Polymer Vol. 37 No. 14, pp. 3101–3109, 1996
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0032-3861/96/$15.00+0.00

LC-poly(ester-amide-imide)s derived from trimellitic acid and 4-aminobenzoic acid

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(Received 7 September 1994; revised 6 October 1995)

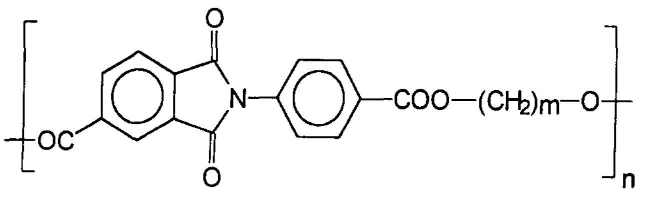
A new mesogene diester based on phenyltrimellitimide was synthesized and used as a condensation monomer in combination with a number of aliphatic diols to render novel poly(ester–amide–imide)s (PEAIs). The melt polycondensation method provided polymers of moderate inherent viscosity, that were characterized by elemental analyses, differential scanning calorimetry, X-ray diffractometry, including synchrotron radiation measurements at different temperatures, optical microscopy with polarized light and thermogravimetric analysis. The glass transition temperatures (T_g) lie in the range 100–130°C, which means a substantial improvement relative to analogous poly(ester–imide)s (PEIs). All the novel PEAIs are thermotropic materials that show a mobile LC-mesophase above the melting temperature. By combining microscopic observations with X-ray diffraction diagrams, the mesophases could be identified as smectic-A phases. PEAIs with even-numbered spacers are semi-crystalline in the solid state, while those with odd-numbered spacers can form a solid smectic glass phase, i.e. a frozen smectic-A phase, upon rapid cooling from the melt. Copyright © Elsevier Science Ltd.

(Keywords: co-polyimides; monomers; synthesis)

INTRODUCTION

In previous work we have reported on the synthesis and evaluation of poly(ester-imide)s (PEIs) derived from *N*-(4′-carboxyphenyl)trimellitimide and aliphatic spacers[1,2]. In spite of the favourable structural factors of the phenylphthalimide unit to work as an efficient mesogen, such as linearity and asymmetrical charge distribution, PEIs from *N*-(4-carboxyphenyl)-4-carboxyphthalimide and aliphatic glycols, e.g. polymers **1a–h**, did not show any stable liquid crystalline mesophase, but they ordered into semi-crystalline solids when correctly annealed, or into smectic glasses when quenched from the molten state[1,2].

Another research group also found short lived monotropic liquid crystalline (LC)-phases upon rapid cooling[3,4].



1a-h (n = 4-10 and 12)

However, *N*-(4-carboxyphenyl)trimellitimide (CPTI) can give rise to enantiotropic nematic polyesters when polycondensed with suitable diphenols[5,6]. Many of these wholly aromatic LC-PEIs showed very poor solubility and high melting temperatures, close to the initial thermal decomposition of the polymers, and consequently, their usefulness as engineering thermoplastics is at least questionable. On the other hand formation of broad nematic phases from combinations of CPTI and diphenols suggests that lengthening of the CPTI unit by one more aromatic ring (functionalized in *para* position) might improve the mesogenic character to such an extent that even polycondensation with aliphatic diols may yield enantiotropic LC-PEIs.

Since polyimides and copolyimides generally show excellent thermal properties, they have found their most interesting applications as heat-resistant polymers and engineering thermoplastics[7,8]. Therefore, it is interesting to investigate the properties of new copolyimides that could be moulded in the thermotropic mesophase state. Thus, in an attempt to extend these investigations to novel thermotropic copolyimides based on phenyltrimellitimide derivatives, the present work was aimed at synthesizing liquid crystalline poly(ester–amide–imide)s (LC-PEAIs) with accessible transformation temperatures that permit a processing of the polymers in the mesophase state. Moreover, thermotropic poly(ester–amide)s have been claimed to show excellent mechanical properties,

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and they do show higher glass transition temperatures T_gs, i.e. higher deflection temperatures, than homologous polyesters[9,10]. Thus, the PEAIs reported in this paper were designed to fulfil three main objectives: to confirm whether a longer rigid unit derived from CPTI would behave as an effective mesogenic unit, to enhance the thermal stability of aliphatic-aromatic copolyimides described earlier, and to make an evaluation of the general properties of the novel polymers.

EXPERIMENTAL

Materials

Trimellitic acid anhydride (TMA) was a gift from BASF-Glasurit, Guadalajara, Spain. It was recrystallized from xylene. 4-Aminobenzoic acid and ethyl-4-aminobenzoate were purchased from Fluka and used without further purification.

Trimellitic anhydride acid chloride (**2**) was prepared by boiling TMA with 1.2 mol thionyl chloride in a solution of tetrahydrofuran (THF) for 1 h. The anhydride acid chloride was isolated by distillation of the solvent and subsequent vacuum distillation of the residue at 165°C/5 mm Hg. The intermediate was then recrystallized from heptane giving rise to fine colourless needles of m.p. 73–74°C (lit.[11], 69°C).

Trimellitic anhydride ethyl ester (**3**): 63.2 g of **2** (0.3 mol) and 14.4 g (0.45 mol) of absolute ethanol were dissolved in 300 ml of dry CH_2Cl_2 and cooled to −60°C (CO_2/acetone) under a dry N_2-atmosphere. 24.2 ml of distilled pyridine (0.3 mol) was added dropwise to the stirred mixture. After the addition was over, the solution was kept at −60°C for 1 h, and then heated to room temperature, where it was stirred for a further 4 h. The reaction mixture was washed with water and dried over Na_2SO_4. After distillation of the solvent the residue was recrystallized from *n*-heptane. Yield: 57.5 g (88%); m.p. 97°C. ^{1}H-n.m.r. (200 MHz, DMSO): δ (ppm) 8.45 (d, 1H), 8.35 (s, 1H), 8.15 (d, 1H), 4.4 (q, 2H), 1.35 (t, 3H).

