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New Polymer Syntheses. 31. Poly(4-mercaptobenzoate) and Copolyester of 4-Mercaptobenzoic Acid and Various 4-Hydroxybenzoic Acids

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ABSTRACT: Poly(4-mercaptobenzoate) with $\overline{\mathrm{DP}}$s above 200 was prepared by thermal condensation of *S*-acetyl-4-mercaptobenzoic acid at temperatures in the range 300–350 °C. Poly(4-mercaptobenzoate) is highly crystalline and insoluble in all common solvents and possesses a reversible first-order solid → solid phase transition at 366 ± 2 °C as revealed by DSC and WAXS measurements. Thermogravimetric analyses show a short-time thermostability up to ca. 410 °C. Partially crystalline copolyesters were obtained by cocondensation of *S*-acetyl-4-mercaptobenzoic acid and 4-acetoxy-, 4-acetoxy-3-bromo-, 4-acetoxy-3-chloro-, and 4-acetoxy-3-methoxybenzoic acid. WAXS patterns, IR spectra, and DSC measurements indicate that these cocondensates are neither blends of homopolyesters nor block copolyesters but copolyesters with nearly random sequences. The DSC traces of copolyesters containing 4-hydroxybenzoic acid (molar ratios 3:1, 1:1, 1:3) display reversible first-order solid–solid phase transitions, at temperatures different from those of the homopolyesters. WAXS measurements conducted with synchrotron radiation at variable temperatures indicate that the high-temperature modification of the copolyesters is almost identical with that of the parent homopolyesters. Furthermore, melting points (T_m's) in the range 380–480 °C were found; yet the melting process is in all cases accompanied by thermal degradation. Thermomechanical analyses demonstrate that the heat-distortion temperatures (HDT's) of the copolyesters may be as high as or even higher than that of poly(4-mercaptobenzoate).

Introduction

From the viewpoint of chemical structure poly(4-hydroxybenzoate), (4-Hybe)$_n$, is the ideal main-chain liquid crystal (LC) polyester. Due to the high degree of crystallinity and an extremely high (theoretical) melting point (>600 °C), it cannot be processed from the melt, because thermal degradation is too rapid at temperatures above 500 °C. In order to obtain polyesters with melting points below 400 °C the chemical structure needs to be modified in such a way that the melting enthalpy is considerably reduced and the melting entropy increased. The lattice energy, which is responsible for the melting enthalpy, is mainly based on van der Waals interactions between the aromatic rings and on the dipole moments of the ester groups. As demonstrated by Xydar,[1-3] a random sequence of monomers such as 4-Hybe, hydroquinone, 4,4′-dihydroxybiphenyl, and terephthalic acid, which prevents a regular array of dipole moments, suffices to reduce the melting point to such an extent that processing is feasible around 400 °C.

Partial and random replacement of "ether oxygens" by sulfur, i.e., random cocondensation of 4-mercaptobenzoic acid (4-Mebe) with 4-hydroxybenzoic acid (4-Hybe), might have a similar effect, because the covalent radius of the sulfur atom is significantly greater than that of oxygen. Thus, it was the purpose of the present work to study syntheses and properties of (co)polyesters containing 4-Mebe. Aromatic copolyesters containing a small percentage of 4-Mebe were claimed as thermotropic engineering plastics in a recent patent,[4] yet without any description of their properties. To the best of our knowledge poly(4-mercaptobenzoate), (4-Mebe)$_n$, and copolyesters of 4-Mebe and various 4-hydroxybenzoic acids have never been reported so far.

Experimental Section

Materials. 4-Aminobenzoic acid and 4-hydroxybenzoic acid were gifts of Bayer AG (Leverkusen, FRG) and were used without further purification. 3-Chloro- and 3-methoxy-4-hydroxybenzoic acid were purchased from Aldrich Co. (St. Louis, MO) and used without purification. 3-Bromo-4-hydroxybenzoic acid was prepared by bromination of 4-hydroxybenzoic acid in water.[5] All hydroxy acids were acetylated by means of excess acetic anhydride in boiling toluene. Marlotherm-S, a mixture of isomeric dibenzylbenzenes, was a gift of Hüls AG (Marl, FRG). It was used without further purification.

***S*-Acetyl-4-mercaptobenzoic Acid Trimethylsilyl Ester.** Crude 4-mercaptobenzoic acid was prepared from 4-aminobenzoic acid according to the procedure of ref 6 and 7. Crude 4-mercaptobenzoic acid (1.0 mol) was dissolved in a solution of 2.5 mol of potassium hydroxyde in 1.4 L of ice-water; 1.3 kg of ice and 1.25 mol of acetic anhydride were added; and the reaction mixture was shaken for 24 h at room temperature. After acidification with concentrated hydrochloric acid 0.6 mol of crude *S*-acetyl-4-mercaptobenzoic acid was isolated by filtration and dried in vacuo at 50 °C (mp 188–200 °C). This crude acid and

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Table I
Results of Polycondensation of *S*-Acetyl-4-mercaptobenzoic Acid in Marlotherm-S

no.	temp, °C	time, h	yield, %	$\overline{\mathrm{DP}}$[c]	elem anal.[d]			
						C	H	S
1	20–250	0.5	98[a]	75	found	62.32	2.94	24.93
	250	17.5	88[b]					
2	20–300	0.5	85[a]	200	found	61.84	2.95	22.95
	300	17.5	82[b]					
3	20–300	1.0	82[a]	200	found	61.46	3.08	22.41
	300	18.0	77[b]					
4	20–350	0.5	69	20	found	62.24	2.98	23.49
	350	17.0						
5	20–300	0.5						
	300	17.5	113[a]	insol	found	61.90	3.10	22.41
	400	1.0	58[b]					
6	20–400	1.0	1		found			
	400	3.5						

[a] Crude polyester after washing with dichloromethane. [b] After extraction with dry acetone. [c] ^{1}H NMR end-group analyses. [d] Calcd for $C_7H_4O_5$ (136.2): C, 61.74; H, 2.97; S, 23.54.

