, Table II), the reaction mixture solidifies with increasing conversion, and later heating to 350 °C does not yield a homogeneous melt. DSC and WAXS measurements (Figure 1B) suggest formation of blocky sequences in combination with phase separation. Obviously, the initially formed crystalline blocks of poly(4-Hybe) do not melt and thus do not transesterify. However, when the reaction temperature is rapidly raised to 350 °C (no. 2, Table II), a homogeneous melt is obtained, and the properties of the resulting copolyesters are almost identical with that of **3c** prepared in Marlotherm-S (no. 3, Table I). Furthermore, the free hydroxy acids were condensed in the presence of excess acetic anhydride (no. 3, Table II, Figure 1A). Compared to other condensations of Table II, both yield and incorporation of 3-chloro-4-Hybe were relatively low. Yet the properties were similar to those of **3c** or of the copolyester prepared by bulk condensation of acetoxybenzoic acids (no. 2, Table II). The difference between the WAXS pattern of Figure 1A and the WAXS pattern of **3c** in Figure 7 is not due to the different synthetic methods but to different treatment of the sample before the X-ray measurements. In the case of Figure 1A–C, films were pressed at 390 °C, whereas the original powders were measured for Figures 5–8.

Both cocondensations of (trimethylsiloxy)benzoyl chlorides (eq 2) gave materials with nearly identical properties. In contrast to all copolyesters obtained from acetoxybenzoic acids or by means of acetic anhydride, these copolyesters were largely amorphous, as indicated by WAXS measurements (Figure 1C) or by thermomechanical studies (Figure 10 and discussion below). ^{1}H NMR and ^{13}C NMR spectra of hydrolyzed samples revealed that the cocondensation of (trimethylsiloxy)benzoyl chlorides involved side reactions that modified the chemical structure of both monomer units. The nature of this chemical modification could not be elucidated, yet the NMR spectra explain why the properties of both "silyl samples" (nos. 4 and 5, Table II) are different from those of all other samples.

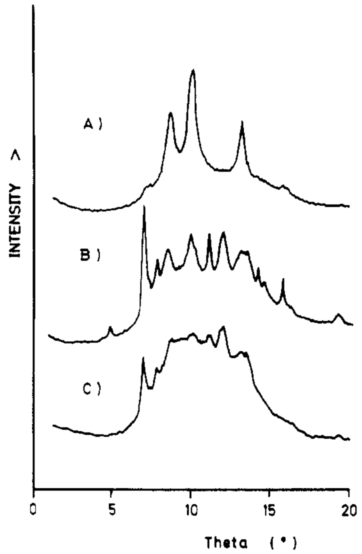
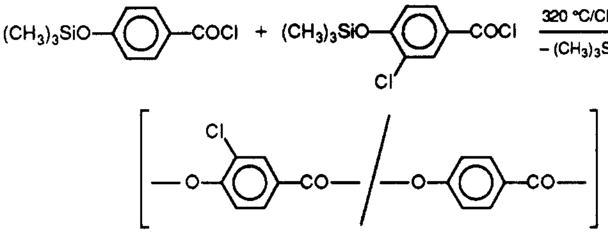


Figure 1. WAXS powder patterns, measured at 20 °C, of films pressed at 390 °C and 200 atm: (A) 1:1 copolyester no. 3, Table II; (B) 1:1 copolyester no. 1, Table II; (C) 1:1 copolyester no. 4, Table II.



(2)

The molar composition of all copolyesters was determined by Cl elemental analysis. In some cases, the copolyesters were completely hydrolyzed in $CD_3OD/NaOD/D_2O$ mixtures, and 360-MHz ^{1}H NMR spectra of the reaction mixture were measured. NMR measurements of intact copolyesters were not feasible, because all samples prepared by the acetate method were crystalline and insoluble in all common solvents. As shown in Figure 2, the ^{1}H NMR signals of hydrolyzed 4-Hybe and 3-chloro-4-Hybe are well separated. Therefore, the molar composition could be calculated from these ^{1}H NMR spectra, and a satisfactory agreement with the Cl elemental analyses was obtained. Regardless of the structure of monomers, all condensations conducted in Marlotherm-S have in common that the rate of incorporation of 3-chloro-4-Hybe is lower than that of 4-Hybe. Obviously, the chlorine atom in the 3-position causes a weak steric hindrance and reduces the nucleophilicity of the OH group.

