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NEW POLYMER SYNTHESES 98. HYPERBRANCHED POLY(ESTER-AMIDE)S DERIVED FROM NATURALLY OCCURRING MONOMERS

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ABSTRACT

Two new multifunctional monomers (1a, 2a) were prepared by acylation of silylated 4-aminobenzoic acid or 3,5-bisaminobenzoic acid with trisacetyl gallic acid chloride. All attempts to prepare soluble hyperbranched homopolyesters from the monomers 1a or 2a failed because of crosslinking. In contrast, copolycondensations of the "branching monomers" 1a or 2a with the trimethylsilyl esters of acetylated vanillic acid or phloretic acid yielded soluble randomly branched copoly(ester-amide)s at a maximum reaction temperature of 220°C or 230°C. As evidenced by ^{1}H NMR spectroscopy, all these copoly(ester-amide)s possess acetamide endgroups in addition to the acetate endgroups due to ester-amide interchange reactions. All copoly(ester-amide)s are amorphous materials with glass-transition temperatures (T_g's) between 170 and 230°C. The T_g's increase with the molar fraction of amide groups.

INTRODUCTION

Biodegradable polymers yielding non-toxic degradation products are typically aliphatic polyesters such as polyglycolide, polylactides, poly(ε -caprolactone), poly(β-hydroxy butyric acid), etc. Such aliphatic polyesters possess low glass-transition temperatures (T_g's in the range of -60 to +60°C), rather low heat distortion temperatures and relatively low mechanical strengths, when

compared to aromatic polyesters. In order to improve these properties, either fully aromatic and semi-aromatic biodegradable polymers need to be synthesized and used as neat materials or as reinforcing components of biodegradable composites.

In this connection, the present work is part of a broader study of aromatic polyesters [1-6] derived from non-toxic naturally occurring monomers, such as 4-hydroxybenzoic acid, vanillic acid, 3-(4-hydroxyphenyl)propionic acid (phloretic acid) and 3,4,5-trihydroxybenzoic acid (gallic acid) [7]. The present work concerns copoly(ester-amide)s containing 4-amino-benzoic acid, which is another monomer familiar to the human metabolism for at least two reasons. Firstly, it is a component of the vitamin folic acid, and secondly, its alkylesters have been used as an analgesic drug over many decades. The synthesis of randomly branched (or hyperbranched) structures has the purpose to reduce the crystallinity, to improve the solubility, and to favor the compatibility with a variety of biodegradable matrix materials. Nearly alternating copolymers of 4-aminobenzoic acid and vanillic acid have already been synthesized [8, 9]. These copoly(ester-amide)s were insoluble in common solvents of low or moderate acidity and the melting process above 400°C was affected by intensive thermal degradation. Since substitution eliminates the classification (and properties) as "naturally occurring monomers", random branching with another naturally occurring monomer (i.e. gallic acid) seemed to be an attractive strategy to improve both solubility and compatibility. In this connection, it should be mentioned that gallic acid is produced by many plants. It is a component of tannins and occurs in this form, for instance, also in red wine.

EXPERIMENTAL

Materials

4-Aminobenzoic acid, thionychloride and chlorotrimethylsilane were gifts of Bayer AG (Leverkusen, FRG) and were used as received. Gallic acid, vanillic acid and 3,5-diaminobenzoic acid were purchased from Aldrich Co. (Milwaukee, Wisc., USA). 3-(4-Hydroxyphenyl)propionic acid was purchased from Lancaster Synth. (Mülheim/Ruhr, FRG). 3,4,5-Trisacetoxybenzoylchloride (m.p. 105°C) was prepared previously [4] by acetylation of gallic acid with an excess of acetic anhydride in refluxing toluene followed by chlorination with refluxing thionylchloride. Acetylated vanillic acid (m.p. 147°C) and its trimethylsilyl ester (m.p. 65-66°C) were prepared as reported previously [9]. Acetylated phloretic acid and its trimethylsilyl ester (n_D^{20} 1.4859) were also synthesized according to the literature [10].

