Layer Structures. 2. Influence of Spacers on Chain Packing and Phase Transitions of Poly(ester-imide)s Derived from N-(4-Carboxyphenyl)trimellitimide

Hans R. Kricheldorf,* Gert Schwarz, and Matthias Berghahn

Institut für Technische und Makromolekulare Chemie, Bundesstrasse 45, D-20146 Hamburg, Germany

Javier de Abajo and José de la Campa

Instituto de Ciencia y Tecnologia de Polimeros, Calle Juan de la Cierva 3, E-28006 Madrid, Spain

Received October 21, 1993; Revised Manuscript Received February 7, 1994.

ABSTRACT: Various poly(ester-imide)s of N-(4-carboxyphenyl)trimellitimide were prepared by transesterification of its dimethyl ester with various aliphatic diols. The following spacers were used: combinations of different α, ω -dihydroxyalkanes, mixtures of 1,12-dihydroxydodecane and tetraethylene glycol, neat di-, tri-, and tetraethylene glycol, and diols containing sulfide groups. Poly(ester-imide)s containing alkane spacers form layer structures in the solid state but neither monotropic nor enantiotropic liquid-crystalline (LC) phases. The three different kinds of solid state observed for these poly(ester-imide)s were interpreted as frozen smectic-A, -B, and -E phases. Spacers containing sulfide bonds yield poly(ester-imide)s which may form two different smectic crystal modifications but again no enantiotropic LC phase. Poly(ethylene oxide) spacers tend to suppress the crystallization and prevent the formation of layer structures. Taking also into account further results from the literature, we interpret the formation of layer structures as a phase separation on the nanometer level.

Introduction

In a previous part of this series¹ the synthesis and properties of poly(ester-imide)s 1a-h were reported. This



class of polyesters is of particular interest for the following reasons. N-(4-Carboxyphenyl)trimellitimide is the least expensive mesogenic dicarboxylic acid known so far, and thus, polymers derived from it may even be of commercial interest.² However, enantiotropic nematic polyesters have only been reported in combination with diphenols.²⁻⁶ In contrast, the semialiphatic poly(ester-imide)s 1a-h do not form an enantiotropic mobile mesophase. Yet, they can adopt three different kinds of layer structures in the solid state, namely, a smectic glass and two different crystal modifications.

In a more recent paper, Pardey et al.⁷ reported that two members of series 1a-h, namely, 1a and 1f, form a short living monotropic liquid-crystalline (LC) phase upon cooling. In this connection the present work had the purpose to improve the knowledge about polyesters derived from N-(4-carboxyphenyl)trimellitimide. The chemical structure and combination of spacers should be varied over a broad range. Their influence on the layer structures in the solid phase should be studied, on the one hand, and the formation of enantiotropic LC phases, on the other hand.

Experimental Section

Materials. The α,ω -dihydroxyalkanes and the oligo(ethylene glycols) were purchased from Aldrich Chemical Co. (Milwaukee,

* Abstract published in Advance ACS Abstracts, March 15, 1994.

WI) and dried for several days over P_4O_{10} in vacuo prior to use. 3-Bromopropanol, 1,4-dimercaptobutane, and 1,6-dimercaptohexane were also purchased from Aldrich Chemical Co. and reacted without further purification (see below). *N*-(4-Carboxyphenyl)trimellitimide was prepared from 4-aminobenzoic acid and trimellitic anhydride (both gifts of Bayer AG, Leverkusen) in dry dimethylformamide by means of acetic anhydride.³ Its esterification is described below.

Dimethyl Ester of N-(4-Carboxyphenyl)trimellitimide. N-(4-Carboxyphenyl)trimellitimide (0.5 mol) was suspended in methanol (1.51) and cooled to ca. -10 °C. Distilled thionyl chloride was then added dropwise with stirring, so that the temperature was kept below 0 °C. After complete addition, the reaction mixture was stirred for 1 h with cooling, for 20 h without cooling, and for 1 h under reflux. Afterward, the clear solution was concentrated in vacuo.