4-Ethoxycarbonyl-*N*-(4′-chlorocarbonylphenyl)-phthalimide (**5**): 12.5 g of 4-aminobenzoic acid (0.09 mol) was added to a solution of 20.0 g of **3** (0.09 mol) in 200 ml of dry THF, and the mixture was refluxed for 4 h. The reaction mixture was then vacuum concentrated and the solid residue isolated by filtration. The residue, without further purification, was dissolved in 300 ml thionylchloride, 1 ml of *N,N*-dimethylformamide was added and the solution refluxed until the evolution of SO_2 subsided. Afterwards the solvent was removed by vacuum distillation, and the solid residue was recrystallized from toluene. Yield: 24 g (75%); m.p. 212°C. ^{1}H-n.m.r. (200 MHz, DMSO): δ (ppm) 8.45 (d, 1H), 8.35 (s, 1H), 8.15 (d, 1H), 8.1 (d, 2H), 7.65 (d, 2H), 4.4 (q, 2H), 1.35 (t, 3H).

4-(4′-Ethoxycarbonylphthalimido)-*N*-(4′-ethoxycarbonylphenyl)benzamide (**6**): 24 g of **5** (67 mmol) was dissolved in 350 ml of THF and cooled down to 0°C. Then a solution of 11.1 g of ethyl-4-aminobenzoate (67 mmol) in 150 ml of THF was added under vigorous stirring and the reaction mixture was heated to 65°C for 1 h and then concentrated to one-third in volume. The solid was filtered off and finally recrystallized from xylene yielding white needles of m.p. 259°C. Yield: 30 g (92%).

^{1}H-n.m.r. (200 MHz, DMSO): δ (ppm) 10.7 (s, 1H), 8.45 (d, 1H), 8.35 (s, 1H), 8.15 (d, 1H), 8.1 (d, 2H), 8.0 (s, 4H), 7.65 (d, 2H), 4.4 (m, 4H), 1.35 (m, 6H). Analysis for $C_{27}H_{22}N_2O_7$: Calcd, C 66.69%, H 4.52%, N 5.76%; Found, C 66.73%, H 4.48%, N 5.82%.

Polycondensation

The polycondensation reactions were carried out in a cylindrical glass vessel fitted with mechanical stirring, gas inlet and outlet tubes. 50 mmol of the diethylester **6**, 50 mmol of a diol spacer (plus an excess, that depended on the diol volatility, to equilibrate the loss of aliphatic monomer), and titanium isopropoxide (30 mg) were weighed into the reactor and heated by means of a metal bath under a blanket of nitrogen. The mixture was heated to approx. 250°C, where the reaction began, and then a gradual temperature ramp was applied over 3–4 h up to a temperature limit of 280°C, the final steps being carried out under a vacuum of approx. 0.1 mm Hg. The last steps proceeded in the solid state for polymers **7a**, **7c** and **7e**.

The crude PEAIs were recuperated by solvent extraction with trifluoroacetic acid (TFA)/CH_2Cl_2 (1:4 in volume) and precipitated by the addition of cold methanol, washed with methanol several times and dried in a vacuum oven at 80°C.

Measurements

Elemental analyses were performed by the Analyses Service of Centro Nacional de Quimica Organica, Madrid. The viscosities were measured in an automated Ubbelohde viscometer thermostated at 25.0 ± 0.1°C on 0.5% polymer solutions in TFA/CH_2Cl_2 (1:4 in volume). The i.r. spectra were recorded on a Perkin-Elmer 457 spectrophotometer using thin polymer films made by evaporation of solutions (DMSO) cast on NaCl crystals. The ^{1}H-n.m.r. spectra were recorded in deuterated DMSO or in a mixture TFA/$CDCl_3$, at 200 MHz with a VARIAN-Gemini-200 spectrometer. The wide angle X-ray scattering (WAXS) powder patterns were obtained on a Siemens D-500 diffractometer at 25°C, by means of Ni-filtered Cu–Kα radiation. The synchrotron radiation measurements ($\lambda = 1.50$ Å) were made at HASYLAB-DESY (Hamburg) at a heating or cooling rate of 20°C min^{-1} in vacuum, using a position sensitive one dimensional detector.

The differential scanning calorimetry (d.s.c.) curves were obtained with a Perkin-Elmer DSC-7 device, in aluminium pans at a heating or cooling rate of 20°C min^{-1}, under nitrogen.

