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POLYANHYDRIDES. XI. POLY(ESTER-ANHYDRIDE)S DERIVED FROM 4-HYDROXYBENZOIC ACID, VANILLIC ACID, AND ALIPHATIC DICARBOXYLIC ACIDS

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ABSTRACT

Poly(ester-anhydride)s, PEA's, built up by 50 mol% ester and 50 mol% anhydride groups were prepared by polycondensation of 0,0'-bistrimethylsilyl 4-hydroxybenzoic acid and various α,ω -alkane-dicarbonylchlorides. The polycondensations were conducted either in bulk or in 1-chloronaphthalene. High yields (up to 94%) were obtained under both reaction conditions, but the higher inherent viscosities resulted from polycondensations in 1-chloronaphthalene. IR- and ^{13}C NMR spectroscopy revealed that reaction temperatures above 200°C cause side reactions such as transacylation and transesterification. Analogous series of polycondensations were conducted with 0,0'-bistrimethylsilyl vanillic acid. The resulting PEA's were amorphous, whereas the PEA's derived from 4-hydroxybenzoic acid are semicrystalline.

INTRODUCTION

In recent years, the interest and research activities in any kind of more or less biodegradable polymers have strongly increased. The two groups of biodegradable polymers which have already found application and are also most promis-

ing for the future are: firstly, polylactones, particularly polyesters of lactic acid, and secondly, starch and starch derivatives. A third group of polymers which may be useful for special applications are polymers containing anhydride groups. Numerous polyanhydrides were synthesized and characterized over the past five decades [1-5]. However, most polyanhydrides described so far, are homopolymers which possess several characteristic disadvantages, with regards to any practical application:

- 1) they are highly crystalline and insoluble in most, if not all, inert solvents
- 2) they are difficult to process from the melt, because of rapid degradation
- 3) they are highly sensitive to hydrolysis, and the rate of hydrolytic degradation is difficult to adjust to the requirements of potential applications.

These difficulties can be overcome by syntheses of poly(ester-anhydride)s, in particular, by those copolyesters containing a variable amount of anhydride groups. In most previous parts of this series [7-11] we have reported on fully aromatic poly(ester-anhydride)s. The present work describes poly(ester-anhydride)s based on 4-hydroxy benzoic acid or vanillic acid, on the one hand, and aliphatic dicarboxylic acids, on the other hand. The aromatic hydroxy acids, were selected as comonomers, because they raise the glass-transition temperature (T_g) and because they occur in the human metabolism, and thus, are harmless degradation products [6].

EXPERIMENTAL

Materials

The aliphatic dicarboxylic acid dichlorides were purchased from Aldrich Co. (Milwaukee, Wisc.) and purified by distillation. 4-Hydroxybenzoic acid and vanillic acid were gifts of Bayer AG. They were silylated with an excess of hexamethyl-disilazane in refluxing toluene [7] and were described in previous publications [7, 12, 13].

Polycondensations

A) *In Bulk*

A silylated hydroxyacid (20 mmol), dicarboxylic acid dichloride (20 mmol) and benzyltriethylammonium chloride (10 mg) were weighed into a cylindrical glass reactor equipped with stirrer, gas-inlet and gas-outlet tubes. The reaction vessel was placed into an oil bath preheated to 110°C. The temperature was then raised in steps of 20°C according to the progress of the polycondensation. The liberated chlorotrimethylsilane was removed with a slow stream of nitrogen. The reaction mixtures

TABLE 1. Polycondensations of Silylated 4-Hydroxybenzoic Acid and Aliphatic Diacid Dichlorides in Bulk