Diethyl Ester of N-(4-Carboxyphenyl)trimellitimide. N-[4-(Chloroformyl)phenyl]trimellitimide chloride (0.13 mol) was suspended in dry ethanol (200 mL), dry pyridine (0.26 mol) was added, and the reaction mixture was refluxed until a nearly clear solution was obtained. The warm solution was filtered and cooled in a refrigerator for 24 h. The crystallized product was then filtered off and recrystallized from ethanol. Yield 81%; mp 148-149 °C. Anal. Calcd for C₂₀H₁₇O₆N (367.4): C, 65.39; H, 4.66; N, 3.75. Found: C, 65.11; H, 4.78; N, 3.66. ¹H NMR (CDCl₉/TMS): $\delta = 1.34-1.52$ (m, 6H), 4.31-4.57 (m, 4H), 7.59 (d, 2H), 8.04 (d, 1H), 8.19 (d, 2H), 8.15 (dd, 1H), 8.60 (s, 1H).

1,12-Dihydroxy-4,9-dithiadodecane. Sodium (0.26 mol) was dissolved in dry ethanol (250 mL), and 1,4-dimercaptobutane (1.3 mol) was added dropwise in an atmosphere of nitrogen. 3-Bromo-1-propanol (0.27 mol) was then added, and after 1 h, the reaction mixture was stirred under reflux for an additional 3 h. After cooling, water (300 mL) was added and the ethanol removed in vacuo. The residue was extracted with three 200-mL portions of diethyl ether. The combined extracts were dried with MgSO₄. The dried ether solution was concentrated, and the product was distilled in vacuo over a short-path apparatus at a bath temperature of 150–160 °C. Yield 20%; n^{20}_{D} 1.5267. Anal. Calcd for C₁₀H₂₂O₂S₂ (238.4): C, 50.38; H, 9.30; S, 26.90. Found: C, 50.51; H, 9.17; S, 27.01. ¹H NMR (CDCl/TMS): $\delta = 1.63-1.95$ (m, 8H), 2.48-2.69 (m, 8H), 2.90-3.35 (m, 2H), 3.71 (t, 4H).

2540



1,14-Dihydroxy-4,11-dithiatetradecane. This spacer was prepared analogously from 1,6-dimercaptohexane. The crude product was freed from solvents in vacuo and recrystallized from diethyl ether/ligroin. Yield 74; mp 39-40 °C. Anal. Calcd for C₁₂H₂₆O₂S₂ (266.5): C, 54.09; H, 9.83; S, 24.06. Found: C, 54.28; H, 9.53; S, 23.90. ¹H NMR (CDCl₃/TMS): $\delta = 1.21-2.01$ (m, 14H), 2.19-2.78 (m, 8H), 3.76 (t, 4H).

Polycondensations. The diethyl ester of N-(4-carboxyphenyl)trimellitimide (12.0 mmol), a diol spacer (12.2 mmol), and titanium tetraisopropoxide (20 mg) were weighed into a cylindrical glass reactor equipped with a mechanical stirrer and gas inlet and outlet tubes. The reaction mixture was placed into a metal bath preheated to 150 °C. The temperature was then raised in a stepwise manner to 230 °C over a period of 4 h. The evolved ethanol was removed with a slow stream of nitrogen. Finally, vacuum was applied for 30 min. The cold polyester was dissolved in CH₂Cl₂/trifluoroacetic acid (volume ratio 4:1), precipitated into methanol, and dried at 80 °C.

With the dimethyl ester, the polycondensation was conducted in the temperature range 160–260 °C and the diols were used in an excess of 5 mol %.

Measurements. The viscosities were measured with an automated Ubbelohde viscometer thermostated at 20 °C. The ¹H NMR spectra were recorded with a Bruker AC-100 FT-NMR spectrometer in 5-mm-o.d. sample tubes. Internal TMS served for shift referencing. The DSC measurements were conducted with a Perkin-Elmer DSC-4 at a heating and cooling rate of 20 °C/min under nitrogen in aluminum pans. The WAXS powder patterns were recorded with a Siemens D-500 using Ni-filtered Cu Ka radiation. The ¹³C NMR CP/MAS spectra were obtained on a Bruker MSL 300 FT NMR spectrometer in ZrO₂ double-bearing rotors at a spinning rate of 4 kHz. A contact time of 1 ms and pulse interval of 4 s were applied.