Silylation of 3,5-Bisaminobenzoic Acid

3,5-Bisaminobenzoic acid (0.5 mol) and hexamethyldisilazane (0.55 mol) were heated in dry toluene (1.4 L) and chlorotrimethylsilane (0.55 mol) was added dropwise with stirring. After 4 hours of reflux, the reaction mixture was cooled, filtered with exclusion of moisture and concentrated *in vacuo.* The product N,N',O-tristrimethylsilyl-3,5-diaminobenzoic acid was isolated by distillation *in vacuo* over a short-path apparatus. Yield 98%, m.p. 74°C (lit.[3]: m.p. 73-74°C).

The silylation of 4-aminobenzoic acid was conducted analogously. Yield of N,O-bistrimethylsilyl-4-aminobenzoic acid: 97%, m. p. 82-84°C (lit. [11]: m.p. 83-84°C).

N-(3,4,5-Trisacetoxybenzoyl)-4-aminobenzoic acid

Bistrimethylsilyl-4-aminobenzoic acid (0.1 mol) and 3,4,5-trisacetoxybenzoylchloride (0.1 mol) were weighed into a 500 ml round flask containing dry dioxane (300 mL) and stirred (with a magnetic bar) for 20 hours at 25°C. Afterwards, the reaction mixture was concentrated *in vacuo*, the residue dissolved in tetrahydrofuran (500 mL), and stirred with 250 ml neutral water for 4 hours at 25°C. The precipitated product was then isolated by filtration, washed with a small amount of diethylether and dried at 65°C *in vacuo*. Yield: 71% , m.p. 231-233°C. Anal. Calcd. for $C_{20}H_{17}NO_9$ (415.4): C 57.13, H 4.13, N 3.37, Found: C 57.49, H 4.21, N 3.56 %. ^{1}H NMR (DMSO-d_6): δ = 2.33 (s, 9H), 7.83-7.92 (m, 6H), 10.63 (s, 1H), 12.79 (s, 1H) ppm.

N,N'-Bis(3,4,5-trisacetoxybenzoyl)-3,5-diaminobenzoic acid

This compound was prepared from silylated 3,5-diaminobenzoic acid (0.075 mol) and 3,4,5-trisacetoxybenzoylchloride (0.15 mol) as described above. Yield: 62%, m.p. 296°C (DSC). Anal. Calcd. for $C_{33}H_{28}N_2O_{16}$ (708.6): C 55.94, H 3.98, N 3.95, found: C 55.64, H 4.06, N 4.15 %. ^{1}H NMR (DMSO-d_6): δ = 2.33 (s, 18H), 7.64 (s, 4H), 8.13 (d, 2H), 8.63 (d, 1H), 10.58 (s, 2H), 13.11 (s, 1H) ppm.

Polycondensations

A) Homopolycondensation of Neat 1a

N(-3,4,5-Trisacetoxybenzoyl)-4-aminobenzoic acid (1a, 10 mmol) was weighed into a cylindrical glass-reactor equipped with a mechanical stirrer, gas-inlet and outlet tubes. The reaction vessel was placed into an oil bath preheated to 150°C and the temperature was rapidly raised to 250°C or 240°C. This temperature was

maintained for 5 hours and the evolved acetic acid was removed with a slow stream of nitrogen. Finally vacuum was applied for 10 minutes.

B) Homopolycondensation of Crude 1b

N(-3,4,5-Trisacetoxybenzoyl)-4-aminobenzoic acid (1a, 10 mmol), hexamethyldisilazane (6 mmol) and dry toluene (15 mL) were weighed into a cylindrical glass-reactor and refluxed for 6 hours. Afterwards, the solvent was removed and the residue was then heated to 230°C or 220°C for 5 hours and the liberated trimethylsilyl acetate was removed with a slow stream of nitrogen.

C) Homopolycondensation of Crude 2b

N,N'-Bis(3,4,5-trisacetoxybenzoyl)-3,5-diaminobenzoic acid (2a, 10 mmol) hexamethyldisilazane (6 mmol) and dry toluene (15 ml) were weighed into a cylindrical glass-reactor and polycondensed as described for B.).

D) Copolcondensation of 2a with 3a or 3b

N,N'-Bis(3,4,5-trisacetoxybenzoyl)-3,5-diaminobenzoic acid (2a, 10 mmol) and 3-acetoxy benzoic acid (3a, 20 mmol) or its trimethylsilyl ester (3b, 20 mmol) were weighed into a cylindrical glass-reactor, equipped with stirrer, gas-inlet and outlet tubes and were polycondensed as described for A.) at 230°C or 220°C. In the case of the polycondensation at 220°C the cold product was dissolved in a mixture of CH_2Cl_2 and TFA (volume ratio 4:1), precipitated into methanol and dried at 90°C *in vacuo*.

