Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

New Polymer Syntheses. 80. Linear, Star-Shaped, and Hyperbranched Poly(Ester-Amide)s from Silicon-Mediated One-Pot Condensations of 3-Acetoxy-, 3,5-Bisacetoxybenzoic Acid, and 3-Aminobenzoic Acid

Hans R. Kricheldorf[a]; Gerd Löhden[a]
[a] Institut für Technische und Makromolekulare Chemie der Universität, Hamburg, Germany

To cite this Article Kricheldorf, Hans R. and Löhden, Gerd(1995) 'New Polymer Syntheses. 80. Linear, Star-Shaped, and Hyperbranched Poly(Ester-Amide)s from Silicon-Mediated One-Pot Condensations of 3-Acetoxy-, 3,5-Bisacetoxybenzoic Acid, and 3-Aminobenzoic Acid', Journal of Macromolecular Science, Part A, 32: 11, 1915 — 1930

To link to this Article: DOI: 10.1080/10601329508009370

URL: http://dx.doi.org/10.1080/10601329508009370

J.M.S.—PURE APPL. CHEM., A32(11), pp. 1915–1930 (1995)

NEW POLYMER SYNTHESES. 80. LINEAR, STAR-SHAPED, AND HYPERBRANCHED POLY(ESTER-AMIDE)S FROM SILICON-MEDIATED ONE-POT CONDENSATIONS OF 3-ACETOXY-, 3,5-BISACETOXYBENZOIC ACID, AND 3-AMINOBENZOIC ACID

HANS R. KRICHELDORF* and GERD LÖHDEN

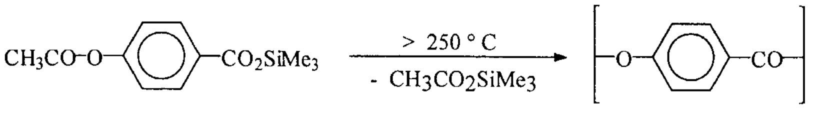
Institut für Technische und Makromolekulare Chemie der Universität
Bundesstr. 45, D-20146 Hamburg, Germany

ABSTRACT

Acylation of *N*,*O*-bistrimethylsilyl-3-aminobenzoic acid with 3-acetoxybenzoylchloride yielded the trimethylsilylester of *N*-(3′-acetoxybenzoyl)-3-aminobenzoic acid, which was polycondensed in situ at 260 or 280°C. Cocondensation with acetylated tetraphenols yielded four-arm star copolymers with a random or preferentially alternating sequence of 3-hydroxy and 3-aminobenzoyl units. Due to ester-amide exchange detected by ^{1}H- and ^{13}C-NMR spectroscopy, the sequences were never perfectly alternating. Methyl groups attached to the star centers allowed the determination of degrees of polymerization by ^{1}H-NMR spectroscopy. Acylation of *N*,*O*-bistrimethylsilyl-3-amino benzoic acid with 3,5-bisacetoxybenzoylchloride yielded a trifunctional monomer, the polycondensation of which yielded a hyperbranched poly(ester-amide). By cocondensation of the trifunctional monomer with acetylated tetraphenyl, star-shaped poly(ester-amide)s with four hyperbranched star arms were obtained. All these poly(ester-amide)s are amorphous materials with glass-transition temperatures in the 190–200°C range and good solubility in polar organic solvents.

INTRODUCTION

This work is part of broader study of synthesis and characterization of telechelic, star-shaped, or dendritic polycondensates such as aromatic polyethers, polyesters, or polyamides. Telechelic polymers are useful as building blocks of tri- or multiblock copolymers. Star-shaped and dendritic polycondensates may be useful as adhesives, compatibilizers, additives, etc. The main problem of syntheses of star-shaped and dendritic polymers by polycondensation of A_2B-type monomers is side reactions resulting in crosslinks. Therefore, this work and related studies [1-7] are based on the polycondensation of silylated monomers. Silylated monomers avoid the presence of acidic protons and thus significantly reduce the risk of acid-catalyzed side reactions. The present work had the purpose to study the synthesis of star-shaped and dendritic poly(ester-amide)s from 3-aminobenzoic acid and 3-hydroxy- or 3,5-bishydroxybenzoic acid. The polycondensation process is based on the reaction of silylated carboxyl groups with acetylated phenol groups (e.g., Eq. 1). This new polycondensation method [8, 9] has the additional advantage that it allows the synthesis of aromatic poly(ester-amide)s in a "one-pot" procedure [10, 11]. Dendritic aromatic polyesters [1, 2, 4, 5] and polyamides [12] prepared by other synthetic methods have been reported in the literature.



(1)

EXPERIMENTAL

Monomers

3-Hydroxybenzoic acid, 3,5-dihydroxybenzoic acid, and 3-aminobenzoic acid were gifts of Bayer AG (Leverkusen, Germany) and were used without further purification. The hydroxy acids were acetylated in refluxing toluene with an excess of acetic anhydride and 1 mL pyridine. The acid chlorides were prepared in refluxing freshly distilled thionylchloride: 3-Acetoxybenzoylchloride, n_D^{20} 1.5422 (n_D^{20} 1.5410 in Ref. 10); 3,5-bisacetoxybenzoylchloride, mp 88-90 (mp 89.5-90°C in Ref. 13).

The 3-aminobenzoic acid was silylated with chlorotrimethylsilane and triethylamine in refluxing toluene and isolated by distillation in vacuo (125-135°C/0.1 mbar). Yield 91%, n_D^{20} 1.4990 (n_D^{20} 1.4995 in Ref. 14).

Trimethylsilyl 3-acetoxybenzoate was prepared as described previously [15]. The tetrafunctional comonomers were prepared as described in the preceding part of this series [11].

Silylated 3-Acetamidobenzoic Acid

3-Aminobenzoic acid (0.3 mol) and chlorotrimethylsilane (0.7 mol) were heated in dry toluene (700 mL), and trimethylamine (0.7 mol) was added dropwise with stirring. The reaction mixture was refluxed for 2 hours and cooled to ~25°C.

Acetylchloride (0.3 mol) dissolved in 50 mL toluene was then added rapidly with stirring, and the reaction mixture was then refluxed for 1 hour. After cooling with ice, the precipitated $Et_3N \cdot HCl$ was filtered off under exclusion of moisture. The filtrate was concentrated in vacuo, and the product was distilled at a pressure of 10^{-2} mbar over a short path apparatus. Yield: 84%.

