New Polymer Syntheses. 50. Whiskers of Poly(4-hydroxybenzoate) by Condensation of Trimethylsilyl 4-Acetoxybenzoate

Hans R. Kricheldorf,* Gert Schwarz, and Frank Ruhser

Institut für Technische und Makromolekulare Chemie der Universität, Bundesstrasse 45, D-2000 Hamburg 13, FRG

Received November 1, 1990; Revised Manuscript Received January 24, 1991

ABSTRACT: Polycondensations of various aprotic derivatives of 4-hydroxybenzoic acid were conducted in Marlotherm-S at 350 or 400 °C. The following potential monomers were studied: phenyl 4-(trimethylsiloxy)-benzoate; trimethylsilyl 4-(trimethylsiloxy)benzoate; ethyl 4-acetoxybenzoate; phenyl 4-acetoxybenzoate; trimethylsilyl 4-acetoxybenzoate. Only the latter monomer gave acceptable yields (up to 60%) of poly(4-hydroxybenzoate). When concentration, reaction time, and temperature were varied, a whiskerlike morphology was found under most circumstances. Slablike crystals were never found even at a high monomer concentrations (0.4 mol/L). Hydrolysis, DSC, and WAXS measurements prove that the whiskers prepared at 400 °C represent chemically and physically rather perfect crystals of poly(4-hydroxybenzoate), whereas those obtained at 350 °C are physically less perfect. At 400 °C fibrous whiskers with lengths above 100 μm and aspect ratios up to 100:1 can be synthesized.

Introduction

The standard method for the synthesis of high molecular weight poly(4-hydroxybenzoate) (polyHBA) is the polycondensation of 4-acetoxybenzoic acid in an inert liquid reaction medium at temperatures in the range 300–400 °C.[1-6] It was recently demonstrated[7] that this polycondensation process involves several types of side reactions, such as formation of diphenyl ether groups, Fries rearrangement, evolution of ketene, etc. Some of these side reaction are most likely catalyzed by acidic protons. 4-Acetoxybenzoic acid and acetic acid are weak acids when measured in water at room temperature, but they are certainly much more acidic above 300 °C in a nonbasic solvent.

It was also found that difunctional byproducts of the polycondensation process may poison the crystal growth of whiskerlike crystals, which represent the chemically and physically most perfect crystals of polyHBA.[7-9] Therefore, it was purpose of the present work to look for a synthesis of polyHBA that proceeds in the absence of acidic protons and to study its usefulness for the preparation of long thin whiskers (length/diameter ratios ≥ 50:1). Such whiskers may be of interest as reinforcing fibers for other matrix polymers. The synthesis of short needlelike polyHBA crystals with a length of a few micrometers was first reported by Tsay et al.[10] Thick columnar whiskers with lengths in the range 10–40 μm were later described by a research group of Toyobo Co.[6,8]

Experimental Section

Materials. 4-Hydroxybenzoic acid and ethyl and phenyl 4-hydroxybenzoate were gifts of Bayer AG (Krefeld-Uerdingen, FRG). They were derivatized without further purification. Acetylation was achieved with an excess of acetic anhydride and a catalytic amount of pyridine in refluxing toluene. Silylation was conducted with trimethylchlorosilane and triethylamine in refluxing toluene. Synthesis and properties of trimethylsilyl 4-(trimethylsiloxy)benzoate were reported.[11] Marlotherm-S, a mixture of isomeric dibenzylbenzenes, was a gift of Huels AG. It was distilled in vacuo.

Trimethylsilyl 4-Acetoxybenzoate. 4-Acetoxybenzoic acid (0.5 mol) was suspended in dry toluene (800 mL) and triethylamine (1.05 mol) was added. This mixture was heated with stirring and trimethylchlorosilane (1.05 mol) was added dropwise. Finally the reaction mixture was refluxed for 2 h, cooled with ice, and filtered under exclusion of moisture. The product was isolated by distillation in vacuo. Yield, 85%; η^{20}_D, 1:4921; bp 104–106 °C (0.05 mbar). Anal. Calcd for $C_{12}H_{16}O_4Si$ (252.34): C, 57.12; H, 6.39. Found: C, 56.71; H, 6.37.

