anhydride IR absorbance was obtained. Attempted polymerization of this dipeptide by the melt condensation yielded a tar.

Since these polymers are considered as biodegradable materials, we have studied their degradation characteristics under physiological conditions (sodium phosphate buffer 0.1 M, pH 7.4, 37 °C). Thick films (1 mm) of aliphatic poly(anhydrides) of adipic acid, sebacic acid, and dodecanedioic acid were completely degraded after 5, 12, and 18 days, respectively. Thick films (1 mm) of aromatic polymers of terephthalic acid and CPP showed a weight loss of 33% and 24%, respectively after 3 months.

A comparative stability study of storage under anhydrous conditions was performed. Poly(SA) prepared by the new method, using PVP, was stable under storage. On the other hand, poly(SA) prepared with TEA followed by water extraction of the TEA·HCl salt was hydrolyzed under storage to an insoluble solid within 1 week. This instability was attributed to the polymer hydrolysis by water molecules entrapped in the polymer bulk during purification.

This study presents one-step polymerization of poly(anhydrides) by solution polymerization at ambient temperature. Either phosgene or diphosgene proved convenient to synthesize pure poly(anhydrides); however, diphosgene is the preferred coupling reagent. In contrast with the traditional use of dehydration agents, the use of insoluble acid acceptors (PVP or inorganic bases) yielded highly pure polymers. The use of various solvent systems is complimentary to the use of the insoluble bases in chloroform. The choice of the right solvent system can be used for precipitating exclusively either the polymer or the amine–acid salt; thus, filtration leads to pure polymers. These methods are advantageous for the polymerization of heat-sensitive dicarboxylic acids such as therapeutically active diacids and poly(anhydrides) of dipeptides.

Acknowledgment. This work supported in part by grants from NOVA PHARMACEUTICALS and N.I.H. (GM26698). We wish to thank Prof. J. Kohn for his help.

Registry No. Phosgene, 75-44-5; diphosgene, 503-38-8; sebacoyl chloride, 111-19-3.

References and Notes

(1) Rosen, H. B.; Chang, J.; Wnek, G. E.; Linhardt, R. J.; Langer, R. *Biomaterials* **1983,** *4,* 131.
(2) Leong, K. W.; Brott, B. C.; Langer, R. *J. Biomed. Mater. Res.* **1985,** *19,* 941.
(3) Leong, K. W.; D'Amore, P.; Marietta, M.; Langer, R. J. *J. Biomed. Mater. Res.* **1986,** *20,* 51.
(4) Leong, K. W.; Kost J.; Mathiowitz, E.; Langer, R. *Biomaterials* **1986,** *7,* 364.
(5) Domb, A. J.; Langer, R. *J. Polym. Sci.* **1987,** *25,* 3373.
(6) Hill, J.; Carrothers, W. H. *J. Am. Chem. Soc.* **1932,** *54,* 1569.
(7) Yoda, N.; Miyake, A. *Bull. Chem. Soc. Jpn.* **1959,** *32,* 1120.
(8) Subramanyam, R.; Pinkus, A. G. *J. Macromol. Sci., Chem.* **1985,** *A22*(1), 23, and references within.
(9) Leong, K. W.; Simonte, V.; Langer, R. J. *Macromolecules* **1987,** *20,* 705.
(10) Matzner, M.; Kurkjy, R. P.; Cotter, R. J. *Chem. Rev.* **1964,** *64,* 645.
(11) Norton Thiokol, Inc. Technical review, diphosgene, 1987.
(12) Kurita, K.; et al. *J. Org. Chem.* **1976,** *41,* 2070.
(13) Oya, M.; Kataki, R.; Nakai, H. *Chem. Lett.* **1973,** 1143.
(14) Shopov, I.; Dramov, S. *Izv. Otd. Khim. Nauki* (*Bulg. Akad. Nauk.*) **1969,** *2*(1), 45; *Chem. Abstr.* **1969,** *71,* 91956w.
(15) Conix, A. *J. Polym. Sci.* **1958,** *29,* 343.
(16) Bodanszky, M., Bodanszky, A., Eds.; *The Practice of Peptide Synthesis*; Springer-Verlag: New York, 1984.
(17) *Encycl. Polym. Sci. Technol.* **1969,** *10,* 640.
(18) Rinderknecht, H.; Ma, V. *Helv. Chim. Acta* **1964,** *47,* 162.
(19) Hill, J. *J. Am. Chem. Soc.* **1930,** *52,* 4110.

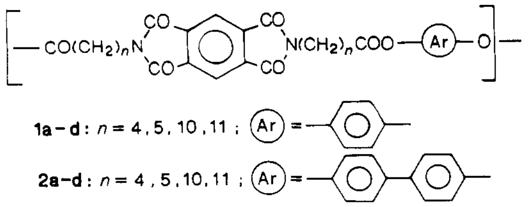
New Polymer Syntheses. 24. Liquid Crystal Poly(ester imides) Derived from Benzophenonetetracarboxylic Dianhydride and ω-Amino Acids

Hans R. Kricheldorf,* Ralf Pakull, and Stefan Buchner

Institut für Technische und Makromolekulare Chemie der Universität, Bundesstrasse 45, D-2000 Hamburg 13, West Germany. *Received October 8, 1987*

ABSTRACT: Six dicarboxylic acids were prepared from benzophenone-3,3′,4,4′-tetracarboxylic dianhydride (BTA) and 4-aminobutyric acid, 5-aminovaleric acid, 6-aminocaproic acid, 7-aminoheptanoic acid lactam, 11-aminoundecanoic acid, and 12-aminododecanoic acid. These diacids were condensed with the diacetates of hydroquinone, 2,6-dihydroxynaphthalene or 4,4′-dihydroxybiphenyl. The resulting poly(ester imides) were characterized by inherent viscosity elemental analyses, differential scanning calorimetry (DSC), observation under polarized light, and WAXS measurements. Formation of a smectic melt was found for almost all polymers containing 4.4′-dihydroxybiphenyl. These thermotropic poly(ester imides) were also characterized by thermomechanical and thermogravimetric analyses, and an odd–even effect was found for the heat-distortion temperatures. Only one poly(ester imide) of hydroquinone formed a mesophase. Because in this case no component of the polymer chain is a mesogen, the formation of a mesophase indicates a special cooperative effect, presumably a charge-transfer interaction, between the aromatic monomer units.

