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The Effects of Diamine Skeleton and Its Substituents on Mesogenicity of Polyamides

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In the series of p-phenylene derivatives the monotropic nematic state was observed in poly(B-ODDA), poly(DMB-ODDA) and poly(CB-ODDA). No mesomorphic state was observed in poly(DCB-ODDA). The nematic state was observed in the series of diphenylmethane derivatives and the bulky alkyl substituent in the ortho position of the diphenylmethane heightens mesogenicity of the series of polyamides.

Aromatic polyamides are well known as lyotropic liquid crystals,1) but there have been a few reports on the thermotropic polyamides.2) The intermolecular hydrogen bonding between the amide linkages increases the thermal stability of the polyamides and so they frequently decompose before the formation of a liquid crystalline state in the melting process. Moreover, there have been no reports on the mesomorphic state of polyamides with only a carbon framework in the main chain.

In this study we synthesize a series of new polyamides by the condensation polymerization of octadecanedicarboxylic acids(ODDA) and aromatic diamines with different skeletons and with different substituents in their ortho positions adjacent to amido linkage of the benzene rings. We studied the phase transition and liquid crystalline state of the polymers by DSC and polarizing microscope observation.

The polyamides were synthesized from ODDA and various diamines of Fig. 1, where the synthetic route is also shown, in the presence of triphenyl phosphite in N-methylpyrrolidone/pyridine(4:1) solution at 373 K for 3 h.3) Diamines used are 1,4-diaminobenzene(B), 1,4-diamino-2-chlorobenzene(CB), 1,4-diamino-2,5-dichlorobenzene(DCB), 1,4-diamino-2,5-dimethylbenzene(DMB), 4,4'-diaminodiphenylmethane(DPM), 4,4'-diamino-3,3'-dimethyldiphenylmethane (DMDPM) and 4,4'-diamino-3,3',5,5'-tetramethyldiphenylmethane(TMDPM). Aromatic diamines(supplied from Nippon Kayaku Co, Ltd.) were recrystallized from methyl ethyl ketone and ODDA (supplied from The Nisshin Oil Mills, Ltd.) was from methanol before use. The obtained polymers were washed with methanol and identified as objectives by IR. IR was measured by an IR spectrophotometer JASCO A 302. The limiting viscosity of the polymers was measured by an Ubbelohde's viscometer in sulfuric acids at 303 K. DSC was measured by a Perkin Elmer DSC 1B at a heating/cooling rate of 10 K min^{-1} from 300 K to over the melting point. The texture was studied by a polarizing microscope, a Nikon Optiphot-pol XTP-11 equipped with a Mettler hot stage FP 82, under crossed polarizers at a heating/cooling rate of 10 K min^{-1}.

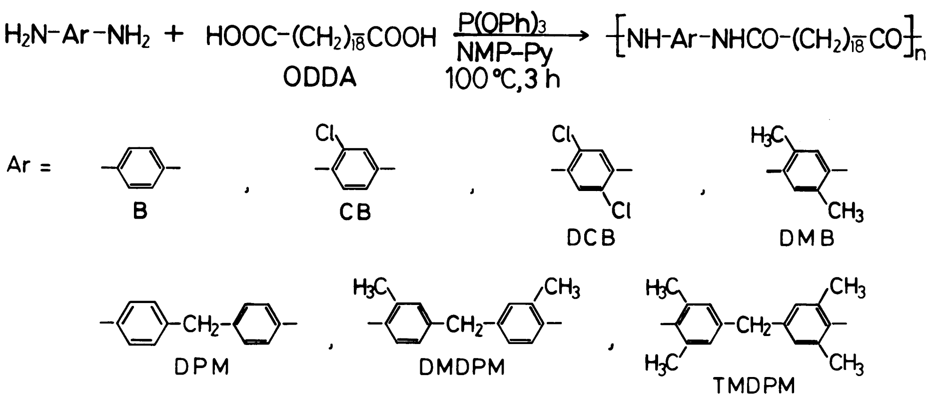

Fig. 1. Synthetic route of polyamides.

In the IR spectra, C=O and N-H stretching was shown around 1650 and 3260 cm^{-1}. This result suggests the presence of amide linkage.