Polym No.	Dicarboxylic acid dichloride	Temp [°C]	Time [h]	Yield ^{a)} [%]	η_{inh}^b [dl/g]	Tg ^{c)} [°C]	Tm ^{c)} [°C]	Elem. formula (Form. weight)	Elemental analyses C H	
1a	adipoyl chloride	110	4.5	89	0.18	23	56	C ₁₃ H ₁₂ O ₅ (248.23)	Calcd 62.90 Found 61.70	4.87 5.01
1b	suberoyl chloride	180	4	91	0.36	21	61	C ₁₅ H ₁₆ O ₅ (276.29)	Calcd 65.21 Found 64.51	5.84 5.96
1c	sebacoyl chloride	200	4	92	0.27	18	65	C ₁₇ H ₂₀ O ₅ (304.34)	Calcd 67.10 Found 67.05	7.30 6.69
1d	dodecandioyl chloride	240	4	94	0.37	21	64	C ₁₉ H ₂₄ O ₅ (332.39)	Calcd 68.66 Found 68.10	7.30 7.38

^{a)} Yields of crude reaction products

^{b)} Measured in CH₂Cl₂ at 20°C with c=2g/l

^{c)} From DSC measurements with a heating rate of 20°C/min (first heating)

were kept at the maximum temperature (see Table 1) for at least 0.5 hours *in vacuo*. The total time required for these polycondensations was in the order of 4-6 hours, depending on the reactivity of the dichloride. The crude polyanhydrides were mechanically isolated after cooling and characterized as crude materials.

B) In 1-Chloronaphthalene

A silylated hydroxy acid (20 mmol), a dicarboxylic acid dichloride (20 mmol) and benzyltriethylammonium chloride (10 mg) were weighed into a 50 ml three-necked round bottom flask and dissolved in dry 1-chloronaphthalene (15 ml). The reaction vessel was placed in an oil bath preheated to 110°C. The temperature was raised in steps of 20°C according to the progress of the polycondensation and the maximum temperature was maintained for several hours (see Tables 2 and 4). The liberated chlorotrimethylsilane was removed with a slow stream of nitrogen. Finally the cold reaction mixture was diluted with CH₂Cl₂ (50 ml) and precipitated into cold diethyl ether (500 ml). The dried polymer was again dissolved in CH₂Cl₂, precipitated into cold diethylether and dried at 40°C *in vacuo*.

Measurements

The inherent viscosities were measured with an automated Ubbelohde viscometer, thermostated at 20°C.

The IR-spectra were recorded on a Nicolet SXB-20 FT IR spectrometer.

The 100 MHz ¹H NMR spectra were recorded on a Bruker AC-100 FT NMR spectrometer in 5 mm o.d. sample tubes.

The 25.4 MHz ¹³C NMR spectra were recorded with the same spectrometer in 10 mm o.d. sample tubes. Internal TMS served for shift referencing in all cases.

The DSC measurements were conducted with a Perkin Elmer DSC-7 in aluminum pans under nitrogen.

The WAXD powder patterns were recorded with a Siemens D-500 diffractometer using CuK_α-radiation.

RESULTS AND DISCUSSION

Syntheses

As reported in previous publications [7, 8], aromatic poly(ester-anhydride)s derived from 4-hydroxybenzoic acids were easily obtained by polycondensation of the silylated 4-hydroxybenzoic acid with dicarboxylic acid dichlorides. Therefore, all syntheses were conducted in such a way that 0,0'-bistrimethylsilyl 4-

TABLE 2. Polycondensations of Silylated 4-Hydroxybenzoic Acid and Aliphatic Diacid Dichlorides in 1-Chloronaphthalene.