Introduction



In a previous part of this series[1] poly(ester imides) derived from pyromellitic anhydride (PMA), ω-amino acids, and various bisphenols, in particular hydroquinone (**1a–d**) or 4,4′-dihdyroxybiphenyl (**2a–d**) were described. These poly(ester imides) were investigated with regard to the formation of mesophases and with regard to their thermomechanical properties. Two interesting results were obtained. First, the polymers **2a–d** did not form a well-defined mesophase, although the 4,4′-dihydroxybiphenyl unit is well-known as a mesogenic group.[2,3] Surprisingly, poly(ester imides) containing hydroquinone (e.g., **1c**) or

0024-9297/88/2221-1929$01.50/0

Table I
Yields and Properties of the Diacids 3a–f Prepared from Benzophenone-3,3′,4,4′-tetracarboxylic Dianhydride and Various Amino Acids

formula (n)	yield, %	mp, °C	elem formula (mol wt)		elem anal C	H	N
3a (3)	88.9	221–223	$C_{25}H_{20}N_2O_9$ (492.45)	calcd	60.68	4.09	5.69
				found	60.99	4.31	5.73
3b (4)	44.2	201–203	$C_{27}H_{24}N_2O_9$ (520.50)	calcd	62.31	4.65	5.38
				found	62.36	4.72	5.54
3c (5)	42.7	190–192	$C_{29}H_{28}N_2O_9$ (548.55)	calcd	63.50	5.15	5.11
				found	63.65	5.23	5.38
3d (10)	56.6	151–153	$C_{39}H_{48}N_2O_9$ (688.82)	calcd	68.00	7.02	4.07
				found	67.88	7.01	4.27
3e (11)	83.1	146–148	$C_{41}H_{52}N_2O_9$ (716.88)	calcd	68.69	7.31	3.91
				found	68.86	7.34	4.31

bis(4-hydroxyphenyl) ether exhibited a mesophase, even though both bisphenols are not mesogenic. Obviously, in this case the pyromellitimide unit plays the role of the mesogen. Second, high heat-distortion temperatures (HDT) were found for both series of poly(ester imides) **1a–d** and **2a–d**. In contrast to most semicrystalline polymers including various thermotropic liquid crystal (LC) polyesters,[4–6] the HDTs of **1a–d** and **2a–d** are related to the melting points and not to the glass-transition temperatures (T_g's). This result means that the crystallites form the coherent matrix and not the amorphous phase.

The present work had the purpose of extending the previous studies to poly(ester imides) derived from 3,3′,4,4′-benzophenonetetracarboxylic acid and ω-amino acids (i.e., monomers **3a–f**).

Experimental Section

Materials. ϵ-Aminocaproic acid, hydroquinone, and 4,4′-dihydroxybiphenyl were gifts of Bayer AG (D-4150 Krefeld-Uerdingen) and were used without purification. All other acids, 2,6-dihydroxynaphthalene, and benzophenone-3,3′,4,4′-tetracarboxylic dianhydride were purchased from Aldrich Co. (St. Louis, MO). The anhydride was recrystallized from a mixture of boiling dioxane and acetic anhydride. The bisphenols were acetylated by means of acetic anhydride in boiling toluene.

***N,N*′-Bis(ω-carboxyalkyl)benzophenone-3,3′,4,4′-tetracarboxylic Diimides 3a–c,e,f.** Benzophenone -3,3′,4,4′-tetracarboxylic dianhydride (0.3 mol) and an ω-aminoacid (0.6 mol) were heated in 600 mL of dry dimethylformamide to 140 °C for 2 h. Acetic anhydride (1.0 mol) was added and heating was continued for additional 2 h. Afterward, the reaction mixture was poured into cold water; the precipitated crude diacids were isolated by filtration and recrystallized from hot dioxane by dropwise addition of water. Yields and properties of the diacids **3a–c**, **e**, and **f** are summarized in Table I.

***N,N*′-Di-*n*-alkylbenzophenone-3,3′4,4′-tetracarboxylic Diimides 7a–f.** An *n*-alkylamine (0.1 mol) was added to the solution of benzophenone-3,3′,4,4′-tetracarboxylic dianhydride (0.05 mol) in 100 mL of dry dimethylformamide, and the reaction mixture was heated for 1 h to 120 °C. Acetic anhydride (0.15 mol) was then added and heating was continued for an additional 2 h. After cooling the reaction mixture was poured into ice water; the crystallized imides were isolated by filtration and recrystallized from warm toluene and ligroin or from diethyl ether. For yields and properties see Table V.

Polycondensations. (A) With Free Diacids (3a–c,e,f). A diacid (**3a–c,e,f**) (50 mmol), an acetylated bisphenol (50 mmol), and 10 mg of magnesium acetate were weighed into a cylindrical, round-bottom glass reactor equipped with gas inlet and outlet tube and with a mechanical stirrer. The mixture of monomers was rapidly heated to 250 °C, where the condensation process started after 30 min; the temperature was gradually raised to 280 °C (long spacers) or 300–310 °C (short spacers). After stirring for 1 h at the final reaction temperature, vacuum was applied for 60 min. The cold poly(ester imides) were dissolved in a mixture of dichloromethane and trifluoroacetic acid (4:1 by volume) precipitated from cold methanol and dried at 80 °C (12 mbar).

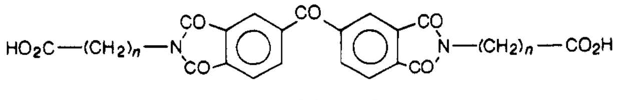
(B) "One-Pot-Procedure" with Azacyclooctan-2-one. Benzophenone-3,3′,4,4′-tetracarboxylic dianhydride (50 mmol) and azacyclooctan-2-one (50 mmol) were heated in the aforementioned glass reactor. After 1 h an acetylated bisphenol (50 mmol) and 10 mg of magnesium acetate were added and the polycondensation was conducted as described above.