The ^{1}H NMR spectra of hydrolyzed polyesters also allowed the calculation of number-average molecular weights from the intensity of the acetate signal as described previously.[8,9] The results listed in Tables I and II clearly indicate that high polymers and not oligomers were prepared. The accuracy and reliability of this method exclusively depends on the chemistry of the condensation process, i.e., on a potential side reaction modifying the end groups. This problem is common to all kinds of end group analyses, but other methods of molecular weight measurements were not applicable to the polyesters of this work.

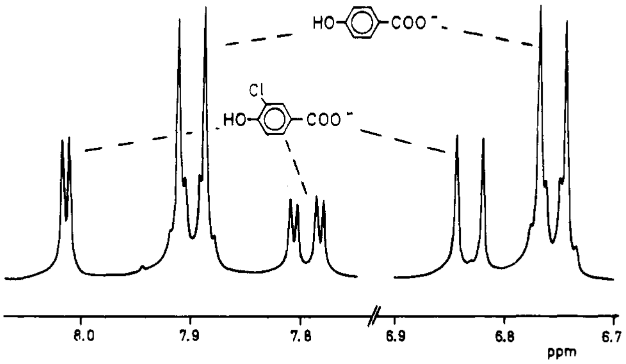


Figure 2. 360-MHz ^1H NMR spectrum of hydrolyzed copolyester measured in a mixture of CD_3OD and 40% $NaOD/D_2O$ (60:40 by volume).

Unfortunately, the insolubility of copolyesters **3a–i** also prevented ^{13}C NMR sequence analyses. The ^{13}C NMR CP/MAS spectra of solid copolyesters did not yield any sequence information owing to broad and overlapping signals. However, the DSC and WAXS patterns of the copolyesters **3a–i** from Table I suggest that these copolyesters possess nearly random sequences. This conclusion is based on the observation that both DSC endotherms and WAXS patterns display a systematic variation with the molar composition of **3a–i**. It is at least evident that the blocks are so short that they do not form a separate phase.

DSC Measurements and Microscopy. All DSC traces were measured with a heating rate of 20 °C/min, and after slow cooling (−20 °C/min) a second heating trace was measured to check the reproducibility of phase transition. All copolyesters (**3a–i**) and the homopolyesters **1** and **2** have in common that no glass transition is detectable in the DSC curves. Thus, from the viewpoint of DSC measurements these copolyesters are highly crystalline materials.

DSC measurements of the homopolyester **1** did not reveal any endotherm (up to 450 °C) in contrast to poly(4-Hybe), which exhibits a sharp reversible first-order transition at ca. 335 °C. This phase transition is well documented in the literature.[2–12] It represents a change from an orthorhombic crystal lattice (below 335 °C) to a pseudohexagonal chain packing (above 335 °C).[11]

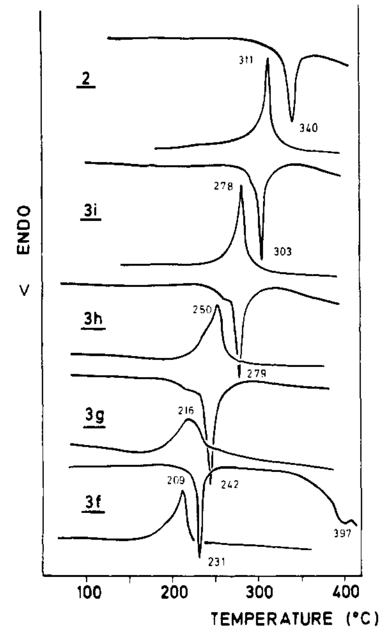


Figure 3. DSC traces of poly(4-Hybe) (**2**) and copolyesters **3i–f**: first heating and first cooling trace were measured with a rate of 20 °C/min.

