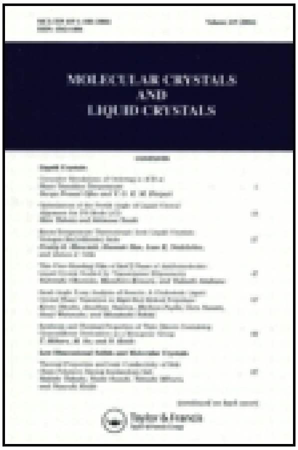

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Thermotropic Polyesterimides Derived From Trimellitic Acid

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THERMOTROPIC POLYESTERIMIDES DERIVED FROM TRIMELLITIC ACID

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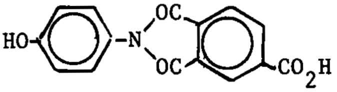
Abstract Two groups of thermotropic poly(ester-imide)s were prepared from trimellitic anhydride (TMA) and various bisphenols. The first group contains α,ω-diamines the second group ω-amino acids as flexible spacers. Both groups possess a layered supermolecular structure in the solid state and form a smectic melt above the melting points. The poly(ester-imide)s with diamine spacers possess a regular primary structure, they crystallize rapidly and reach a high degree of crystallinity. Furthermore, they show unusually high heat-distortion temperatures (HDTs) which are directly related to their melting points.

INTRODUCTION

Numerous polyimides were synthesized and characterized in the past three decades, because building blocks with imide structures possess a high thermostability, a good chemical stability and a low inflammability[1,2]. Due to their good qualities as engineering plastics numerous poly(ether-imide)s, poly(ester-imide)s and poly(amide-imide)s were also commerciallized by various chemical companies[1,2]. Yet to be best of our knowledge liquid crystalline (LC) polyimides have not been described so far, although the flat geometry of aromatic imide groups and their strong dipole forces suggest that they might be good mesogens.

In a first attempt to synthesize thermotropic poly(ester-imide)s with high thermostability and high heat-distortion temperatures, N-(4-hydroxyphenyl)trimellitic acid (1) was prepared and cocondensed with 4-hydroxybenzoic acid at various molar ratios[3)]. Further copoly(ester-imide)s were obtained by cocondensation with terephthalic acid or 1,4-cyclohexane diacid and hydroquinone. Yet, none of these copoly(ester-imide)s formed a mesophase at temperatures below 420°C. Therefore, all further attempts to synthesize thermotropic poly(ester-imide)s which can be processed at temperatures below 380°C concentrated on structures with aliphatic spacers in the backbone.



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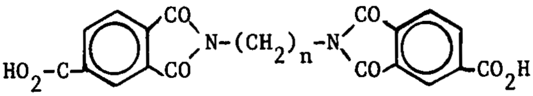
RESULTS AND DISCUSSION

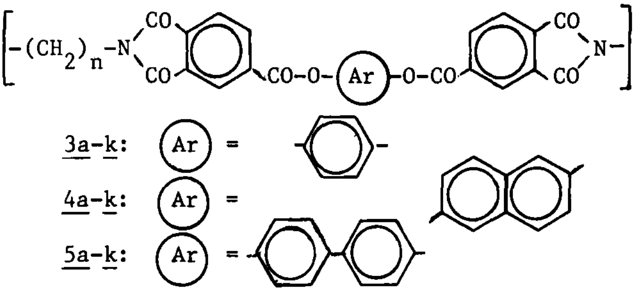
A) Poly(ester-imide)s of trimellitic acid and α,ω-diamines

The poly(ester-imide)s prepared from TMA may be subdivided into two groups. The first group contains spacers derived from aliphatic α,ω-diamines, whereas the spacers of the second group were introduced in the form of aliphatic ω-amino acids. The poly(ester-imide)s of the first group are based on synthesis and polycondensation of the diacids 2a-2k.



2a-k (n = 4-12)

The poly(ester-imide)s based on the diacids 2a-k consist of three classes of thermotropic polymers which are characterized by the bisphenols used for their synthesis. With hydroquinone the series 3a-k was obtained[4)], with 2,6-dihydroxynaphthalene series 4a-k[4)] and with 4,4'-dihydroxybiphenyl series 5a-k[5)]. All these poly(ester-imide)s were prepared by bulk condensations of the diacides 2a-k with the bisacetates of the aforementioned bisphenols in the presence of magnesium acetate. When in the case of 3k hydroquinone was replaced by methylhydroquinone or phenylhydroquinone, only amorphous products were obtained. The thermotropic character was also lost, when in the case of 4k 2,6-dihydroxynaphthalene was replaced by the 1,4-, 1,5- or 2,7-isomer$^{4)}$.