Polycondensations. Trimethylsilyl 4-acetoxybenzoate (10, 20, or 40 mmol) was dissolved in 95 mL of dry Marlotherm-S, and this mixture was immersed into a metal bath preheated to 280–300 °C (using a two- or three-necked glass vessel). The temperature was then rapidly raised to 350 or 400 °C. Finally the reaction mixture was cooled and diluted with acetone and the precipitated polyHBA was isolated by filtration and washed several times with hot acetone.

Measurements. DSC traces were measured at a heating rate of 20 °C/min with a Perkin-Elmer DSC-4 in aluminum pans under nitrogen. WAXS powder patterns were obtained from a Siemens D-500 powder refractometer using Ni-filtered Cu Kα radiation. SEM micrographs were obtained on a Leitz AMR 1600 T instrument with an acceleration potential of 10 kV. All samples were coated with gold on a Balzers SC-040 instrument.

Results and Discussion

Syntheses. The following five aprotic derivatives of 4-hydroxybenzoic acid were subjected to polycondensation: ethyl 4-acetoxybenzoate (**1a**), phenyl 4-acetoxybenzoate (**1b**), trimethylsilyl 4-acetoxybenzoate (**1c**), phenyl 4-(trimethylsiloxy)benzoate (**2a**), and trimethylsilyl 4-(trimethylsiloxy)benzoate (**2b**). It has been previously demonstrated[7,12] chemically and physically almost perfect whiskers of polyHBA may be prepared at high reaction temperatures (e.g., 350 or 400 °C) provided that the reaction time is optimized. Since the reactivity of the aprotic monomers **1a–c** and **2a,b** is lower than that of 4-acetoxybenzoic acid, polycondensations were only conducted at 350 and 400 °C.

The reaction conditions used for polycondensation of **1a,b** and **2a,b** are listed in Table I. The results clearly indicate that these "monomers" are not reactive enough to give satisfactory yield and molecular weights of polyHBA. Significantly better results were obtained from silylated 4-acetoxybenzoic acid (eq 1). The data listed in Table II show that yields up to 60% may be obtained, but in most cases yields were below 50%. From this point of view polycondensations of the free acid (eq 2) are more successful because yields in the range of 70–80% may be obtained.[7] However, the morphology of polyHBA resulting

0024-9297/91/2224-3485$02.50/0

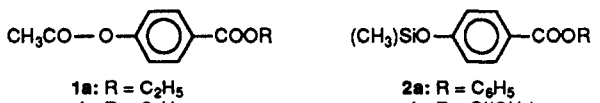
Table I
Polycondensations of Various Aprotic Derivatives of 4-Hydroxybenzoic Acid

no.	monomer	concn, M	temp, °C	time, h	yield, %
1	ethyl 4-acetoxybenzoate	0.1	350	16	0
2	ethyl 4-acetoxybenzoate	0.1	400	4	0
3	ethyl 4-acetoxybenzoate	0.1	400	8	0
4	phenyl 4-acetoxybenzoate	0.1	350	16	0
5	phenyl 4-acetoxybenzoate	0.1	400	8	0
6	phenyl 4-acetoxybenzoate	0.2	350	16	0
7	phenyl 4-acetoxybenzoate	0.2	400	8	0
8	phenyl 4-acetoxybenzoate	0.4	350	16	0
9	phenyl 4-acetoxybenzoate	0.4	400	8	3
10	phenyl 4-(trimethylsiloxy)-benzoate	0.1	350	16	0
11	phenyl 4-(trimethylsiloxy)-benzoate	0.1	400	8	0
12	phenyl 4-(trimethylsiloxy)-benzoate	0.2	350	16	0
13	phenyl 4-(trimethylsiloxy)-benzoate	0.2	400	8	0
14	phenyl 4-(trimethylsiloxy)-benzoate	0.4	350	16	6
16	phenyl 4-(trimethylsiloxy)-benzoate	0.4	400	8	7
17	trimethylsilyl 4-(trimethylsiloxy)benzoate	0.1	350	16	0
18	trimethylsilyl 4-(trimethylsiloxy)benzoate	0.1	400	8	0
19	trimethylsilyl 4-(trimethylsiloxy)benzoate	0.2	350	16	0
20	trimethylsilyl 4-(trimethylsiloxy)benzoate	0.2	400	8	0