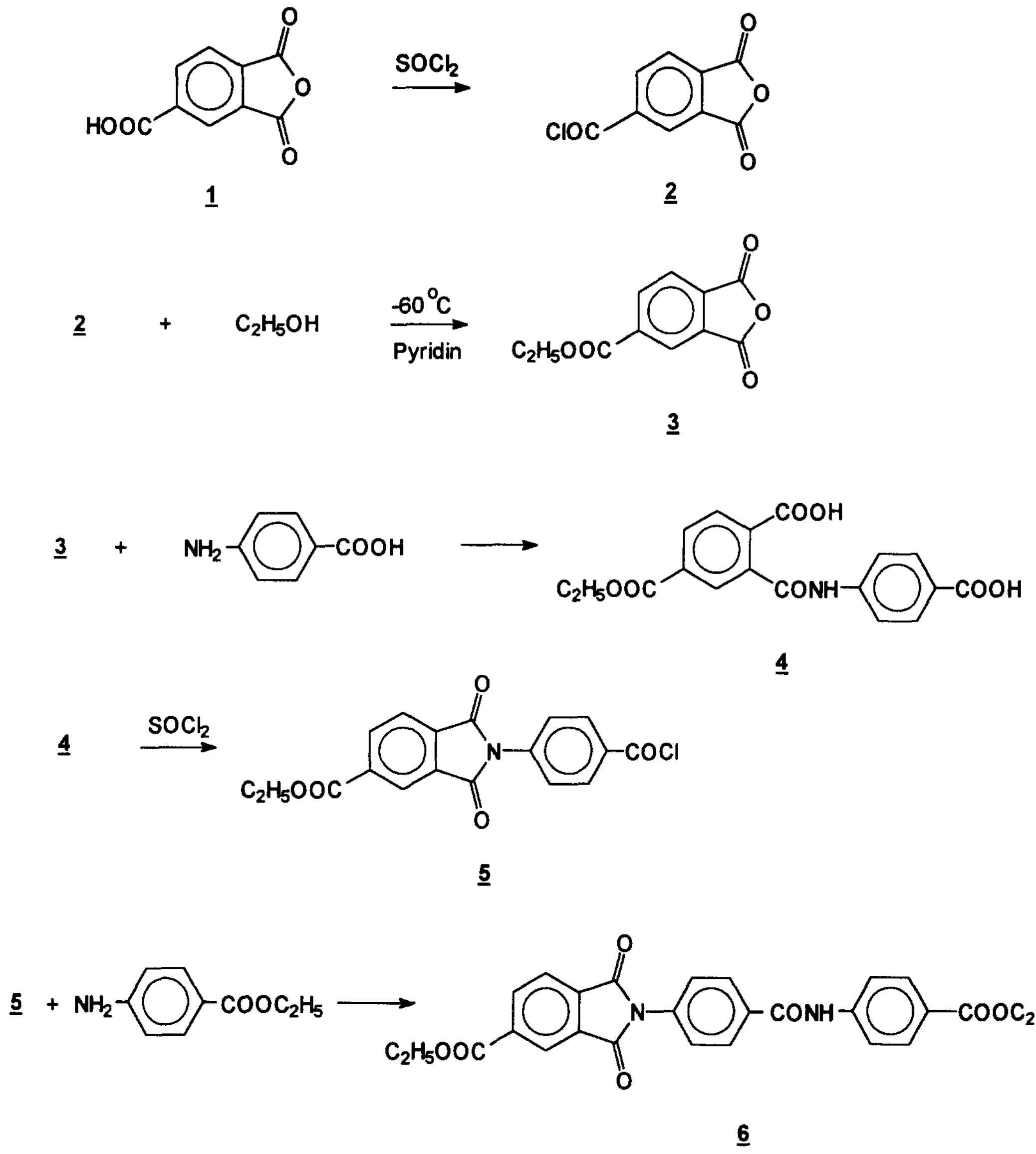
Thermogravimetrical analyses (t.g.a.s) were performed with a Perkin-Elmer TGS-2 device, under nitrogen at a heating rate of 10°C min^{-1}.

Microscope observations were made with an optical microscope Olympus BH-2 fitted with crossed polarizers. The temperature was controlled in 1°C range by means of a computerized Linkam THM 600 heat controller.

RESULTS AND DISCUSSION

Synthesis of monomers and polymers

A new monomer was synthesized and characterized as a preliminary step in the preparation of LC-PEAIs containing trimellitimide units. It was prepared following the synthetic route shown in *Scheme 1*. Starting



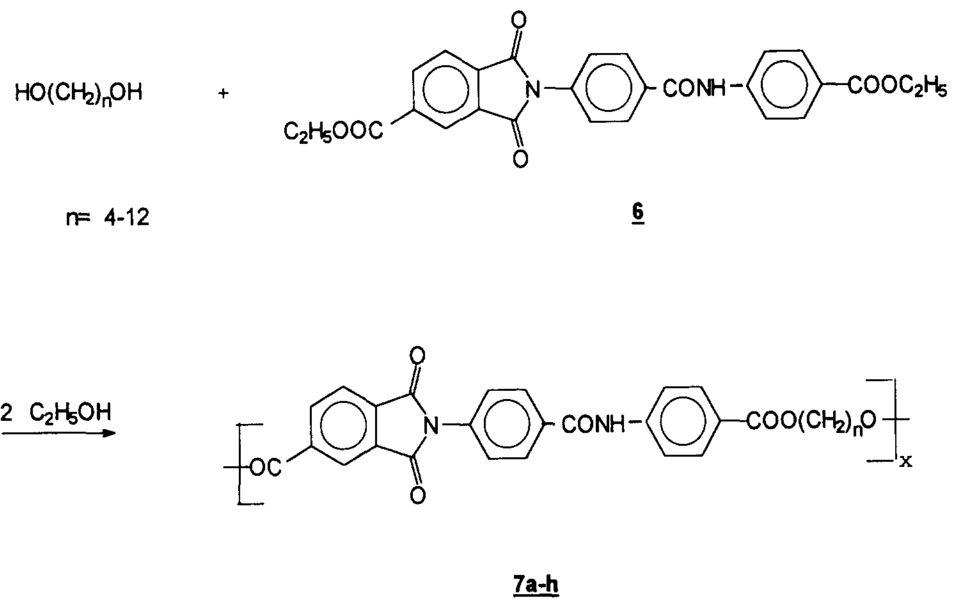
Scheme 1

materials employed were 4-aminobenzoic acid, ethyl 4-amino-benzoate (benzocaine), and trimellitic anhydride (**1**). The overall yield was 55% based on trimellitic anhydride. The most hazardous step was that of closing the imide ring by treating the amic acid **4** with thionyl chloride at relatively high temperature. It is well known that the side product HCl can attack the amide linkage to give a chloride and a primary amide (von Braun reaction[12]). It seems, however, that the ring closing is a fast reaction, so that the concentration of imide rings grows very rapidly relative to the rate of formation of HCl, arising from the reaction of $SOCl_2$ with the carboxylic acid. A yield of more than 70% clearly speaks for this assumption.

PEAIs were prepared from **6** and aliphatic diols as shown in *Scheme 2*. Only in the case of long chains ($n = 10$, 12) or odd-numbered spacers the reaction proceeded in the melt. Polymers **7a**, **7c** and **7e** solidified at the end of the reaction, so that the last step of the process was carried out in the solid state. Maximum polycondensation temperature was limited to 280°C to avoid thermal degradation of the polymers, and variable excess of diol was used to balance the loss of the aliphatic monomer at the severe reaction conditions. A molar excess of up to 50% had to be used for the most volatile diols ($n = 4$, 5).