Analyses calculated for $C_{18}H_{15}NO_7$ (357.3): C 60.51, H 4.23, N 3.92; found C 60.33, H 4.13, N 3.65%. ^1H NMR (in DMSO-d_6/TMS): δ 2.31 (s, 6H), 7.26–8.39 (m, 7H), 10.5 (s, 1H), 13.0 (s, 1H) ppm.

N-(3′,5′-Bisacetoxybenzoyl)-3-aminobenzoic Acid (6)

N-*O*-Bistrimethylsilyl-3-aminobenzoic acid (0.1 mol) was dissolved in dry toluene (250 mL), and 3,5-bisacetoxybenzoylchloride (0.1 mol) was added with stirring. After 20 hours the precipitated solid was filtered off, washed with a little cold toluene, and suspended in ethanol (200 mL). After stirring for 12 hours, the crystallized product was isolated by filtration and recrystallized from a dimethylformamide/water mixture. Yield 76%, mp 244–246°C.

Analyses calculated for $C_{18}H_{15}NO_7$ (357.3): C 60.51, H 4.23, N 3.92; found C 60.33, H 4.13, N 3.65%. ^1H NMR (in DMSO-d_6/TMS): δ 2.31 (s, 6H), 7.26–8.39 (m, 7H), 10.5 (s, 1H), 13.0 (s, 1H) ppm.

Polycondensations

With 3-Acetoxybenzoylchloride

Dry toluene (20 g) and *N*,*O*-bistrimethylsilyl-3-aminobenzoic acid (25 mmol) were weighed into a cylindrical glass reactor equipped with a glass stirrer and gas inlet and outlet tubes. 3-Acetoxybenzoylchloride (25 mmol) was added and the reaction mixture was stirred for 12 hours at 20–25°C. Chlorotrimethylsilane and toluene were then removed with a slow stream of nitrogen upon heating to 50°C. The residual monomer was heated to 260°C for 2 hours, to 270°C for 1 hour, to 280°C for 2.5 hours, and finally a vacuum of 10^{-1} mbar was applied for 10 minutes. After cooling, the product was dissolved in a mixture of CH_2Cl_2 and trifluoroacetic acid (volume ratio 4:1), precipitated into cold methanol, and dried at 120°C in vacuum.

With 3,5-Bisacetoxybenzoylchloride

3,5-Bisacetoxybenzoylchloride (15 mmol) was reacted with *N*,*O*-bistrimethylsilyl-3-aminobenzoic acid (15 mmol) in dry toluene (20 mL) as described above. The monomer thus obtained was heated to 230°C for 45 minutes, to 240°C for 45 minutes, to 250°C for 75 minutes, to 260°C for 30 minutes, and finally a vacuum of $\sim 10^{-1}$ mbar was applied for 10 minutes.

Copolycondensations of Tetraphenols

The polycondensations were conducted as described above, but an acetylated tetraphenol was added from the beginning.

With Silylated 3-Acetamidobenzoic Acid

Trimethylsilyl-3-acetamidobenzoate (25 mmol) and trimethylsilyl-3-acetoxybenzoate (25 mmol) were weighed into a cylindrical glass reactor equipped with a stirrer and gas inlet and outlet tubes. The monomers were heated to -260°C for 2 hours, to 270°C for 1 hour, and to 280°C for 2.5 hours. The cold reaction product was dissolved in CH_2Cl_2 containing 20 vol% trifluoroacetic acid and precipitated into methanol. Yield 75%, $\eta_{inh} = 0.15$ dL/g (at 20°C, $c = 2$ g/L in CH_2Cl_2:trifluoroacetic acid 4:1 by volume.

Analyses calculated for $C_{14}H_9NO_3$ (239.2): C 70.29, H 3.79, N 5.86; found C 69.01, H 3.85, N 6.07%.

The ^{1}H-NMR spectrum indicates the presence of acetate and acetamide endgroups in a molar ratio of 1:2.

Measurements

The viscosities were measured with an automated Ubbelhode viscometer thermostated at 25°C.

The IR spectra were recorded from KBr pellets used in a Nicolet SXB-30 FT-IR-spectrometer.

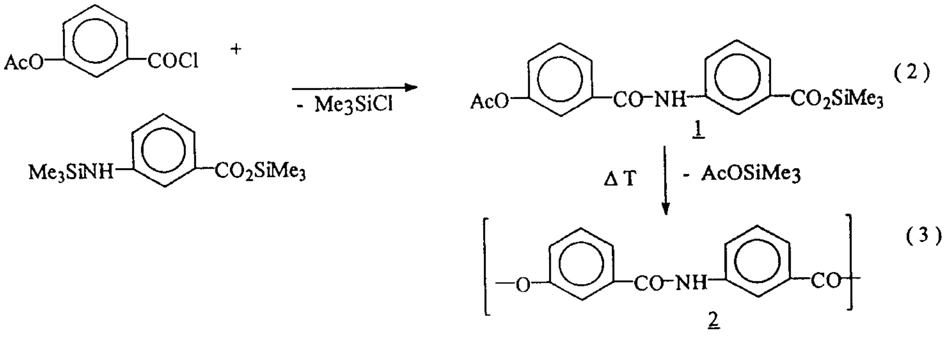
The DSC measurements were conducted with a Perkin-Elmer DSC-7 in aluminum pans under nitrogen.

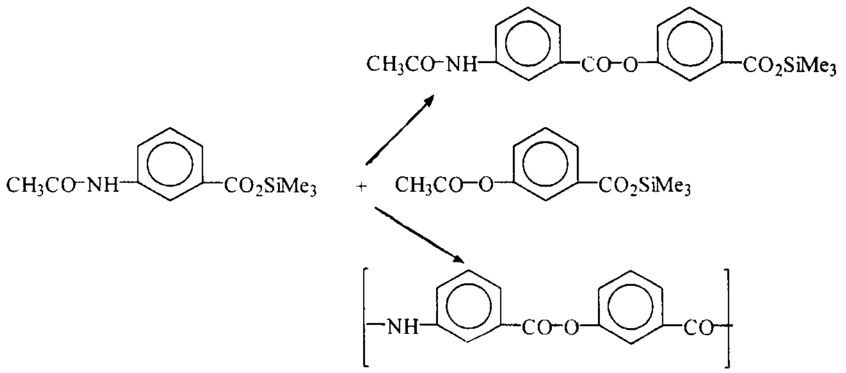
The 100 MHz ^{1}H-NMR spectra were recorded with a Bruker AC-100 FT-NMR spectrometer in 5 mm o.d. sample tubes. The 25.4 MHz ^{13}C-NMR spectra were recorded on the same instrument using 10 mm o.d. sample tubes. For both kinds of NMR measurements a 4:1 (by volume) mixture of $CDCl_3$ and trifluoroacetic acid containing TMS was used as the solvent.