Measurements. The inherent viscosities were measured with an automated Ubbelohde viscosimeter thermostated at 25 °C. Solutions of 100 mg of polymer in 50 mL of a 4:1 (by volume) mixture of dichloromethane and trifluoroacetic acid were used for all measurements. The DSC traces were measured at a heating or cooling rate of 20 °C/min on a Perkin-Elmer DSC-4 in aluminum pans. The thermomechanical analyses were conducted with a Perkin-Elmer TMS-2 at a heating rate of 10 °C/min under a load of 0.05 or 1.0 kg/mm². The thermogravimetric analyses were obtained on a Perkin-Elmer TGS-2 at a heating rate of 10 °C/min in air.

The wide-angle X-ray (WAXS) measurements at room temperature were taken on a Siemens D-500 with two circle goniometer using Ni-filtered Cu Kα radiation (λ = 1.54 Å). The time-resolved WAXS measurements at elevated temperatures were performed on a synchrotron radiation beamline[7] (λ = 1.50 Å) at HASYLAB, DESY, Hamburg, by using a vacuum furnace and a one-dimensional, position-sensitive detector. The heating rates were 20 °C/min and the accumulation times for one spectrum were 10 s.

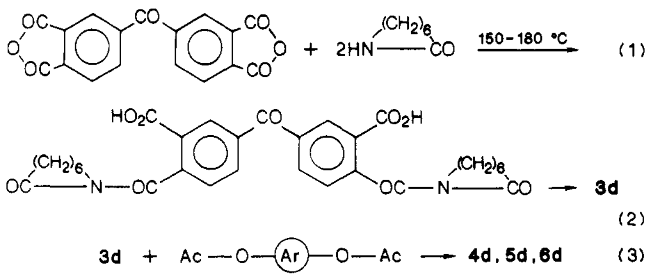
Results and Discussion

(A) Syntheses. All poly(ester imides) described in the present work **4a–f**, **5a–f**, and **6a–f** were obtained by polycondensation of the diacids **3a–f** with the diacetates of hydroquinone, 2,6-dihyroxynaphthalene or 4,4′-dihydroxyphenyl. The diacids **3a–c** and **3e,f** were prepared by condensation of BTA with the corresponding ω-amino acids. In order to avoid high temperatures for completion of the cyclization step, acetic anhydride was used as dehydrating reagent. The diacid **3c** was described by several authors.[8] Nonetheless, yields and properties of all diacids used in this work (**3a–c** and **3e,f**) are summarized in Table I.

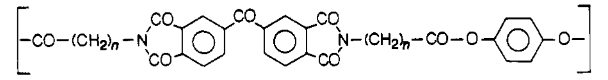


3a, $n = 3$ **3d**, $n = 6$
b, $n = 4$ **e**, $n = 10$
c, $n = 5$ **f**, $n = 11$

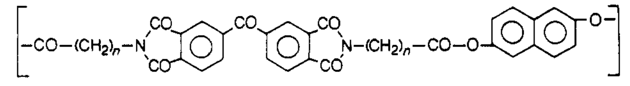
Owing to the high costs of 7-aminoheptanoic acid the diacid **3d** was prepared in a different way. BTA and 1-azacyclooctan-2-one were reacted at temperatures up to 170 °C (eq 1,2). The resulting crude diacid was then condensed with a bisphenol acetate without isolation and purification (eq 3). It was demonstrated in a previous paper dealing with the synthesis of poly(ester imides) from trimellitic anhydride and ω-amino acids or lactams that such "one-pot procedures" give satisfactory results. Also



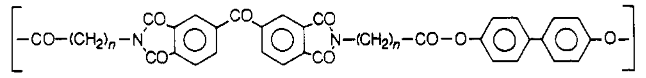
in this work ^{13}C NMR spectra confirmed that the poly(ester imides) **4d**, **5d**, and **6d** do not contain blocks of nylon 8, which might have been formed by polymerization of 1-azacyclooctan-2-one. The ^{13}C NMR spectra of **4d**, **5d**,



4a, n=3 **4d**, n=6
b, n=3 **e**, n=10
c, n=5 **f**, n=11



5a, n = 3 **5d**, n = 6
b, n = 4 **e**, n = 10
c, n = 5 **f**, n = 11



6a, n = 3 **6d**, n = 6
b, n = 4 **e**, n = 10
c, n = 5 **f**, n = 11

and **6d** agreed well with those of poly(ester imides) prepared from isolated diacids (e.g., **3c**). The yields of all poly(ester imides) fall into the range of 82–98% and mainly depend on losses during the mechanical workup. Despite their crystallinity all poly(ester imides) are soluble in a mixture of dichloromethane (DCM) and trifluoroacetic acid (TFA), so that reprecipitation and viscosity measurements were feasible. In all three series (**4a–f**, **5a–f**, **6a–f**) the poly(ester imides) prepared from the diacids **3a–c** possess lower inherent viscosities than those derived from **3d–f** (Tables II–IV). This observation and the dark color of the products obtained from **3a–c** suggest that the diacids with shorter aliphatic chains are thermally less stable and undergo slight decomposition during the condensation. Nonetheless, satisfactory elemental analyses were obtained in all cases.

(B) DSC Measurements and Microscopic Characterization. All poly(ester imides) of this work were characterized by DSC measurements with a heating or cooling rate of 20 °C/min and by observation in a microscope under polarized light. In contrast to LC poly(ester imides) described in previous parts of this series[1,5,10] (e.g., **1a–d** and **2a–d**) all poly(ester imides) derived from diacids **1a–f** contain an amorphous fraction which allowed the determination of glass transition temperatures (T_g's). The T_g's exhibit the obvious tendency to decrease with increasing length of the spacer (Tables II–IV).