Results and Discussion

Syntheses. All poly(ester-imide)s derived from aliphatic diols (2a-d, 3a,b, 4a-c, 5a-c, and 6a-g) (Chart 1) were prepared by Ti(OBu)₄-catalyzed transesterification of dimethyl N-(4-carboxyphenyl)trimellitimide (eq 1). This method has the advantage that acid-catalyzed side reactions are avoided. For comparison, the homopolyester 1c was prepared by two different methods: (a) transesterification according to eq 1 and (b) alcoholysis of the



(Alk) = divalent aliphatic spacer

dichloride of N-(4-carboxyphenyl)trimellitimide in bulk (eq 2) (a method used in ref 7). ¹H NMR spectroscopy

$$CKO^{CO} N - O - COCI + HO - (CH_2)_6 - OH - 1c (2)$$

revealed that the sample prepared by the acidolytic method (labeled 1c') contains ether groups (Figure 1). These ether groups are obviously formed by HCl-catalyzed side reaction of the alcohol groups. Such ether groups were never found when the transesterification method was used, and thus the transesterification method was preferred for all polycondensations of this work. The new sulfide spacers **7a**,**b** required for the syntheses of **3a**,**b** and **4a**-**c** were prepared by nucleophilic substitution of 3-bromopropanol according to eq 3. The yields and properties of poly(ester-

$$2HO - (CH_2)_3 - Br + HS - (CH_2)_n - SH + 2NaOEt -2NaBr. - 2EtOH + O - (CH_2)_3 - S - (CH_2)_n - S - (CH_2)_3 - OH$$
(3)
$$HO - (CH_2)_3 - S - (CH_2)_n - S - (CH_2)_3 - OH$$
(3)
$$7a, n = 4$$

b, n = 6

imide)s 2a-d are listed in Table 1, those of poly(esterimide)s 3a,b and 4a-c in Table 2, those of 5a-c in Table 3, and those of 6a-g in Table 4.

The 100-MHz ¹H NMR spectra of all polyesters were measured in a mixture of CDCl₃ and trifluoroacetic acid (volume ratio 4:1). As illustrated by Figures 1-3 the chemical shifts and intensity ratios of the aliphatic and

	yield (%)	η_{inh}^{a} (dL/g)	elem form (form wt)		elem	anal.		Т _б (°С)	$T_{m1}^{b,c}$ (°C)	$T_{m2}^{b,d}$ (°C)	<i>T</i> _c ^{b,e} (°C)
polym					% C	% H	% N				
2a	95	0.72	C ₂₈ H ₃₁ NO ₆	calcd	70.03	6.54	2.93	44	159-163	180-185	113
			(477.5)	found	70.13	6.65	2.99				
2b	92	1.28	$C_{54}H_{58}N_2O_{12}$	calcd	69.98	6.26	3.02	54	141-142	157 - 159	119
			(927.0)	found	69.69	6.40	3.31				
2c	91	0.51	C ₅₃ H ₅₆ N ₂ O ₁₂	calcd	69.74	6.14	3.07	54	$115 - (120)^{f}$	155-156	99
			(913.0)	found	69.57	6.20	3.14				
2d	86	0.48	C52H54N2O12	calcd	69.49	6.01	3.12	60	138-139	159-160	123
			(899.0)	found	69.19	6.30	3.40				

Table 1. Yields and Properties of Poly(ester-imide)s 2a-d

^a Measured at 25 °C with c = 5 g/L in CH₂Cl₂/trifluoroacetic acid (volume ratio 4:1). ^b From DSC measurements with a heating/cooling rate of 20 °C/min. ^c Second heating (after cooling from the isotropic melt with a cooling rate of -20 °C/min). ^d Third heating after annealing 15-20 °C below T_{m2} . ^e First cooling trace (cooling rate -20 °C/min). ^f After annealing at 70 °C.

Table 2. Tields and Properties of Poly(ester-imide)s 3a.b at
--

	vield	ninba		elem anal.						T	d spacing	
polym	(%)	(dL/g)	(form wt)		% C	% H	% N	% S	(•Ĉ)	(°C)	(°C)	(Å)
3a	98	0.54	$C_{26}H_{27}NO_6S_2$ (513.6)	calcd found	60.89 60.60	5.30 5.32	2.73 2.67	12.48 12.56	39	101¢	134 ^d 144 ^e	26.7
3b	98	0.46	$C_{28}H_{31}NO_6S_2$ (541.7)	calcd found	62.09 62.22	5.77 5.84	$2.59 \\ 2.52$	$11.84 \\ 11.48$	31	92	128	30.4
4a	99	0.61	$C_{132}H_{139}N_5O_{30}S_8$ (2532.0)	calcd found	62.62 62.79	5.53 5.43	2.77 2.68	10.13 10.18	41	104	149	26.7
4b	94	0.66	$C_{54}H_{58}N_2O_{12}S_2$ (991.2)	calcd found	65.44 66.73	5.90 6.30	2.83 2.62	6.47 5.97	42	108	156	26.9
4c	88	0.65	$C_{138}H_{151}N_5O_{30}S_2$ (2423.8)	calcd found	68.38 68.44	6.28 6.36	2.89 2.77	2.65 2.76	44	120	163	27.6