RESULTS AND DISCUSSION

Linear and Star-shaped Poly(Ester-amide)s

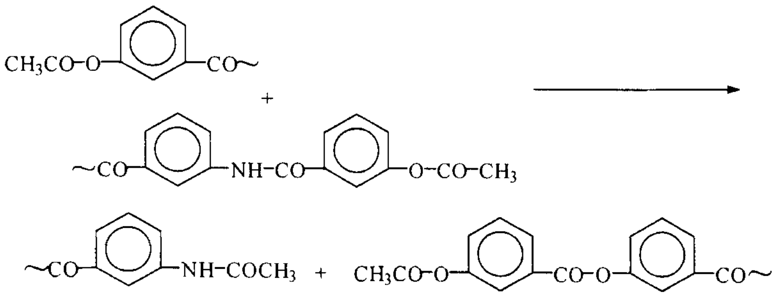
In order to test the usefulness of the synthetic approach underlying this work, linear poly(ester-amide)s (**2**) and star-shaped poly(ester-amide)s with four linear star arms (**3b**, **4b**) were synthesized first. Meta-substituted hydroxy- and aminobenzoic acids were used as starting materials instead of para-substituted compounds to obtain soluble polymers. 3-Aminobenzoic acid was silylated with chlorotrimethyl-



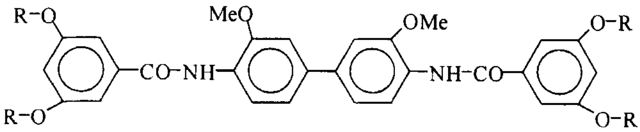


(4)

(5)

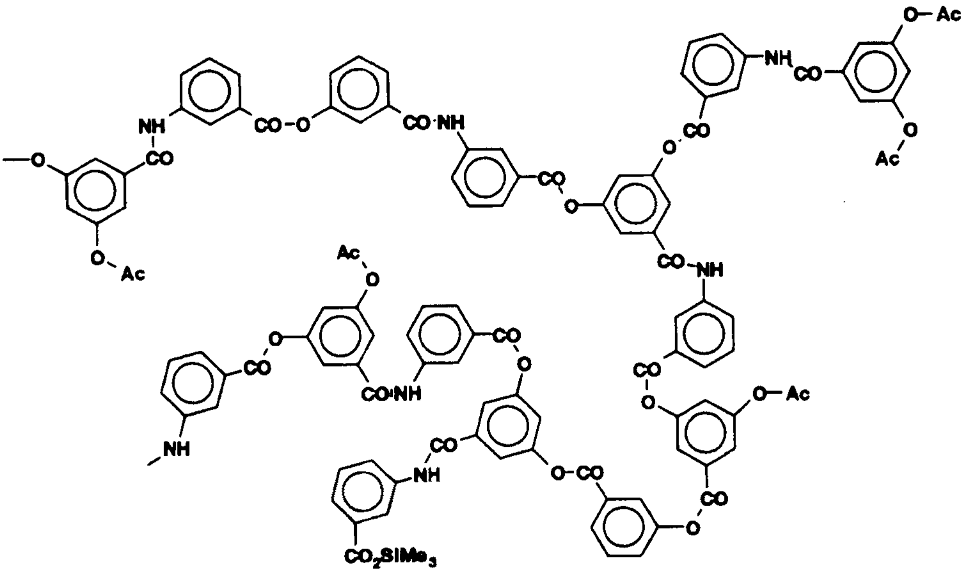


(6)

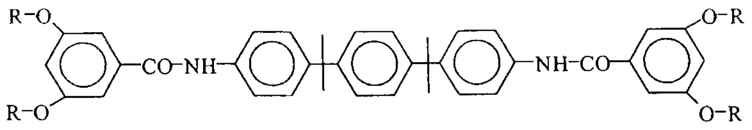


3 a - c

a : R = Acetyl b : R = poly(ester-amide) 2 c : R = poly(ester-amide) 7

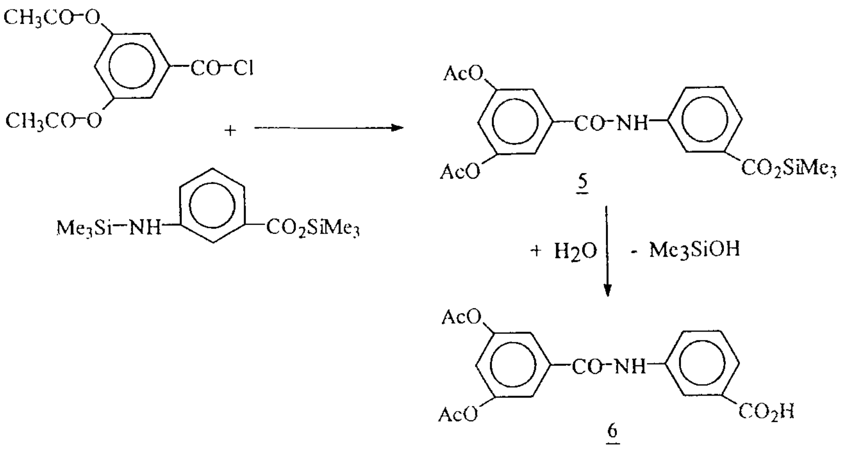


7

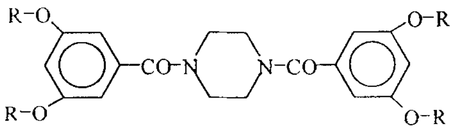


4a - c

a : R = Acetyl b : poly(ester-amide) 2 c : poly(ester-amide) 7



(7)



8a - b

a : R = Acetyl b : R = poly(ester-amide) 7

silane and triethylamine in the usual way. 3-Acetoxybenzoylchloride prepared by standard methods served as the second building block. When both reactants were combined in an inert solvent (e.g., toluene) at moderate temperatures (< 50°C), a selective and almost quantitative acylation of the silylated amino group took place (Eq. 2). Evaporation of both solvent and chlorotrimethylsilane yielded the crude monomer **1** which was polycondensed in bulk without further purification or characterization.