The DSC measurements of the poly(ester imides) **6a–e** display two endotherms in the first and second heating traces (Figure 1). Observation under the microscope in polarized light revealed that these poly(ester imides) form a mesophase in the temperature range defined by both endotherms (Table IV). The texture of the mesophase is similar to the granular texture previously described for other poly(ester imides) with a regular sequence of spacer and other poly(ester imides) with a regular sequence of spacer and aromatic mesogen.[1,5,9,10] This texture was found to be characteristic of a smectic phase and the X-ray measurements of poly(ester imides) **4e** discussed below confirm this conclusion. A comparison of the poly(ester imides) **6a–e** with regard to the mesophase revealed that the temperature range narrows with increasing length of the spacer. Such a tendency is also known from other thermotropic polyesters with regular sequence of spacers and mesogen. Therefore, it is not surprising that no mesophase is observable in the case of **6f**.

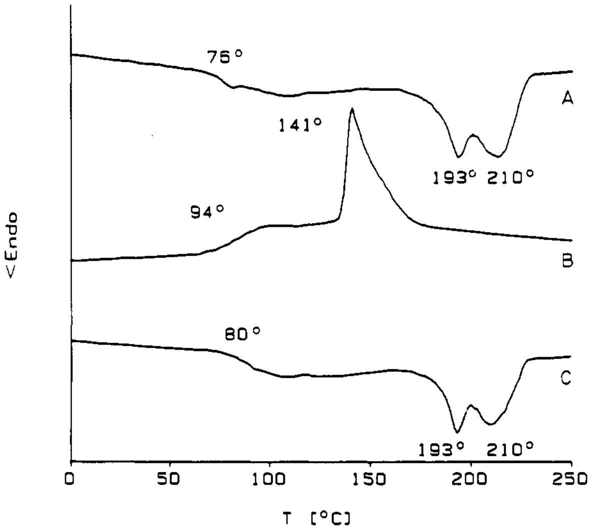


Figure 1. DSC measurements of poly(ester imide) **6e** (heating and cooling rates = 20 °C/min): (A) first heating; (B) first cooling; (C) second heating.

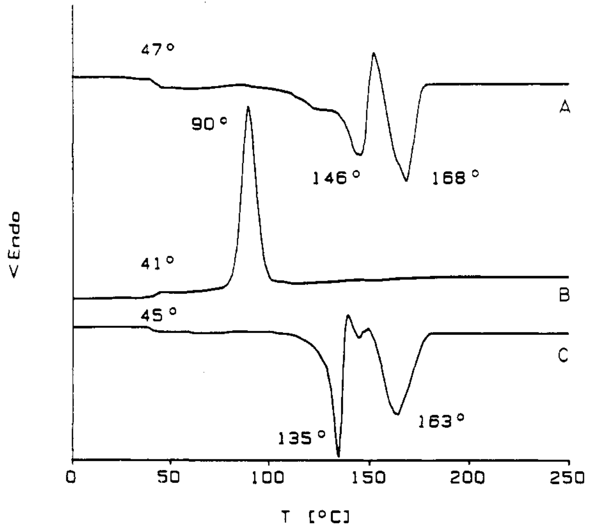


Figure 2. DSC measurements of poly(ester imide) **4e** (heating and cooling rates = 20 °C/min): (A) first heating; (B) first cooling; (C) second heating.

The poly(ester imides) **4a–f** and **5a–f** have in common that most members of both series do not form a mesophase. The members with short spacers ($n \leq 6$) are entirely amorphous and have the appearance of a brownish transparent glass. Even annealing above the glass transition temperature did not result in crystallization. In the case of **4e** and **5e** two endotherms are detectable in the DSC traces (Figure 2). Yet, observation under the microscope in polarized light confirmed the existence of a mesophase only for **4e**. This mesophase displays the typical granular texture of a smectic phase. The existence of a mesophase in the case of **4e** is of particular interest, because in contrast to the dihydroxybiphenyl unit of series **6a–f** neither hydroquinone nor 2,6-dihydroxynaphthalene possess mesogenic character.

Table II
Yields and Properties of Poly(ester imides) Prepared from *N*,*N*′-Bis(ω-carboxyalkyl)-3,3′,4,4′-benzophenonetetracarboxylic Diimides 4a–f and Hydroquinone

formula (*n*)[a]	yield, %	η_{inh},[b] dL/g	T_g,[c] °C	T_{m_1},[c] °C	T_{m_2},[c] °C	mesophase,[d] °C	elem formula (mol wt)		elem anal		
									C	H	N
4a (3)	83	0.36	119				$C_{31}H_{22}N_2O_9$ (566.53)	calcd	65.72	3.91	4.95
								found	65.25	3.95	5.04
4b (4)	92	0.21	109				$C_{33}H_{26}N_2O_9$ (594.58)	calcd	66.66	4.41	4.71
								found	66.71	4.43	4.91
4c (5)	91	0.30	84				$C_{35}H_{30}N_2O_9$ (622.64)	calcd	67.52	4.86	4.50
								found	67.48	4.92	4.61
4d (6)	84	0.40	79	133	147		$C_{37}H_{34}N_2O_9$ (650.69)	calcd	68.30	5.27	4.31
								found	68.36	5.43	4.45
4e (10)	93	0.47	47	146	168	136–167	$C_{45}H_{50}N_2O_9$ (762.91)	calcd	70.85	6.61	3.67
								found	70.87	6.62	3.73
4f (11)	97	0.40	46	143			$C_{47}H_{54}N_2O_9$ (790.96)	calcd	71.37	6.88	3.54
								found	71.45	6.97	3.69

[a] Number of methylene groups in the spacer. [b] Measured with *c* = 2 g/L at 25 °C in dichloromethane/trifluoroacetic acid (4:1 by volume). [c] From DSC measurements conducted at a heating rate of 20 °C/min. [d] As observed in a microscope under polarized light.