DSC curves of the polyamides with p-phenylene derivatives are shown in Fig. 2. In the first heating process of poly(B-ODDA), three endothermic peaks, which corresponds to crystalline-crystalline phase transitions, are observed. In the first cooling process only one exothermic peak is observed. At a lower temperature of this thermal anomaly, a

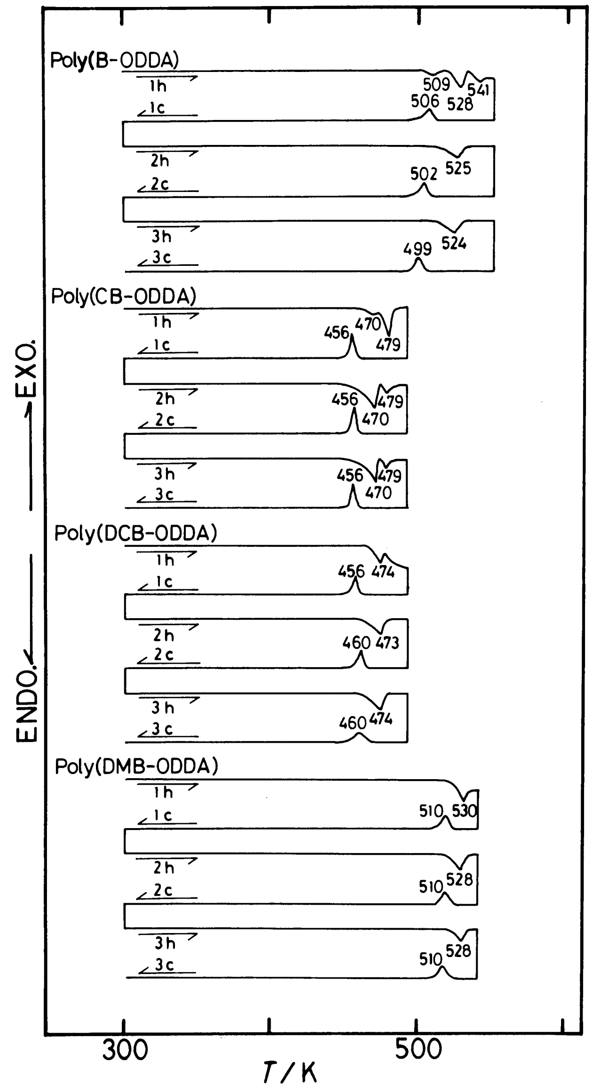

Fig. 2. DSC curves of polyamides of ODDA and 4,4'-diaminobenzene derivatives.

schlieren texture was observed in the microscope under crossed polarizers. A photograph of of poly(B-ODDA) at 489 K in the first cooling process is shown in Fig. 3. It suggests that the mesophase is nematic. In poly(CB-ODDA) and poly(DMB-ODDA) nematic schlieren textures are also observed only in the cooling processes. No mesomorphic state was observed in poly(DCB-ODDA).

The DSC curves of polyamides with diphenylmethane derivatives are shown in Fig. 4. In the first heating process of poly(TMDPM-ODDA), two endothermic peaks are observed and in the first cooling process only one exothermic peak is observed. In the polarizing microscope observation, the nematic schlieren texture was also observed between two endothermic peaks in the first heating and below the exothermic peak in the first cooling process. These textures are retained untill room temperature. In poly(DMDPM-ODDA) the similar liquid crystalline texture was observed only in the cooling process. In poly(DPM-ODDA) the liquid crystalline texture was not observed in both the heating and cooling processes.

The phase transition temperature of polyamides with a different type of mesogen in the first heating process and limiting viscosity are shown in Table 1. The values of limiting viscosity suggest the formation of polymers. In poly(TMDPM-ODDA) enantiotropic mesomorphism was observed. In poly(B-ODDA), poly(CB-ODDA), poly(DMB-ODDA) and poly(DMDPM-ODDA) monotropic mesomorphism

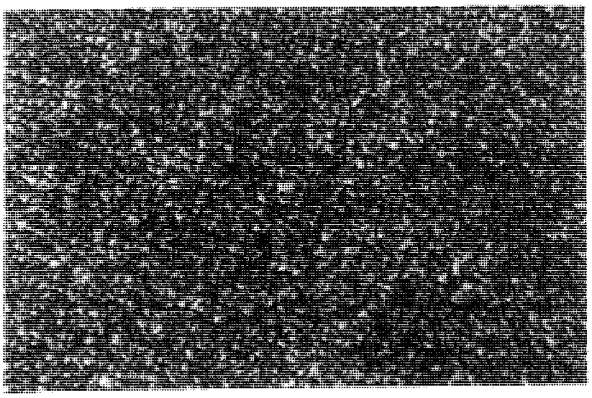

Fig. 3. Polarizing microscope photograph of poly(B-ODDA) at 489 K in the first cooling process.