^a Measured at 20 °C with c = 2 g/L in CH₂Cl₂/trifluoroacetic acid (volume ratio 4:1). ^b From DSC measurements with a heating rate of 20 °C/min. ^c After annealing at 70 °C for 12 h. ^d After annealing at 110 °C for 16 h. ^c After annealing at 125 °C for 16 h.

Table 3. Yields and Properties of Poly(ester-imide)s 5a-c

	vield	nLQ	elem form		elem	ТЬ	Τ ¢		
polym	(%)	(dL/g)	(form wt)		% C	% H	% N	(°Č)	(°C)
5 a	99	0.41	$C_{20}H_{15}NO_7$ (381.3)	calcd	63.00 62.15	3.93 4 21	3.67	101	138
5b	94	0.26	$C_{22}H_{19}NO_8$ (425.4)	calcd	62.11 61.67	4.50	3.30 3.19	63	106
5c	88	0.40	$C_{24}H_{23}NO_9$ (469.4)	calcd found	61.41 61.10	4.90 5.20	2.99 3.00	52	101

^a Measured at 25 °C with c = 2 g/L in CH₂Cl₂/trifluoroacetic acid (volume ratio 4:1). ^b From DSC measurements with a heating rate of 20 °C/min. ^c After annealing ~ 20 °C below the given $T_{\rm m}$.

Table 4. Yields and Properties of Copoly(ester-imide)s 6a-g

yield $\eta_{inh}{}^a$ polym (%) (dL/g)		elem form		elem a	anal.	T.º	T-16	T_{m2}^{b}	T.º		
		(dL/g)	(form wt)		% C	% H	% N	(°C)	(°Ĉ)	(°C)	(°Č)
6a.	87	0.34	C ₂₅₂ H ₂₅₄ N ₁₀ O ₈₁	calcd	64.14	5.43	2.97	49	102		
			(4718.80)	found	62.04	5.31	2.79				
6b	94	0.43	C256H262N10O78	calcd	65.05	5.59	2.96	50	102		
			(4726.91)	found	63. 9 0	5.51	2.85				
6c	85	0.48	C260H270N10O75	calcd	65.95	5.75	2.96	48	104		
			(4735.02)	found	64.01	5.60	2.80				
6d	86	0.46	C284H278N10O72	calcd	66.85	5.91	2.96	47	100	146	58
			(4743.12)	found	66.02	5.93	3.12		(83)		
6e	97	0.56	Core Hore N10Oco	calcd	67.75	6.07	2.95	49	124	157	86
	•••	0.00	(4751.23)	found	67.82	6.31	3.10		(85)		00
6 f	84	0.47	Coro Hood N10Occ	caled	68.64	6.23	2.94	50	126	160	97
	01	0.11	(4759.35)	found	68.99	6.35	2.71		(89)	100	01
6g	92	0.49	C276H202N10O63	calcd	69.53	6.38	2.94	53	(00)	162	112
- 0			(4767.46)	found	69.50	6.60	2.78	20	(99)		

^a Measured at 25 °C with c = 5 g/L in CH₂Cl₂/trifluoroacetic acid (volume ratio 4:1). ^b From DSC measurements with a heating rate of 20 °C/min. °From DSC measurements with a cooling rate of -20 °C/min.

aromatic protons confirm the expected structures, which are in agreement with the elemental analyses listed in Tables 1-3.