0.62 mol of chlorotrimethylsilane were dissolved in 1.2 L of dry toluene, and upon heating 0.62 mol of triethylamine was added dropwise under stirring. The reaction mixture was refluxed for 30 min, cooled, and filtered under exclusion of moisture. The product was isolated by distillation over a short-way apparatus under a vacuum of 0.1 mbar at bath temperatures ranging from 170 to 190 °C, yield 35%.

Anal. Calcd for $C_{12}H_{16}O_3SSi$ (268.4): C, 53.69; H, 6.02; S, 11.94. Found: C, 53.37; H, 5.62; S, 12.53. ^{1}H NMR ($CDCl_3$/TMS): δ = 0.39 (s), 243 (s), 7.45 (d, J = 8 Hz), 8.05 (d, J = 8 Hz) ppm.

***S*-Acetyl-4-mercaptobenzoic Acid.** Crude *S*-acetyl-4-mercaptobenzoic acid trimethylsilyl ester (0.35 mol) was dissolved in 1.5 L of ethyl acetate and stirred for 30 min with 1 L of 0.5 N hydrochloric acid. The organic layer was separated, dried with sodium sulfate, and concentrated in vacuo. Upon portionwise addition of ligroin three fractions of white crystalline product were obtained: fraction 1, yield 30%, mp 198–201 °C (ref 8, 202.5–203.5 °C); fraction 2, yield 50%, mp 190–199 °C; fraction 3, yield 10%, mp 187–196 °C. Anal. Calcd for $C_9H_8O_3S$ (196.2), fraction 1: C, 55.08; H, 4.12; S, 16.34. Found: C, 55.50; H, 4.11; S, 16.48.

Poly(4-mercaptobenzoate) (Table I). *S*-Acetyl-4-mercaptobenzoic acid, 100 mmol, and 100 mg of magnesium oxide were suspended in 100 mL of Marlotherm-S and heated under stirring in a nitrogen atmosphere at the temperaures given in Table I. After cooling the reaction mixture was diluted with dichloromethane; the crystalline polyester was isolated by filtration, washed with dichloromethane, and dried at 60 °C in vacuo. The crude product was finally extracted for 24 h with hot acetone in a Soxhlet apparatus and dried again.

Cocondensations. (A) *S*-Acetyl-4-mercaptobenzoic acid, 50 mmol, and 50 mmol of an acetyl hydroxy acid were condensed in 100 mL of Marlotherm-S as described above. Reaction times, temperatures, and results are summarized in Table II.

(B) *S*-Acetyl-4-mercaptobenzoic acid, 50 mmol, 50 mmol of an acetylated hydroxy acid, and 100 mg of magnesium oxide were heated under nitrogen in a 50-mL round-bottom flask with a ground-glass joint. Condensation started at ca. 250 °C and the initially formed melt of monomers gradually solidified with increasing conversion despite increasing reaction temperature (see Table III). After cooling the copolyesters were mechanically powdered, extracted with hot acetone, and dried at 60 °C in vacuo. Reaction times, temperatures, and results are summarized in Table III.

Measurements. The IR spectra were measured on a Perkin-Elmer Md 257 with KBr disks containing ca. 3 mg of polyester in 250 mg of KBr. The DSC measurements were conducted with a Perkin-Elmer DSC-4 in aluminum pans at a heating (and cooling) rate of 20 °C/min. The thermomechanical analyses (penetration method) were conducted with a Perkin-Elmer TMS-2

Table II
Cocondensation of *S*-Acetyl-4-mercaptobenzoic Acid with Various Acetylated Aromatic Hydroxy Acids in Marlotherm-S

no.	comonomer	molar[a] ratio	temp, °C	time, h	yield, %	elem formula (mol wt)	elem anal.			
								C	H	S
1	4-acetoxybenzoic acid	3:1	20–300	0.5	100[b]	$C_{14}H_8O_3S$	calcd	65.61	3.16	12.51
			300	17.0	75[c]	(256.3)	found	65.50	3.08	12.34
2	4-acetoxybenzoic acid	1:1	20–300	0.5	125[b]	$C_{28}H_{16}O_5S_3$	calcd	63.61	3.06	18.19
			300	17.0	64[c]	(528.6)	found	63.43	2.96	18.05
3	4-acetoxybenzoic acid	1:3	20–300	0.5	145[b]	$C_{28}H_{16}O_7S$	calcd	67.73	3.25	6.46
			300	17.0	73[c]	(496.5)	found	67.61	3.23	6.33
4	4-acetoxy-3-chlorobenzoic acid	1:1	20–300	0.5	84[b]	$C_{14}H_7ClO_3S$	calcd	57.84	2.43	11.03
			300	17.0	67[c]	(290.7)	found			
5	4-acetoxy-3-methoxybenzoic acid	1:1	20–300	0.5	63[b]	$C_{15}H_{10}O_4S$	calcd	62.92	3.53	11.20
			300	17.0	55[c]	(286.3)	found	62.98	3.46	11.24
6	4-acetoxybenzoic acid, 4-acetoxy-3-methoxy benzoic acid	1:1:1	20–300	0.5	91[b]	$C_{22}H_{14}O_6S$	calcd	65.01	3.48	7.89
			300	17.0	31[c]	(406.4)	found	65.23	3.19	8.99

[a] Molar ratio: *S*-acetyl-4-mercaptobenzoic acid/comonomer. [b] Crude product. [c] After extraction with acetone.