Table II
Polycondensations of Trimethylsilyl 4-Acetoxybenzoate in Marlotherm-S

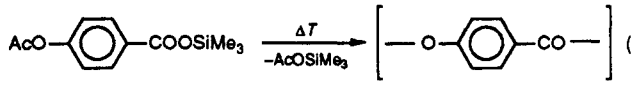
no.	monomer concn, M	temp, °C	time, h	yield, %	morphology
1	0.05	350	16	35	needlelike whiskers
2	0.1	350	16	38[a]	fibrous whisker
3	0.1	400	2	32	needlelike whiskers
4	0.1	400	4	39	needlelike
5	0.1	400	8	42[b]	needlelike whiskers
6	0.2	350	4	33	leaflike
7	0.2	350	8	46	seaweedlike
8	0.2	350	16	59	seaweedlike
9	0.2	400	2	48	fibrous whiskers
10	0.2	400	4	35	fibrous whiskers
11	0.2	400	8	37	fibrous whiskers
12	0.4	350	4	36	leaflike
13	0.4	350	16	53[c]	seaweedlike
14	0.4	400	2	39	fibrous whiskers
15	0.4	400	4	44	fibrous whiskers
16	0.4	400	6	38	fibrous whiskers

[a] DP = 110 by end-group analysis. [b] DP = 105 by end-group analysis. [c] DP = 130 bp end-group analysis.

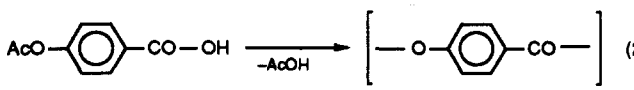


1a: R = C_2H_5
b: R = C_6H_5
c: R = $Si(CH_3)_3$

2a: R = C_6H_5
b: R = $Si(CH_3)_3$



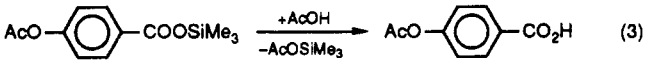
(1)



(2)

from the polycondensation of 4-acetoxybenzoic acid at concentrations ≥0.1 M is different from that obtained by condensation of **1c**.

When 5 mol % of 4-acetoxybenzoic acid is added to the reaction mixture, reaction rate and yield slightly increase. This result is obvious, because the 4-acetoxyenzoic acid is considerably more reactive and because the liberated acetic acid may generate additional 4-acetoxybenzoic acid by desilylations of **1c** (eq 3). However, this result does



(3)

not give any information on the reaction mechanism that is operating when pure trimethylsilyl 4-acetoxybenzoate is condensed at temperatures ≥350 °C. A direct interaction of silyl ester and acetoxy groups via a cyclic or ionic transition state may be involved.

For a proper understanding of this new polycondensation method the following observations are important. Rigorous exclusion of OH groups by silanization of the glass walls and distillation of Marlotherm-S under nitrogen did not show a significant effect. Chloride ions (1 mol % relative to monomer) added in the form of benzyltriethylammonium chloride did not show a catalytic effect. When dibutyltin dimethoxide or titanium(IV) butoxide were added to a polycondensation of **1c** at 350 °C (16 h, 1 M), the reaction mixture turned black and a low yield of deeply colored material was isolated. When 4-acetoxybenzoic acid was condensed at 350 or 400 °C, various additives had a negative influence on the crystal growth of whiskers.[7] For all these reasons the synthesis of the whiskers described below was conducted with pure **1c**.

Further results that may help to characterize the polycondensation process of **1c** were obtained from polycondensations of silylated terephthalic acid. When this monomer was heated with 4,4′-dihydroxybiphenyl or silylated 4,4,′-dihydroxybiphenyl (concentration 0.2 M) in Marolotherm-S at 400 °C for 4 h no polyester was formed. In contrast, crystalline poly(biphenylene terephthalate) was isolated in a yield of 71%, when 4,4′-diacetoxybiphenyl was used as reaction partner under the same conditions.

These results and those of Tables I and II clearly indicate that a successful polycondensation of monomers with silylated carboxyl group requires an acetylated phenol group as reaction partner. Further studies on the synthesis of polyarylates from silylated carboxylic acids will be described in a future part of this series.

Characterization. Several samples of polyHBA isolated from the polycondensation of **1c** were subjected to ^1H NMR end-group analyses. This method, described previously,[3] provides a crude estimation of the average degree of polymerization ($\overline{DP}$). The results listed in footnotes of Table II indicate that polycondensations of **1c** indeed yield polyHBA with $\overline{DP}$'s above 100.