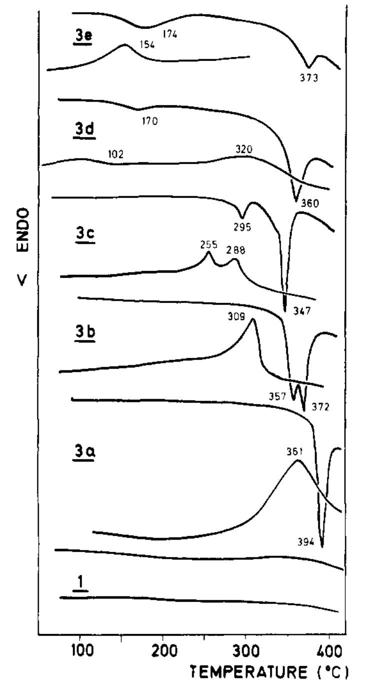
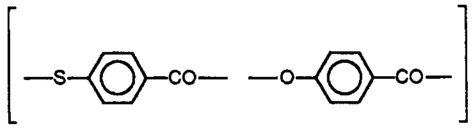


Figure 4. DSC traces of copolyesters **3e–a** and poly(3-chloro-4-Hybe) (**1**): first heating and first cooling trace measured with a rate of 20 °C/min.



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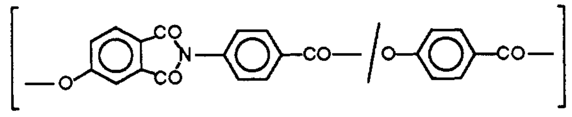

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The DSC measurements of copolyesters **3a–i** revealed two types of endotherms. Copolyesters rich in 4-Hybe units (**3e–i**) possess an endotherm in the temperature range 190–330 °C, which indicates the same change of modifications already known from pure poly(4-Hybe). The increasing molar fraction of 3-chloro-4-Hybe units reduces the temperature of this phase transition (Figure 3). A similar behavior was found for copolyester of 4-mercaptobenzoic acid and 4-Hybe (**4**).[15] However, in the case of copolyesters **5** the temperature of the solid → solid phase transition rises with increasing molar fraction of the imide unit.[16] No satisfactory explanation exists as to why two classes of copolyesters of 4-Hybe exist with respect to the temperature dependence of this reversible phase transition. The copolyesters **3a–c** display an endotherm in the temperature range between 360 and 400 °C, which represents a true melting process. This melting point possesses a minimum at a molar ratio of 1:1, when the molar fraction of 3-chloro-4-Hybe is systematically varied (Figure 4). The melt possesses a high viscosity at temperatures below 420 °C, and stirring is not feasible at temperatures below 360 °C, when the polycondensation has reached its final conversion. Microscopic observation of **3b** and **3c** with crossed polarizers revealed that the melt does not freely flow up to temperatures of 480 °C, where beginning thermal degradation

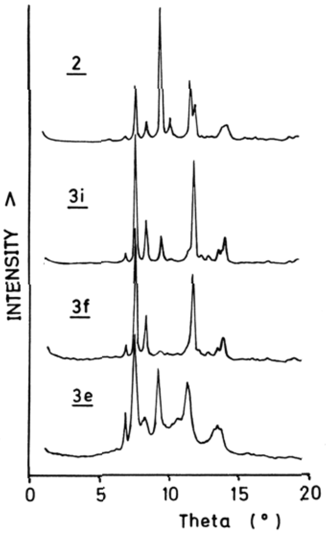

Figure 5. WAXS powder patterns (measured at 20 °C) of poly(4-Hybe) (**2**) and copolyesters **3i**, **3f**, and **3e** (all samples "as polymerized").

affects further observation. Even when slight shear forces were applied with a spatula, no mobility was detectable. Nonetheless, upon annealing for approximately 30 min at 450 °C or 5–10 min at 480 °C a treated schlieren texture which is typical for the nematic phase of liquid-crystalline main-chain polyesters is observable. This observation agrees well with the recently reported finding of a schlieren texture for oligomeric poly(4-Hybe) above 300 °C.[6] Thus, it is clear that the copolyesters of 4-Hybe and 3-chloro-4-Hybe may be called thermotropic engineering plastics.