E) Copolcondensation of 1a with 4 and 5

N(-3,4,5-Trisacetoxybenzoyl)-4-aminobenzoic acid (1a) VA (4) and PhA (5) were weighed in various feed ratios into a cylindrical glass-reactor and polycondensed at 220°C as described for E.).

F) Copolcondensation of 2a with 4 and 5

N,N'-Bis(3,4,5-trisacetoxybenzoyl)-3,5-diaminobenzoic acid (2a), VA (4) and PhA (5) were weighed in various feed ratios into a cylindrical glass-reactor and polycondensed at 220°C as described above.

Measurements

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

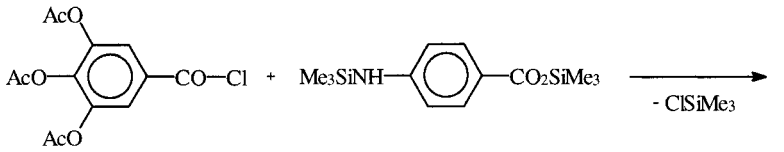
The 100 MHz ^1H NMR spectra were recorded on a Bruker AC 100 FT-NMR spectrometer in 5 mm o.d. sample tubes.

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

RESULTS AND DISCUSSION

Syntheses of Monomers

For the present work, two new multifunctinal monomers (1a and 2a) derived from gallic acid (GA) were synthesized. The acid chloride of acetylated GA was used as starting material in both cases. It was reacted with bissilylated 4-aminobenzoic acid at room temperature (Equation 1). Under such mild conditions the silylation protects the carboxyl group against the attack of the acid chloride, whereas the amino group is slightly activated, so that a clean reaction occurs. The silylated intermediate 1b was not isolated but directly hydrolyzed with neutral water to yield the monomer 1a (Equation 2). It is another advantage of the silylated carboxyl groups that a quantitative hydrolysis is feasible with neutral water, so that the acetate groups are not affected. An analogous reaction sequence involving silylated 3,5-diaminobenzoic acid yielded the monomer 2a via the silylated intermediate 2b. Difunctional monomers used in this work (but described before) were the 3-acetoxybenzoic acid (3a) and its trimethylsilyl ester (3b), and the trimethylsilyl esters of acetylated vanillic acid (VA) 4 or phloretic acid (PhA) 5. The monomers were preferentially used in the silylated form, because previous studies have shown [3-6] that in most cases the syntheses of hyperbranched polyesters are more successful when silylated carboxyl groups are involved. Lower concentrations or the absence of acidic protons reduces acid catalyzed side reactions such as the Fries arrangement, and thus, reduces the risk of crosslinking.



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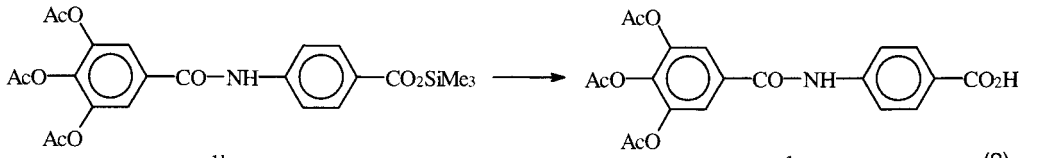
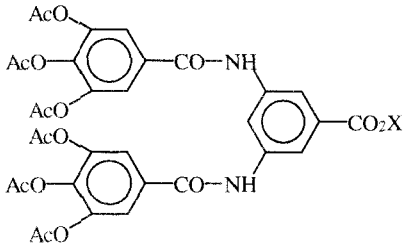
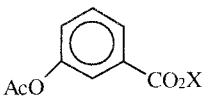


1b 1a (2)



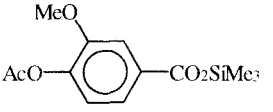
2a : X = H

2b : X = $SiMe_3$



3a : X = H

3b : X = $SiMe_3$



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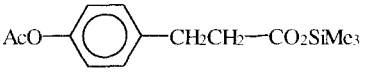

5

Polycondensations

At first, several attempts were made to prepare the hyperbranched homo-poly(ester-amide)s of the monomers 1a and 2a. In the case of 1a two polycondensations were conducted in the molten state at 250°C or at 240°C but both polycondensations resulted in heavily crosslinked products. A third and fourth experiment were performed in such a way that 1a was silylated with hexamethyldisilazane in refluxing toluene, and the crude trimethylsilyl ester 1b was then heated to 230 or 220°C in bulk. Yet, crosslinked products were obtained in both cases.