The reaction temperatures of these polycondensations were varied between 260, 280, and 300°C (Table 1). Soluble poly(ester-amide)s, PEAs, were obtained at 260 and 280°C, whereas the highest temperature resulted in an insoluble, crosslinked product. The spectroscopic characterization of the soluble PEAs gave further

TABLE 1. Polycondensation of Silylated *N*-(3′-Acetoxybenzoyl)-3-aminobenzoic Acid by a One-Pot Procedure

	Comonomer	Monomer[a]/comonomer	Maximum temperature, °C	Yield, %	η_{inh},[b] dL/g	DP[c]	T_g,[d] °C	Elemental analyses	C	H	N
1	–	–	260	45	0.22	–	190	Calcd	70.29	3.79	5.85
								Found	69.05	3.96	5.40
2	–	–	280	52	0.23	–	192	Calcd	70.29	3.79	5.85
								Found	68.87	4.16	5.30
3	–	–	300	–	Insoluble	–	190	Calcd	70.29	3.79	5.85
								Found	68.56	4.05	5.40
4	**3a**	30/1	280	48	0.08	26	186	Calcd	69.01	3.87	5.70
								Found	68.01	4.30	5.89
5	**3a**	60/1	280	42	0.14	55	186	Calcd	69.97	3.83	5.77
								Found	68.05	4.30	6.47
6	**3a**	90/1	280	43	0.24	80	193	Calcd	70.07	3.82	5.80
								Found	68.11	4.19	5.50
7	**4a**	30/1	280	60	0.09	35	193	Calcd	70.30	3.98	5.63
								Found	69.01	4.22	5.68
8	**4a**	60/1	280	52	0.16	60	193	Calcd	70.30	3.89	5.74
								Found	69.14	4.16	5.93
9	**4a**	90/1	280	56	0.26	90	192	Calcd	70.39	3.86	5.77
								Found	69.18	4.11	5.88

[a] Molar feed ratio of monomer and tetrafunctional comonomer (star centers).
[b] Measured at 25°C with $c = 2$ g/L in DMF.
[c] Apparent DP as determined by ^{1}H-NMR spectroscopy.
[d] From DSC measurements with a heating rate of 20°C/min.

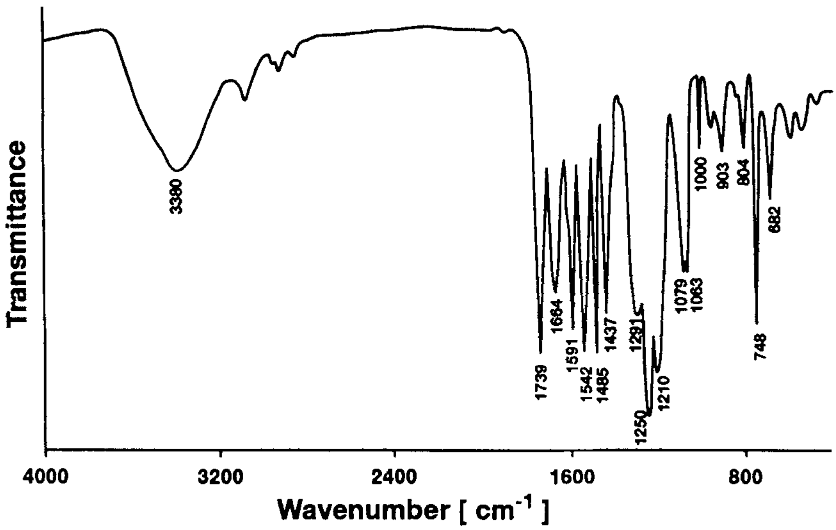


FIG. 1. IR spectrum (KBr pellet) of the poly(ester amide) prepared from monomer **1** at 280°C in bulk (No. 2, Table 1).

interesting information. The IR spectra displayed the expected separate bands of ester (1737 ± 2 cm^{-1}) and amide groups (1662 ± 2, 1590 ± 2, 1544 ± 2 cm^{-1}), Fig. 1. The ^1H-NMR spectra measured in DMSO (Fig. 2) revealed the existence of two acetyl signals at 2.0 and 2.3 ppm which were assigned to acetamide and acetate endgroups. The ^{13}C-NMR spectra confirmed the existence of both kinds of end-

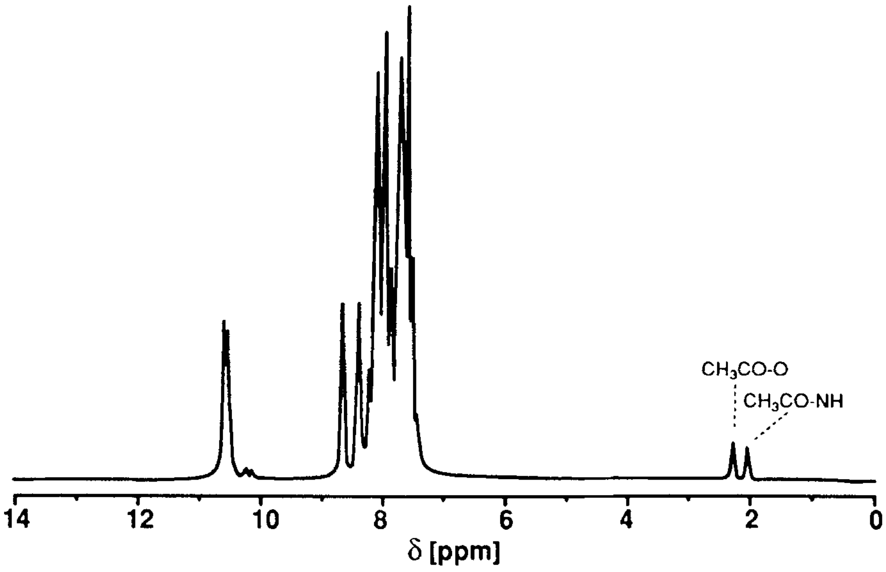


FIG. 2. 100 MHz ^1H-NMR spectrum of the poly(ester-amide) prepared from **1** at 280°C in bulk (the DMSO and H_2O signals were removed).

TABLE 2. ^{1}H- and ^{13}C-NMR Chemical Shifts δ^a of Selected Protons and Carbons in Poly(Ester-amide)s **2** and **7**

Residue[b]	δ of ^{1}H-NMR signals, ppm	δ of ^{13}C-NMR signals, ppm	
$CH_3CO-O-Ar$	2.30	169.0	20.7
$CH_3CO-NH-AR$	2.06	168.7	24.0
Ar—CO—O—Ar (**2**)	—	165.8/164.5	—
Ar—CO—NH—Ar (**2**)	10.58, 10.64	163.7/164.5	—
OCH_3 in **3a–c**	3.94	—	—
CH_3 in **4a–c**	1.59	—	—
CH_2 in **8a–b**	3.50	—	—

[a] Measured in DMSO-d_6 with internal TMS.

