

EFFECT OF SEQUENCE STRUCTURE ON THE THERMOTROPIC LIQUID CRYSTALLINE PROPERTIES OF POLYESTERAMIDES BASED ON DIMETHYLBENZIDINE, BISPHENOL-A AND *p*-TEREPHTHALYL CHLORIDE*

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Abstract A series of thermotropic liquid crystalline polyesteramides with different sequence structure based on dimethylbenzidine (DMBD), bisphenol-A(BPA) and *p*-terephthalyl chloride (TPC) was synthesized by changing the feeding order of monomers in low temperature solution polycondensation system. By means of NMR and a computer program the sequence structure parameters were measured. The effect of sequence structure on liquid crystalline phase transition temperature of PEAs obtained was investigated.

Keywords Liquid crystal; Polyesteramide; Sequence structure; Melting temperature

INTRODUCTION

The liquid crystalline polyamides such as poly(*p*-phenylene terephthalamide) (PPTA), copolyamides modified based on PPTA which are lyotropic liquid crystalline polymers^[1] and aromatic-aliphatic copolyamides which are thermotropic polymers^[2] were reported. Some of them were applied to industry^[3]. Many kinds of thermotropic liquid crystalline polyesters and copolyesters have become commercial products^[4]. Polyesteramide (PEA) is either a new or an old type of polymers containing amide group and ester group in the backbone^[5-6]. But the studies on synthesis, properties and structure of liquid crystalline polyesteramides have been an important area for recent ten years. In this area the effect of sequence structure on the liquid crystalline behaviour is very interesting.

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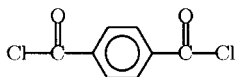
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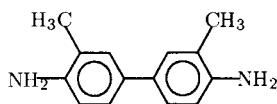
As considered for all other copolymers the sequence structure affects obviously the properties of polymers. It should be noted that the melting temperature affected more strongly by sequence structure of copolymers is very important for study on liquid crystalline phase transition behaviour of thermotropic liquid crystalline polymers.

EXPERIMENTAL

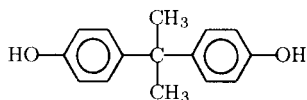
The polyesteramides (PEAs) were synthesized from *p*-terephthalyl chloride,



dimethylbenzidine



and bisphenol-A



by low temperature solution polycondensation in a solvent system consisting of *N*-methylpyrrolidone (NMP) and anhydrous lithium chloride (LiCl). Triethylamine (TEA) was used as acid acceptor (AA) in polycondensation reactions. The sequence structure parameters of polymer chain including random degree (B), number average chain length (Ln), polyamide segment length (Lna) and polyester segment length (Lne) were determined by means of H^1 -NMR spectra and a computer program for the resolution of H^1 -NMR spectra with overlapping peaks and the calculation of chain sequence structure parameters^[7]. The proton NMR spectra were recorded on FX-90Q NMR spectrometer with a Fourier transform accessory at 90 MHz and 100°C. The solution of polymers used were approximately 2–3%(w/w) in NMP/LiCl (3%W/V). The thermal properties of polyesteramides were measured by DuPont-990 differential scanning calorimeter under nitrogen atmosphere at a heating rate of 10°C/min. The inherent viscosity was determined with an Ubbelohde type viscosimeter at 0.5 g/dl polymer concentration at 30°C.

RESULTS AND DISCUSSION

The chain sequence structure of PEAs produced by different feeding methods of monomers

The four feeding methods, as shown in Table 1, were used to obtain PEAs with different chain sequence structure, which were based on $-\text{OH}/\text{NH}_2 = 1.0$ (mol.). Table 2 summarizes the inherent viscosity (η_{inh}) and sequence structure parameters, polyamide length (Lna), polyester segment length (Lne) and random degree (B) of PEAs produced.

Table 1 The feeding methods of monomers used

Code	Feeding order
I	(BPA+DMBD) $\rightarrow$ AA $\rightarrow$ TPC
II	BPA $\rightarrow$ AA $\rightarrow$ TPC $\rightarrow$ DMBD
III	BPA $\rightarrow$ AA $\rightarrow$ TPC ₁ * $\rightarrow$ DMBD $\rightarrow$ TPC ₂ *
IV	DMBD $\rightarrow$ AA $\rightarrow$ TPC ₁ $\rightarrow$ BPA $\rightarrow$ TPC ₂

* TPC₁/TPC₂ = 1.0 (mol)

Table 2 Sequence structure parameters of PEAs produced

Method	I	II	III	IV
η_{inh} (dl/g)	0.82	0.85	0.84	0.66
Lna	4.16	2.84	3.55	4.09
Lne	4.22	2.61	3.26	4.13
B	0.48	0.74	0.59	0.49

Comparing the Ln and B of PEA-1 with that of PEA-2, it is clearly that the PEA-2 produced by the method-II in which BPA and DMBD were separately added and the first step was the reaction of BPA with TPC has larger B value and smaller Ln value than that of PEA-1 produced by method-I in which BPA and DMBD were mixed and then added. These data show that the prepolycondensation of BPA with TPC is favourable for the preparation of PEA with larger B and smaller Ln . Usually the reaction activity of amine group of DMBD is higher than that of hydroxy group of BPA in Schotten-Baumann reaction^[8]. The higher activity of the monomers affect the sequence structure of PEA in this polycondensation system more obviously. This result is the same as that obtained from the study on sequence structure of aromatic-aliphatic copolyamides based on TPC, *p*-phenylene diamine (PPD) and aliphatic diamine (ADA)^[9].