Optical microscopy and scanning electron microscopy (SEM) revealed the most interesting result of this work: whiskerlike crystals were formed under most reaction condition, in particular at high conversions (e.g., after 8–16 h at 350 °C or after 2 h at 400 °C). At 400 °C reaction times longer than 8 h were not taken into consideration to avoid thermal degradation. The formation of whiskers at monomer concentrations of 0.4 mol/mL (approximately 10 wt %) indicates that the silylation of the monomer reduced side reactions. Polycondensations of the free acid never gave whiskers at concentrations >0.3 M[6-8,12] and long fibrous whiskers were only obtained at concentrations ≤0.05 M.[7]

A closer inspection of the crystals isolated from the condensations listed in Table II revealed the following

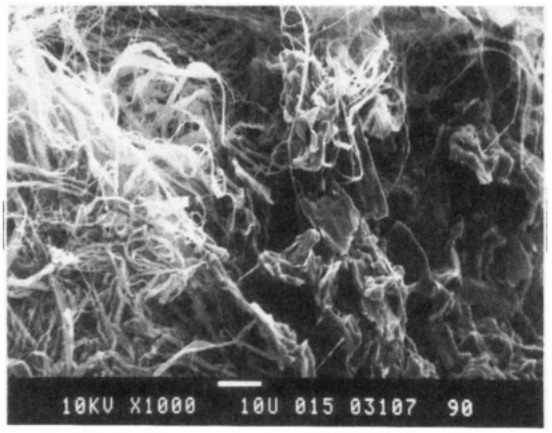


Figure 1. SEM micrograph of polyHBA isolated from condensation of **1c** (0.4 mol/L) at 350 °C for 16 h (no. 13, Table II).

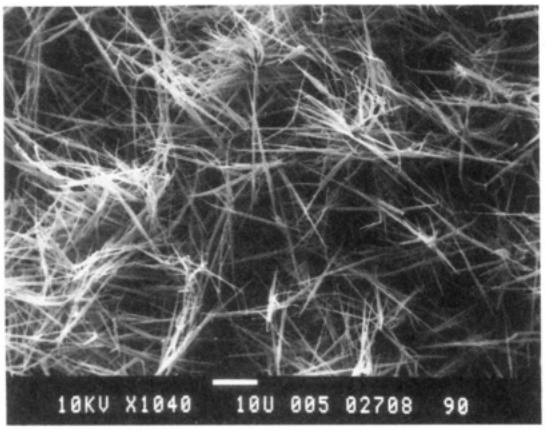


Figure 2. SEM micrograph of polyHBA isolated from condensation of **1c** (0.1 mol/L) at 400 °C for 4 h (no. 4, Table II).

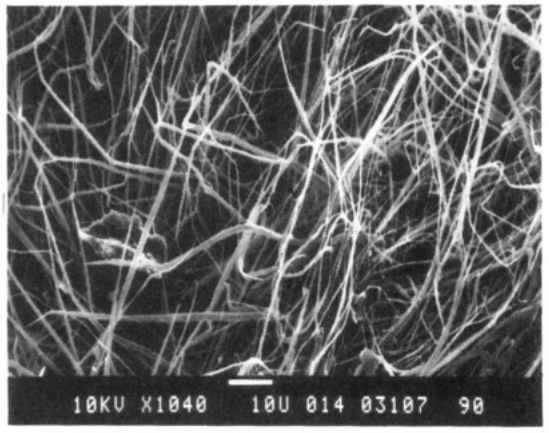


Figure 3. SEM micrograph of polyHBA isolated from condensation of **1c** (0.4 mol/L) at 400 °C for 4 h (no. 15, Table II).

tendencies. When the polycondensation of **1c** was conducted at 350 °C, needlelike crystals were formed at the lowest concentrations of 0.05 M and long reaction times (16 h). At 0.1 M and higher concentrations needles are replaced by fibrous whiskers and/or a "seaweedlike" morphology (Figure 1). At short reaction times (≤4 h) a leaflike or lamellar morphology is observable. When the polycondensation of **1c** was conducted at 400 °C, again long needlelike crystals were formed at the lowest concentration (0.1 M, see Figure 2). These needles may have lengths of around 20–40 μm and a thickness of ca. 1 μm. At higher concentrations long, thin fibers are formed with lengths above 100 μm and diameters of 1–3 μm (Figure 3). The reaction time does not have a significant influence on the morphology, when times of ≥8 h at 350 °C and ≥2 h at 400 °C are considered.