Polym No.	Dicarboxylic acid dichloride	Temp [°C]	Time [h]	Yield ^{a)} [%]	η_{inh}^b [dl/g]	T _g ^{c)} [°C]	T _m ^{c)} [°C]	Elem. formula (Form. weight)	Elemental analyses C H	
1a'	adipoyl chloride	110	6	90	0.18	25 23 ^{d)}	(78)123 172 ^{d)}	C ₁₃ H ₁₂ O ₅ (248.23)	Calcd 62.90 Found 61.84	4.87 5.05
1b'	suberoyl chloride	180	8	94	0.33	24 26 ^{d)}	(78)144 (64)156 ^{d)}	C ₁₅ H ₁₆ O ₅ (276.29)	Calcd 65.21 Found 64.75	5.84 5.91
1c'	sebacoyl chloride	200	24	92	0.61	20	74 - 70 ^{d)}	C ₁₇ H ₂₀ O ₅ (304.34)	Calcd 67.10 Found 67.08	7.30 6.62
1d'	dodecandiyl chloride	250	8	89	0.66	20	65	C ₁₉ H ₂₄ O ₅ (332.39)	Calcd 68.66 Found 67.45	7.30 7.41

a) Yields of crude reaction products

b) Measured in CH₂Cl₂ at 20°C with c=2g/l

c) From DSC measurements with a heating rate of 20°C/min (first heating)

d) From DSC second heating curves

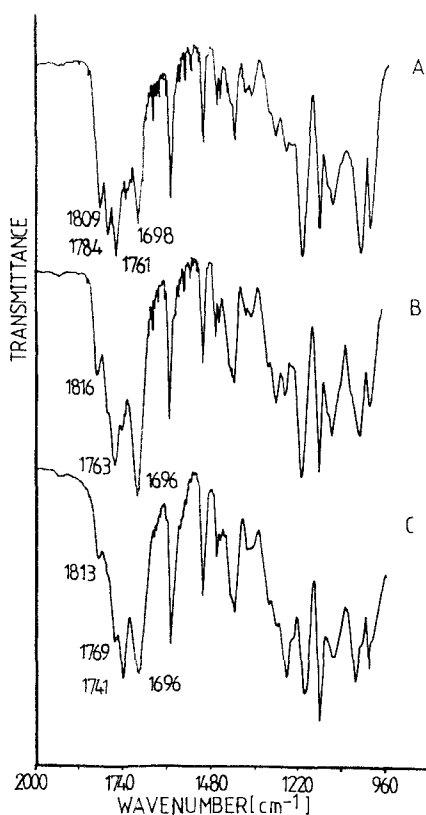


Figure 1. IR-spectra (films cast on NaCl) of the poly(ester-anhydride)s **1d** prepared at different reaction temperatures: A) 200°C, B) 240°C, C) 280°C.

hydroxybenzoic acid or *O,O'*-bistrimethylsilyl vanillic acid were reacted with α,ω -alkane dicarbonyl dichlorides (Equation 1). From previous syntheses of polyesters and poly(ester-anhydride)s [7, 8], it was clear that chloride ions were needed as catalysts. Furthermore, it was known that a temperature of 100°C was required as minimum reaction temperature. Therefore, the only open question was the maximum reaction temperature.

In order to find the upper limit of the reaction temperature three polycondensations of silylated 4-hydroxybenzoic acid with sebacoyl chloride were conducted in bulk (method A), so that the final reaction temperature was limited to 200°C, 240°C or 280°C. The product (**1c**) obtained at 280°C was not completely soluble in CHCl_3 or tetrahydrofuran, and thus, NMR spectra were not recorded. The IR-spectra (Figure 1), and the ^{13}C NMR spectra (Figure 2) proved that significant