The feeding method III is also a good one for obtaining the PEA with large B and smaller Ln .

Effect of sequence structure of PEA on melting temperature (T_m)

It was reported^[10] that PEA was a thermotropic, nematic liquid crystalline polymers and the liquid crystalline region ranges from T_m to the degradation temperature (T_d).

Fig. 1 shows the DSC curves for PEA-1, PEA-2 and PEA-3 produced by feeding method I, II and III respectively.

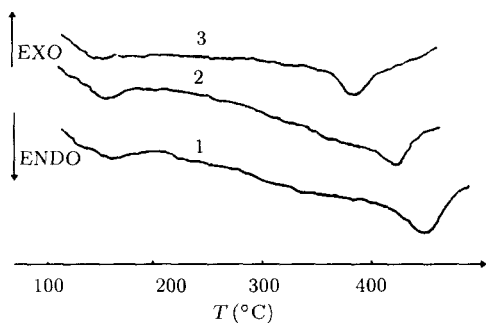


Fig.1 DSC curves of PEAs

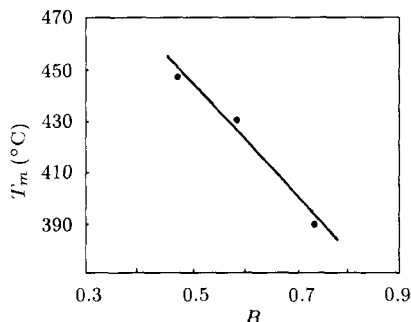


Fig.2 Relationship between T_m and B of PEA

Fig.2 and Fig.3 show the nearly linear relations of T_m with (B) and with (Ln) . The melting temperature is more strongly affected by the sequence structure of PEAs, which have the same chain composition.

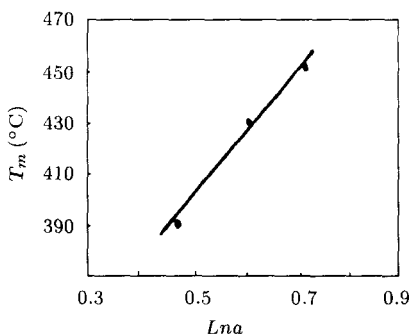


Fig.3 Relationship between T_m and Lna of PEA

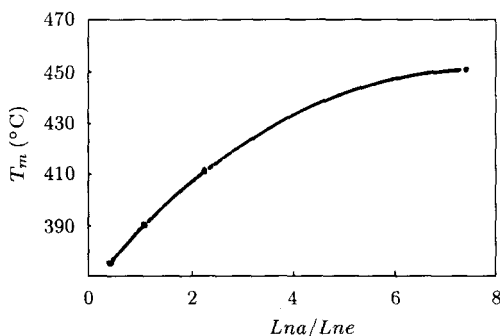


Fig.4 Variation of T_m of PEAs with Lna/Lne

Effect of chain composition of PEAs on T_m and degradation temperature (T_d)

As mentioned above the effect of sequence structure on T_m is obvious for PEA with the same chain composition. Due to the presence of intermolecular hydrogen bonds in polyamide segments, the chain composition i.e. the ratio of polyamide and polyester sequence average length in PEA, is also an important factor affecting the T_m for PEA with nearly the same random degree. Table 3 lists the T_m , T_d and the sequence structure parameters of PEAs produced by different mol. ratio of BPA/DMBD.

As indicated by these data in Table 3, the values of Lna/Lne are in accord with the mol. ratio of DMBD/BPA approximately, which is a direct evidence for the

accuracy of analysis method used for the elucidation of sequence structure of PEAs synthesized. The relation of Lna/Lne and T_m is evidenced in Fig.4, the T_m of PEAs increases with the increase of the ratio of Lna/Lne .

Table 3 Chain composition and sequence structure of PEA

DMBD/BPA (mol.)	T_m^* (°C)	T_d^* (°C)	Lna^{**}	Lne^{**}	B	Lna/Lne
20/80	345	415	/	/	/	/
30/70	375	/	2.27	5.42	0.63	0.43
50/50	390	425	2.83	2.61	0.74	1.08
70/30	410	/	5.40	2.36	0.61	2.29
90/10	450	/	22.00	3.00	0.38	7.33

* Measured by DSC

** Lna : Polyamide sequence length Lne : Polyester sequence length

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