Yields and elemental analyses obtained for the series of PEAIs have been summarized in *Table 1*. The i.r. spectra of all PEAIs are nearly identical and do not exhibit characteristic differences between samples with odd or even spacers (*Figure 1*). Three C=O bands are detectable at $1780\,cm^{-1}$ (imide group), $1720\,cm^{-1}$ (imide + ester group), and $1670\,cm^{-1}$ (amide group). Of particular interest is the N-H band at $3380-3400\,cm^{-1}$. A typical value for strong symmetrical H bonds of aromatic polyamides is $3300 \pm 20\,cm^{-1}$. Thus, the N-H band of PEAIs suggests that the hydrogen bond does not link two amide groups, but rather an amide and an imide or an ester group.

The polymers were also characterized by measuring their inherent viscosities and by ^{1}H-n.m.r. spectroscopy. The viscosities must be considered only as moderate (see *Table 1*) and are indicative of polymers with comparatively low molecular weights. However, peaks corresponding to end groups appeared as very small or negligible signs in the ^{1}H-n.m.r. spectra of the polymers. As an example, the spectrum of polymer **7f** has been reported in *Figure 2*. Although the current



Scheme 2

Table 1 Results of the polycondensation of monomer **6** with various glycols

Polymer	n	Yield (%)	Elem. formula (Form. weight)		Elemental analysis C	H	N	$\eta_{inh.}$ (λ) dl g^{-1}
7a	4	92	$C_{27}H_{20}N_2O_7$	Calc.	66.97	4.13	5.78	0.44
			(484.48)	Found	67.20	4.40	6.04	
7b	5	91	$C_{28}H_{22}N_2O_7$	Calc.	67.50	4.41	5.62	0.51
			(498.50)	Found	67.80	4.60	5.81	
7c	6	94	$C_{29}H_{24}N_2O_7$	Calc.	67.96	4.72	5.47	0.36
			(512.52)	Found	68.09	4.90	5.73	
7d	7	82	$C_{30}H_{26}N_2O_7$	Calc.	68.43	4.98	5.32	0.40
			(526.55)	Found	68.76	4.76	5.53	
7e	8	87	$C_{31}H_{28}N_2O_7$	Calc.	68.88	5.22	5.18	0.44
			(540.57)	Found	68.58	4.89	5.21	
7f	9	91	$C_{32}H_{30}N_2O_7$	Calc.	69.30	5.45	5.05	0.51
			(554.60)	Found	69.53	5.78	5.21	
7g	10	76	$C_{33}H_{32}N_2O_7$	Calc.	69.71	5.67	4.93	0.50
			(568.63)	Found	69.55	5.38	5.01	
7h	12	92	$C_{35}H_{36}N_2O_7$	Calc.	70.45	6.08	4.69	0.55
			(596.68)	Found	70.29	6.17	4.81	

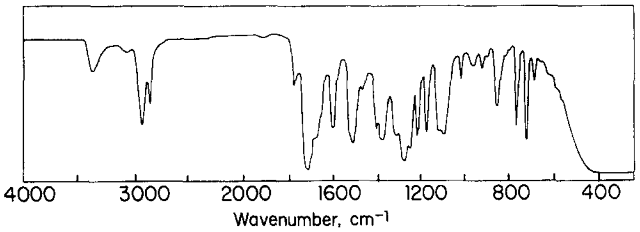


Figure 1 I.r. spectrum of PEAI **7g** (KBr pellet)

PEAIs show limited solubility in common organic solvents, they are soluble in protonated acid solvents, or very polar solvents such as DMSO. Thus, ^{1}H-n.m.r. spectra could be readily obtained in deuterated DMSO.

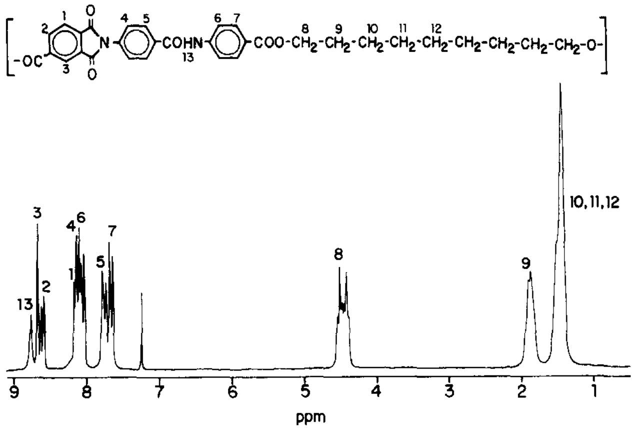


Figure 2 ^{1}H n.m.r. spectrum of polymer **7f** ($n = 9$) recorded in $CDCl_3$/TFA

Table 2 Thermal properties of PEAIs

Polymer	n	T_g^a (°C)	T_m^a (°C)	T_i^a (°C)	ΔH^a (J g^{-1})	ΔT^b (°C)	T_d^c (°C)
7a	4	130	310	374	12.5	56	415
7b	5	129	272	368	10.6	96	410
7c	6	107	315	354	11.0	40	413
7d	7	106	193	337	13.5	144	410
7e	8	105	281	349	12.0	68	412
7f	9	100	198	331	12.0	133	405
7g	10	102	236	331	12.0	95	402
7h	12	74	260	300	8.0	40	405

[a] From d.s.c. measurements with a heating rate of 20°C min^{-1}

[b] Temperature range of the mesophase as defined by d.s.c. measurements

[c] Temperature of 5% loss of weight, from t.g.a. measurements with a heating rate of 10°C min^{-1}