Table III
Cocondensation of *S*-Acetyl-4-mercaptobenzoic Acid with Various Acetylated Aromatic Hydroxy Acids in the Melt (MgO as Catalyst)

no.	comonomers	molar[a] ratio	temp,[b] °C	time,[b] °C	yield, %	elem formula (mol wt)	elem anal.			
								C	H	S
1	4-acetoxybenzoic acid	1:1	180, 250	0.5, 0.5	91	$C_{14}H_8O_3S$	calcd	65.61	3.15	12.51
			300, 300V	1.0, 1.0		(256.3)	found	65.76	3.09	12.35
2	4-acetoxy-3-bromobenzoic acid	1:1	150, 250	0.5, 0.5	89	$C_{14}H_7BrO_3S$	calcd	50.16	2.11	9.57
			300, 300V	1.0, 0.5		(335.2)	found	51.18	2.02	9.52
3	4-acetoxy-3-chlorobenzoic acid	1:1	180, 250	0.5, 0.5	97	$C_{14}H_7ClO_3S$	calcd	57.84	2.43	11.03
			300, 300V	1.0, 1.0		(290.7)	found			
4	4-acetoxy-3-methoxybenzoic acid	1:1	150, 250	0.5, 0.5	91	$C_{15}H_{10}O_4S$	calcd	62.92	3.53	11.20
			300, 300V	1.0, 1.0		(286.3)	found	61.60	3.40	10.40
5	4-acetoxy-3-bromo- and 4-acetoxy-3-methoxybenzoic acid	1:1:1	150, 250	0.5, 0.5	93	$C_{22}H_{13}BrO_6S$	calcd	54.44	2.71	6.61
			280, 280V	1.0, 0.3		(485.3)	found	54.03	2.73	7.00

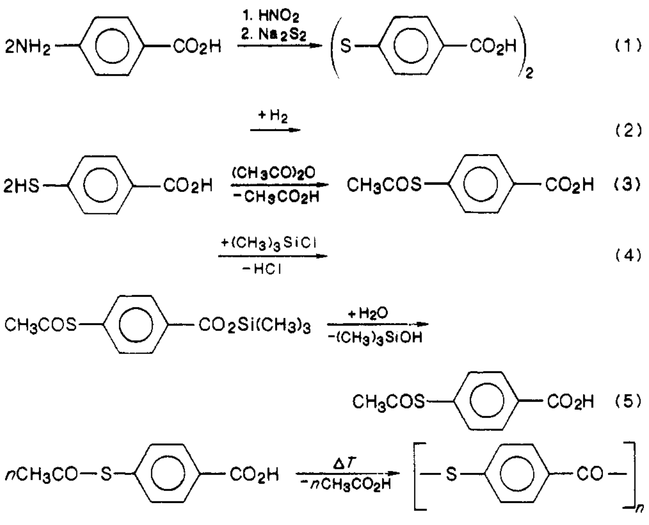
[a] Molar ratio: *S*-acetyl-4-mercaptobenzoic acid/comonomer. [b] The temperature was raised in a stepwise manner (V means vacuum). [c] Calcd for Br, 23.84%; found, 21.42. [d] Calcd for Cl, 12.19%.

under a pressure of 1 kg/mm^2 at a heating rate of 50 °C/min. The samples used for the TMA measurements were pressed to small pieces of film at a temperature of 330–340 °C under a pressure of ca. 5 MPa (50 atm) and cooled in air. The thermogravimetric analyses were conducted with a Perkin-Elmer TGS-2 at a heating rate 10 °C/min in air.

The WAXS powder patterns (e.g., Figure 6) were obtained on a Siemens D-500 diffractometer with a Cu Kα radiation and a Ni filter. For the set of slits between radiation source and scintillation detector angles of 10°, 1°, 0.1°, and 0.05° were chosen. The diagrams were recorded in steps of δ = 0.1° with a radiation time of 20 s/data point. The synchrotron radiation measurements were conducted at a wavelength of 1.50 Å with a one-dimensional position-sensitive detector at HASYLAB, DESY, in Hamburg, FRG.[9] A heating rate of 20 °C/min (in a vacuum furnace) and an accumulation time of 10 s for one powder pattern were used.

Results and Discussion

Poly(4-mercaptobenzoate). To the best of our knowledge poly(4-mercaptobenzoate), (4-Mebe)$_n$, has not been described so far. Therefore its synthesis and characterization were attempted prior to a study of its copolyesters. Because highly crystalline high molecular weight poly(4-hydroxybenzoate), (4-Hybe)$_n$, is best prepared by thermal condensation of 4-acetoxybenzoic acid in an inert reaction medium, such as Marlotherm-S,[10,11] the same approach was used for the preparation of (4-Mebe)$_n$. The synthesis of 4-Mebe and S-acetyl-4-Mebe starting from 4-aminobenzoic acid (eq 1–3) was described by several authors.[6-8] However, all attempts to reproduce these procedures yielded neither pure 4-Mebe nor pure S-acetyl-4-Mebe, despite several recrystallizations. Therefore, the crude S-acetyl-4-Mebe was silylated and the relatively pure trimethylsilyl ester isolated after distillation was hydrolyzed (eq 4 and 5). The monomer obtained in this way was sufficiently pure.



The condensation of S-acetyl-4-Mebe (eq 6) was conducted at four different temperatures between 250 and 400 °C (Table I). The crude polyester 1 which crystallized from the reaction medium was extracted with acetone to remove residual Marlotherm-S, oligomers, and byproducts. The elemental analyses and all measurements were conducted with such intensively purified samples. As expected (4-Mebe)$_n$ has many properties in common with (4-Hybe)$_n$, for instance a high degree of crystallinity, and thus, insolubility in all common solvents. Hence, crude information on the molecular weights was only obtainable by ^{1}H NMR end-group analysis of the acetyl group after hydrolysis of the polyester in an NMR tube.[10] The results indicate that high molecular weights (M_n > 100) require reaction temperatures ≥ 300 °C. However, both yields and elemental analyses demonstrate that prolonged heating at 400 °C leads to substantial degradation. In other words, optimum condensation conditions require temperatures in the range 300–350 °C. The lower thermostability of (4-Mebe)$_n$ compared to (4-Hybe)$_n$ is also evident in thermogravimetric analyses. In contrast to (4-Hybe)$_n$, (4-Mebe)$_n$ displays a step in its degradation curve (Figure 1). The origin of this stepwise degradation could not be elucidated.