Properties of Poly(ester-imide) 2a (1h). When the poly(ester-imide)s **2b-d** were examined by optical microscopy with crossed polarizers, no enantiotropic liquidcrystalline (LC) melt was detectable. Even a monotropic LC phase with sufficient lifetime for unambiguous identification (>5 min) was not observable. In agreement with these findings, the DSC measurements of 2a (1h) displayed only one sharp endotherm in the heating trace (Figure 4A) with a maximum around 161 ± 2 °C. This endotherm was detectable regardless of whether the sample was slowly or rapidly cooled. It was also independent of any annealing at temperatures below 100 °C. The same endotherm (and thus modification) was reported for 1h (2a) in a previous



Figure 1. 100-MHz¹H NMR spectrum of poly(ester-imide) 1c', prepared by polycondensation of 1,6-hexanediol and N-[4'-(chloroformyl)phenyl]trimellitimide chloride in bulk.



Figure 2. 100-MHz ¹H NMR spectrum of poly(ester-imide) 3b.



Figure 3. 100-MHz ¹H NMR spectrum of poly(ester-imide) 5c. paper.¹ However, in contrast to other members of series 1a-g, a second high-melting modification was previously not found for 1h (2a).¹ In the present work, 2a (1h) was subjected to extensive annealing at 170 °C, i.e., in the isotropic melt immediately above T_{m1} . As illustrated by



Figure 4. DSC measurements (heating rate 20 °C/min) of poly-(ester-imide) 1h (2a): (A) second heating after cooling from the melt with a rate of -20 °C/min; (B) after annealing at 170 °C for 3 h; (C) after annealing at 170 °C for 24 h.



Figure 5. WAXS powder patterns of poly(ester-imide) 1h (2a): (A) after quenching from the isotropic melt; (B) after annealing at 70 °C for 1 h; (C) after annealing at 170 °C for 24 h.

Figure 4 (curves B and C), prolonged annealing indeed generated a second modification (denoted II) with an endotherm in the temperature range 180–185 °C. Microscopic observation of the annealing process with crossed polarizers revealed the appearance of birefringent particles with irregular shape, whereas the formation of spherulites was not observed.

¹³C NMR CP/MAS measurements of the glassy state and of both quasicrystalline modifications, I and II,

Table 5. Layer Distances (d) of Poly(ester-imide)s 1e-h and 2b-d As Calculated from the X-ray Reflections

homopoly- (ester–imide)s	d _{mead} (A)	d _{max,trans} ^a (A)	d _{max.gauche} b (A)	copoly- (ester–imide)s	d _{mead} (A)	
1h(2a)(n=12)				2b		
quenched	26.8			quenched	26.0	
modific I	26.8	30.1	26.4	modific I	25.0	
modific II	26.8			modific II	26.0	
lg(n = 10)				2c		
quenched	25.2	27.6	24.6	quenched	26.0	
modific I	25.2			modific I	25.0	
				modific II	25.2	
1f(n = 9)				2d		
quenched	22.1	26.3	23.7	quenched	25.2	
modific I	21.6			-		
1e(n = 8)						
quenched	22.6			modific I	24.5	
modific I	22.6	25.1	22.6	modific II	25.2	
modific II	22.2					

^a Maximum lengths of the repeating units calculated for spacers with all-trans conformation. ^b Maximum lengths of the repeating units calculated for spacers with all-gauche conformation.

revealed that the spacers prefer gauche conformations. Only one relatively broad signal at 31 ppm was found without any side peak or shoulder, indicating the presence of trans conformations. The absence of any order in the spacer layers means that the spacers do not contribute any reflection to the WAXS patterns of modification II. These results confirm that the different modifications of 2a (1h) almost exclusively originate from different conformations and "chain packings" of the aromatic building blocks.

Slow heating or annealing above the $T_{\rm g}$ (but below the $T_{\rm m}$ of modification I) results in a narrowing of the broad reflection around $2\theta = 20^{\circ}$ whereas the small-angle reflections (d spacing) remain constant (Figure 5B). This change may be interpreted as a gradual formation of a nearly hexagonal packing of the aromatic building blocks, or, in other words, the gradual formation of a frozen smectic-B phase. Both smectic glass and solid smectic-B phase involve a certain conformational disorder of the imide units resulting from the rotation of the phenylene ring relative to the phthalimide group around the C-N σ bond (ω in 8). The noncoplanarity of both ring systems gives the entire aromatic building blocks a somewhat cylindrical shape, which favors a more or less perfect hexagonal array.