Table III
Yields and Properties of Poly(ester imides) Prepared from *N*,*N*′-Bis(ω-carboxyalkyl)-3,3′,4,4′-benzophenonetetracarboxylic Diimides 5a–f and 2,6-Dihydroxynaphthalene

formula (*n*)[a]	yield, %	η_{inh},[b] dL/g	T_g,[c] °C	T_{m_1},[c] °C	T_{m_2},[c] °C	mesophase,[d] °C	elem formula (mol wt)		elem anal.		
									C	H	N
5a (3)	85	0.37	139				$C_{35}H_{24}N_2O_9$ (616.58)	calcd	68.18	3.92	4.54
								found	68.16	3.92	4.50
5b (4)	83	0.32	116				$C_{37}H_{28}N_2O_9$ (644.64)	calcd	68.94	4.38	4.35
								found	69.17	4.44	4.44
5c (5)	90	0.32	99				$C_{39}H_{32}N_2O_9$ (672.70)	calcd	69.64	4.80	4.16
								found	69.47	4.90	4.27
5d (6)	84	0.60	92				$C_{41}H_{36}N_2O_9$ (700.75)	calcd	70.28	5.18	4.00
								found	70.22	5.29	4.09
5e (10)	84	0.64	58	149	169		$C_{49}H_{52}N_2O_9$ (812.97)	calcd	72.39	6.48	3.45
								found	72.35	6.50	3.56
5f (11)	88	0.57	57	163			$C_{51}H_{56}N_2O_9$ (841.02)	calcd	72.84	6.71	3.33
								found	72.72	6.73	3.49

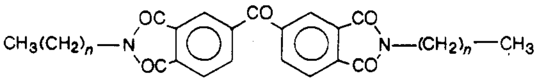
[a] Number of methylene groups in the spacer. [b] Measured with *c* = 2 g/L at 20 °C in dichloromethane/trifluoroacetic acid (4:1 by volume). [c] From DSC measurements conducted at heating rate of 20 °C/min. [d] As observed in a microscope under polarized light.

Table IV
Yields and Properties of Poly(ester imides) Prepared from *N*,*N*′-Bis(ω-carboxyalkyl)-3,3′,4,4′-benzophenonetetracarboxylic Diimides 6a–f and 4,4′-Dihydroxybiphenyl

formula (*n*)[a]	yield, %	η_{inh},[b] dL/g	T_g,[c] °C	T_{m_1},[c] °C	T_{m_2},[c] °C	mesophase,[d] °C	elem formula (mol wt)		elem anal.		
									C	H	N
6a (3)	88	0.31	120	268	315	272–320	$C_{37}H_{26}N_2O_9$ (642.63)	calcd	69.16	4.08	4.36
								found	69.11	4.14	4.33
6b (4)	95	0.32	111	279	309	281–305	$C_{39}H_{30}N_2O_9$ (670.68)	calcd	69.84	4.51	4.18
								found	70.30	4.55	4.18
6c (5)	83	0.46	105	197	221	203–228	$C_{41}H_{34}N_2O_9$ (698.74)	calcd	70.48	4.91	4.01
								found	70.74	4.97	4.14
6d (6)	92	0.31	90	194	212	208–224	$C_{43}H_{38}N_2O_9$ (726.79)	calcd	70.06	5.27	3.85
								found	70.72	5.35	3.87
6e (10)	82	0.66	76	193	210	200–216	$C_{51}H_{54}N_2O_9$ (839.01)	calcd	73.01	6.49	3.34
								found	73.09	6.62	3.44
6f (11)	82	0.55	59	182			$C_{53}H_{58}N_2O_9$ (867.06)	calcd	73.42	6.74	3.23
								found	73.43	6.74	3.50

[a] Number of methylene groups in the spacer. [b] Measured with *c* = 2 g/L at 20 °C in dichloromethane/trifluoroacetic acid (4:1 by volume). [c] From DSC measurements conducted at heating rate of 20 °C/min. [d] As observed in a microscope under polarized light.

Also for the poly(ester imides) derived from pyromellitic anhydride and hydroquinone (**1a–e**), formation of a mesophase was observed. Yet, it could be demonstrated that the pyromellit imide unit itself is a mesogenic group. In the case of **4e** the situation is quite different because the benzophenone imide unit is not mesogenic. This statement is based on a theoretical and an experimental argument. First, the benzophenone system cannot adopt a coplanar conformation, because the protons in ortho position relative to the keto group partially overlap in the coplanar state. The solid-state conformation of aromatic poly(ether ketones) provides clear evidence for this interpretation.[11] The experimental argument originates from synthesis and characterization of the model imides **7a–g** (Table V).



7a, *n* = 3
b, *n* = 5
c, *n* = 7
d, *n* = 9
7e, *n* = 11
f, *n* = 13
g, *n* = 15

With exception of **7d** only one endotherm is detectable in the DSC heating traces. In the case of **7d** two closely

Table V
Melting Points and Elemental Analysis of the *N*,*N'*-Dialkylbenzophenonetetracarboxylic Diimides

no. of aliph carbons	mp, °C	elem formula (mol wt)		elem anal. C	H	N
4 (**7a**)	146–148	$C_{25}H_{24}N_2O_5$ (432.23)	calcd	69.47	5.60	6.47
			found	69.28	5.71	6.21
6 (**7b**)	138–139	$C_{29}H_{32}N_2O_5$ (488.61)	calcd	71.29	6.55	5.73
			found	71.01	6.68	5.55
8 (**7c**)	133–135	$C_{33}H_{40}N_2O_5$ (544.73)	calcd	72.76	7.40	5.14
			found	72.49	7.68	5.00
10 (**7d**)	130–132	$C_{37}H_{48}N_2O_5$ (600.82)	calcd	73.97	7.99	4.66
			found	73.69	8.15	4.43
12 (**7e**)	128–130	$C_{41}H_{56}N_2O_5$ (656.95)	calcd	74.96	8.59	4.26
			found	74.73	8.80	3.99
14 (**7f**)	127–129	$C_{45}H_{64}N_2O_5$ (713.05)	calcd	75.80	8.98	3.93
			found	75.58	9.11	3.81
16 (**7g**)	127–129	$C_{49}H_{72}N_2O_5$ (769.1)	calcd	76.52	9.36	3.64
			found	76.45	9.44	3.57

neighboring endotherms were found; yet under the microscope again only one melting or crystallization process was observable. A mesophase was never detected.