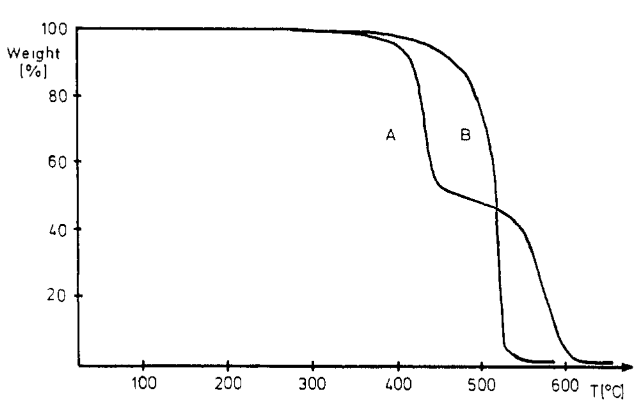


Figure 1. Thermogravimetric analyses of (A) poly(4-mercaptobenzoate) (no. 2, Table I) and (B) poly(4-hydroxybenzoate)[9] measured at a heating rate of 10 °C/min in air.

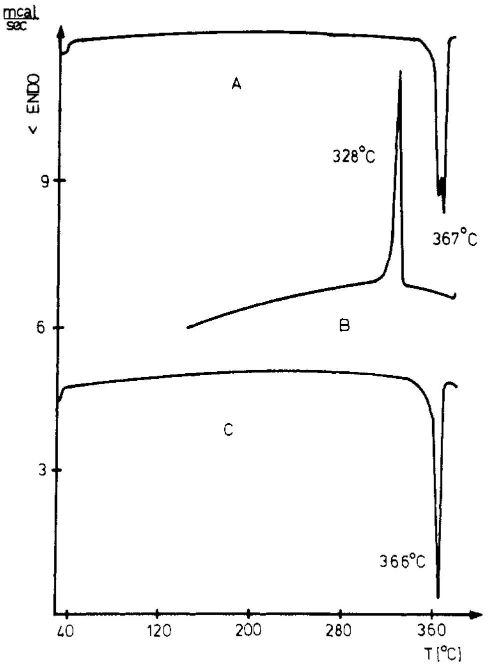


Figure 2. DSC traces of poly(4-mercaptobenzoate) (no. 3, Table I) measured at a heating (cooling) rate of 20 °C/min: (A) first cooling; (C) second heating.

DSC measurements revealed a reversible first-order transition with an endotherm at 366 ± 2 °C and an exotherm at 328 ± 2 °C, when a heating and cooling rate of 20 °C/min was applied (Figure 2). Observation under the polarizing microscope revealed that this first-order transition does not indicate a melting process, because the samples remained solid above 370 °C. Thus, this solid → solid transition is closely analogous to that described for poly(4-Hybe).[1,10-12]

This conclusion was confirmed by WAXS measurements in the temperature range 30–430 °C (Figure 3). These measurements were conducted by means of synchrotron radiation at a heating rate of 20 °C/min, so that a WAXS pattern was taken every 30 s. The plot of Figure 3 dem-

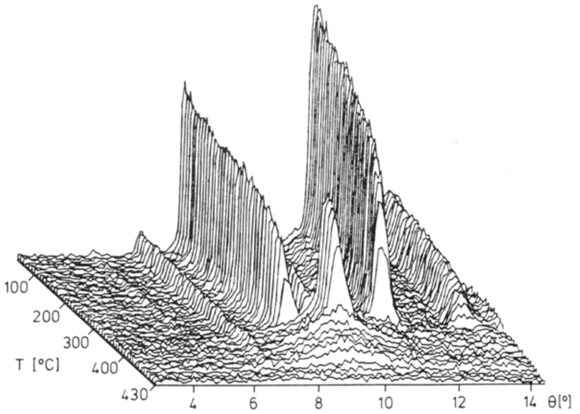


Figure 3. WAXS powder patterns of poly(4-mercaptobenzoate) (no. 3, Table I), measured with synchrotron radiation at a heating rate of 20 °C/min.

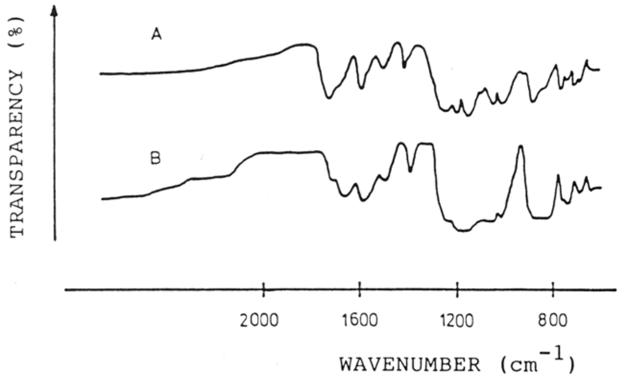
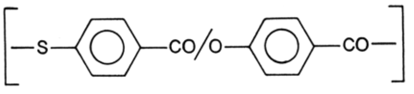


Figure 4. IR spectra (measured in KBr) of (A) the blend of poly(4-Hybe) and poly(4-Mebe), molar ratio 1:1, and (B) 1:1 copolyester (**2b**) of 4-Hybe and 4-Mebe (no. 2, Table II).

onstrates that the three strong reflections of the low-temperature modification of poly(4-Mebe) at $\vartheta = 9.6°$, 12.8°, and 13.9° disappear between 365 and 370 °C. Above 370 °C two reflections are detectable, a weak one at $\vartheta = 6.7°$ and a strong one at $\vartheta = 9.5°$ (Figure 3). Above 400 °C these reflections fade away due to thermal degradation. When poly(4-Hybe) was measured with synchrotron radiation under identical conditions, again a weak reflection at $\vartheta = 6.9°$ and a strong reflection at $\vartheta = 9.7°$ was found.[1,13] The similarity of these reflections suggests that the high-temperature modification of poly(4-Mebe) and poly(4-Hybe) are nearly identical. The slight differences result from the greater covalent radius of sulfur compared to oxygen.