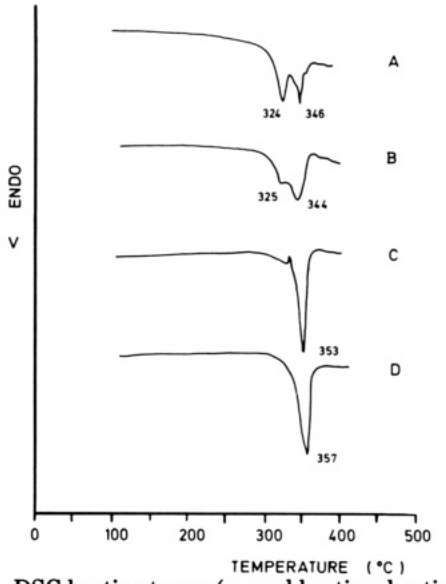


Figure 4. DSC heating traces (second heating, heating rate 20 °C/min) of polyHBA: (A) condensation 4 h/350°C/0.2 M (no. 6, Table II); (B) condensation 8 h/350 °C/0.2 M (no. 7, Table II); (c) condensation 2 h/400 °C/0.1 N (no. 3, Table II); (D) condensation 8 h/400 °C/0.1 M (no. 5, Table II).

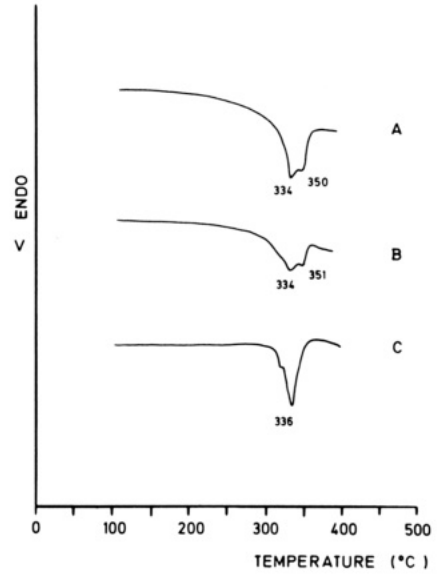


Figure 5. DSC heating traces (second heating, heating rate 20 °C/min) of polyHBA: (A) condensation 16 h/350 °C/0.05 M (no. 1, Table II); (B) condensation 16 h/350 °C/0.01 M (no. 2, Table II); (C) condensation 16 h/350 °C/0.04 M (no. 13, Table II).

Most samples were also characterized by DSC measurements conducted at a heating rate of 20 °C/min. As demonstrated for the polycondensation of 4-acetoxybenzoic acid,[7-12] the shape and temperature of the first endotherm (α-transition) are sensitive to the perfection of the crystallites and, thus, to the reaction conditions. The second endotherm at 440 °C is not useful for analytical purposes, because it is too weak and because repeated heating (and cooling) to 470–480 °C causes partial decomposition of the sample.

The DSC measurements revealed that nearly perfect crystallites with one sharp endotherm at 356 ± 2 °C (Figure 4C,D) were only obtainable by polycondensations at 400 °C. Reaction times ≥2 h and variation of the concentration (0.1–0.4 M) do not show a significant influence on the DSC traces. Due to the lower reactivity of the trimeth-

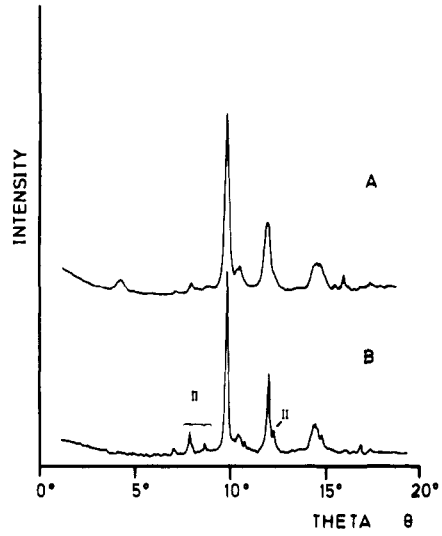


Figure 6. WAXS powder pattern of polyHBA: (A) condensation 4 h/350 °C/0.2 M (no. 6, Table II); (B) condensation 2 h/400 °C/0.4 M (no. 14, Table II).