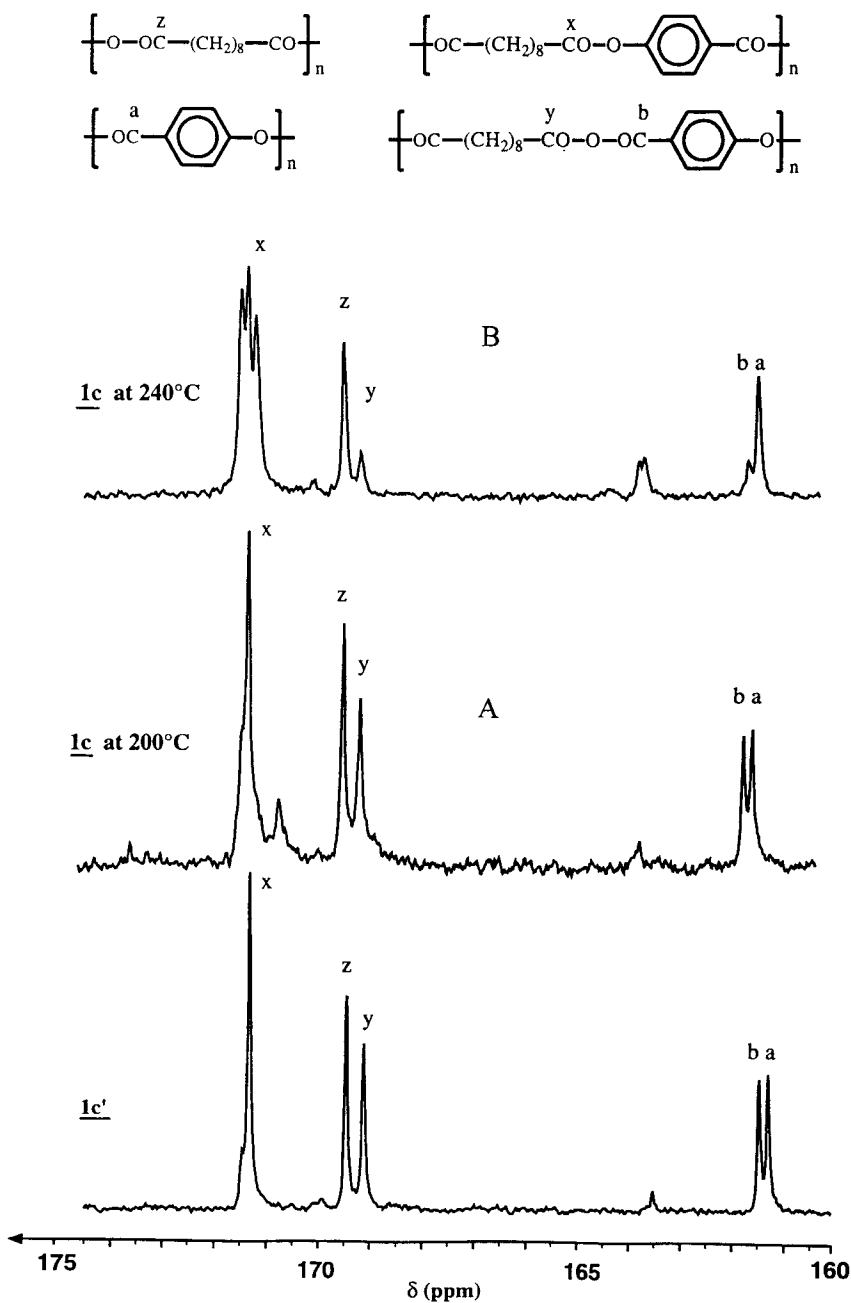
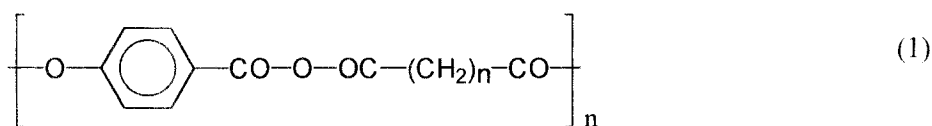
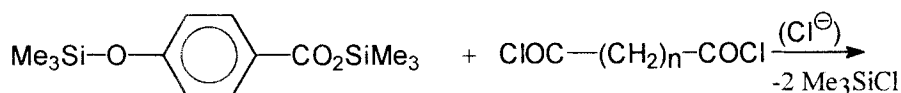


Figure 2. 25.4 MHz ^{13}C NMR spectra of poly(esteranhydrides) **1c**: A) prepared at 200°C, B) prepared at 240°C.