These results demonstrate that the mesophase of **4e** is formed despite the absence of mesogenic groups. Obviously, special interaction between the bisphenol and the benzophenone imide unit is responsible for the observed smectic phases. This interaction is most likely a weak charge-transfer (CT) complexation. In order to obtain more evidence for the existence of CT complexes, solutions of disacetylhydroquinone and model imide **7c** were studied by means of UV spectroscopy. Unfortunately, no evidence for the formation of a CT complex was obtained. However, this negative result does not disprove a weak CT interaction in the molten state. The UV spectra were recorded with 10^{-4} M solutions, and thus, the probability of CT complex formation in the molten state is by a factor 10^{10} higher. A more detailed study on the role of CT complexes for the formation of mesophases is in progress.

X-ray Measurements. In order to obtain more information on the supermolecular order of the poly(ester imides) **4a**,**f**, **5a–f**, and **6a–f**, WAXS powder patterns were measured at room temperature. The X-ray patterns of all poly(ester imides) have three features in common (Figure 3). First, the amorphous halo is weak, indicating a relatively high degree of crystallinity. Second, strong reflections are observable around $\vartheta = 10°$, representing the lateral distances of the chains which are on the order of 4.5–5.0 Å. The structure of these reflections varies with the length of the spacers (Figure 3) possibly due to different elementary cells. Third, up to five sharp reflections are detectable at small angles ($\vartheta = 1.5–6.5°$) which represent the first and higher order reflections of an almost perfect layered supermolecular order. Due to the great d-spacings of poly(ester imides) **6a–f**, their first order reflections were not perfectly measurable under the conditions of wide-angle X-ray scattering (Figure 3).

The layer planes of this crystal lattice are more or less perpendicular to the chain axis and possess identical d-spacings. The d-spacings calculated from the small-angle reflections are slightly shorter than the lengths of the fully extended repeating units. Obviously the repeating units are tilted relative to the layer planes. When the d-spacings of poly(ester imides) **6a–f** are plotted versus the number of methylene units in the spacers, an overall increase with the spacer length is detectable (Figure 4). However, an irregular odd–even effect seems to exist which was also observed for the poly(ester imides) **1a–e** and **2a–e**. Obviously, the tilt angles of the repeating units relative to the layer planes vary with the number of methylene groups. The different patterns of the reflections between $\Theta = 9°$ and 15° may be taken as an additional hint for differences of the chain packing. In this connection it is noteworthy that a similar, but regular, odd–even effect of the d-spacings was found for poly(ester imides) prepared from trimellitic anhydride and α,ω-diamines.[5,10] A more detailed

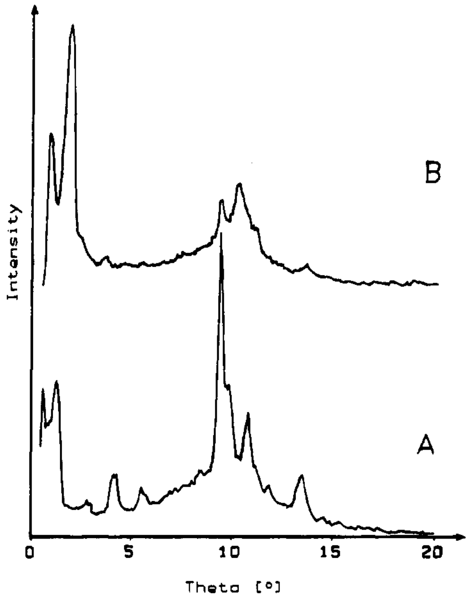


Figure 3. WAXS powder patterns measured at ca. 25 °C: (A) poly(ester imide) **6a**; (B) poly(ester imide) **6f**.

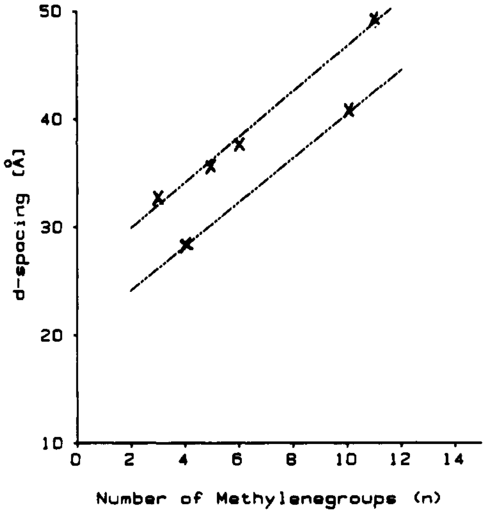


Figure 4. Plot of d-spacings (as calculated from the small-angle X-ray reflections) versus the number of methylene groups of the spacers in polymers **6a–f**.

Table VI
Heat Distortion Temperatures (HDTs) and Thermostabilities of Poly(ester imides) Prepared from the Diacids 3a–f and Various Bisphenols

formula (*n*)[a]	T_g,[b] °C	T_{m_1},[b] °C	HDTs A[c]	HDTs B[d]	temp with the wt loss[e] 1%	5%	10%	20%
4a (3)	119		128	113	309	350	368	387
4c (5)	84		92	83	343	385	403	424
4e (10)	46	135	82	66	294	357	391	427
5a (3)	139		190	155	325	350	371	392
5c (5)	99		100	95	356	355	379	423
5e (10)	58	169	164	144	334	377	404	441
6a (3)	120	268	139	115	293	350	364	381
6b (4)	111	279	277	133				
6c (5)	105	197	102	101	335	375	395	430
6d (6)	88	194	195	83				
6e (10)	70	195	197	165	280	368	391	428
6f (11)	59	182	155	58				

[a] Number of methylene groups in the spacer. [b] From DSC measurements with a heating rate of 20 °C/min. [c] Pressure 0.05 kg/mm^2 at a heating rate of 10 °C/min. [d] Pressure 1.0 kg/mm^2 at a heating rate of 10 °C/min. [e] Heatin rate 10 °C/min in air.