The high melting point of 2a prevented polycondensations of the neat monomer in bulk. Silylation of 2a with hexamethyldisilazane in refluxing toluene followed by polycondensation of the crude trimethylsilyl ester 2b at 230°C or 220°C yielded again a crosslinked product. In other words, all attempts to prepare soluble "homopolymers" of the monomers 1a, 1b, 2a, and 2b failed. The most likely origin of crosslinking is the thermal Fries-rearrangement which generates new functional groups, such as OH and ketogroups. At temperatures below 200°C, the Fries-rearrangement certainly needs acid catalysis. However, a non-catalyzed thermal Fries-rearrangement seems to be the main degradation reaction of most aromatic polyesters above 400°C [12, 13]. 1% of such side reactions (which is enough for an efficient crosslinking) may also occur below 300°C due to the numerous acetate

groups of the monomers 1a, 2a/b and of the resulting poly(ester-amide)s. Possibly an enolization of the aromatic amide group followed by a condensation of the resulting OH group is another source of crosslinks.

The monomer 2a was then copolycondensed with 3-acetoxybenzoic acid (3a) or its trimethylsilyl ester (3b) to find out if there is a chance to obtain soluble copolymers. The results summarized in Table 1 demonstrate that a reaction temperature of 230°C was too high and gave crosslinked products, whereas a temperature of 220°C allowed the isolation of completely soluble copoly(ester-amide)s. Such a strong influence of small differences in the temperature on the properties of hyperbranched polyesters has already been reported by several authors [14-17], and was thus not surprising.

On the basis of these results, the monomer 1a was copolycondensed with 4 and 5 in various feed ratios as described in Table 2. With a maximum reaction temperature of 220°C, completely soluble copolymers were obtained in all experiments. Their solubilities were summarized in Table 3. An analogous series of copolycondensations was conducted with mixtures of the monomers 2a, 4 and 5 (Table 4) at 230°C. Again, four soluble copoly(ester-amide)s were isolated. These copoly(ester-amide)s were soluble in acidic media such as dichloroacetic acid (DCA) or mixtures of trifluoroacetic acid (TFA) with either dichloromethane or chloroform (Table 5), but they were insoluble in non-acidic solvents such as DMSO or DMF. From this point of view, they were significantly less soluble than their counterparts derived from monomer 1a. However, their complete dissolution in acidic solvents proved the absence of crosslinks.

Characterization of the Copoly(ester-amide)s

When elemental analyses of the soluble copoly(ester-amide)s were performed after drying at 90 or 120°C, the C and H values were significantly lower than the calculated ones (Tables 2 and 4) whereas, the experimental N-values were higher. Higher C and H values were found after drying at 200°C and the evolution of small amounts of methanol and trifluoroacetic acid (TFA) was detected. We have also observed for other hyperbranched polyesters and poly(ester-amide)s that these polymers tend to hold back polar solvents and non-polar solvents so that intensive drying above the glass transition temperature is required.

For the ^{1}H NMR measurements, two different solvents were used: $CDCl_3$ + TFA and dimethylsulfoxide-d_6 (DMSO-d_6). As illustrated by spectra in Figures 1 and 2, the former solvent mixture has the advantage that no solvent signals appear in the shift range of the aliphatic protons (0-5 ppm). Therefore, the nearly equimolar

TABLE 1. Copolymerization of Monomers 2a with 3a or 3b in Bulk (5 Hours)