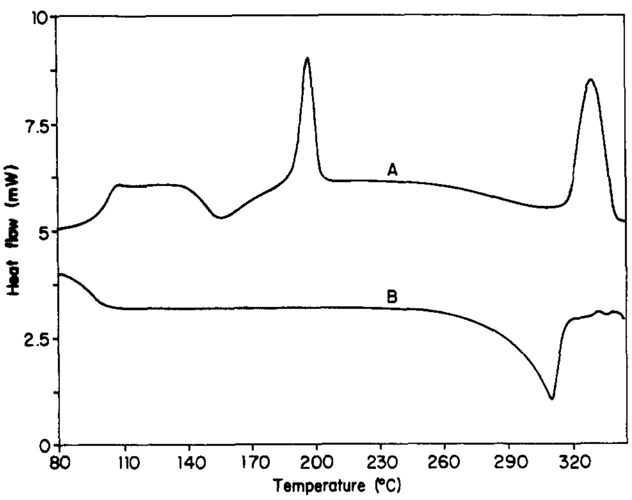


Figure 3 D.s.c. curves of polymer **7f** ($n = 9$): (A) first heating; (B) first cooling

Properties

The thermal behaviour of the current PEAIs was first investigated by d.s.c. In all cases an inflection of the d.s.c. curve was detected about 100°C, attributable to T_g temperature. Polymers **7a** and **7b** showed T_g values a little higher, about 130°C, in agreement with their density of aromatic rigid units and hydrogen bonding. The values are clearly higher than the T_g values of homologous poly(ester imide)s[1]. Even for the polymers with the longest spacer ($n = 12$), the T_g value was about 30°C higher than that of the homologous poly(ester imide)[1]. The presence of both amide groups and 4-substituted benzene rings in the mesogenic unit would account for this increase in T_g.

At higher temperatures, all the PEAIs exhibited two clear endotherms: T_m, assigned to the transformation from the solid semi-crystalline state to a LC-phase, and T_i, indicating the transformation of the LC-phase to an isotropic polymer melt. The values of T_m and T_i for the set of PEAIs are listed in *Table 2*. Polymers with odd-numbered spacer groups showed the greater range of stable mesophase, as it is the rule for main-chain LC-polymers consisting of alternating mesogens and polymethylene spacers[13]. The temperature range of mesophase stability is maximum for polymer **7d** ($n = 7$).

Neat endotherm peaks appeared in the first runs, while on cooling at 20°C min^{-1} from the isotropic melt only the exotherm corresponding to the isotropic LC-phase transformation could be seen, with a drastic lowering of the free enthalpy associated to the transformations. This effect has been illustrated in *Figure 3*, where the d.s.c. traces have been reproduced for polymer **7f** ($n = 9$). Therefore, the T_m data listed in *Table 2* were taken from the first runs. Furthermore, the polymer melts are not stable at high temperature, i.e. above 340°C, although the initial decomposition temperatures, as measured by t.g.a., are about 400°C. At these temperatures and above, transesterification, transamidation reactions, and the interchange of amide and ester groups take place, leading to a different sequence of building blocks within the main chain. After quenching the samples from the melt, d.s.c. traces were obtained that greatly differed from those of the first runs. The fact that clear transitions could not be measured on the cooling runs, suggests also that the current PEAIs have an inherent difficulty to develop regular, organized supramolecular structures if the conditions are not very favourable. Nevertheless, annealing at an adequate temperature, can promote high degrees of crystallinity, particularly in the case of polymers with even-numbered spacers ($n = 6$), as can be drawn from the diagrams of *Figures 4* and *5*. Cooling of odd-numbered PEAIs from the isotropic melt rendered an apparently non-crystalline solid that did not show a melting endotherm on subsequent d.s.c. runs. Nonetheless, the WAXS powder patterns exhibited middle angle reflection which indicates the existence of a layer structure in the solid state. This finding and the observation of a smectic-A phase above T_g, mean that the solid state is a frozen smectic-A phase in these cases.

The existence of a true enantiotropic LC-phase was confirmed by optical microscopy. In all cases, a bâttonet texture typical for a smectic-A phase was observed (see *Figure 6*). The bâttonets move and smear out on shearing between glass plates proving that a mobile smectic LC-phase exists. The enthalpy changes found at T_i (*Table 2*) also agree with the transition from a smectic LC-phase to an isotropic melt.

With regard to the ability of the current PEAIs to form enantiotropic LC-mesophases, in contrast to polymers of the series **1a–h**, the justification must lie in the fact that the BATI unit is considerably longer than the CPTI unit (*Figure 7*). Because of the lateral extension of the aromatic building block, the length/diameter ratio, which is responsible for the mesogeneity, is now sufficiently

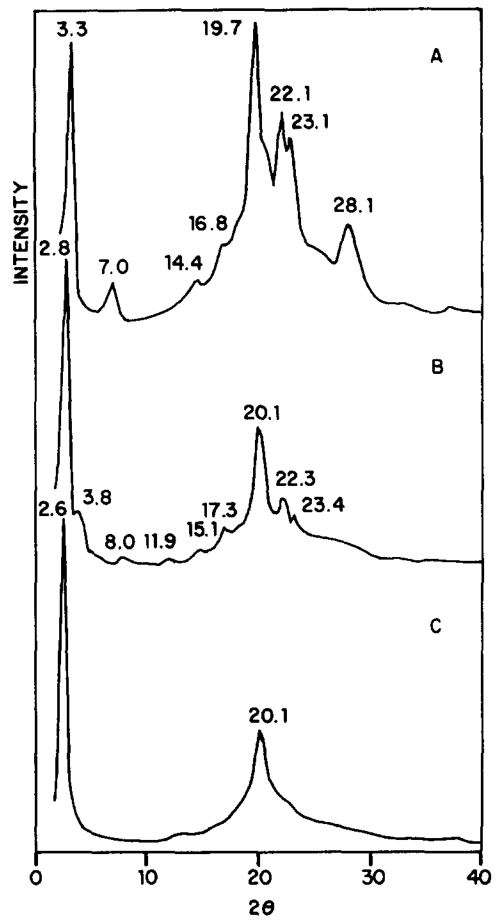


Figure 4 WAXS powder patterns of PEAIs: (A) **7a** ($n = 4$); (B) **7e** ($n = 8$); (C) **7h** ($n = 12$)

