

Note

ODD-EVEN EFFECT OF LYOTROPIC LIQUID CRYSTALLINE PROPERTIES OF AROMATIC-ALIPHATIC COPOLYAMIDES

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Abstract A series of aromatic-aliphatic copolyamides containing different aliphatic diamine units was synthesized by low temperature solution polycondensation. The liquid crystalline critical concentration (c^*) and liquid crystalline critical temperature (T^*) of these copolyamides exhibited an odd-even zigzag effect with the odd-even variation of carbon atom number in the aliphatic diamines used.

Keywords Odd-even effect, Copolyamide, Lyotropic, Phase transition

INTRODUCTION

The physical properties of many kinds of organic compounds such as melting temperature show a zigzag variation with the odd-even change of the number of carbon atoms in the aliphatic compound chain. This phenomenon is called the odd-even effect.

For low molecular weight liquid crystals, many physical properties such as nematic-isotropic transition temperature, orientation entropy, elastic constant, heat capacity and so on, also exhibit zigzag variation with the increase of methylene units in terminal alkyl or alkoxy group^[1-4]. For polymers, and especially for thermotropic liquid crystal polymers (LCPs), the same zigzag variation with odd-even change of the number of carbon atom in flexible spacer was also studied^[5-9].

However, the odd-even effect of lyotropic LCPs was rarely reported. The authors have reported the liquid crystalline (LC) properties of lyotropic aromatic-aliphatic copolyamide solutions^[10, 11]. In this paper the odd-even effect of the lyotropic LC properties of aromatic-aliphatic copolyamide was studied.

EXPERIMENTAL

Preparation of Copolyamides

Ten kinds of aromatic-aliphatic copolyamides were synthesized by low temperature solution polycondensation of *p*-terephthalyl chloride (TPC) with *p*-phenylene diamine (PPD) and aliphatic diamines (ADA).

Measurements

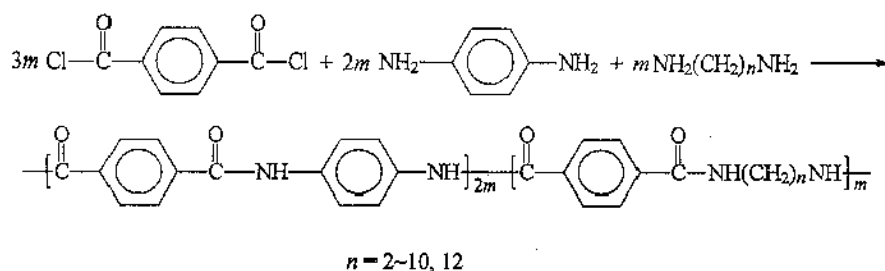
Inherent viscosity η_{inh}

Inherent viscosity was measured by Ubbelohde viscometer at 30°C in 98% sulfuric acid.

$$\eta_{inh} = (1/c) \ln(t/t_0)$$

c : concentration of copolyamide solution which was about 0.5g/dL; t_0 : time that the solvent used passed the capillary of the viscometer; t : time that the polymer solution passed the capillary of the viscometer.

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Critical concentration (c^*) and critical temperature (T^*)

The polymer solutions of different concentration in 100% sulfuric acid were prepared for each kind of copolyamides. The concentration of the solutions ranged from 10.80% (W/W) to 12.00% (W/W) with a concentration interval of about 0.1%. The solutions were kept for several hours at 25 °C and then their optical birefringence was observed under an Olympus BH-2 polarizing optical microscope (POM) at 25 °C. The concentration at which the birefringence was just observed was called the liquid crystalline critical concentration (c^*) of the lyotropic LC copolyamide. Copolyamide solutions of concentration higher than c^* at 25 °C were used for measurement of the liquid crystalline critical temperature (T^*). At T^* the birefringence has just disappeared under a POM with a hot stage, the temperature of which was controlled to increase from 25 °C at a rate of 10 K/min.

RESULTS AND DISCUSSION

Odd-Even Effect of c^*

The copolyamide samples used in this work were carefully selected to have similar sequence structure and inherent viscosity. Table 1 and Fig. 1 show the c^* of the copolyamides produced from ADA containing different numbers of methylene groups and the odd-even zigzag variation. Copolyamides containing odd numbers of methylene groups have lower c^* than that of the adjacent copolyamides containing even numbers of methylene groups. It is contrary to the odd-even effect of the melting temperature for thermotropic liquid crystalline copolymers. It may be explained by the possibility of forming hydrogen bonds between the amide groups and sulfuric acid which was the solvent for this system, and the copolyamides containing odd numbers of methylene groups have stronger hydrogen bonds due to the conformation of the methylene segments in the copolyamide chain.