All poly(ester-imide)s 3a-k, 4a-k and 5a-k were characterized by DSC-measurements at a heating rate of 20°C and by microscopic observation under polarized light. The DSC traces exhibit in most cases two endotherms (Tm_1 and Tm_2) which represent the transition from the solid state to a smectic melt (Tm_1) and the smectic → isotropic transition (Tm_2) respectively. The second endotherm is in several cases difficult to detect, because the enthalpy change is low (2-6 kJ/mol), because it extents over a broader temperature range than Tm_1, and because it is affected by thermal decomposition of the poly(ester-imide)s.

Because the bisphenol has an influence of the length of the mesogenic group it also influences the stability of the anisotropic melt. In the case of hydroquinone the temperature range of the mesophase is on the order of 10 - 20°C, in the case of 2,6-dihydroxynaphthalene on the order of 20 - 50°C and for 4,4'-dihydroxybiphenyl 60 - 120°C. Thus, the poly(ester-imide)s 5a-k are best suited for mechanical processing from the mesophase. Furthermore, a plot of Tm_1 and Tm_2 versus the spacer lenght (FIGURE 1) demonstrates that Tm_1 obeys a distinct odd-even effect in contrast to Tm_2[5)].

The regular sequence of aliphatic spacer and aromatic mesogen suggests that the mesophase of 3a-k, 4a-k and 5a-k is smectic. This suggestion was confirmed in two ways. First microscopic observation under plarized light revealed a "granular texture". This texture differs largely from the mobile droplets with "schlieren texture" which were observed in the case of random copolyesters prepared from the diacids 2a-k, hydroquinone bisacetate and 4-acetoxybenzoic acid. The smectic nature of the mesophases of 5k was also confirmed by WAXS-measurements conducted by means of synchrotron radiation in the temperature range of 20 - 320°C (see below)[5)].

When WAXS powder patterns of the crystalline poly(esterimide)s 3a-k and 5a-k were measured at room temperature a broad reflection were found in all cases at $\vartheta = 10^\circ$. Other aromatic polyesters with unsubstituted phenylene units also display such reflections which represent the lateral distances (ca. 4.5 Å) of directly neighboring chains. More interesting are the sharp reflection found at small angles (1st to 5th order) indicating a layered supermolecular structure. As demonstrated in FIGURE 2 the d-spacings of the layers calculated from the small angle reflections parallel the lengths of the repeating units. Interestingly, these d-spacings displays a strong odd-even effect although the slopes of the even and the odd series are nearly identical[4,5)]. This finding suggests that the spacers of both the even and odd series possess the same tilt against the layer plane. The shorter d-spacings of the odd series also suggest

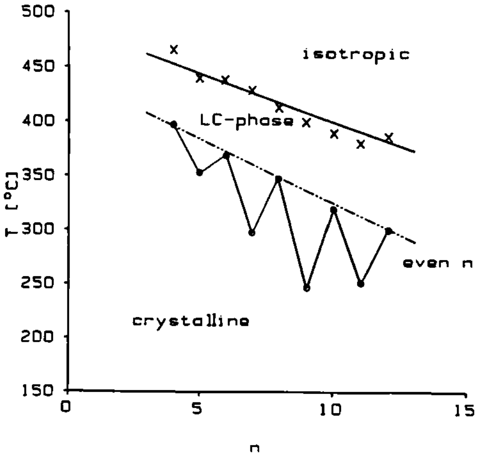


FIGURE 1. Phase transitions of the poly(ester-imide)s 5a-k

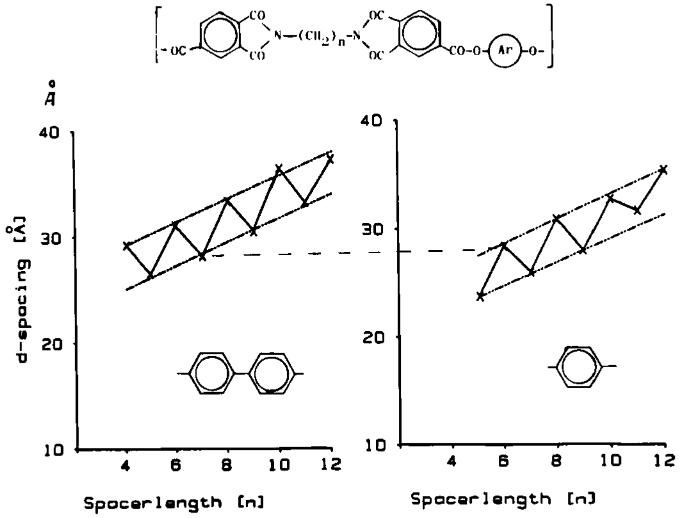
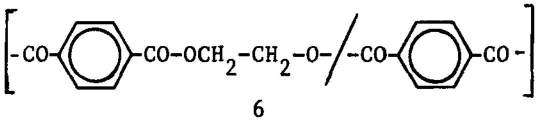


FIGURE 2. d-Spacings of the layer planes of the poly(ester-imide)s 5a-k

that their mesogens are stronger tilted than the mesogens of the even series.