Molar feed ratios	Reaction Temp. (°C)	Yield (%)	η_{inh} [a] (dl/g)	T_g [b] (°C)	Elem. Formula (Formula weight)	Elemental Analyses	C	H	N
2a / 3a = 1/2	220	70	0.17		$C_{47}H_{36}N_2O_{20}$ (948.8)	Calcd.	59.50	3.82	2.95
						Found	58.48	3.60	3.17
2a / 3a = 1/2	230	crosslinked							
2a / 3b = 1/2	220	90	0.25		$C_{47}H_{36}N_2O_{20}$ (948.8)	Calcd.	59.50	3.82	2.95
						Found	58.51	3.69	3.21
2a / 3b = 1/2	230	crosslinked							

a) measured at 20°C with c = 2 g/l in CH_2Cl_2/TFA (volume ratio 4:1)

b) from DSC measurements with a heating rate of 20°C/min

TABLE 2. Copolycondensation of Monomers 1a, 4, and 5 in Bulk at 220°C (5 Hours)

Exp. No.	Molar feed ratios 1a / 4 / 5	Yield (%)	η_{inh} [a] (dl/g)	T_g [b] (°C)	Elem. Formula (Formula weight)	Elemental Analyses	C	H	N
1	1/6/0	69	0.27	174	$C_{66}H_{49}NO_{25}$ (1256.1)	Calcd.	63.11	3.93	1.12
						Found	62.02	3.78	1.52
2	1/4/0	78	0.42	195	$C_{50}H_{37}NO_{19}$ (955.8)	Calcd.	62.83	3.90	1.47
						Found	61.29	3.78	1.73
3	1/2/0	78	0.39	207	$C_{34}H_{25}NO_{13}$ (655.6)	Calcd.	62.29	3.84	2.14
						Found	61.03	3.68	2.40
4	1/1/1	83	0.43	192	$C_{35}H_{27}NO_{12}$ (653.6)	Calcd.	64.32	4.16	2.14
						Found	62.63	4.05	2.42

a) measured at 20°C with c = 2 g/l in CH_2Cl_2/TFA (volume ratio 4:1)

b) from DSC measurements with a heating rate of 20°C/min

TABLE 3. Solubilities of the Copoly(ester-amide)s Derived from 1a

Molar feed ratios 1a / 4 / 5	CH_2Cl_2/ TFA 4:1	$CHCl_3$/ TFA 4:1	m-Cresol	DMSO	DCA	NMP	DMF
1/6/0	+	+	+	+	+	+	+
1/4/0	+	+	+	+	+	+	+
1/2/0	+	+	+	+	+	+	-
1/1/1	+	+	+	+	+	+	+

TABLE 4. Copolycondensation of Monomers 2a, 4, and 5 in Bulk at 230°C (5 Hours)

Exp. No.	Molar feed ratios 1a / 4 / 5	Yield (%)	η_{inh} [a] (dl/g)	T_g [b] (°C)	Elem. Formula (Formula weight)	Elemental Analyses	C	H	N
1	1/6/0	77	0.44	202	$C_{79}H_{60}N_2O_{32}$	Calcd.	61.24	3.90	1.81
					(1549.3)	Found	59.52	3.73	2.21
2	1/4/0	80	0.33	212	$C_{63}H_{48}N_2O_{26}$	Calcd.	60.58	3.87	2.24
					(1249.0)	Found	58.39	3.66	2.41
3	1/2/0	84	0.33	229	$C_{47}H_{36}N_2O_{20}$	Calcd.	59.50	3.82	2.95
					(948.8)	Found	58.16	3.74	2.89
4	1/1/1	88	0.31	189	$C_{48}H_{38}N_2O_{19}$	Calcd.	60.89	4.05	2.96
					(946.8)	Found	59.41	3.85	2.92

a) measured at 20°C with c = 2 g/l in CH_2Cl_2/TFA (volume ratio 4:1)

b) from DSC measurements with a heating rate of 20°C/min

TABLE 5. Solubilities of the Copoly(ester-amide)s Derived from 2a

Molar feed ratios 1a / 4 / 5	CH_2Cl_2/ TFA 4:1	$CHCl_3$/ TFA 4:1	m-Cresol	DMSO	DCA	NMP	DMF
1/6/0	+	+	+	-	+	-	-
1/4/0	+	+	-	-	+	-	-
1/2/0	+	+	-	-	+	-	-
1/1/1	+	+	-	-	+	+	-