Table 1. The c^* of lyotropic LC copolyamides

Number of methylene groups in ADA	2	3	4	5	6	7	8	9	10	12
c^* % (W/W)	11.6	11.0	11.5	11.3	11.5	11.3	11.6	11.5	11.6	11.8
η_{inh} (dL/g)	1.83	1.90	1.85	1.71	1.75	1.76	1.76	1.70	1.62	1.80

Odd-Even Effect of T^*

As can be seen from Fig. 2, the LC critical temperature (T^*) of lyotropic copolyamides with odd numbers of methylene groups is higher than that of the adjacent copolyamides containing even numbers of methylene groups. If the possibility of forming hydrogen bonds is also the most important factor resulting in the odd-even effect of T^* , then the observed change direction of T^* and c^* with the variation of the odd-even number of methylene groups is reasonable.

Odd-Even Effect of c^* at High Temperature

The T^* of copolyamides containing different numbers of methylene group at different concentrations were measured. Then a phase transition diagram was obtained for all samples which is shown in Table 2 and Fig. 3. From Fig. 3 the c^* of every copolyamide samples at any temperatures of the given temperature range can be

obtained, and then the odd-even effect curves of c^* can be plotted different temperatures. Figure 4 only shows the curves at 130°C and 100°C.

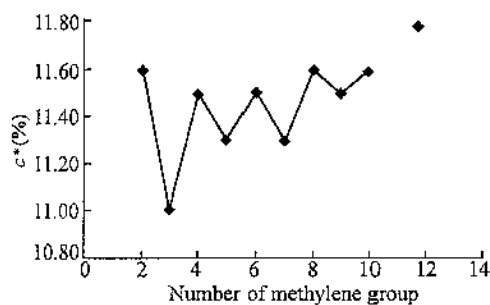


Fig. 1 The odd-even effect of c^* at 25°C for copolyamides

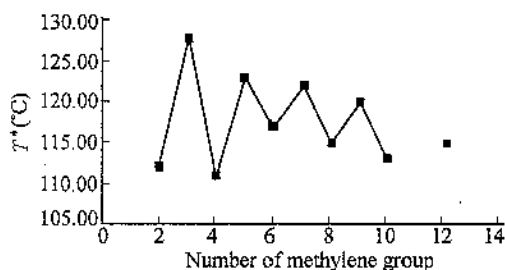


Fig. 2 The odd-even effect of T^* for copolyamides ($c = 15\%$ W/W)

Table 2. The T^* of lyotropic copolyamides at different solution concentration

Methylene number of ADA used		2	3	4	5	6	7	8	9	10	12	
		T^* (°C)										
Concentration of polymer solution (<i>W/W</i>) (%)	12.0	45	53	45	52	43	51	42	50	42	41	
	12.5	58	69	60	67	58	64	53	62	55	55	
	13.0	76	87	75	85	75	80	66	81	71	75	
	14.0	95	108	90	96	90	96	90	97	89	92	
	15.0	112	128	111	123	117	122	105	120	113	115	
	16.0	128	142	124	139	127	132	111	125	121	124	
	17.0	141	155	140	150	136	148	132	140	132	130	
	18.0	153	168	152	162	148	155	145	146	143	140	

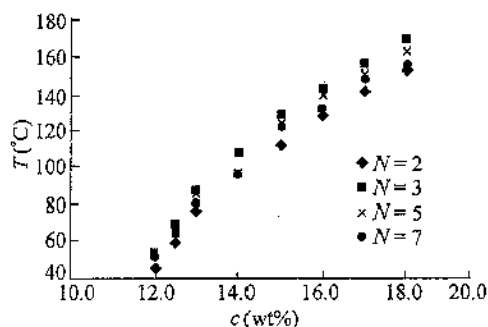


Fig. 3 The phase transition diagram

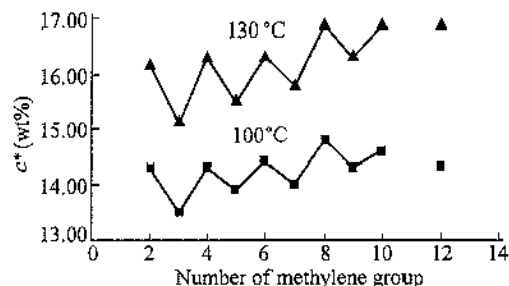


Fig. 4 The odd-even effect of c^* at high temperatures for copolyamides

The general trend of the variation of the zigzag curves at high temperatures (Fig. 4) is the same as that at room temperature (Fig. 1), but the difference of c^* values between two adjacent lyotropic copolyamides which contain odd and even number of methylene groups is obviously larger at higher temperatures than that at lower temperatures.

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