After annealing at 170 °C, the WAXS pattern of Figure 5C was obtained. It demonstrates that modification II is characterized by layers with highly ordered imide building blocks. Taking into account that the layer distance did not change (Table 5), we may label this modification smectic-E. This means that the mesogens form a kind of orthorhombic order in the a-b plane (with the c axis parallel to the main chain). A true orthorhombic crystal lattice is, of course, not formed, because an adequate order in the c direction does not exist. This hypothesis allows the interpretation of the sharp reflections at 5.4 and 3.9 Å as direct distances between neighboring mesogens in the a-bplane. Furthermore, when upright mesogens are present in all three kinds of solid state (and the measured d spacings do not indicate any change), then the assumption of frozen smectic-A, -B, and -E phases is a consistent and logical series of increasing two-dimensional order.



Figure 6. DSC measurements (heating rate $20 \,^{\circ}$ C/min) of copoly-(ester-imide) 2d: (A) after annealing at 70 $^{\circ}$ C for 24 h; (B) after slow cooling (-10 $^{\circ}$ C/min) from the isotropic melt; (C) after annealing at 140 $^{\circ}$ C for 6 h.

When the mesogens are tilted, the corresponding sequence of two-dimensional order would be smectic-C, smectic-F or -I, and smectic-H. A definite proof for perfectly upright mesogens cannot be offered. However, the measured d spacings are in good agreement with the values calculated for upright mesogens and spacers with gauche conformations (Table 5). At least a predominance of gauche conformations is confirmed by the ¹³C NMR CP/MAS spectrum of 2a, which displays one intense CH_2 signal between 34 and 28 ppm and a maximum at 31 ppm (for comparison, see Figure 11). ²H NMR measurements of 2a with a deuterated spacer (to be published in a future paper) support this interpretation, indicating a high mobility of the spacers in the solid state. The assumption of tilted mesogens in combination with spacers having gauche conformations should result in experimental dspacings 2-6 Å below the measured values. In other words, all available data clearly favor the hypothesis of upright mesogens and thus the existence of solid smectic-A, -B, and -E phases.

Properties of Copoly(ester-imide)s 2b-d. The thermal properties and chain packing of copolyesters **2b-d** were found to resemble largely those of homopolyester **2a** (1h). As illustrated by Figures 6 and 7, **2d** (and also **2b,c**) can adopt two modifications, which are almost identical with those of **2a** (1h), the main difference being lower melting points. Another difference is detectable in the first heating trace, namely, a third endotherm at relatively low temperature. This endotherm does not appear when the samples are slowly cooled from the isotropic melt (Figure 6B) or annealed for a short time at 100-120 °C. A satisfactory explanation for this low-temperature endotherm cannot be offered at this time.

A third characteristic difference between 2a (1h) and 2b-d concerns the layer distances (d spacings) calculated from the small-angle reflection. The results listed in Table 5 indicate that the thermal history (quenching, annealing, etc.) has little influence on the d spacings of the homopolymers 1e-h which allows for easier comparison with



Figure 7. WAXS powder patterns of copoly(ester-imide) 2d: (A) after annealing at 70 °C for 24 h; (B) after slow cooling from the isotropic melt; (C) after annealing at 140 °C for 6 h.

copolymers 2b-d. As previously reported, the poly(esterimide)s show an "odd-even effect" for their d spacings, and this is the reason for the relatively low experimental values of 1f. Such an odd-even effect cannot exist and dose, in fact, not exist for the copolymers; thus, a comparison of 1f and 2c is not very informative. Therefore, the most interesting and easiest to interpret comparison is that between 1e and 1h (2a), on the one hand, and 1h (2a) and 2d, on the other hand.

In the case of 2b-d a random sequence of the different spacers has the consequence that on average 50% of all spacers in one layer are short spacers. Hence, the maximum layer distance is given by the length of the fully extended short spacer. The experimental values of 2dindeed confirm this consideration, because they agree well with the value calculated for 1e. This means that the short and long spacers in 2b-d also represent two different populations of conformations: the short spacers adopt the all-trans conformation and the long spacers are more or less coiled. A schematic illustration of the layer structure of 2d is given in Figure 8.

Properties of Poly(ester-imide)s 3a,b and 4a-c. Poly(ester-imide)s **3a,b** and **4a-c** have several properties in common with those of **2a-d**. As revealed by optical microscopy with crossed polarizers, neither **3a,b** nor **4a-c** form an enantiotropic LC phase or a monotropic LC phase with a lifetime of several minutes.