The synchrotron radiation measurements of 5k conducted at a heating and cooling rate of 20°C/min revealed that the first and second order small angle reflection still exist in the mesophase, thus confirming a smectic structure. Furthermore, the synchrotron data indicate that the crystallization is nearly complete within one minute. The agreement with this result DSC measurements showed that cooling with a rate of ca. -200°C/min does not suppress the crystallization of 3a-k and 5a-k in the case of longer spacers ($n \geq 8$) even quenching of molten samples with liquid nitrogen did not yield amorphous materials, so that the glass-transition temperatures (Tg) could not be measured. In contrast, rapid cooling of molten samples of series 4a-k yields a partially amorphous material. Obviously the lower symmetry of the 2,6-dihydroxynaphthalene unit strongly affects the rate of crystallization.



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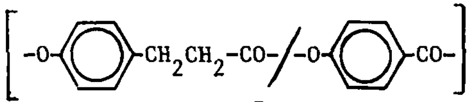

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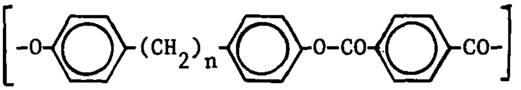

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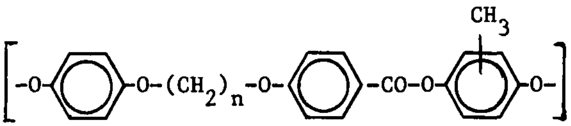

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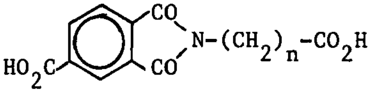
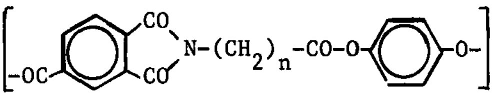
An aspect of particular interest are the heat-distortion temperatures (HDTs) of LC-polyesters in general and those of

LC-poly(ester-imide)s in particular. When LC-polyesters with aliphatic spacer in the main chain were characterized by means of the penetration method at high pressure (e.g. 1 kg/mm^2, comparable with the "Vicat-A" test) the following results were obtained. The PET/PHB copolymers 6[6] show HDTs as low as their Tg's, i.e. in the range of 80-90°C[5]. Similarily low HDTs corresponding to Tg's in the range of 50 - 70°C were found for copolyester of β-(4-hydroxyphenyl)propionic and 4-Hybe (7)[7]. In both cases the random sequences and low degrees of crystallinity may be blamed for these poor mechanical properties. However, several LC-polyesters with a regular sequence of pacer and aromatic mesogen, do not give better results. For instance polyesters prepared from alkylene bisphenols and terephthalic acid (8) or other dicarboxylic acids[8] and the polyesters of structure 9[9] all possess HDTs close to their Tg's. Also the poly(ester-imide)s 4a-k show such an unsatisfactory behavior[4] and thus support the prejudice that aliphatic spacers are detrimental for high HDTs[9]. However, when the poly(ester-imide)s 3a-k and 5a-k were measured under the same conditions HDTs related to the melting points (Tm) were found. Depending on the spacer lenght these HDT, may be as high as 370°C (for 5a[5,10]. Furthermore, the thermomechanical measurements do not show any yielding of the films at Tg (in the range of (90-130°C) even after rapid cooling of the molten samples[5]. Obviously, the rapid crystallization along with a high degree of crystallinity produce a network of crystallites which resist the mechanical pressure regardless of the glass-transition. Whether a special morphology contributes to this extraordinary mechanical properties is the object of current investigations.

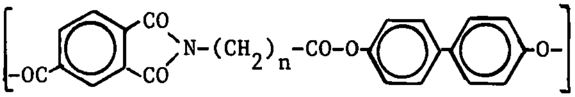
B) Poly(ester-imide)s of trimellitic acid and ω-amine acid



10a-f
(n = 3-6,11,12)



11a-f



12a-f

The second group of thermotropic poly(ester-imide)s derived from TMA are based on the condensation of the diacids 10a-f with hydroquinone (11a-f) or with 4,4'-dihydroxybiphenyl (12a-f)[11]. The diacids can be prepared by condensation of trimellitic anhydride with ω-amino acids or with lactams, provided that the ring size of lactam is higher than seven (n > 5). In this way three relatively inexpensive monomers (12c, e and f) are obtainable. Furthermore, is it worth mentioning that the condensation of trimellitic anhydride either with ω-amino acid or lactam and the subsequent polycondensation with an acetylated bisphenol may be conducted in an "one-pot procedure".