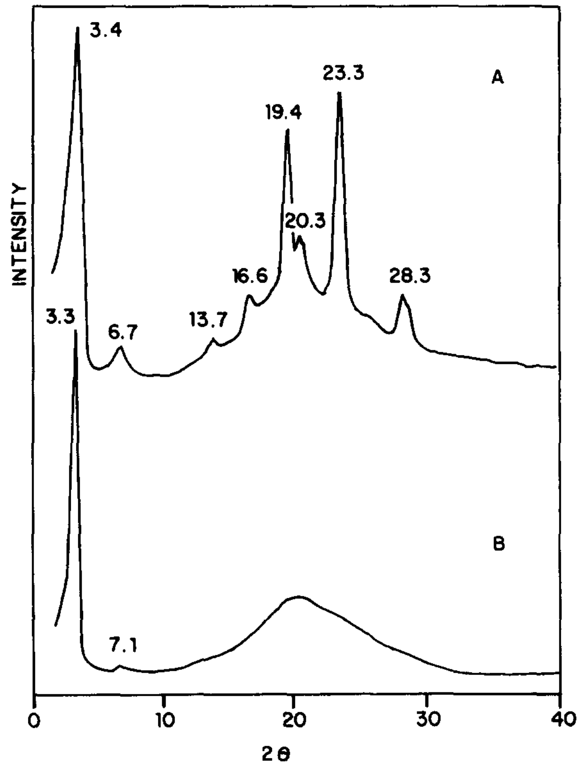


Figure 5 WAXS powder patterns of PEAIs: (A) **7b** ($n = 5$) annealed; (B) **7d** ($n = 7$) quenched

Figure 6 The formation of the smectic S_A-phase in the form of bâttonets upon cooling of PEAI **7f** from the isotropic melt

high, despite a slight deviation from linearity[14]. The strong interactions promoted by the amide groups are surely working also for the stabilization of the layered supermolecular structure observed for the current PEAIs.

It is worth commenting that, as it generally happens, PEAIs with an even number of atoms in the spacer have higher transition temperatures than those with an odd number of atoms.

X-ray measurements

X-ray diffraction patterns of all PEAIs were measured at room temperature and at elevated temperatures for the following reasons: 1) to confirm the interpretation of the texture observed by optical microscopy with crossed polarizers; and 2) to obtain at least some rough information on the chain packing in the solid state. However, a detailed study of the crystal structures was not intended in this work.

The WAXS powder patterns of some PEAIs recorded at 25°C are given in *Figures 4* and *5*. All WAXS patterns exhibited a middle angle reflection (MAR) in the range of $2\theta = 2.5$–$3.5°$ which indicates the existence of a layer structure in the solid state. The exact values of these MARs are listed in *Table 3* and plotted against the number of CH_2-groups of the spacers in *Figure 8*. This plot reveals that the layer distances (d-spacings) of the PEAIs have the tendency to show an odd–even effect.

Table 3 EAXS and synchrotron measurements of layer distances at room temperature and in the S_A-mesophase

			WAXS measurements at 25°C[a]		Synchtrotron radiation	
Polymer	*n*		2*θ*	*d*-spacing	T (°C)	*d*-spacing
7a	4	1st order	3.6	24.5	350	25.5
		2nd order	7.0	25.2		
7b	5	1st order	3.8	23.2	350	26.2
		2nd order	3.8	23.4		
7c	6	1st order	5.7	15.5	320	25.3
		2nd order	–	–		
7d	7	1st order	3.6	24.5	270	25.0
		2nd order	3.6	24.7		
7e	8	1st order	3.0	29.4	305	27.1
		2nd order	–	–		
7f	9	1st order	3.3	26.7	300	27.9
		2nd order	–	–		
7g	10	1st order	2.8	31.5	285	29.0
		2nd order	–	–		
7h	12	1st order	27	32.7	280	31.0
		2nd order	–	–		

[a] Recorded after annealing at 120°C

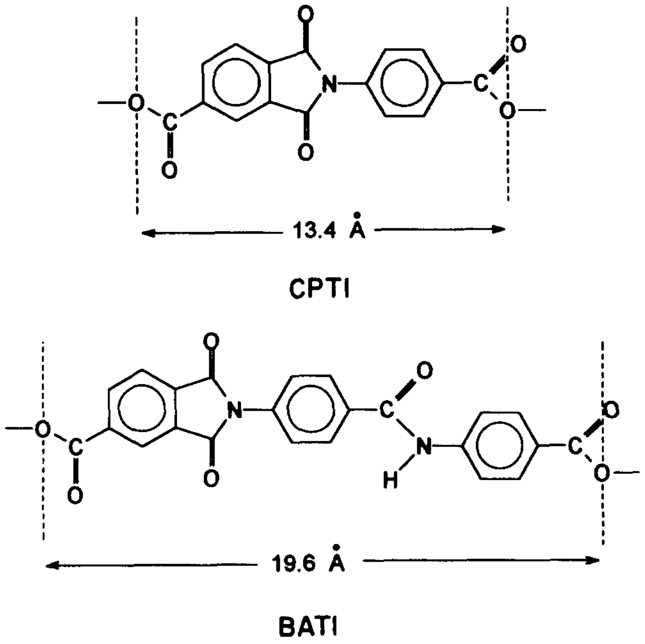


Figure 7 Geometry of mesogens as calculated by a force field program

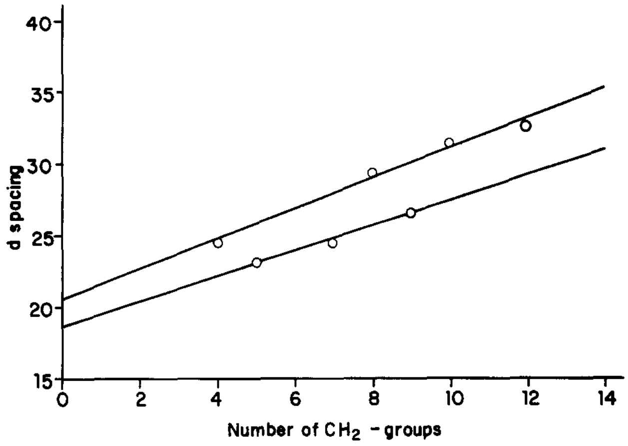


Figure 8 Layer distances measured at room temperature (WAXS) vs. the number of methylene groups in the spacer

The finding of this odd-even effect is satisfactory, because also the melting temperatures show a strong odd–even effect (*Table 2*). This observation means that the crystal lattices of the PEAIs with odd-spacers are less stable than those of the even-numbered spacers. In principle two explanations may account for this finding:

I) The mesogens of the odd-numbered PEAIs are tilted relative to the layer plane in contrast to the mesogens of the even-numbered PEAIs, and this tilting is energetically less favorable for the crystal lattice.