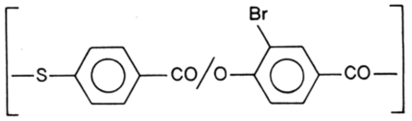
The high-temperature modification of both homopolyesters is most likely a pseudohexagonal packing of chains,[14] where individual aromatic rings or chain segments have sufficient space to rotate around the σ-bonds in the para position. The reflections at $\vartheta = 9.5°$ or 9.7° represent the lateral distances needed to allow rotation of the aromatic rings, at least as a cooperative process or after slight distortion of neighboring chains. Typical for the higher segmental mobility in the high-temperature modification of poly(4-Hybe) is the greater specific volume,[1] the ductility under high pressure,[1] and the occurrence of chemical reactions, such as transesterification.[10,11] On the other hand, this high-temperature modification may not be called a liquid-crystalline phase, because three arguments contradict this designation. First, the WAXS reflections of the high-temperature modification of poly(4-Mebe) and poly(4-Hybe) are as sharp as those of the low-temperature modifications. Second, the materials recovered from the aluminum pans used for DSC-measurements up to 400 °C are powders and not a molten mass. Third, no liquefaction is observable under the microscope, even when slight shear forces are applied.

Copolyesters: Synthesis and Spectroscopic Characterization. *S*-Acetyl-4-Mebe was cocondensed with the following monomers: 4-acetoxybenzoic acid; 4-acetoxy-3-bromobenzoic acid; 4-acetoxy-3-chlorobenzoic acid; 4-acetoxy-3-methoxybenzoic acid. By means of these comonomers the binary copolyesters **2a–c** and **3–5** were prepared along with the ternary copolyester **6**. Two series of cocondensations were conducted (Tables II and III). For the first series of condensations an inert, liquid reaction medium (Marlotherm-S) was used, whereas the condensation of the second series was conducted in the melt with magnesium oxide as catalyst. Regardless of the reactions all copolyesters were highly crystalline and insoluble in all common solvents, so that characterization in solution was not feasible. Hence, NMR spectroscopic evidence for the formation of more or less random sequences could not be obtained, since the ^{13}C NMR CP/MAS spectra of solid copolyesters did not exhibit any sequence effects.



2a-c

2a, molar ratio 3:1
b, molar ratio 1:1
c, molar ratio 1:3



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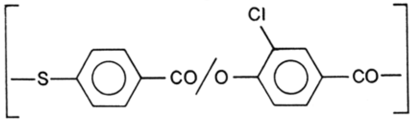

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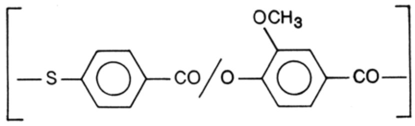

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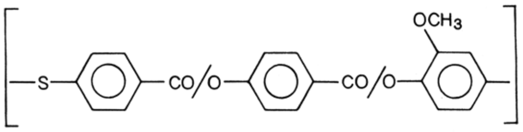

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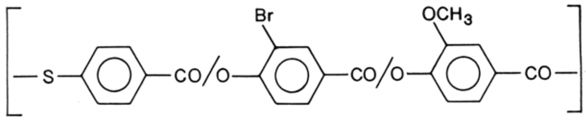

7

In order to obtain clear evidence whether the alleged copolyesters are true copolyesters with a more or less random sequence, the copolyesters **2a–c** were compared with the parent homopolyesters by three methods: IR spectroscopy, WAXS, and DSC measurements. As demonstrated in Figure 4, a comparison of the 1:1 copolyester **2b** with a blend of the homopolyesters yielded two different IR spectra. It is, for example, characteristic for the copolyesters that the C=O stretch vibration of the 4-Hybe units (1720 cm^{-1}) is reduced in intensity relative to the C=S stretch vibration (1630 cm^{-1}) in contrast to the homopolyesters. This observation was confirmed by the comparison of copolyesters **2a**, **2b**, and poly(4-hydroxy-

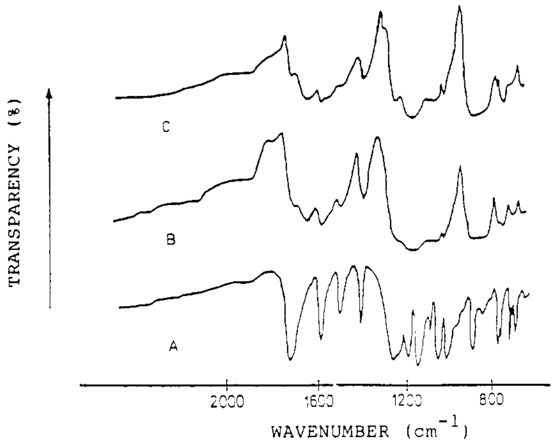

Figure 5. IR spectra (measured in KBr) of (A) poly(4-hydroxybenzoate), (B) 1:1 copolyester **2b**, and (C) 1:3 copolyester **2c**.