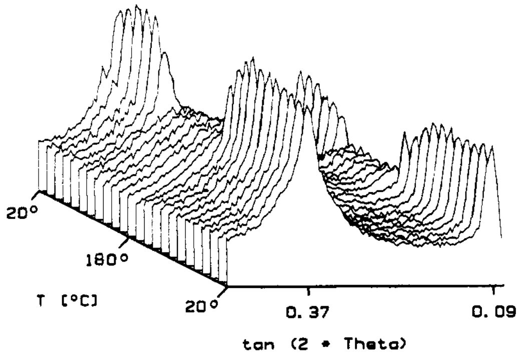


Figure 5. WAXS powder patterns of poly(ester imide) **4e** measured with synchrotron radiation at a heating rate of 20 °C/min; the time difference between individual patterns is approximately 40 s.

study of chain packing and morphology of the poly(ester imides) **1**–**6** is in progress.

Since the poly(ester imide) **4e** is noteworthy for its mesophase without mesogens, the smectic nature of the molten state between T_{m_1} and T_{m_2} should be confirmed by X-ray measurements. Therefore WAXS measurements of **4e** were conducted at variable temperature by means of synchrotron radiation. WAXS patterns were measured every 20 s at a heating or cooling rate of 20 °C/min in the temperature range 20–180 °C. The plot of Figure 5 (every second picture) displays the melting (and crystallization) process by the broadening of the $\vartheta = 10°$ reflection, which indicates the decreasing order of the lateral chain packing.

Three individual pictures extracted from this series clearly demonstrate that the second-order reflections of the layer planes still exists in the molten state at 150 °C (Figure 6B). It is even detectable at 180 °C (Figure 6, pattern C) when a partial transition to the isotropic melt has taken place. Thus, these WAXS measurements definitely prove that the poly(ester imide) **4e** forms a smectic phase despite the absence of mesogenic groups.

Thermomechanical and Thermogravimetric Analyses. Thermomechanical analyses of various thermotropic poly(ester imides) (e.g., **1a**–**e** and **2a**–**e**) conducted by means of the penetration method had revealed interesting results.[1,5,9,10] When highly symmetrical monomer units such as hydroquinone or 4,4′-dihydroxybiphenyl and pyromellitic imide were combined, high heat-distortion temperatures (HDTs) were found, which are directly related to the melting process and not to the glass transition. In addition to the technical advantage, such high HDTs provide the information that the crystalline phase forms the coherent matrix and not the amorphous phase. Such a morphology is relatively rare, and most thermotropic polyesters, in particular random copolyesters, indeed possess the inverse morphology, i.e., crystallites embedded in an amorphous matrix.[4–6] Systematic thermomechanical analyses of thermotropic poly(ester imides) have demonstrated that the appearance of high HDTs is highly sensitive to a variation of the chemical structure. When highly symmetrical monomer units, e.g., hydroquinone, are replaced by less symmetrical ones, e.g., 2,6-dihydroxynaphthalene, the HDTs decrease from T_m to T_g.[9] Obviously, the chemical structure influences the rate of crystallization and the degree of crystallinity, which both govern the formation of networks of crystallites.

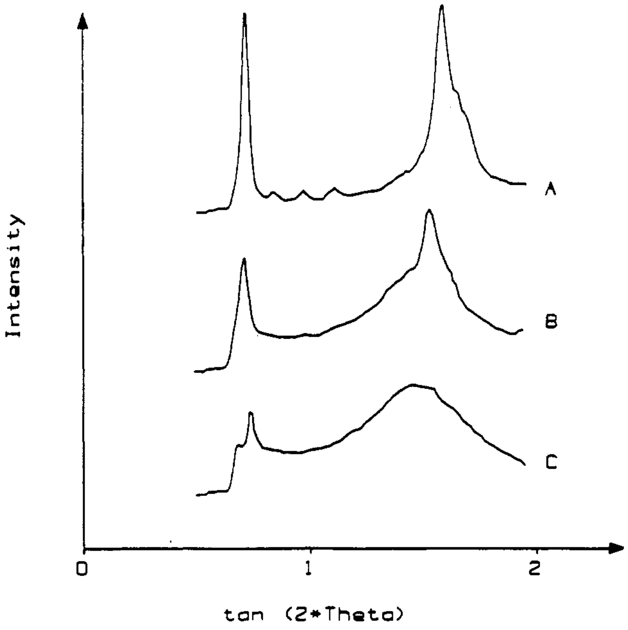


Figure 6. WAXS powder patterns of poly(ester imide) **4e** measured with synchrotron radiation at (A) 25 °C, (B) 150 °C, and (C) 180 °C.

In this connection thermomechanical analyses of the poly(ester imides) derived from BTA are of interest because the benzophenone imide unit is neither a mesogen nor a highly symmetric building block. The results of the thermomechanical analyses, conducted at a heating rate of 10 °C/min under two different pressures, are listed in Table VI. Under high load (1.0 kg/mm^2, corresponding to the "Vicat-A" test) most HDTs agree more or less with the T_g's (Figure 7C). Yet, two exceptions are noteworthy, namely, the poly(ester imides) **5e** and **6e** (to a lesser extent also **4e**). The HDTs of these poly(ester imides) are related