WAXS Measurements. WAXS powder patterns of all homo- and copolyesters were measured at room temperature. It is well-known from poly(4-Hybe) that this homopolyester can adopt two different othorhombic cells:[11] modification I with a = 7.52 Å, b = 5.70 Å, and c = 12.49 Å; modification II with a = 3.77 Å, b = 11.06 Å, and c = 12.89 Å. In samples prepared by thermal condensation of 4-acetoxybenzoic acid, reflections of both modifications are usually present (Figure 5), yet modification I strongly predominates. Incorporation of 3-chloro-4-Hybe stabilizes modification II, even when less than 10 mol % is present as indicated by the powder pattern of **3i** in Figure 5. A similar situation was found for the incorporation of N-(4-carboxyphenyl)-4-hydroxyphthalimide.[16] Modification II remains the predominant modification up to a molar fraction of 20–25% 3-chloro-4-Hybe (**3f**, Figure 5).

When WAXS patterns of copolyesters **3f** and **3i** were measured with synchrotron radiation at higher temperature, a change of modification was observable in both cases. One sharp and intensive reflection was found at ϑ = 9.5° (Figure 6), indicating a pseudohexagonal chain packing nearly identical with that of modification III of pure poly(4-Hybe). The temperature of this phase transition is identical with the endotherm found in the heating traces of the DSC measurements (Figure 3), and both types of measurements agree in that this phase transition is completely reversible with a "hysteresis effect" of ca. 25–30 °C.

The WAXS patterns of copolyesters **3f–i** are also noteworthy for the fact that no halo is detectable in addition to the reflections of modification II. This finding suggests that these copolyesters, like pure poly(4-Hybe), possess 90% or more crystallinity. However, when the molar fraction of 3-chloro-4-Hybe increases above 25%, the powder pattern changes. Positions and intensities of the sharp reflections vary, and the halo of an amorphous phase also appears (**3e**, Figure 5; **3c,d**, Figure 7). The amorphous fraction reaches its maximum at a composition near 1:1 (**3c**), as expected for a random or nearly random sequence of both monomer units.

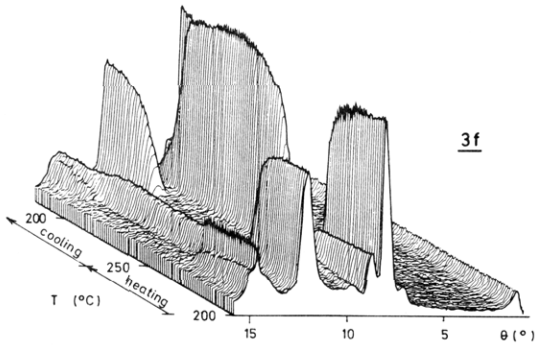

Figure 6. WAXS powder patterns of copolyester **3f** ("as polymerized") measured with synchrotron radiation (λ = 1.5 Å) at variable temperature.

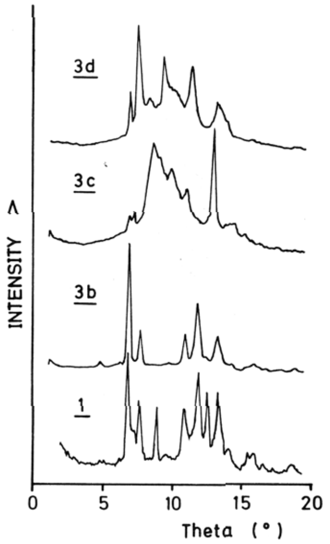

Figure 7. WAXS powder patterns (measured at 20 °C) of copolyesters **3d**, **3c**, and **3b** and homopolyester **1** (all samples "as polymerized").

At first glance, these WAXS patterns do not agree well with the DSC measurements displayed in Figure 4. The DSC traces show a sharp endotherm (at 347 °C) for **3c** and suggest a largely crystalline character for **3c**. However, WAXS measurements conducted with synchrotron radiation at higher temperatures allow at least a satisfactory interpretation of the endotherms of **3a–e**. As demonstrated for **3c** in Figure 8, these copolyesters undergo a true melting process. All sharp reflections disappear, and only a halo is observable above the phase transition. The existence of a true melting process and the assumption of a random sequence are then in good agreement with the DSC traces of Figure 4, because the minimum T_m is found for the 1:1 copolyester **3c**.