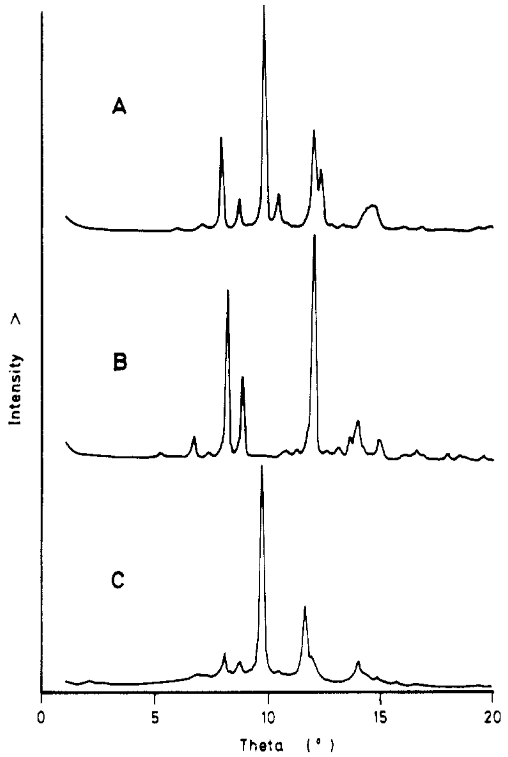

Figure 6. WAXS powder patterns measured at 25 °C: (A) poly(4-Hybe), ref 9; (B) poly(4-Mebe) no. 2, Table I; (C) 1:1 copolyester **2b** (no. 2, Table II).

benzoate) shown in Figure 5. Furthermore, the C=O and C=S vibrations are not resolved in the spectrum of the blend, whereas both are separately observable (although poorly resolved) in the spectra of the copolyesters. The IR spectra of copolyester **2b** and the blend of poly(4-Hybe) and poly(4-Mebe) display additional differences in the fingerprint region. Thus the IR spectra suggest that the copolyesters **2a–c** do not possess a blocky sequence.

The WAXS powder patterns are less informative in this respect (Figure 6). The WAXS pattern of the 1:1 copolyester might well result from a superposition of the patterns of both homopolyesters. Nonetheless, Figure 6 also demonstrates that the crystal lattices of the low-temperature modifications of poly(4-Hybe) and poly(4-Mebe) are quite different from their high-temperature modifications. Another interesting result of the WAXS measurements concerns the degree of crystallinity. Because both IR spectroscopy and DSC measurements (see below) indicate that the copolyesters **2a–c** and **3–5** are true copolyesters, it is noteworthy that neither the WAXS patterns of the copolyesters prepared in Marlotherm-S nor those obtained by bulk condensation display an amorphous halo (Figure 6B). This observation suggests that the copolyesters like the homopolyesters possess an unusually high degree of crystallinity (>50%). Similar results were obtained for copolyesters of 4-Hybe and substituted 4-hydroxybenzoic acids.[15] Furthermore, it should be emphasized that according to the WAXS patterns, copolyesters prepared in Marlotherm-S and by bulk condensation possess almost identical degrees of crystallinity.

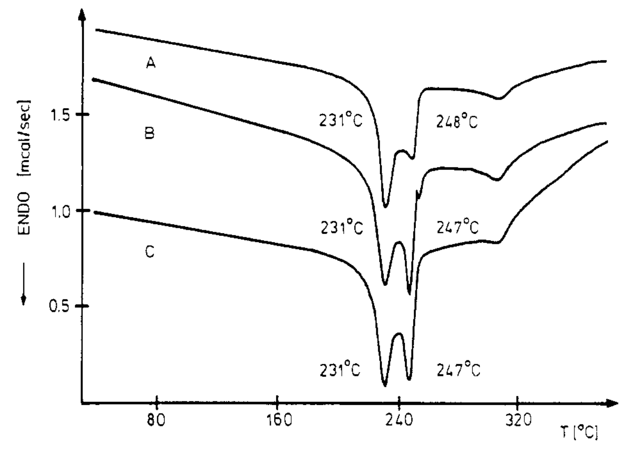

Figure 7. DSC traces of the 1:1 copolyester **2b** (no. 2, Table II) measured at a heating (cooling) rate of 20 °C/min: (A) second heating after slow cooling; (B) third heating after annealing for 15 min at 245 °C; (C) fourth heating after quenching with liquid nitrogen.

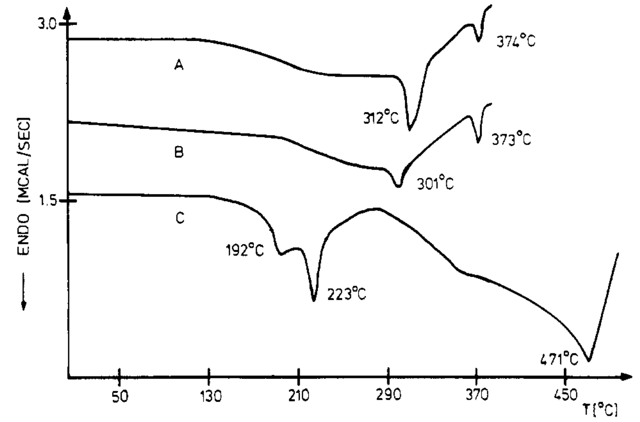

Figure 8. DSC traces (heating and cooling rate 20 °C/min) of (A) first heating of 3:1 copolyester **2a** (no. 1, Table II), (B) second heating of 3:1 copolyester **2a** (no. 1, Table II), and (C) first heating of 1:3 copolyester **2c** (no. 3, Table II).

Thermal Properties of Copolyesters. DSC measurements of the copolyesters **2a–c** conducted at a heating rate of 20 °C/min revealed the following features. At least two endotherms are detectable in the heating traces of all samples (Figures 7–9). Yet, whereas those endotherms are relatively sharp and conspicuous in the DSC traces of samples prepared in Marlotherm-S (Figures 7 and 8), they are barely detectable in the heating curve of the sample **2b** prepared by bulk condensation (curve B in Figure 9). This finding indicates that the synthesis procedure has an influence on the supermolecular structure of these copolyesters, although the WAXS pattern are almost identical.