[b] AR = 3-substituted benzoyl unit.

groups (Table 2). This result is the first indication that intensive amide/ester exchange reactions took place (e.g., Eq. 4) in the course of these polycondensations. This interpretation is confirmed by the following observations. Two NH signals were found in the ^{1}H-NMR spectra, obviously resulting from the diads 3-aminobenzoyl-3-aminobenzoyl and 3-oxybenzoyl-3-aminobenzoyl. Furthermore, the ^{13}C-NMR spectra exhibited three CO signals with an intensity ratio close to 1:2: 1 (Fig. 3). This pattern is typical for a random sequence when the signals of the alternating diads 3-oxybenzoyl-3-aminobenzoyl and 3-aminobenzoxyl-3-oxybenzoyl overlap. The signal of the 3-oxybenzoyl-3-oxybenzoyl diad was unambiguously assigned by comparison with the homopolyester of 3-hydroxybenzoic acid. Last but

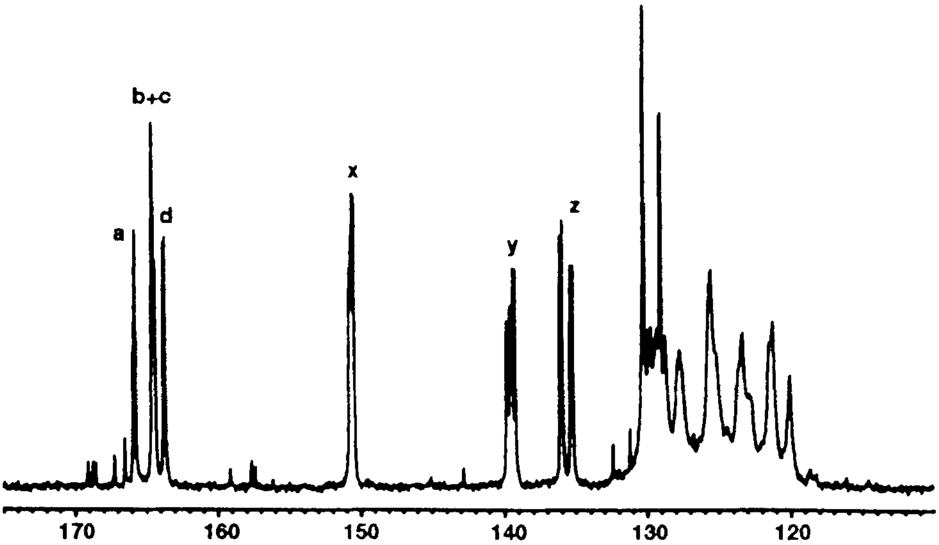


FIG. 3. 25.4 MHz ^{13}C-NMR spectrum of the poly(ester-amide) prepared from **1** at 280°C.

not least, all quaternary carbons of the 3-aminobenzoyl and 3-oxybenzoyl units displayed a splitting into four peaks of nearly equal intensity (Fig. 4). These signal patterns fit in with a random sequence of four triads. Thus, all spectroscopic results taken together clearly prove that the polycondensation of **1** at 280°C yielded a random sequence and at 260°C a nearly random sequence of the different monomer units.

In order to obtain more insight into the reactivity of the acetamide (end)-groups, a cocondensation of silylated 3-acetoxybenzoic acid and silylated 3-acetamidobenzoic acid was conducted in bulk at temperatures up to 280°C. Provided that the acetate groups solely participate in the condensation process, mainly a dimer and a few higher oligoesters containing acetamide endgroups should be formed (Eq. 4). The alternative would be the formation of a random copoly(ester-amide) with equal amounts of acetate and acetamide endgroups (Eq. 5). The experimental result was a low molar mass copoly(ester-amide) with a molar composition of 1:1 and acetate and acetamide endgroups in a ratio of 1:2. This result demonstrates that the acetamide groups contribute to the polycondensation process, although with lower reactivity than the acetate groups.

The ^{1}H-NMR signals of the acetyl endgroups allowed calculation of the average degree of polymerization (DP). For both samples 1 and 2 of Table 1, a DP around 20 was found, corresponding to a number-average molecular weight (M_n) around 4800 g/mol. This relatively low value is understandable considering that the formation of acetamide groups slows the chain growth process. As illustrated by Eq. (6), the ester-amide exchange involving an acetate endgroup does not directly affect the molecular weight. In order to obtain higher molecular weights and a star-shaped structure, monomer **1** was polycondensed with the tetrafunctional comonomers **3a** and **4a**. The syntheses and properties of these comonomers were described in the preceding part of this series [11].

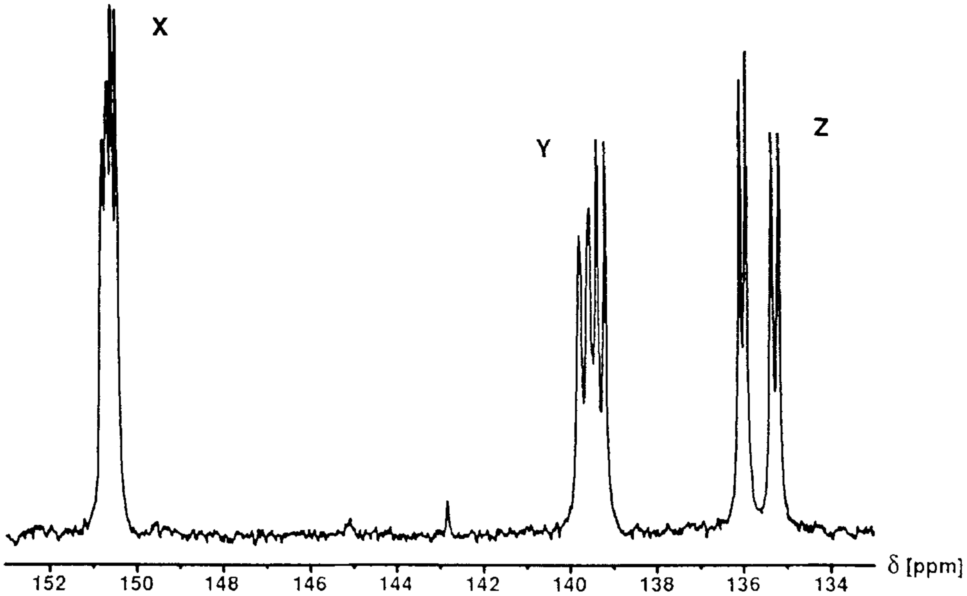


FIG. 4. 25.4 MHz ^{13}C-NMR spectrum of the poly(ester-amide) prepared from **1** at 280°C.