side reactions occurred at 240 and 280°C. At 200°C, only acyl interchange reactions had occurred in agreement with previous studies of other polyanhydrides 9. The IR spectra of the PEA's prepared at 200°, 240°, or 280° showed that the CO-bands of the anhydride groups at $1811\pm 5\text{cm}^{-1}$, $1782\pm 5\text{cm}^{-1}$ and $1765\pm 5\text{cm}^{-1}$ loose intensity with increasing reaction temperature. However, the side reaction responsible for this trend were not elucidated. When other dicarboxylic acid dichlorides were used, it was learned from repeated polycondensations that the maximum temperature which could be used to prevent major side reactions depends largely on the reactivity of the dicarboxylic acid chloride. Whereas 240°C was still useful in the case of dodecane-diyl dichloride the temperature had to be lowered to 110°C in the case of succinyl chloride. The reaction conditions and the results of the most successful polycondensation experiments conducted in bulk are compiled in Table 1.



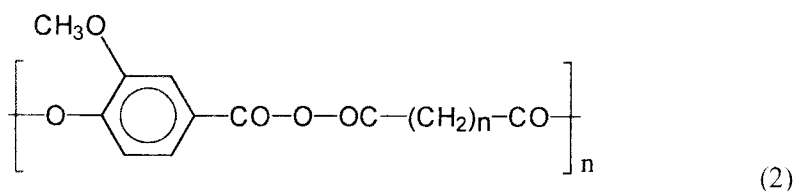
1 a - d

a: n = 4

b: n = 6

c: n = 8

d: n = 10



2 a - e

a: n = 2

b: n = 4

c: n = 6

d: n = 8

e: n = 10

An analogous series of polycondensations was conducted in 1-chloronaphthalene which is a good inert solvent for numerous polyesters. The reaction condition and results are summarized in Table 2. Despite the lower concentration of the reactants higher molecular weights (viscosities) were obtained for the PEA's 1**b**-1**d**. In the case of 1**a'** the inherent viscosity was the same as that of 1**a** prepared in bulk. A comparison of the PEA's prepared by methods A or B also revealed that the yields, the elemental analyses and the ^1H NMR spectra were nearly identical. More detailed information was extracted from the ^{13}C NMR spectra (Figures 2 and 3). As demonstrated previously[14, 15] the CO-signals are particularly sensitive to sequence effects and may indicate transacylation and transesterification reactions. In the case of 1**c** and 1**d** the counterparts 1**c'** and 1**d'** gave nearly the same spectra as illustrated in Figure 2. These ^{13}C NMR spectra proved that the polycondensations were accompanied by intensive transacylation reactions, so that an equilibrium between homo- and heteroanhydride groups was obtained. However, significant differences were detectable when 1**a** was compared with 1**a'** or 1**b** with 1**b'** (Figure 3). Whereas the spectra of 1**a** and 1**b** resembled those of 1**c** and 1**d**, the spectra of 1**a'** and 1**b'** indicated that further interchange reactions (most likely transesterification) had occurred. The spectrum of 1**b'** prepared at 180°C resembled the spectrum of 1**b**, when prepared at 240°C (Figure 2). Particularly conspicuous is the reduced concentration of the mixed anhydride groups. As discussed below, these differences in the chemical structure have consequences for the properties of 1**a'** and 1**b'**.

Two more series of PEA's (2**a**-2**e** and 2**a'**-2**e'**) were prepared by polycondensation of silylated vanillic acid with aliphatic dicarboxylic acid dichlorides. Again method A and method B were applied, and the reaction conditions and results compiled in Tables 3 and 4. High yields were obtained by both methods. With exception of 1**a'** the elemental analyses were satisfactory in both series, and the ^1H NMR spectra were identical. The inherent viscosities did not show a clear tendency. Slightly higher values were obtained by method A for 2**b** and 2**e**, whereas method B gave higher values for 2**c'** and 2**d'**. Furthermore, the ^{13}C NMR spectra of both series of PEA's were nearly identical. Transacylation had occurred in all polycondensations. A trend towards additional interchange reactions was detectable for the more reactive acid chlorides.