Repeated heating and cooling of the copolyesters **2a–e** between 30 and 380 °C revealed that the endotherms are reproducible, even though the temperature and intensity (or transition enthalpy) of the transition change slightly

Table IV
Thermal Properties of Homo- and Copolyesters of 4-Mercaptobenzoic Acid (4-MeBe)

no.	(co)polyester (molar ratio)	synth method	T_m(dec),[a] °C	HDT,[b] °C	wt loss at the given temp, °C[c]			
					5%	10%	20%	50%
1	(4-Mebe)$_n$	no. 2, Table I		318	400	419	430	475
2	(4-Mebe)$_n$	no. 4, Table I			408	423	432	504
3	(4-Mebe/4-Hybe)$_n$ (3:1) (**2a**)	no. 1, Table II	444	315	400	420	430	505
4	(4-Mebe/4-Hybe)$_n$ (1:1) (**2b**)	no. 1, Table III	412 ± 2	356–364	404	423	431	516
5	(4-Mebe/4-Hybe)$_n$ (1:3) (**2c**)	no. 3, Table II	471 ± 1	345	412	427	439	524
6	(4-MeBe/3-bromo-4-Hybe) (**3**)	no. 3, Table III		170	355	375	395	516
7	(4-Mebe/3-chloro-4-Hybe) (**4**)	no. 4, Table II		187				
8	(4-Mebe/3-methoxy-4-Hybe) (**5**)	no. 6, Table II	385 ± 2	151–155	320	363	380	455
9	(4-Mebe/4-Hybe/3-methoxy-4-Hybe) (**6**)	no. 6, Table II		207				
10	(4-Mebe/3-bromo4-Hybe/3-methoxy-4-Hybe) (**7**)	no. 5, Table III		340				

[a] From DSC measurements with a heating rate of 20 °C/min. [b] From thermomechanical analyses with a heating rate of 10 °C/min and a pressure of 1 kg/mm². [c] From thermogravimetrical analyses with a heating rate of 10 °C/min in air.

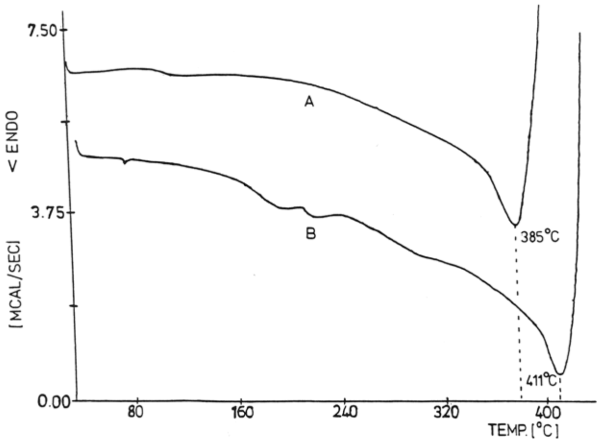

Figure 9. DSC traces (heating rate 20 °C/min): (A) first heating of the copolyester **5** prepared from 3-methoxy-4-hydroxybenzoic acid (no. 5, Table III); (B) first heating of the 1:1 copolyester **2b**, prepared by bulk condensation (no. 1, Table III).

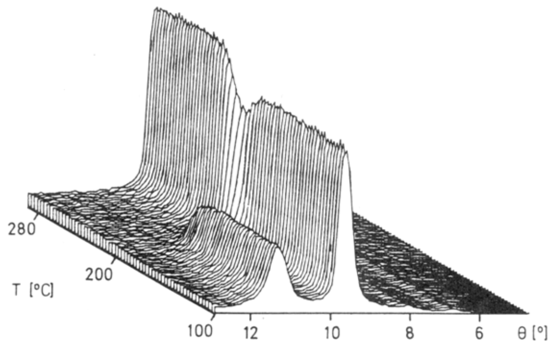

Figure 10. WAXS powder patterns of the 1:1 copolyester **2b** (no. 2, Table II) measured with synchrotron radiation at a heating rate of 20 °C/min.

after the first heating (Figures 7 and 8). The temperatures of the corresponding phase transitions depend on the composition of the copolyesters and have a minimum at the ratio 1:3 (**2c**) (curve C in Figure 8). In order to elucidate the nature of these phase transitions, WAXS powder patterns of **2b** (no. 2, Table II) were measured by synchrotron radiation between 100 and 300 °C. At a heating rate of 20 °C/min a picture was taken every 10 s (Figure 10). These X-ray measurements display the existence of a weak reflection at 6.8° and a sharp, intensive reflection at 9.6° at temperatures above the phase transition. Obviously this copolyester adopts the same high-temperature modification as the parent homopolyesters. The depression of this phase transition by approximately 100 °C suggests that the copolyesters **2a–c** possess more or less random sequences. However, even in the case of an overall randomness of composition and sequence, a certain degree of chemical heterogeneity and block length distribution may exist between individual chains. This heterogeneity may explain why two phase transitions are detectable in all DSC traces of **2a–c**. In this connection it is again worth noting that the samples recovered from the DSC measurements were powdery and that no liquefaction was observable under the microscope. Thus, it is evident that also the phase transitions of the copolyesters do not indicate the formation of a nematic melt.

In the case of copolyesters **3–7** a weak endotherm was detectable in the first heating trace of **4** (no. 4, Table II), whereas all other DSC measurements demonstrated the absence of reversible phase transition. This result is not surprising, because even the homopolyesters of substituted 4-hydroxybenzoic acids do not undergo reversible changes of modification.[11] To the best of our knowledge, any detailed study of the crystal structure of substituted poly(4-hydroxybenzoates) is lacking so far. Therefore, no further interpretation of these results can be given at the current state of affairs.