The cocondensation of **1** with **3a** or **4a** should allow control of the average molecular weight by variation of the monomer/comonomer ratio. The viscosity and NMR data (endgroup analyses) listed in Table 1 confirm this expectation. **3a** and **4a** have the additional advantage that they possess methyl groups yielding singlet ^{1}H-NMR signals which allow the calculation of DP and M_n values. The results obtained from the ^{1}H-NMR signals of the comonomers (Fig. 5) prove that the comonomers were almost completely incorporated into the PEAs, so that the apparent DPs agree fairly well with the feed ratios.

These apparent DPs are maximum values, and the true DPs may be somewhat lower because neither the viscosities nor the NMR spectra prove absolutely that all linear chains were attached to the star centers. The intensities of the acetyl signals indeed suggest that all samples (4–9, Table 1) contain a small fraction of linear species. Nonetheless, these experiments confirm that star-shaped PEAs can be synthesized in a "one-pot-procedure" without crosslinking.

In connection with these cocondensations, the interesting observation was made that the extent of ester/amide exchange depends largely on the reaction conditions. As illustrated by Fig. 5, the signal of the acetamide endgroups was weak

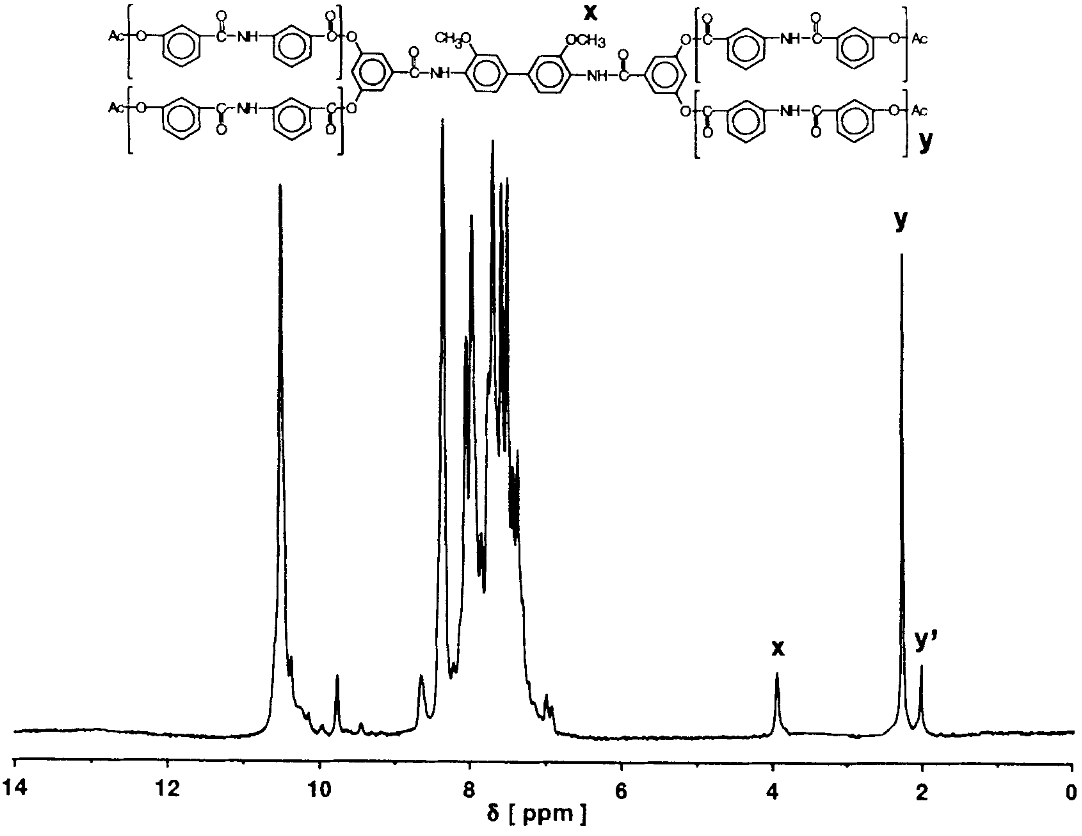


FIG. 5. 100 MHz ^{1}H-NMR spectrum of the poly(ester-amide) **3b** prepared with a monomer/star center ratio of 30:1.

TABLE 3. Polycondensation of *N*-(3,5-Bisacetoxybenzoyl)3-aminobenzoic Acid or Its Trimethylsilylester

		Maximum				Elemental analyses				Solubilities[d]		
Polymer	Monomer	temperature, °C	Yield, %	η_{inh},[b] dL/g	T_g,[c] °C		C	H	N	CH_2Cl_2/TFA[d]	DMF[d]	NMP[d]
1	**6**	240	75[a]	0.10	195	Calcd	64.65	3.73	4.71	+	+	+
						Found	64.01	3.92	4.52			
2	**6**	260	65 (crude)	–	193	Calcd	64.65	3.73	4.71	–	–	–
						Found	63.26	4.02	4.86			
3	**6**	280	50 (crude)	–	194	Calcd	64.65	3.73	4.71	–	–	–
						Found	63.58	3.92	4.56			
4	**5**	240	73[a]	0.10	186	Calcd	64.65	3.73	4.71	+	+	+
						Found	63.67	3.86	4.82			
5	**5**	260	69[a]	0.18	197	Calcd	64.65	3.73	4.71	+	+	+
						Found	63.00	3.92	4.69			
6	**5**	280	63 (crude)	–	200	Calcd	64.65	3.73	4.71	–	–	–
						Found	62.70	3.56	4.60			

[a] Determined after precipitation into methanol.

[b] Measured at 25°C with $c = 2$ g/L in DMF.

[c] From DSC measurements with a heating rate of 20°C/min.

[d] TFA = trifluoroacetic acid, DMF = dimethylformamide, NMP = *N*-methylpyrrolidone.