Thermal Properties

All PEA's were subjected to DSC measurements with a heating and cooling rate of 20°C/min. A somewhat surprising result was found for the PEA's derived from 4-hydroxybenzoic acid, because all those PEA's proved to be semicrystalline

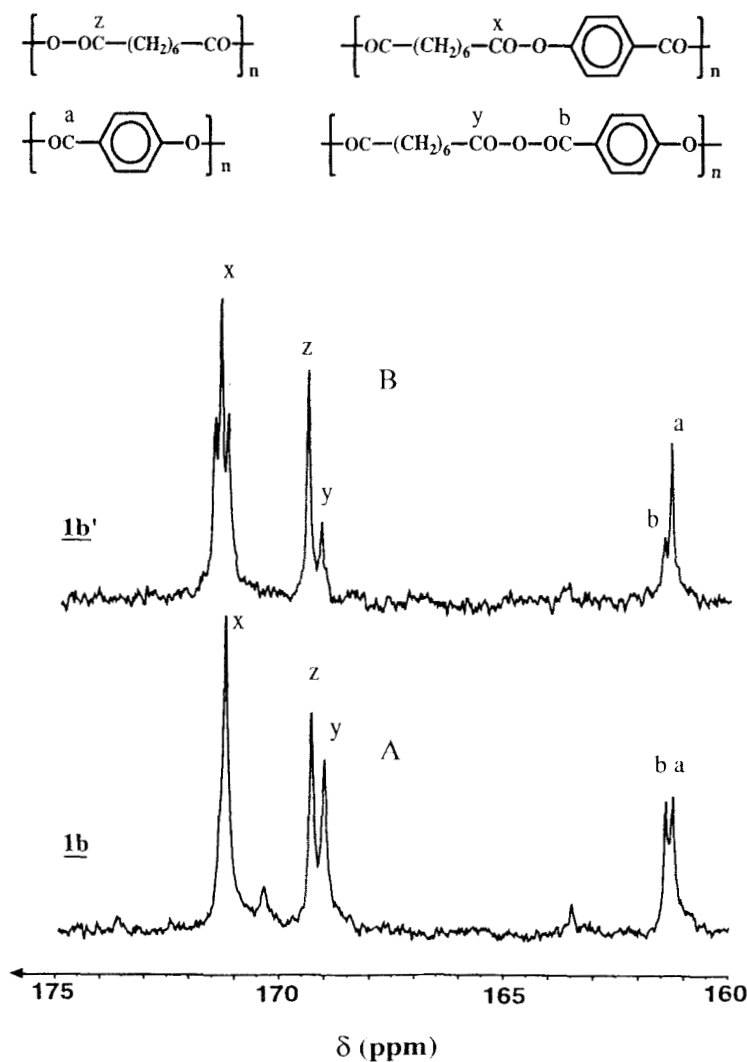


Figure 3. 25.4 MHz ^{13}C NMR spectra of A) PEA 1b and B) PEA 1b'.

regardless of the synthetic method. One melting endotherm in the temperature range of 56–65°C was observable in the first heating curve of 1a–1d, the intensity of which was reduced in the second heating trace. Furthermore, the glass-transition steps (Tg's) were found in the temperature range of 18–23°C. Surprisingly, no clear-cut trend toward lower Tg's or Tm's was detectable, when dicarboxylic acid with longer aliphatic chains were used for the syntheses. Whereas, the Tg's of the PEA's 1a'–1d' were similar to these of 1a–1d the Tm's of 1b'–1d' interesting deviations. Not

TABLE 3. Polycondensations of Silylated Vanillic Acid and Aliphatic Diacid Dichlorides in Bulk.