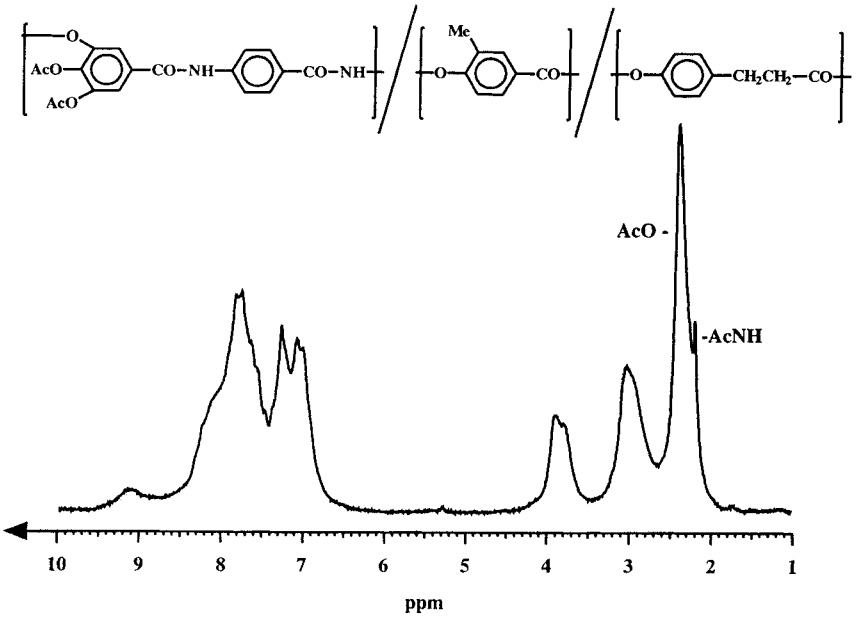

Figure 1. 100 MHz ^{1}H NMR spectrum (in $CDCl_3$/TFA) of the copoly(ester-amide) prepared from equimolar amounts of the monomers 1a, 4 and 5 (No. 4, Table 2).

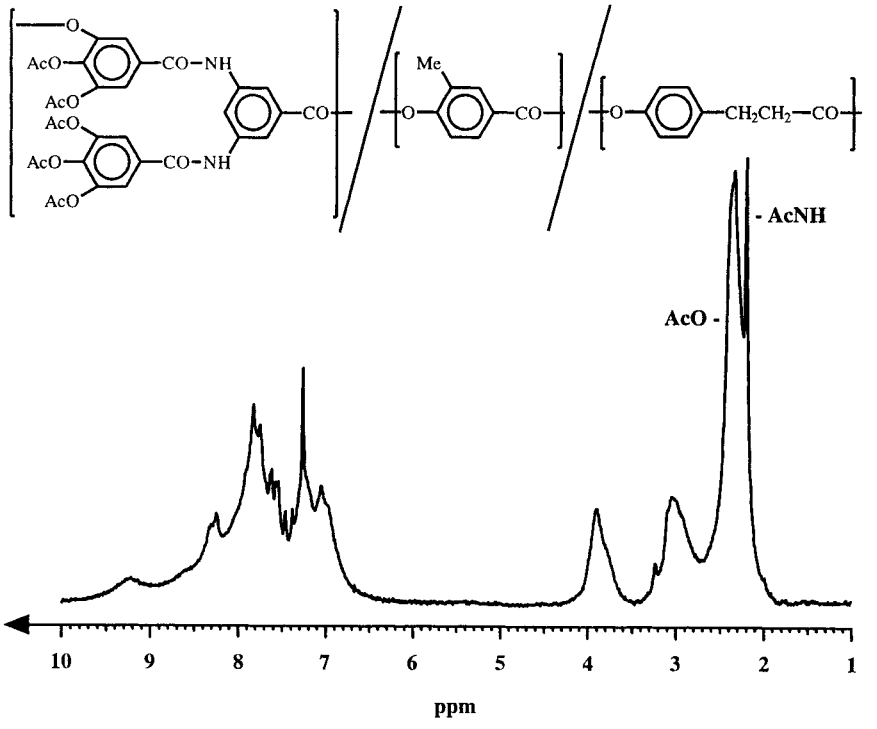

Figure 2. 100 MHz ^{1}H NMR spectrum (in $CDCl_3$/TFA) of the copoly(ester-amide) prepared from equimolar amounts of the monomers 2a, 4 and 5 (No. 4, Table 4).