ylsilyl ester compared to free 4-acetoxybenzoic acid, perfect crystallites with only one sharp endotherm were never obtained at 350 °C. At this lower temperature both time and concentration play a role. At short reaction times the α-endotherm appears at 323 ± 2 °C with a shoulder or second peak at 336–346 °C (Figures 4A and 5). The second peak (or shoulder) increases at the expense of the low-temperature endotherm with increasing reaction time (Figure 4B). Lower monomer concentrations favor the formation of perfect crystallites, as indicated by the intensity of the endotherm around 350 °C in Figure 5. This tendency may be explained by a slower crystal growth at low concentrations. This tendency also fits in with the results of Japanese authors,[8] who isolated needlelike whiskers from polycondensations of 4-acetoxybenzoic acid at 330 °C at low concentrations (<0.1 mol/L).

The WAXS powder patterns seem to be less sensitive to a variation of the reaction conditions, but they confirm the conclusions drawn from the DSC measurements. The reflections of a sample prepared at 350 °C (4 h; 0.2 M, see Figure 6A) are by 20–40% broader than those of whiskers prepared at 400 °C (Figure 6B). The greater line width of all reflections suggests that the crystallites prepared at 350 °C are conformationally and positionally disordered. Also in the case of 4-acetoxybenzoic acid it was observed that condensations conducted for 2–4 h at 400 °C favor the formation of rather perfect whiskers. However, it is worth noting that changes of the morphology not directly parallel the physical perfection of crystallites. The present work and previous results obtained with 4-acetoxybenzoic acid demonstrate that the successful growth of whiskers also depends on the absence of reactive impurities and byproducts.

Conclusions

The above discussed results indicate that the polycondensation of trimethylsilyl 4-acetoxybenzoate deviates from that of the free acid in three points. First, the reactivity is significantly lower, the yields of polyHBA are lower, and higher reaction temperatures (≥350 °C) are required. Second, the slablike crystals typical of the polycondensation of 4-acetoxybenzoic acid in concentrated solutions (>0.2 M) were never formed. Third, long thin fibers (aspect ratios up to 100:1), never reported before, can be obtained from polycondensations at 400 °C with high monomer concentrations. Such whiskers are of particular interest as reinforcing fibers in other matrix polymers.

References and Notes

(1) Economy, J.; Storm, R. S.; Matkovich, M. T.; Cottis, S. G.; Nowak, B. E. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2207.
(2) Economy, J.; Cottis, S. G.; Nowak, B. E., Carborundum Co. Ger. Offen 2055948, 1970; *Chem. Abstr.* **1971**, *74*, 54559k.
(3) Kricheldorf, H. R.; Schwarz, G. *Makromol. Chem.* **1983**, *184*, 475.
(4) Kricheldorf, H. R.; Schwarz, G. *Polymer* **1984**, *25*, 520.
(5) Lieser, G.; Schwarz, G.; Kricheldorf, H. R. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1599.
(6) Endo, S.; Kimura, K.; Ohta, T.; Kato, Y., Toyobo Co. U.S. Patent 4,673,724, 1987
(7) Kricheldorf, H. R.; Ruhser, F.; Schwarz, G. *Makromol. Chem.*, in press.
(8) Yamashita, Y.; Kato, Y.; Endo, S.; Kimura, K. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 687.
(9) Kricheldorf, H. R.; Schwarz, G. *Polymer* **1990**, *31*, 481.
(10) Tsay, J.; Volksen, W.; Economy, J. *Polym. Prepr.* **1982**, *23* (1), 266.
(11) Schwarz, G.; Alberts, H.; Kricheldorf, H. R. *Liebigs Ann. Chem.* **1981**, 1257.
(12) Taesler, C.; Petermann, J.; Kricheldorf, H. R.; Schwarz, G. *Makromol. Chem.*, submitted for publication.

Registry No. Marlotherm-S, 26898-17-9; phenyl 4-(trimethylsiloxy)benzoate, 133472-78-3; trimethylsilyl 4-(trimethylsiloxy)benzoate, 2078-13-9; ethyl 4-acetoxybenzoate, 13031-45-3; phenyl 4-acetoxybenzoate, 24262-65-5; trimethylsilyl 4-acetoxybenzoate, 133472-79-4; poly(4-hydroxybenzoate), 133472-80-7; poly(4-hydroxybenzoate) (SRU), 26099-71-8.