Finally, it is worth noting that the copolyesters rich in 3-chloro-4-Hybe (**3a,b**) exhibit powder patterns that differ clearly from those of the other copolyester. Furthermore, a different powder pattern is found for the homopolyester **1** (Figure 7). Again an amorphous halo is absent, and the degree of crystallinity obviously approach values ≥90%.

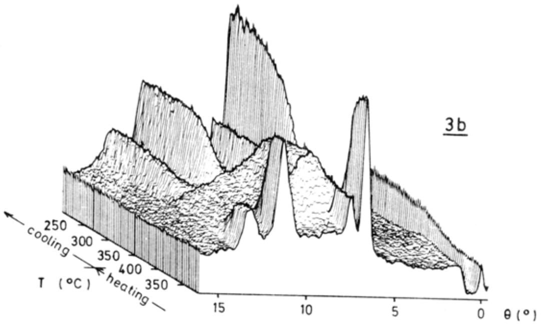

Figure 8. WAXS powder patterns of copolyester **3b** ("as polymerized") measured with synchrotron radiation (λ = 1.5 Å) at variable temperature.

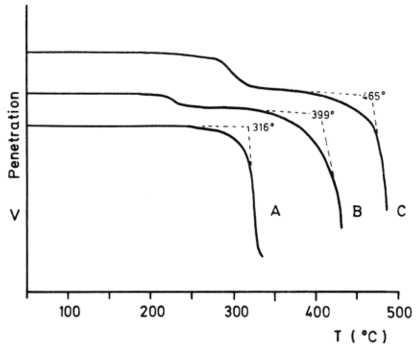

Figure 9. Penetration measurements (heating rate 10 °C/min, load 1 kg/mm^2) of films pressed for 30 s at 390 °C: (A) copolyester **3c**; (B) copolyester **3f**; (C) copolyester **3i**.

Thermomechanical (TMA) and Thermogravimetric Analyses (TGA). The existence of a melting process in the case of copolyesters **3a–e** suggested that films can be pressed at high temperature and under high pressure. The films were pressed at 390 °C for 10 or 30 s. Temperatures above 400 °C and longer evacuation times were technically not feasible. As expected for rapidly crystallizing materials, the films obtained in this way were not transparent and were relatively brittle due to the sinter process, because a homogeneous melt could not be obtained under the given circumstances. Nonetheless, there films were tough enough to allow penetration measurements. These measurements were conducted at a heating rate of 10 °C/min under a load of 1 kg/mm^2 (similar to the Vicat-A test).

The results obtained from copolyesters **3c**, **3f**, and **3i** are illustrated in Figure 9. The temperature where the mechanical resistance completely breaks down rises with increasing molar fraction of 4-Hybe units. Interestingly, the TMA curves of **3f** and **3i** also display a slight decrease of the mechanical resistance at the temperature where the DSC traces indicate the solid → solid phase transition (Figure 5). This effect is more pronounced for **3i** than for **3f**. All TMA curves of Figure 9 have in common that a glass transition is not detectable. This result is worth noting, because copolyester **3c** contains a considerable amorphous fraction as indicated by the WAXS patterns of the original powder (Figure 7) and of the pressed film (Figure 1A is also representative for pressed **3c**). It is also worth noting that the heat distortion temperatures found after 10 or 30 s of pressing vary by ca. 20 °C. Longer pressing times raised the HDT of most samples; yet in one case a slight decrease was observed.

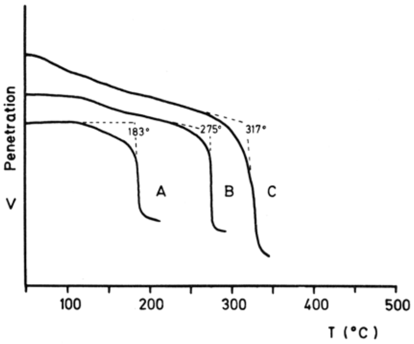

Figure 10. Penetration measurements (heating rate 10 °C/min, load 1 kg/mm^2) of films pressed at 390 °C: (A) 1:1 copolyester no. 5, Table II, pressed for 10 s; (B) 1:1 copolyester no. 4, Table II, pressed for 10 s; (C) 1:1 copolyester no. 4, Table II, pressed for 30 s.