II) The mesogens of both series are upright but the conformations of the odd-numbered spacers are different from those of the even-numbered spacers in such a way that the odd-numbered PEAIs contain a high fraction of *gauche* conformations. More *gauche* conformations entail shorter layer distances, and they represent a high energy level, so that less energy (i.e. a lower temperature) is required for the melting of the PEAIs.

Unfortunately the results of this study do not allow a clearcut decision whether hypothesis I or hypothesis II is correct. As illustrated by *Figure 8*, the *d*-spacings of the even-numbered PEAIs yield a length of 20.5 Å upon extrapolation to zero $-CH_2-$ groups. This distance is in fair agreement with the length of an extended mesogen (19.5 Å) calculated by computer modelling with a force-field program[15]. A value of 19.0 Å was found by extrapolation of the odd-numbered PEAIs. These extrapolations also yield different slopes for the series of even- and odd-numbered PEAIs. The flatter slope of the odd-series corresponds to a 'pitch' of 0.85–0.90 Å per CH_2-group, whereas a 'pitch' of 1.05–1.10 Å was found

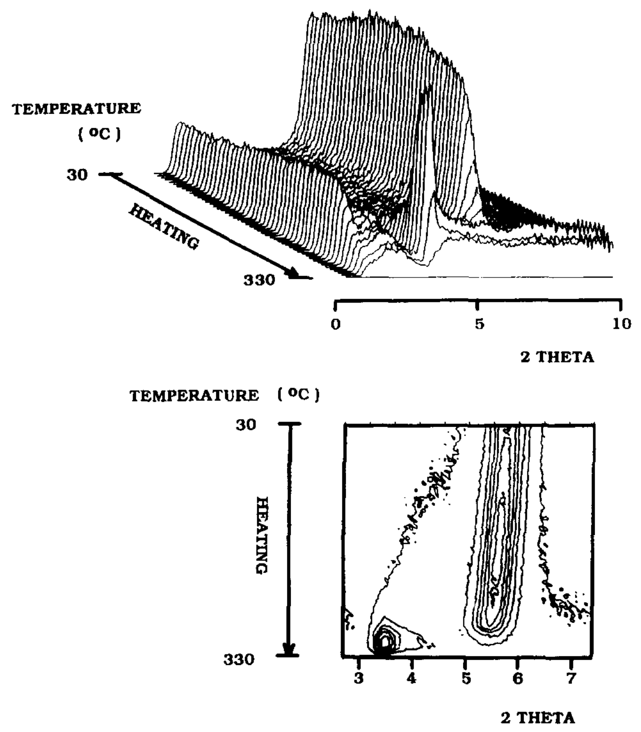


Figure 9 WAXS powder patterns of polymer **7c** ($n = 6$)

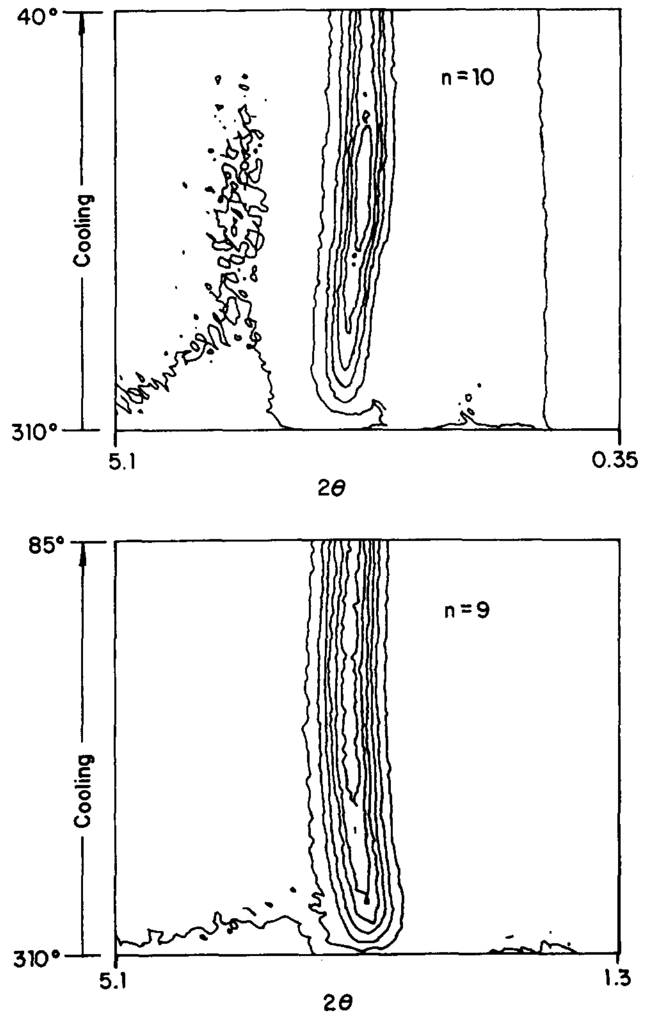


Figure 10 Contour plots of the synchrotron radiation measurements of PEAIs **7f** and **7g**