Poly(ester-imide)s 3a,b and 4a-c are again semicrystalline materials which form a layer structure in the solid state. However, the DSC measurements revealed that the sulfide groups of the spacers affect both the kinetic and the thermodynamic aspects of the crystallization. The thermodynamic aspect (i.e., a lower melting enthalpy) is evidenced by the lower melting points of 3a,b compared to 1h (2a) (Table 2). The negative influence on the crystallization kinetics is detectable when samples of 3a,band 4a are cooled from the isotropic melt at rate of -20°C/min. No crystallization takes place even at this low cooling rate. The higher content of the dodecamethylene



Figure 8. Schematic illustration of the layer structure of copoly-(ester-imide) 2d.



Scattering angle 2Θ

Figure 9. WAXS powder patterns of (A) poly(ester-imide) 4a annealed at 65 °C for 44 h and (B) poly(ester-imide) 3a annealed at 65 °C for 44 h.

spacer in 4b,c accelerates the crystallization, and one or two endotherms show up in the second heating trace. In analogy to 2a-d, 3a,b and 4a-c can form two more or less crystalline modifications. Annealing at temperatures ≥ 100 °C yields in all five cases the higher melting modification II (T_{m_2} in Table 2). Annealing, betwen T_g and 80 °C yields the lower melting modification I (T_{m_1} in Table 2). In analogy to 1h (2a), poly(ester-imide)s 3a,b show a kinetic preference for the formation of modification I. Yet, in the case of 4a-c slowly conducted heating/cooling cycles favor the formation of modification II. The T_{m_1} and T_{m_2} listed in Table 2 show how an increasing content of the dodecanediol unit raises the melting points of both modifications.

The WAXS powder patterns of **3a**, **b** and **4a**-**c** are almost identical with those of **2a**-**d**. When **3a**, **b** and **4a**-**c** are rapidly cooled from the melt, a frozen smectic-A phase (or smectic glass) is obtained with a sharp small-angle reflection representing the layer distances and with a broad halo around $2\theta = 20^{\circ}$. The formation of modification I is characterized by a sharper reflection around 2θ :20° in analogy to the WAXS patterns of Figures 5B and 7B. The WAXS patterns of modification II are nearly identical for all samples, with sharp reflections at 5.4, 4.6, 3.9, and 3.2 Å (Figure 9). Obviously, all these reflections originate from the lateral order of the imide units in their layers without any contribution from the spacers, in agreement



Figure 10. WAXS powder patterns of (A) poly(ester-imide) 5c annealed at $65 \,^{\circ}C$ for $3 \,^{\circ}days$, (B) copoly(ester-imide) 6b annealed at $65 \,^{\circ}C$ for 8 h, and (C) copoly(ester-imide) 6f annealed at $65 \,^{\circ}C$ for 8 h.

with the WAXS patterns of 2a-d. Thus, the most important information extracted from the studies of 3a,band 4a-c is the finding that none of these poly(esterimide)s forms an LC phase despite significantly lower melting temperatures compared to those of 1a-h or 2a-d.

Properties of Poly(ester-imide)s 5a-c and 6a-g. Poly(ester-imide)s 5a-c and 6a-g agree completely with all other poly(ester-imide)s of this work in that they do not form a LC phase. However, a characteristic difference, and the most conspicious property, of 5a-c is their tendency to form an amorphous isotropic phase. Even after 1 day of annealing, crystallization was not detectable. Annealing over a period of 3 days (at 120 °C for 5a and 80 °C for 5b.c) was necessary to induce partial crystallization. The reflections between $2\theta = 10^{\circ}$ and $2\theta = 30^{\circ}$ agree with those of other poly(ester-imide)s in this work (Figure 10), but a small-angle reflection indicating a layer structure $(2\theta = 1.65^{\circ})$ was never found in the case of 5a-c. These findings obviously mean that the polar spacers can easily "dissolve" the polar imide groups (and vice versa), and the tendency of forming layer structures is almost completely lost.

The copoly(ester-imide)s of series 6a-h show the expected influence of the dodecamethylene spacer. Increasing molar fraction of this aliphatic chain favors the crystallization kinetically and thermodynamically. It induces again the formation of layer structures (Figure 10C) and of two crystal modifications (Table 4). Clearly, the polarity of the spacer plays a decisive role in the kinetic and thermodynamic tendency to form a layer structure. The ¹³C NMR CP/MAS spectra of **6b**-h display separate signals for the tetraethylene glycol spacer and for the dodecane unit and indicate again a predominance of gauche conformations in the latter case (Figure 11).