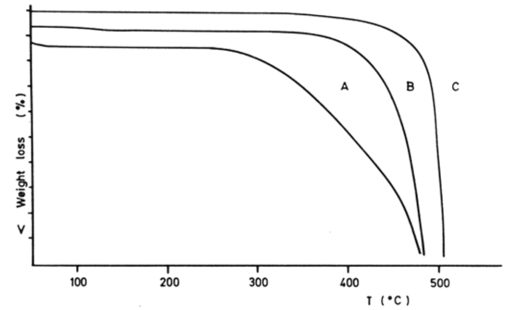

Figure 11. Thermogravimetric analyses conducted at a heating rate of 10 °C/min in air: (A) 1:1 copolyester no. 5, Table II; (B) 1:1 copolyester no. 4, Table II; (C) 1:1 copolyester no. 3, Table II.

The TMA curves obtained from the 1:1 copolyesters prepared from (trimethylsiloxy)benzoyl chlorides (nos. 4 and 5, Table II) are quite different from those of all other samples (Figure 10). In agreement with a mainly amorphous character, low HDTs were found for both samples. It is a satisfactory result of these measurements that three different methods (DSC, WAXS, and TMA) show a good agreement on crystallinity and on the nature and temperatures of phase transitions.

Finally, thermogravimetric measurements were conducted with a heating rate of 10 °C/min in air. The results summarized in Table III demonstrate that the thermostability of poly(3-chloro-4-Hybe) (**1**) is as high as that of poly(4-Hybe) (**2**).[8,9] Hence, it is not surprising that also the copolyesters **3a–i** possess a high thermostability with 5% loss of weight in the temperature range 500–510 °C. However, this high thermostability is only characteristic for copolyesters prepared from acetoxybenzoic acids (eq 1), whereas the samples prepared from (trimethylsiloxy)benzoyl chlorides exhibit significantly lower values (Figure 11). A similar difference was also observed for pure poly(4-Hybe) prepared by different synthetic methods.[8,9]

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Registry No. 1 (homopolymer), 90385-55-0; 1 (SRU), 85609-98-9; 2 (homopolymer), 30729-36-3; 2 (SRU), 26099-71-8; (1)(2) (copolymer), 124921-53-5; (4-acetoxybenzoic acid)(3-chloro-4-acetoxybenzoic acid) (copolymer), 124921-51-3; (3-chloro-4-(trimethylsiloxy)benzoyl chloride)(4-(trimethylsiloxy)benzoyl chloride) (copolymer), 124921-52-4.

Polycondensation Catalyzed by a Palladium Complex. 2. Synthesis and Characterization of Main-Chain Type Liquid Crystalline Polymers Having Distyrylbenzene Mesogenic Groups

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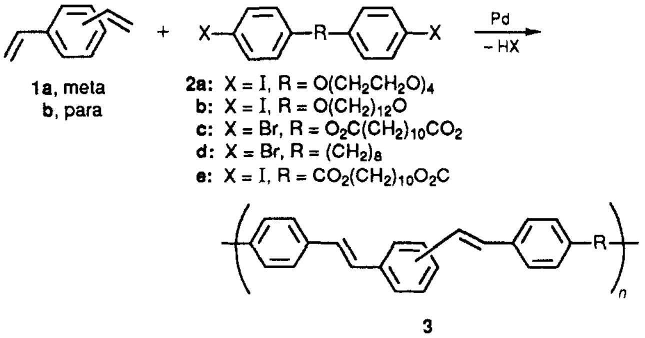
Received April 19, 1989; Revised Manuscript Received September 12, 1989

ABSTRACT: Polymers having *trans,trans*-distyrylbenzene units in the main chain were synthesized by the Heck reaction of *p*-(or *m*-)divinylbenzene with bis(halobenzene) derivatives that have a flexible chain such as a longer alkyl or poly(oxyethylene) group. The product polymers exhibited thermotropic liquid crystallinity, which was characterized by using DSC and an optical microscope with cross-polarizers. Smectic textures were observed in the mesophases of polyesters and polyethers derived from *m*-divinylbenzene.