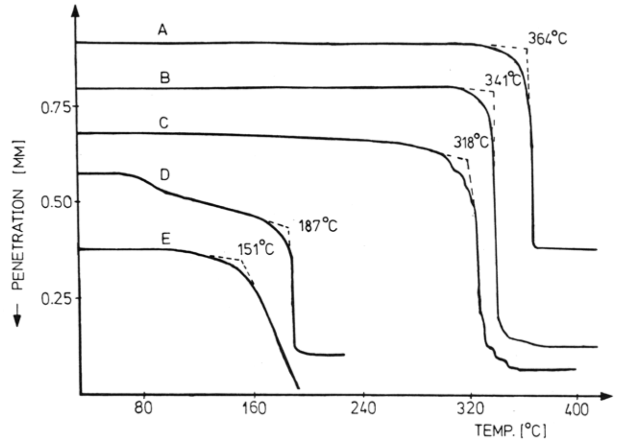

Figure 11. Thermomechanical analyses conducted and a pressure of 1 kg/mm² at a heating rate of 5 °C/min: (A) 1:1 copolyester **2b** (no. 1, Table II); (B) ternary polyester **8** (no. 3, Table III); (C) poly(4-mercaptobenzoate) (no. 3, Table I); (D) copolyester **4** (no. 4, Table II); (E) copolyester **5** (no. 6, Table II).

In addition to reversible solid–solid transitions, the DSC traces of copolyesters **2–7** exhibit endotherms of a true melting process (Figure 9 and curve C in Figure 8). Unfortunately, the melting process is in all cases accompanied by severe thermal degradation and thus never represents a thermodynamically controlled phase equilibrium. Nonetheless, the T_m values listed in Table IV demonstrate that incorporation of sulfur into the chain of poly(4-Hybe) effects the expected depression of the melting point. Introduction of substituents such as bromine or methoxy groups lowers the melting point further; yet all these structural modifications also reduce the thermostability of these polyesters. This destabilizing effect of the substituents is also evident from the thermogravimetric measurements summarized in Table IV. Thus, mechanical processing from the melt (e.g., extrusion) is not feasible without the risk of thermal degradation, and the copolyesters of 4-Mebe are not well suited as thermotropic engineering plastics. This conclusion is supported by the observation that the bulk condensations (Table IV) never yielded stirrable melts. Even in the case of the terpolyesters **6** and **7** the reaction mixtures solidified, when vacuum was applied at the final reaction temperature of 320 °C.

Despite the high melting points of poly(4-Mebe) and its copolyesters, small pieces of coherent films could be pressed at temperatures between 320 and 340 °C when a pressure of 5 MPa was maintained for several minutes. At first glance this result is surprising, yet it should be kept in mind that the experimental temperatures were either above or at least close to the temperature of the first-order transitions where the more mobile high-temperature modification is formed. Under high pressure a small fraction of mobile chains may have a lubricating effect, and thus, a complete phase transition is obviously not necessary for deformation under high pressure.

The coherent, though brittle, films were used for thermomechanical analyses by the penetration method. A pressure of ca. 10 MPA (1 kg/mm^2, comparable with the "Vicat-A" test) was applied at a heating rate of 10 °C/min. The heat-distortion temperatures (HDT's) listed in Table IV demonstrate, on the one hand, that indeed all homo- and copolyesters yield to high pressure at temperatures below the true melting points. On the other hand, it is interesting to see that the HDT's of the copolyester **2a–c** and even of the terpolyester **7** are as high or higher than the HDT of the homopolyester. These high HDT's are clearly a consequence of the high degrees of crystallinity of all samples.

In this connection it is worth noting that the HDT's of the copolyester **2a–c** are also significantly higher than their first-order transitions. This result is another clearcut argument against a nematic nature of the high-temperature modification. The exact HDT's slightly depend on temperature and time used for the preparation of the films (no. 4 and 8, Table IV). Several copolyesters (no. 6–9, Table IV) showed relatively low HDT's, presumably close to their T_g's which were not measurable by DSC. Interestingly, in three cases (**2b**, **4**, and **5**) a comparison of samples prepared by bulk condensation and solution condensation revealed that the HDT's may largely depend on the synthetic procedure. HDT's above 300 °C were found for the products of bulk condensations but HDT's below 200 °C for the products of solution condensations. Obviously, the synthetic procedure modifies the morphology which in turn influences the mechanical properties. However, a thorough study of these complex relationships was beyond the scope of this work.

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Registry No. *S*-Acetyl-4-mercaptobenzoic acid trimethylsilyl ester, 115797-41-6; 4-mercaptobenzoic acid, 1074-36-8; *S*-acetyl-4-mercaptobenzoic acid, 24197-62-4; chlorotrimethylsilane, 75-77-4; *S*-acetyl-4-mercaptobenzoic acid (homopolymer), 115797-61-0; *S*-acetyl-4-mercaptobenzoic acid (SRU), 51325-00-9; (*S*-acetyl-4-mercaptobenzoic acid)(4-acetoxybenzoic acid) (copolymer), 115797-62-1; (*S*-acetyl-4-mercaptobenzoic acid)(4-acetoxy-3-chlorobenzoic acid) (copolymer), 115797-63-2; (*S*-acetyl-4-mercaptobenzoic acid)(4-acetoxy-3-methoxybenzoic acid) (copolymer), 115797-64-3; (*S*-acetyl-4-mercaptobenzoic acid)(4-acetoxybenzoic acid)(4-acetoxy-3-methoxybenzoic acid) (copolymer), 115797-65-4; (*S*-acetyl-4-mercaptobenzoic acid)(4-acetoxy-3-bromobenzoic acid) (copolymer), 115797-66-5; (*S*-acetyl-4-mercaptobenzoic acid)(4-acetoxy-3-bromobenzoic acid)(4-acetoxy-3-methoxybenzoic acid) (copolymer), 115797-67-6.

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