TABLE 4. Copolycondensation of Monomers with Tetrafunctional Comonomers (star centers)

Polymer	Comonomer	Monomer[a]/Comonomer	Yield, %	η_{inh},[b] dL/g	DP[c]	T_g,[d] °C	Elemental analyses	C	H	N
1	**8a**	30/1	63	0.21	55	196	Calcd	64.35	3.80	4.75
							Found	63.44	4.23	4.84
2	**8a**	60/1	57	0.23	70	197	Calcd	64.49	3.77	4.73
							Found	63.37	3.90	4.86
3	**8a**	90/1	54	0.30	90	196	Calcd	64.55	3.75	4.72
							Found	63.34	3.71	4.65
4	**3a**	30/1	58	0.09	40	185	Calcd	64.41	4.00	4.66
							Found	63.10	3.71	4.46
5	**3a**	60/1	67	0.14	65	191	Calcd	64.52	3.87	4.68
							Found	63.13	3.67	4.53
6	**3a**	90/1	63	0.18	75	194	Calcd	64.56	3.82	4.69
							Found	63.62	3.91	5.02
7	**4a**	30/1	76	0.12	30	194	Calcd	65.11	3.89	4.62
							Found	63.80	3.76	4.53
8	**4a**	60/1	73	0.16	55	191	Calcd	64.89	3.81	4.66
							Found	63.30	3.70	4.40
9	**4a**	90/1	81	0.20	85	197	Calcd	64.81	3.78	4.68
							Found	63.70	4.14	4.76

[a] Molar feed ratio of monomer and comonomer.

[b] Measured at 25°C with c = 2 g/L in DMF.

[c] Apparent DP as determined by ^{1}H-NMR spectroscopy.

[d] From DSC measurements with a heating rate of 20°C/min.

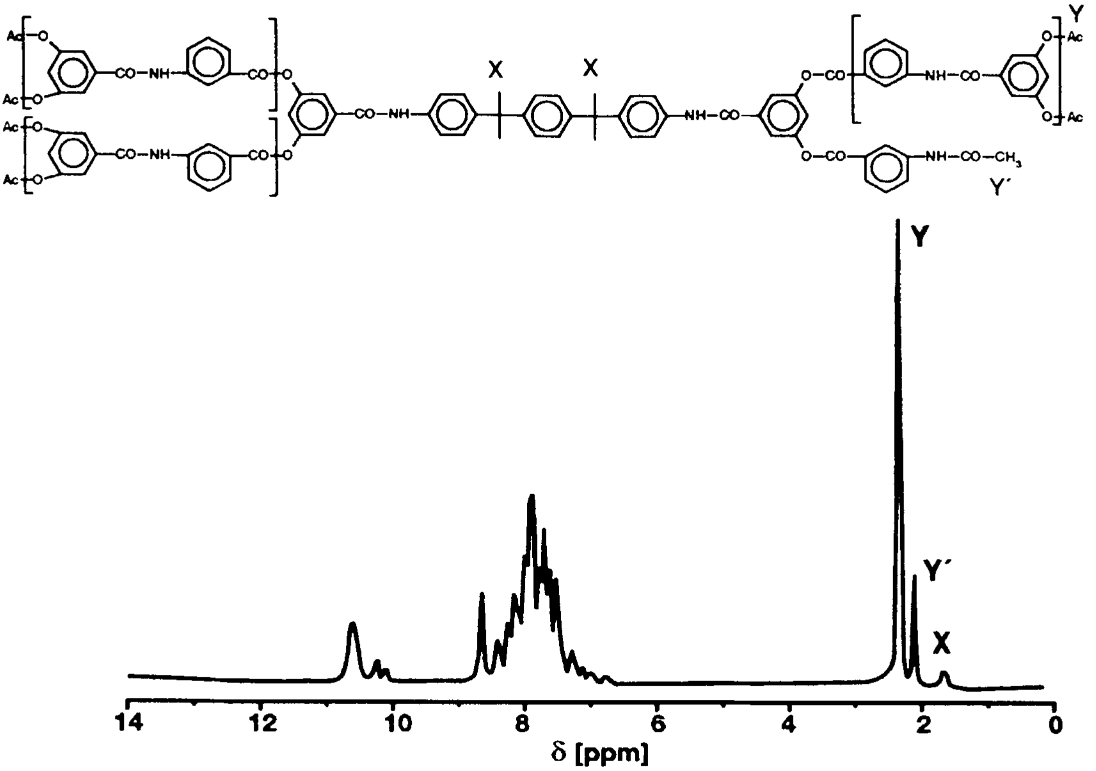


FIG. 6. 100 MHz ^{1}H-NMR spectrum of the poly(ester-amide) **4c** prepared with a monomer/star center ratio of 50:1.

compared to that of the acetate groups, and only one NH signal was detectable. This means that the sequence of this star-shaped PEA was mainly alternating. Similar results were obtained for the other samples prepared from **3a**, whereas the sequences of PEAs derived from **4a** were in between randomness and alternating. The reasons for the different rates of ester/amide exchange were not elucidated in this study. It is possible that traces of HCl resulting from the hydrolysis of chlorotrimethylsilane played the role of a catalyst in the randomization process.

Dendritic Poly(Ester-amide)s

The synthetic approach described above was modified in such a way that 3,5-bisacetoxybenzoylchloride was used for the acylation of silylated 3-aminobenzoic acid (Eq. 7). The success of this acylation was checked by desilylation of crude monomer **5** with ethanol. In this way, monomer **6** with free carboxyl group was prepared without isolation of intermediates. Both monomers **5** and **6** were polycondensed in bulk at three different temperatures (Table 3). The polycondensation of monomer **6** ("acetate method") yielded only a soluble PEA when the reaction temperature was lowered to 240°C. A soluble PEA with higher viscosity was obtained from the silylated monomer (**5**) even at 260°C. These results confirm previ-