Introduction

Very recently, we have reported a novel polycondensation catalyzed by a palladium complex.[1] Polyester and polyamide having cinnamoyl units were synthesized by the Heck reaction,[2] i.e., a coupling reaction between aryl halide moieties and C═C double bonds of acrylic derivatives. Some of the product polymers showed mesophases. This article deals with the further investigation of this novel polycondensation,[3] preparing liquid crystalline (LC) polymers that consist of distyrylbenzene groups in the main chains.[4,5]

It is well-known that a main-chain type thermotropic LC polymer consists of two constituents, i.e., a rigid segment such as biphenyl group or stilbene group and a flexible segment such as an alkyl or poly(oxyethylene) chain.[6] Therefore, the following reaction has been attempted: the combination of divinylbenzenes 1 with compounds 2 having two halophenyl groups that are connected to each other with a spacer chain.



1a, meta
b, para

2a: X = I, R = $O(CH_2CH_2O)_4$
b: X = I, R = $O(CH_2)_{12}O$
c: X = Br, R = $O_2C(CH_2)_{10}CO_2$
d: X = Br, R = $(CH_2)_8$
e: X = I, R = $CO_2(CH_2)_{10}O_2C$

3

Experimental Section

Materials. *m*- and *p*-divinylbenzene were prepared according to a reported method.[7] Monomers of **2a** (mp 87 °C from MeOH) and **2b** (mp 105 °C from $CHCl_3$–EtOH) were obtained by the reaction of 4-iodophenol with diethylene glycol bis(2-bromoethyl) ether and with 1,12-dibromododecane, respectively, according to a method described in the literature.[8] The monomers **2c** (mp 82 °C from $CHCl_3$) and **2e** (mp 70 °C from $CHCl_3$–EtOH) were prepared respectively by the reactions of 4-bromophenol with dodecanedioyl dichloride and of 4-iodobenzoyl chloride with 1,10-decanediol. Another monomer, **2d** (mp 58 °C from hexane), was prepared by the coupling reaction between 4-bromobenzyl bromide and hexamethylene bis(magnesium bromide) in the presence of dilithium tetrachlorocuprate as a catalyst.[9] Palladium acetate and tri-*o*-tolylphosphine (POT) were used without purification. DMF, pyridine, and tri-*n*-butylamine were distilled over CaH_2.

Polymerization. A typical procedure was as follows. To a solution of $Pd(OAc)_2$ (4.48 mg, 0.02 mmol), POT (12.2 mg, 0.04 mmol), and **2a** (0.598 g, 1 mmol) in 6 mL of DMF was added **1a** (0.130 g, 1 mmol) and tri-*n*-butylamine (0.740 g, 4 mmol) under Ar atmosphere. After 5 h at 100 °C, the reaction mixture was poured into 100 mL of MeOH. The precipitated polymer was filtered, washed with ether, and then dried in vacuo (a yellowish powder, 0.455 g). When the product polymer was soluble in an organic solvent, the polymer was purified by reprecipitation into ether after removal of the insoluble catalyst by filtration.

Measurement. ^1H NMR spectra were recorded on a JEOL GX-400 spectrometer (400 MHz). IR spectra were recorded on a Hitachi Model 260-50 infrared spectrophotometer. DSC analysis was carried out by employing a SEIKO DSC 200 (heating and cooling rate = 10 °C/min). All phase transition temperatures were read at the tops of the endothermic or exothermic peaks. A Nikon optical polarizing microscope equipped with a Mettler FP52 hot stage was employed for observation of thermal transition and anisotropic texture. TGA was carried out by employing a Shimazu TGC-30 (heating rate = 10 °C/min). Molecular weights of product polymers were estimated by GPC (polystyrene standards, $CHCl_3$ as an eluent, and Shodex A803 as a column). Intrinsic viscosity was measured by using the Ubbelohde viscometer.

Results and Discussion

Polycondensation. Polycondensation between equimolar amounts of 1 and 2 was carried out at 75–120 °C in DMF or pyridine in the presence of $Pd(OAc)_2/2POT$ as a catalyst and tri-*n*-butylamine as a base to produce

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