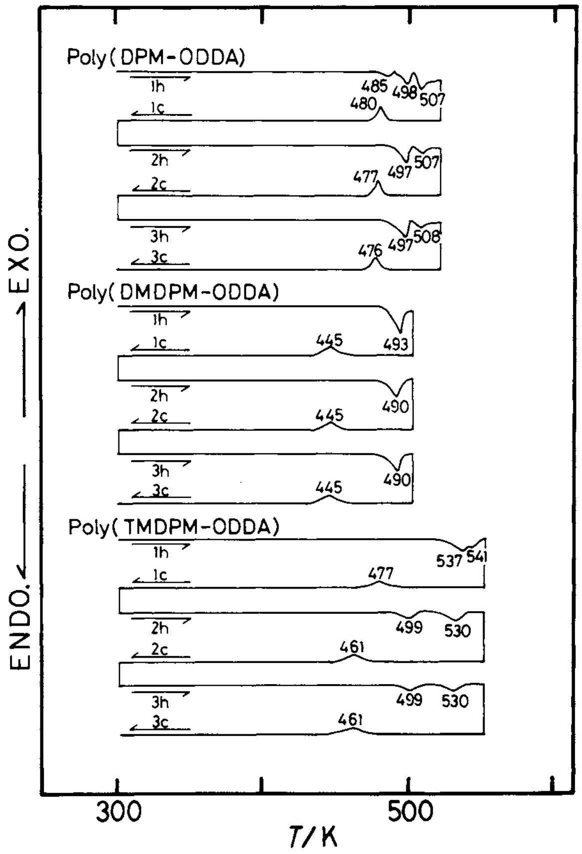

Fig. 4. DSC curves of polyamides of ODDA and 4,4'-diaminodiphenylmethane derivatives.

Table 1. Phase Transition Temperature and Limiting Viscosity of Polyamides

Polyamides	K_1[a)]		K_2[a)]		K_3[a)]		N[b)]		I[c)]	$[\eta]$[d)]/dl g^{-1}
Poly(B-ODDA)	•	509	•	528	•	541	•	[506]	•	0.35
Poly(CB-ODDA)	-		•	470	•	479	•	[456]	•	0.19
Poly(DCB-ODDA)	-		-		•	474	-		•	0.08
Poly(DMB-ODDA)	-		-		•	530	•	[510]	•	0.22
Poly(DPM-ODDA)	•	485	•	498	•	507	-		•	0.12
Poly(DMDPM-ODDA)	-		-		•	493	•	[445]	•	0.32
Poly(TMDPM-ODDA)	-		-		•	537	•	541	•	0.18

a) K_i: crystal i (i=1-3). b) N: nematic. c) I: isotropic liquid.
d) $[\eta]$: limiting viscosity.

was observed. In poly(DCB-ODDA) and poly(DPM-ODDA) no mesomorphic state was found. In the polyamides of p-phenylene derivatives, comparing the molar volume of Cl and CH_3 group, the former is a little larger than the latter, but the mesogenicity of the former is smaller. The reason is explained by an interpretation that high polarity of the lateral chlorine atom prevents formation of liquid crystals. In poly(B-ODDA), the length of the rigid core of the mesogen seems to be rather short, because it has only one phenyl ring in the mesogen. It is, therefore, interesting that such a poly(B-ODDA) forms monotropic liquid crystals. The interchain hydrogen bonding between the amide linkages in the polyamide will play an important role in the formation of the liquid crystalline state. In the polyamides of diphenylmethane derivatives, the mesogenicity increases with the increase of bulkiness of ortho substituent of 4,4'-diphenylmethane, although usually the increase of lateral width of the mesogen prevents the formation of liquid crystalline state. This may be interpreted that effect on the mesogenicity of the weakning of the interchain hydrogen bonding is superior to that of the increase of the lateral width. The results of IR spectra of polyamides will be described elsewhere to account for the relation between hydrogen bonding and liquid crystalline state.

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