Polym No.	Dicarboxylic acid dichloride	Temp [°C]	Time [h]	Yield ^{a)} [%]	η_{inh}^b [dl/g]	Tg ^{c)} [°C]	Tm ^{c)} [°C]	Elem. formula (Form. weight)	Elemental analyses C H	
2a	succinyl chloride	110	8	85	0.12	40	-	C ₁₂ H ₁₀ O ₆ (250.21)	Calcd 57.65 Found 58.35	4.03 5.82
2b	.adipoyl chloride	110	8	91	0.18	24	-	C ₁₄ H ₁₄ O ₆ (278.26)	Calcd 60.43 Found 61.03	5.07 5.61
2c	suberoyl chloride	180	6	91	0.36	9	-	C ₁₆ H ₁₈ O ₆ (306.31)	Calcd 62.74 Found 61.03	5.92 6.12
2d	sebacoyl chloride	200	6	89	0.27	3	-	C ₁₈ H ₂₂ O ₆ (304.34)	Calcd 64.66 Found 63.51	6.63 6.64
2e	dodecandioyl chloride	240	4.5	95	0.37	3	-	C ₂₀ H ₂₆ O ₆ (362.42)	Calcd 66.28 Found 66.51	7.23 7.32

a) Yields of crude reaction products

b) Measured in CH₂Cl₂ at 20°C with c=2g/l

c) From DSC measurements with a heating rate of 20°C/min (first heating)

TABLE 4. Polycondensations of Silylated Vanillic Acid and Aliphatic Diacid Dichlorides in 1-Chloronaphthalene.

Polym No.	Dicarboxylic acid dichloride	Temp [°C]	Time [h]	Yield ^{a)} [%]	η_{inh}^b [dl/g]	Tg ^{c)} [°C]	Tm ^{c)} [°C]	Elem. formula (Form. weight)	Elemental analyses C H	
2a'	succinyl chloride	110	8	83	0.13	57	-	C ₁₂ H ₁₀ O ₆ (250.21)	Calcd 57.65 Found 55.52	4.03 4.81
2b'	.adipoyl chloride	110	12	88	0.16	22	-	C ₁₄ H ₁₄ O ₆ (278.26)	Calcd 60.43 Found 59.61	5.07 5.33
2c'	suberoyl chloride	180	12	96	0.40	13	-	C ₁₆ H ₁₈ O ₆ (306.31)	Calcd 62.74 Found 62.64	5.92 6.02
2d'	sebacoyl chloride	200	24	91	0.49	12	-	C ₁₈ H ₂₂ O ₆ (304.34)	Calcd 64.66 Found 64.07	6.63 6.73
2e'	dodecandioyl chloride	240	8	88	0.34	4	-	C ₂₀ H ₂₆ O ₆ (362.42)	Calcd 66.28 Found 66.28	7.23 7.14

v

a) Yields of crude reaction products

b) Measured in CH₂Cl₂ at 20°C with c=2g/l

c) From DSC measurements with a heating rate of 20°C/min (first heating)

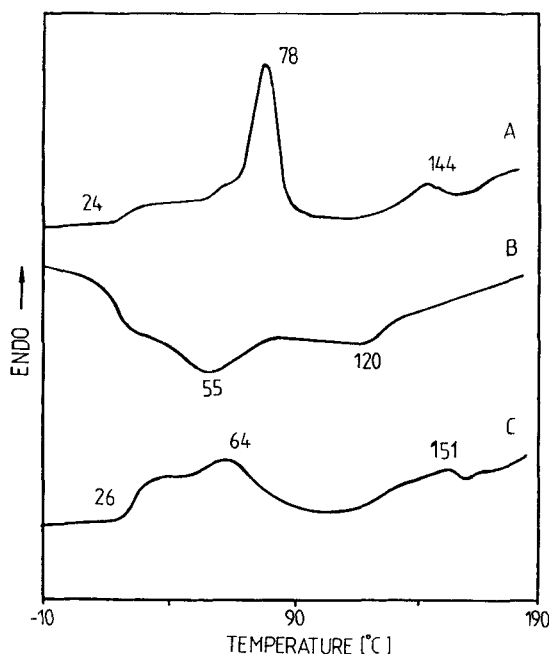
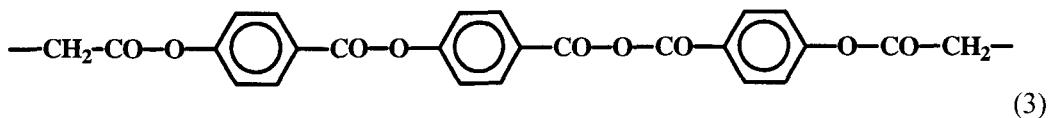