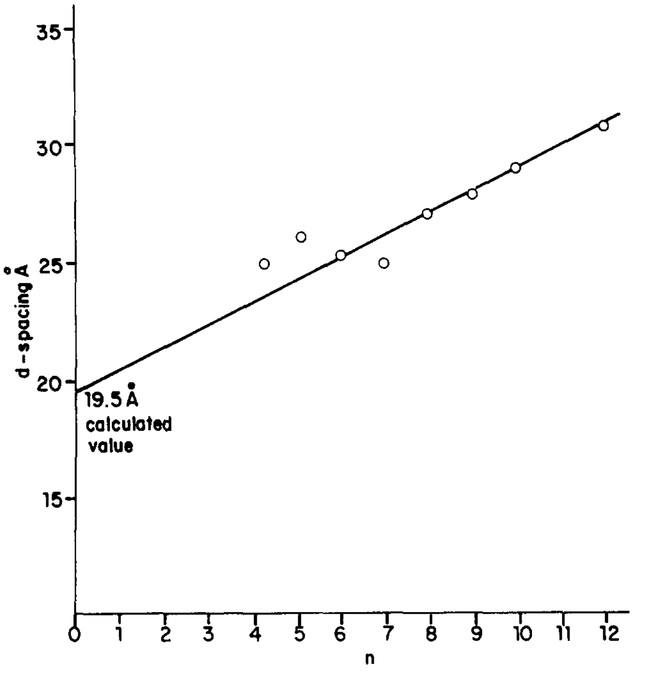


Figure 11 Layer distances of the smectic phases of PEAIs vs. the number of methylene groups in the spacer as determined from synchrotron radiation measurements

for the even PEAIs. The theoretical value for an all-*gauche* spacer is 0.9 Å, and 1.24 Å for an all-*trans* spacer. Therefore the extrapolations of the *d*-spacings, depicted in *Figure 8*, favour hypothesis II, but do not allow a definite decision.

The wide angle reflections allow the following conclusions. In the case of **7a** and **7e**, the existence of several sharp reflections between $2\theta = 10-30°$ (*Figures 4A* and *4B*) indicates an orthorhombic type of the lateral arrangement of the mesogens. Taking into account an upright position of the mesogens, this means that a smectic-E type of layer structure was formed. The difference between a smectic-E mesophase and a smectic-E-like crystal structure consists of differences in the long range order, and shall not be studied in this work. On increasing the length of the spacer, the orthorhombic type of lateral order changes to a hexagonal order, which is almost perfect in the case of **7h** (*Figure 4C*). In other words, **7h** adopts a smectic-B type layer structure in the solid state.

In the case of odd-numbered PEAIs, again smectic-E phases were observed when the samples were annealed (*Figure 5A*). However, quenching from the melt or precipitation from solution produced a smectic glass without any wide angle reflection (*Figure 5B*). Taking into account an upright position of the mesogens, this phase may be called frozen smectic-A phase.

X-ray measurements at higher temperatures (up to 350°C) were conducted with synchrotron-radiation at a heating rate of $20°\mathrm{C\,min}^{-1}$. As illustrated by *Figures 9* and *10* a strong MAR was found for all PEAIs in the molten state. The *d*-spacings calculated from these MARs are listed in *Table 3*. Their plot against the number of CH_2-groups allows a satisfactory extrapolation (*Figure 11*). The extrapolated distance of 19.5 Å is in perfect agreement with the calculated length of an upright mesogen. Hence, the synchrotron radiation measurements confirm the existence of a smectic-A phase for all PEAIs, in full agreement with the texture discussed above (*Figure 6*).

The *d*-spacings found for PEAIs **7a** and **7b** are somewhat larger than expected from the extrapolation of the higher PEAIs (*Figure 11*). A higher content of *trans* conformations might be an adequate, but speculative, explanation. Anyway, these greater *d*-spacings do not affect the conclusion that all PEAIs form a smectic-A phase in the melt. Another interesting aspect of the X-ray measurements of **7a** and **7b** is the observation that the MAR does not change its position upon cooling. That means the mesogens are in both cases also upright in the solid state, a result which clearly favours hypothesis II.

Quite unexpected properties were found for PEAI **7c**. A *d*-spacing of 16 Å was found for the solid state, a value which largely deviates from the *d*-spacings of all other polymers. However, the synchrotron radiation measurements of *Figure 9* demonstrate that the unusual layer structure of the solid state changes dramatically at T_m, so that a normal smectic-A phase is formed. Slight changes of the *d*-spacings were also observed for all higher PEAIs (*Figure 10*). The layer distances of the odd-numbered PEAIs expand a little and the *d*-spacings of the odd PEAIs shrink. This result is in satisfactory agreement with all aforementioned measurements and interpretations. All PEAIs adopt the same tilt angle for the mesogen and the same population of conformations in the melt, but even- and odd-PEAIs form slightly different layer structures in the solid state, due to somewhat different conformations of the spacers.

CONCLUSIONS

4-(4′-Ethoxycarbonylphthalimido)-*N*-(4′-ethoxycarbonyphenyl) benzamide has proved to be a suitable condensation monomer for the preparation of PEAIs by polycondensation with aliphatic diols in a conventional ester interchange process in the melt. The current PEAIs form an enantiotropic LC-phase, in contrast to other previously reported PEIs prepared from aliphatic diols and shorter phenylphthalimide containing monomers. Mesophase intervals ranging from 40 to 140°C have been observed. Due to lower melting temperatures, the PEAIs with an odd-number of CH_2-groups in the spacer possess a broader temperature range of the LC-phase. A smectic-A phase could be identified for all the PEAIs of this series by means of polarizing microscopy and X-ray diffraction measurements at elevated temperatures. This result fits well in with the observation that most smectic polyimides form a smectic-A phase[16–18].

ACKNOWLEDGEMENTS

The financial support provided by the A. von Humboldt Foundation through the programme Forschungskooperation Europa is greatfully acknowledged. H.R. is indebted to the Deutsche Forschungsgemeinschaft for the concession of a post-doc. grant.

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