Discussion

The findings reported above and some results reported in the literature¹ allow the discussion of two interesting



Figure 11. 75.4-MHz ¹³C NMR CP/MAS spectrum of copoly-(ester-imide) 6d: X = signal of the tetraethylene glycol unit; Z = signal of the dodecane spacer (central carbons).

aspects. The first important aspect is the mesogenic character of N-(4-carboxyphenyl)trimellitimide. The observation that none of the poly(ester-imide)s described in this work form a stable LC phase clearly indicates that the imide dicarboxylic acid is a poor mesogen. Particularly informative are 3a and 3b, because these poly(esterimide)s form layer structures in the solid state, whereas no LC melt is formed despite low melting temperatures. In other words, the isotropization temperatures of a hypothetical LC phase must be lower than 100 °C. In contrast, poly(ester-imide)s of N-(4-carboxyphenyl)trimellitimide and various diphenols form highly stable nematic melts with isotropization temperatures above 450 °C. This discrepancy suggests that the mesogenic character strongly depends on the presence of an aromatic ester group. This suggestion is confirmed by the synthesis of poly(ester-imide)s 9a-c from the semiaromatic spacers 10a-e. As will be reported in a future part of this series, the poly(ester-imide)s 9b (n = 3) and 9d (n = 5) form enantiotropic LC phases.



The second aspect of importance concerns the formation of layer structures in the solid state. As reported previously,¹ the poly(ester-imide)s 1a-h form layers corresponding to the lengths of the repeating units, even when quenched from the isotropic melt. The resulting solid mesophase may be called smectic glass, because absolutely no order is detectable inside the layers. The layers formed by copoly(ester-imide)s 2h-d are slightly more ordered. In contrast, poly(ester-imide)s 5a-c do not form layers at all and are even reluctant to crystalline. These properties of 5a-c may be understood in terms of a good compatibility

between imide unit and spacer, or, in other words, the spacers can dissolve the potential mesogens. These observations suggest that the formation of layers by poly-(ester-imide)s 1a-h, 2a-d, 3a,b, and 4a-c may be understood as phase separation on the molecular level (or on the nanometer scale). It has clearly nothing to do with any ordered structure of the mesogens or spacers inside the layers. This suggestion is confirmed by results of Noël et al.,8 who found that polyesters derived from 4,4"terphenyldicarboxylic acid and oligo(ethylene glycol)s (11) form layers in the solid and in the liquid-crystalline state. These polyesters represent the inverse distribution of polar and nonpolar units compared to 1a-h or 2a-d. The mesogen is nonpolar and the spacers are highly polar. It is obviously a regular sequence of polar and nonpolar building blocks which creates a layer structure in the solid state. Whether this layer structure can be maintained in the liquid state is another question.

References and Notes

- Kricheldorf, H. R.; Schwarz, G.; de Abajo, J.; de la Campa, J. G. Polymer 1991, 32, 942.
- (2) Irwin, R. S. U.S. Patent 4,176,223, 1979 (to E. I. du Pont de Nemours and Co.).
- (3) Kricheldorf, H. R.; Domschke, A.; Schwarz, G. Macromolecules 1991, 24, 1011.
- (4) de Abajo, J.; de la Campa, J. G.; Kricheldorf, H. R.; Schwarz, G. Eur. Polym. J. 1992, 28, 261.
- (5) Kricheldorf, H. R.; Hüner, R. J. Polym. Sci., Part A: Polym. Chem. 1992, 30, 337.
- (6) Kricheldorf, H. R.; Bruhn, C.; Rusanov, A.; Komarova, L. J. Polym. Sci., Part A: Polym. Chem. 1993, 31, 279.
- (7) Pardey, R.; Zhang, A.; Gabori, P. A.; Harris, F. W.; Cheng, S. Z. D.; Aducci, J.; Facinelli, J. V.; Lenz, R. W. Macromolecules 1992, 25, 5060.
- (8) Noël, C.; Friedrich, C.; Bosio, L.; Strazielle, L. Polymer 1984, 25, 1281.