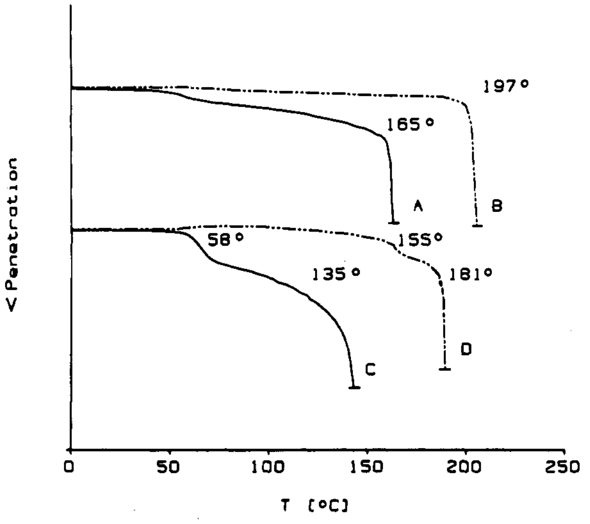


Figure 7. Thermomechanical analyses conducted by the penetration method at a heating rate of 10 °C/min: (A) poly(ester imide) **6e**, pressure 0.05 kg/mm^2; (B) **6e**, pressure 1.0 kg/mm^2; (C) poly(ester imide) **6f**, pressure 0.05 kg/mm^2; (D) **6f**, pressure 1.0 kg/mm^2.

to the melting process; in other words they correspond to the beginning of the melting endotherm in the DSC traces (Figures 1C and 7A,B). In these cases the crystallites form a coherent phase, and it is worth noting that a spacer with 10 methylene groups exactly fits with the length of a benzophenone imide unit. Obviously the molecular dimensions of these poly(ester imides) with $n = 10$ favor a high degree of crystallinity and an optimum morphology. Furthermore, it is worth mentioning that the thermomechanical measurements conducted at low pressure indicate a kind of odd-even effect in the series **6a–f**. This observation underlines that the mechanical properties of thermotropic poly(ester imides) are highly sensitive to slight variations of the primary structure.

Finally, thermogravimetric analyses were conducted at a heating rate of 10 °C/min in air. The results summarized in Table VI suggest that any thermoplastic processing should be limited to temperatures below 330 °C. The poly(ester imides) **4a–f**, **5a–f**, and **6a–f** are 40–50 °C less thermostable than the previously described poly(ester imides) prepared from trimellitic anhydride.[5,10] Yet, it must be taken into account that the molar fraction of aliphatic groups compared at identical spacer length is nearly twice as high in the case of **4–6**. Nonetheless, it is to be noted that the poly(ester imides) **4–6** are inferior to those derived from trimellitic anhydride with regard to both thermostability and thermomechanical properties.

Acknowledgment. We thank the Bundesministerium für Forschung und Technik for financial support (Grant 03C195/1).

Registry No. 3a, 104677-73-8; **3b**, 114505-30-5; **3c**, 71685-31-9; **3d**, 114505-31-6; **3e**, 114505-64-5; **3f**, 114505-32-7; **4a** (copolymer), 114505-60-1; **4a** (SRU), 114505-39-4; **4b** (copolymer), 114505-61-2; **4b** (SRU), 114505-40-7; **4c** (copolymer), 114505-62-3; **4c** (SRU), 114505-41-8; **4d** (copolymer), 114505-63-4; **4d** (SRU), 114505-42-9; **4e** (copolymer), 114505-65-6; **4e** (SRU), 114505-43-0; **4f** (copolymer), 114505-66-7; **4f** (SRU), 114505-44-1; **5a** (copolymer), 114505-67-8; **5a** (SRU), 114505-45-2; **5b** (copolymer), 114505-68-9; **5b** (SRU), 114505-46-3; **5c** (copolymer), 114505-69-0; **5c** (SRU), 114505-47-4; **5d** (copolymer), 114505-70-3; **5d** (SRU), 114505-48-5; **5e** (copolymer), 114505-71-4; **5e** (SRU), 114505-49-6; **5f** (copolymer), 114505-72-5; **5f** (SRU), 114505-50-9; **6a** (copolymer), 114505-73-6; **6a** (SRU), 114505-51-0; **6b** (copolymer), 114505-74-7; **6b** (SRU), 114505-52-1; **6c** (copolymer), 114505-75-8; **6c** (SRU), 114505-53-2; **6d** (copolymer), 114505-76-9; **6d** (SRU), 114505-54-3; **6e** (copolymer), 114505-77-0; **6e** (SRU), 114505-55-4; **6f** (copolymer), 114505-78-1; **6f** (SRU), 114505-56-5; **7a**, 6097-14-9; **7b**, 114505-33-8; **7c**, 114505-34-9; **7d**, 114505-35-0; **7e**, 114505-36-1; **7f**, 114505-37-2; **7g**, 114505-38-3.

References and Notes

(1) Part 23 of this series: Kricheldorf, H. R.; Pakull, R. *Polymer*, in press.
(2) Asrar, J.; Toricemi, H.; Wabanabe, S.; Krigbaum, W. R.; Ciferri, A.; Preston, J. *J. Polym. Sci., Polym. Phys. Ed.* 1983, *21*, 1119.
(3) Ober, K. C.; Jin, J.; Lenz, R. W. *Adv. Polym. Sci.* 1984, *59*, 103.
(4) Kricheldorf, H. R.; Conradi, A. *J. Polym. Sci., Polym. Chem. Ed.* 1987, *25*, 489.
(5) Part 20 of this series: Kricheldorf, H. R.; Pakull, R. *Macromolecules* 1988, *21*, 551.
(6) Hugnh-ba, G.; Cluff, E. F. In *Polymeric Liquid Crystals*; Blumstein, A., Ed.; Plenum: New York–London; p 232.
(7) Elsner, G.; Riekel, C.; Zachmann, H. G. *Adv. Polym. Sci.*, Phys. Ed. 1982, *20*, 719.
(8) Korshak, V. V.; Babchinitzer, T. M.; Kazaryan, L. G.; Vasilev, V. A.; Genin, Y. V.; Asriel, A. Y.; Vygodsky, Y. S.; Churochkina, N. A.; Vinogradova, S. V.; Tsrankin, D. Y. *J. Polym. Sci., Polym. Phys. Ed.* 1980, *18*, 247.
(9) Kricheldorf, H. R.; Pakull, R. *Polymer* 1987, *28*, 1772.
(10) Part 22 of this series: Kricheldorf, H. R.; Pakull, R.; Buchner, S. *J. Polym. Sci., Polym. Chem. Ed.*, in press.
(11) Lovinger, A. J.; Davis, D. D. *Macromolecules* 1986, *19*, 1861.