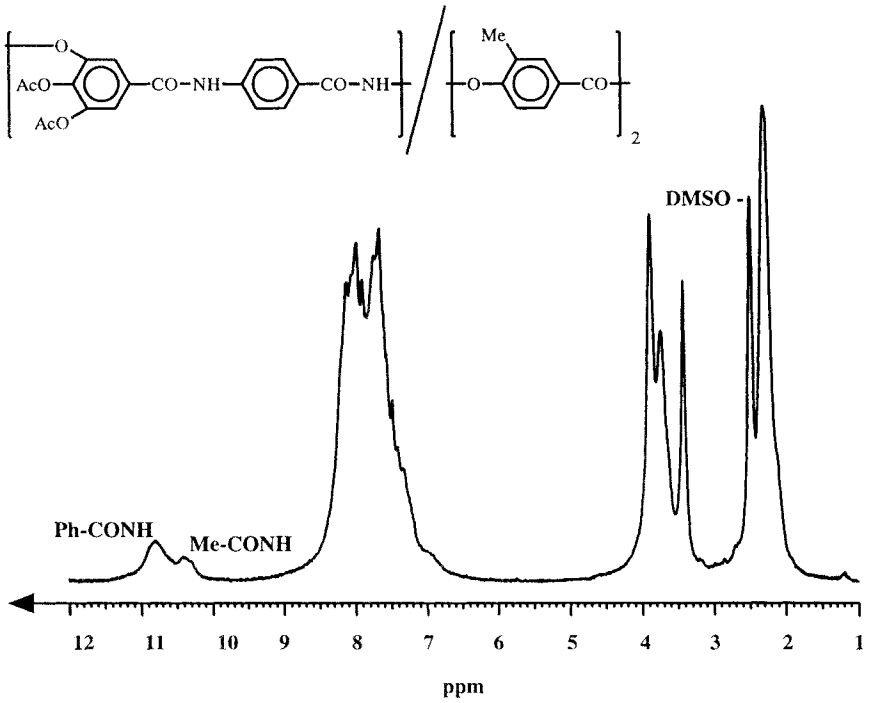

Figure 3. 100 MHz ^{1}H NMR spectrum (in DMSO-d_6) of the copoly(ester-amide) prepared from 1a and a double amount of 4 (No. 3, Table 2).

incorporation of the monomers 4 and 5 was evidenced in the case of the polymers No. 4, Table 2 and No. 4, Table 4 (Figures 1 and 2). These spectra also display a sharp signal at 2.2 ppm originating from acetamido groups. The existence of this signals proves that ester-amide interchange reaction have occured to a significant extent. This finding is in good agreement with what has been reported for the syntheses of other hyperbranched poly(ester-amide)s [10, 18, 19]. The ^{1}H NMR spectra recorded in DMSO-d_6 (Figure 3) have the advantage that two kinds of NH-signals are detectable between 10 and 11 ppm. These signals confirm that all poly(ester-amide)s of this work contain sizable amounts of N-acetyl-4-amino-benzoyl endgroups. Unfortunately, we could not detect any group of signals allowing for a determination of the degree of branching.

Both the WAXD powder patterns and the DSC measurements confirm that all the copoly(ester-amide)s listed in Tables 1, 2 and 4 are amorphous materials. From the T_g's compiled in Tables 2 and 4, three trends can be deduced. Firstly, the

comparison of polymers Nos. 1-3 shows in both Tables increasing T_g's with higher concentration of amide groups (i.e. lower molecular fraction of VA units). Secondly, an analogous trend is obvious when the poly(ester-amide)s of Table 2 are compared with those of Table 4. Thirdly, the incorporation of phloretic acid improves the segmental mobility, and thus, reduces the T_g's.

CONCLUSION

Two new multifunctional monomers were prepared from trisacetyl gallic acid and 4-aminobenzoic acid or 3,5-diaminobenzoic acid. However, all attempts to prepare soluble hyperbranched homopoly(ester-amide)s failed, even when the carboxylic groups were silylated. Soluble, amorphous randomly branched copolymers were obtained from difunctional monomers such as 3-hydroxybenzoic acid, vanillic acid and phloretic acid. Therefore, the multifunctional monomers have at least demonstrated their usefulness as "branching comonomers" for syntheses of randomly branched copoly(ester-amide)s built up by non-toxic, naturally occurring monomers.

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