Sequence Structure and Thermotropic Liquid Crystalline Properties of Aromatic–Aliphatic Polyesteramides Based on Dimethylbenzidine, Hexamethylene Glycol and *p*-Terephthalyl Chloride[†]

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ABSTRACT: Thermotropic aromatic–aliphatic liquid crystalline polyesteramides (PEAs) with different sequence structures were synthesized from dimethylbenzidine (DMBD), hexamethylene glycol (HG), and *p*-terephthalyl chloride (TPC) by different feeding order of monomers. Structure parameters, number average length (L_n) and random degree (B), were obtained by NMR and a computer program. The relation of sequence structure and liquid crystalline phase transition behavior of PEAs obtained was studied.

KEY WORDS Polyesteramide / Liquid Crystal / Sequence Structure /

Polyesteramides synthesized from three monomers, *p*-terephthalylchloride (TPC), dimethylbenzidine (DMBD), and hexamethylene glycol (HG), were thermotropic liquid crystalline polymers and their liquid crystalline behavior was reported.¹ The polyesteramides obtained were random or block polymers because of the different reactivity of –OH and –NH₂ with –COCl. The effect of distribution of two chain segments, polyester chain segment and polyamide chain segment, which exhibited different rigidity on properties of polymers, specially on liquid crystalline phase transition, was obvious.^{2,3}

In this paper polyesteramides with different sequence distributions were synthesized by changing the feeding order of monomers and the relationship between liquid crystalline properties and sequence structure was studied.

EXPERIMENTAL

The monomers, TPC, DMBD, and HG, were used for obtaining the polyesteramides (PEAs) by low temperature solution polycondensation.⁴ Number average sequence length (L_n) and random degree (B), which characterized the sequence distribution of polyesteramide chain segments, were obtained by ¹H NMR spectra and a computer program for the resolution of NMR spectra with overlapping peaks.^{5,6} The Unity-200 NMR spectrometer was used for recording NMR spectra of polyesteramides and the solution used was approximately 2–3% (w/w) in NMP/LiCl (3% w/v). The liquid crystalline phase behavior was determined by Du-Pont 1090 DSC under N₂ at heating rate of 10°C min^{–1}. The inherent viscosity (η_{inh}) measurement was found with a Ubbelohde type viscosimeter at 0.5 g dL^{–1} polyesteramide concentration at 30°C.

RESULTS AND DISCUSSION

Synthesis of PEAs with Different Sequence Structures

Using different feeding orders, as shown in Table I, PEAs which exhibited different sequence structures but were based on same mole ratio of –OH group and –NH₂ were synthesized. The Table II listed η_{inh} , B , and L_n of PEAs produced and NMR data, in which the P_{dt} , P_{dth} , P_{hth} , P_{dt} , and P_{ht} represent the mol ratio of DTD, DTH, HTH, DT, and HT chain structure units and the P_{dh} and P_{hd} represent the possibility of H and D monomer

Table I. The feeding methods of monomers

Code	Feeding methods
I	(HG + DMBD) → AA ^a → TPC
II	HG → AA → TPC → DMBD
III	HG → AA → TPC ₁ ^b → DMBD → TPC ₂ ^b
IV	DMBD → AA → TPC ₁ → HG → TPC ₂

^a Acid acceptor. ^b TPC₁/TPC₂ = 1 (mol).

Table II. NMR data and sequence parameters of PEAs by different feeding methods

Feeding methods	I	II	III	IV
η_{inh} (dL g ^{–1})	0.62	0.51	0.63	0.70
P_{dt}	0.3735	0.3696	0.3676	0.3783
P_{dth}	0.2434	0.2625	0.2532	0.2439
P_{hth}	0.3831	0.3678	0.3792	0.3778
P_{dt}	0.4952	0.5009	0.4942	0.5003
P_{ht}	0.5048	0.4991	0.5058	0.4997
P_{dh}	0.2458	0.2620	0.2562	0.2438
P_{hd}	0.2411	0.2629	0.2503	0.2441
L_n^a	4.07	3.82	3.90	4.10
L_n^b	4.15	3.80	4.00	4.10
B	0.49	0.53	0.51	0.49

^a Sequence length of polyamide segment. ^b Sequence length of polyester segment.

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Figure 1. The relation of T_m and B . Figure 2. The relation of T_m and L_{na} .

Figure 3. The DSC curves of PEAs. 1, DMBD/HG = 50/50 (mol); 2, DMBD/HG = 20/80 (mol).

units after D and H monomer units in the polymer chain, respectively.

Table II shows that B of PEAs produced by method I and method IV in which the DMBD was added into the reaction system at first step were less than that of PEAs obtained by methods II and III in which the HG was fed into reaction system at first step. This proves that the methods in which the monomer with less reactivity hydroxy group, HG, was fed at first step reaction into polycondensation system are favorable for obtaining PEAs with bigger B and smaller L_n .⁷

The difference between the B of aromatic PEAs produced from TPC, DMBD, and bisphenol A (BPA) by I and IV and that of PEAs produced by II and III in last study⁸ is bigger than the difference between the B of aromatic-aliphatic PEAs obtained by I and IV and that of PEAs obtained by II and III in this study. The reason is that the reactivity of aliphatic hydroxy group with TPC is bigger than that of aromatic hydroxy group with TPC. Thus the difference of reactivity with TPC between the amine group of DMBD and the hydroxy group of BPA is also bigger than that of reactivity with TPC between the amine group of DMBD and the hydroxy group of HG in the unequilibrium polycondensation system.

Effects of Sequence Structures of PEAs on Melting Temperature (T_m)

Because of differences of rigidity between polyamide

Table III. Phase transition temperature of PEAs

DMBD/HG/mol	$T_m/^\circ\text{C}^a$	$T_i/^\circ\text{C}^a$	$T_d/^\circ\text{C}^a$	L_{na}	L_{ne}	B	L_{na}/L_{ne}
20/80	154	256	327	3.92	16.26	0.32	0.24
40/60	253	276	—	3.47	5.00	0.49	0.69
50/50	268	298	400	3.82	3.80	0.53	1.01
60/40	313	No	—	5.04	3.32	0.52	1.52

^a By DSC.

Figure 4. T_m and T_i of PEAs vary with L_{na}/L_{ne} .

and polyester segments T_m was more strongly affected by the L_{na} or B of PEAs synthesized by method II and $-\text{OH}/-\text{NH}_2 = 1$ (mol). Figures 1 and 2 show that a little change of L_{na} or B could make the T_m of PEAs change a lot.

On Chain Composition of PEAs

PEAs with different chain composition were synthesized by changing molar ratio of DMBD/HG and method II. The L_{na}/L_{ne} should approximately be equal to DMBD/HG (mol) if the accuracy of analysis method of L_n is enough.

As indicated by DSC curves (Figure 3) and data in Table III the liquid crystalline phase transition temperature (T_i) of PEAs could be observed.

As shown in Figure 4 with increasing rigid polyamide chain segment length, T_m and T_i of PEAs produced increased but the change of T_m was much greater.

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