Figure 4. DSC measurements (heating/cooling rate 20°C/min) of PEA 1b' prepared in 1-chloronaphthalene: A) first heating, B) first cooling, C) second heating.

only was the strongest melting endotherm shifted to higher temperatures (70–80°C), a second, albeit weaker endotherm was present in the heating traces of 1a' and 1b'. (Figure 4). This difference (when compared with 1a and 1b) is also reflected in the WAXS powder patterns. As illustrated by Figure 5, the crystallinity of 1a' and 1b' was higher than that of 1a and 1b. A speculative explanation of these results is based on the assumption that 1a' and 1b' contains dimmeric blocks of 4-hydroxybenzoic acid (Equation 3) resulting from transesterification.



Both DSC measurements and WAXS powder patterns of all PEA's prepared from vanillic acid proved that these polymers are completely amorphous. In contrast to the thermal properties of the PEA's of 4-hydroxybenzoic acid and the

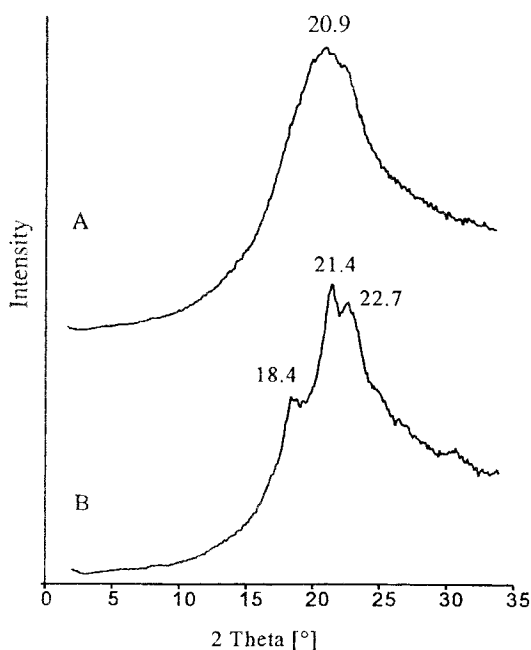


Figure 5. WAXD powder pattern of: A) PEA 1a prepared in bulk, B) PEA 1a' prepared in 1-chloronaphthalene.

PEA's 2a-e and 2a'-2e' display a clear trend of the Tg's, which decrease with increasing lengths of the dicarboxylic acids. However, it is difficult to understand why the Tg's of 2d,e (or 2d',e') are lower than those of 1c,d (or 1c',d').

CONCLUSION

The polycondensation of silylated 4-hydroxybenzoic acid or vanillic acid with aliphatic dicarboxylic acid dichlorides allows the syntheses of poly(ester-anhydride)s consisting of nontoxic degradation products. Polycondensation in 1-chloronaphthalene yields in most cases slightly higher molecular weights, but side reaction may be more pronounced. Regardless of the reaction medium, the maximum reaction temperature needs careful optimization. The PEA's derived from 4-hydroxybenzoic acid differ from the amorphous PEA's of vanillic acid by their semicrystalline character.

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