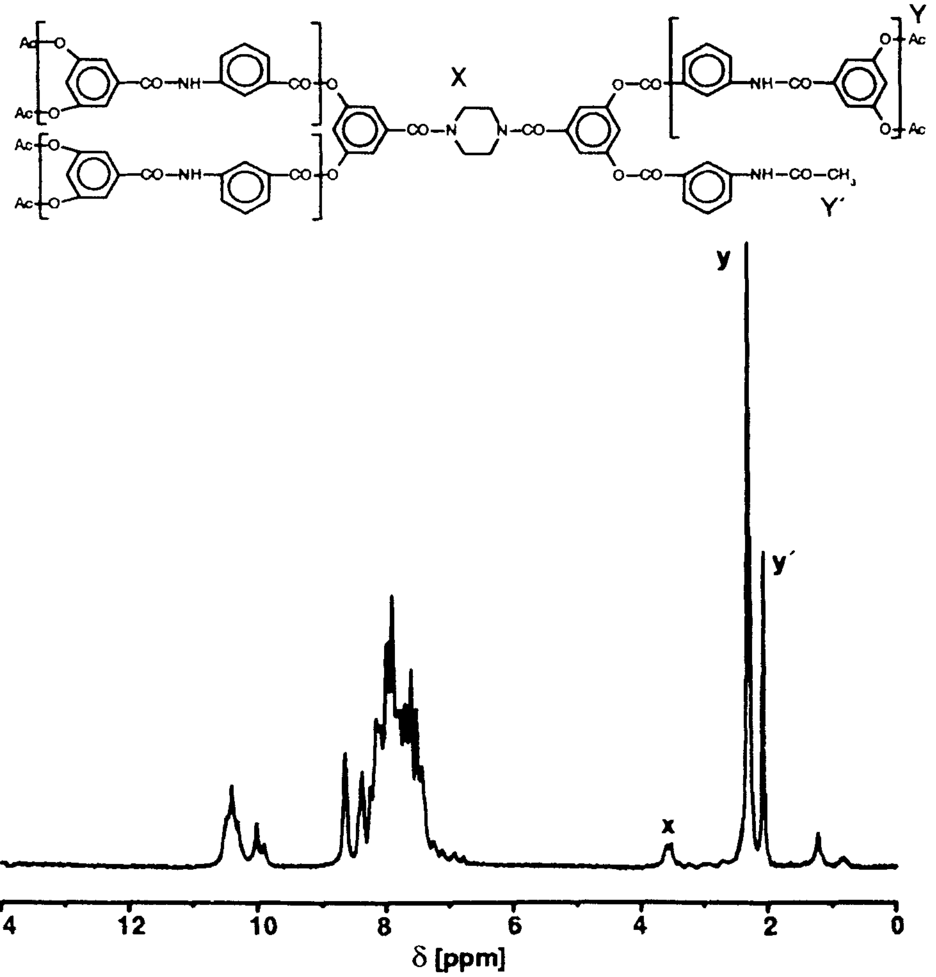


FIG. 7. 100 MHz ^{1}H-NMR spectrum of the poly(ester-amide) **8c** prepared with a monomer/star center ratio of 30:1.

ous studies indicating that free carboxyl groups catalyze more side reactions which cause crosslinking. Nonetheless, both ^{1}H- and ^{13}C-NMR spectra show evidence that the polycondensation of **5** involves an ester/amide exchange reaction, resulting in the formation of acetamide endgroups.

Finally, monomer **5** was polycondensed with the tetrafunctional comonomers **3a**, **4a**, and **8a**. The monomer/comonomer ratios were varied from 30 to 60 to 90. With a reaction temperature of 260°C, soluble dendritic and star-shaped PEAs were obtained in all nine experiments (Table 4). The viscosities increase in all three series with the monomer/comonomer ratio, indicating the expected incorporation of the comonomers. ^{1}H-NMR spectroscopy not only confirmed the successful incorporation of the star centers **3a**, **4a**, and **8a** (Figs. 6 and 7), it also allowed determination of the apparent DPs by quantification of the comonomer signals.

When compared to the feed ratios, these DPs deviate largely in the case of **8a** and **3a** for low monomer/comonomer ratios. This deviation is mainly a result of fractionation because lower oligomers were found in the filtrate after evaporation of the solvent mixture. Again it should be emphasized that the NMR spectroscopic DPs are maximum values and the true DPs may be lower. The finding that the viscosities of PEAs based on **8a** are higher than those of PEAs derived from **3a** or **4a** is surprising. An analogous discrepancy was found for the cocondensations of **3a**, **4a**, and **8a** with other monomers [11]. In the other words, this effect is systematic, but a reasonable explanation cannot be put forward at this time.

Finally, it should be mentioned that the detection of the piperazine ring in the PEAs **8b** requires the ^{1}H-NMR spectra to be measured at temperatures $\geq$ 80°C. Only at such high temperatures is rotation around the amide bonds frequent enough to detect a broad CH_2 signal. The NMR spectroscopic properties of polyamides based on piperazine are well documented in the literature [16, 17].

REFERENCES

[1] H. R. Kricheldorf, Q.-Z. Zang, and G. Schwarz, *Polymer, 23*, 1821 (1982).
[2] C. J. Hawker and J. M. Fréchet, *J. Am. Chem. Soc., 112*, 7638 (1990).
[3] H. R. Kricheldorf and T. Adebahr, *Makromol. Chem., 194*, 2103 (1993).
[4] H. R. Kricheldorf and O. Stöber, *Makromol. Chem., Rapid Commun., 15*, 87 (1994).
[5] S. R. Turner, B. I. Voit, and T. H. Mourey, *Macromolecules, 26*, 4617 (1993).
[6] A. E. Feiring and E. R. Wonchoba, *J. Polym. Sci., Polym. Chem. Ed., 32*, 389 (1994).
[7] H. R. Kricheldorf, X. Chen, and M. Al-Masri, *Macromolecules, 28*, 2118 (1995).
[8] H. R. Kricheldorf, G. Schwarz, and F. Ruhser, *Ibid., 24*, 3485 (1991).
[9] H. R. Kricheldorf and D. Lübbers, *Makromol. Chem., Rapid Commun., 12*, 691 (1991).
[10] H. R. Kricheldorf and G. Löhden, *Makromolecules, 27*, 1669 (1994).
[11] H. R. Kricheldorf and G. Löhden, *Makromol. Chem.*, In Press.
[12] Y. H. Kim, *J. Am. Chem. Soc., 114*, 4947 (1992).
[13] H. R. Eisenhauer and K. P. Link, *Ibid., 75*, 2046 (1953).
[14] V. P. Kozyukov, N. V. Mironova, and U. F. Moronov, *Zh. Obshch. Khim., 48*, 2541 (1978).
[15] H. R. Kricheldorf and O. Stöber, *Makromolecules*, In Press (New Polymer Syntheses. 78).
[16] H. R. Kricheldorf and K.-H. Rieth, *J. Polym. Sci., Polym. Lett. Ed., 16*, 379 (1978).
[17] Y. Mitron, R. McGarvey, and H. Morawetz, *Macromolecules, 2*, 154 (1968).

Received July 19, 1994
Revision received January 26, 1995