Even though the poly(ester-imide)s 14a-f and 15a-f are homopolymers from the viewpoint of their components they may contain random sequences of three different, but isomeric, repeating units due to the asymmetry of the diacids 10a-f. This kind of sequence isomerism has the consequence that the melting points of 11a-f and 12a-f are lower than those of poly(ester-imide)s 3a-k and 5a-k. Yet, despite this difference most properties of 11a-f and 12a-f are very similar to those of the other poly(ester-imide)s.

For instance, the DSC measurements display in the heating traces two endotherms which indicate a solid → smectic and a smectic → isotropic transition. This interpretation agrees with microscopic studies under polarized light which revealed the formation of a birefringent mobile phase with "granular texture". Also in analogy to 3a-k and 5a-k the temperature range of the mesophase is relatively small, when hydroquinone is used as monomer (eg. 15°C for 11e and f), and borader for the polyesters of 4,4'-dihydroxybiphenyl (eg. 60-70°C for 12e and f).

The WAXS patterns of 11a-f and 12a-f show again a close analogy to those of 3a-k and 5a-k indicating a layered supermolecular structure with d-spacings slightly shorter than a fully extented repeating unit. The X-ray pattern of a fiber spun from the anisotropic melt of 12f displays the small angle reflections of the layers on the meridian and the $\partial = 10^{\circ}$ reflection on the equator (FIGURE 3). Here like in the case of 3a-k the chain axis parallel the fiber axis whereas the layer planes are perpendicularily oriented.

Different properties of 3a-k and 5a-k, on the one hand, and 11a-f or 12a-f, on the other hand, were found with regard to crystallization and heat-distortion temperatures. Due to the less regular primary structure 11a-f and 12a-f crystallize less rapidly and less perfectly. Upon quenching from the isotropic melt the poly(ester-imide)s 11a-f may be obtained in the amorphous state. The thermomechanical analyses conducted with the penetration method at a pressure of $1 kg/mm^2$ revealed that the HDTs of 11a-f and 12a-f are significantly lower than their melting points (Tm_1). Interestingly, random copolyesters of 11e and 4-hydroxybenzoic acid do not show higher HDTs despite a considerably higher content of mesogenic aromatic units.

Finally, it is worth noting that the poly(ester-imide)s 3a-k, 4a-k, 5a-k, 11a-f and 12a-f possess similar thermostabilities. 5 % loss of weight occured at temperatures between 370 and 400°C, when the thermogravimetric measurements were conducted at a heating rate of 10°C/min in air. In all series the thermostability decreases with the length of the spacers which are more sensitive to oxydation than the mesogens. Nonetheless, mechanical processing is feasible up to temperatures of 340 - 350°C.

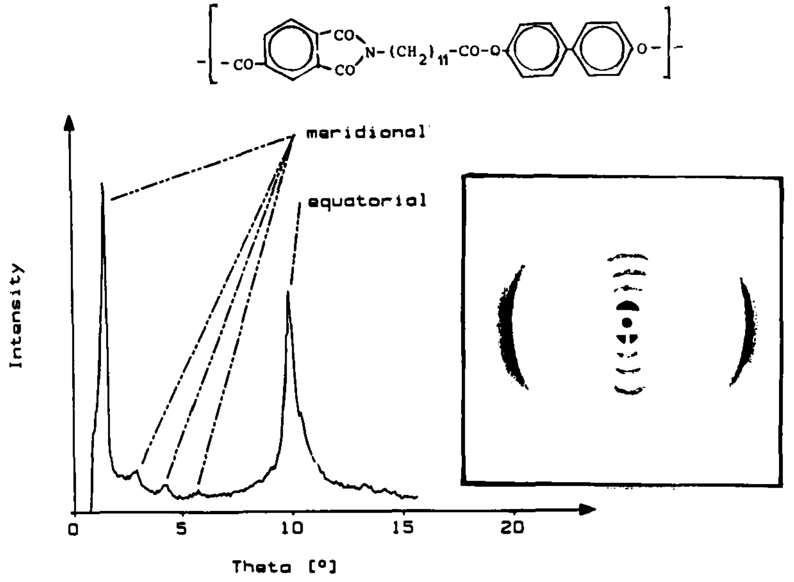


FIGURE 3. WAXS powder pattern and fiber pattern of poly(ester-imide) 12f

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