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Phase transition in polyamides

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SUMMARY

A series of poly(3,3',5,5'-tetraethyldiphenylmethane-1,m-alkanedicarboxamide(poly(TEDPM-ADA(m=8-18))) were synthesized from 1,m-alkanedicarboxylic acids(ADA(m=8-18)) and 4,4'-diamino-3,3',5,5'-tetraethyldiphenylmethane by use of direct polycondensation in the presence of triphenylphosphite. The enantiotropic nematic liquid crystals were observed in the m=12-18 and monotropic liquid crystals were observed in the m=8-11 in poly(TEDPM-ADA). Mesogenicity of the polyamides increases with an increase in the number of methylene spacers, m.

INTRODUCTION

Many thermotropic polymers containing segments of rigid-rods in the main chain have been studied. Most of them are polyesters.

Amide linkage seems an excellent candidate for the construction of durable liquid crystalline polymers because they have high thermal stability and molecular rigidness. Although aromatic polyamides are known to form lyotropic liquid crystals(1), there have been only a few reports on thermotropic liquid crystalline polyamides(2). The most offending characteristic of aromatic polyamides is their high melting points, which is due to the increase of interchain hydrogen bonding(3), and their high melting point prevents the appearance of mesomorphic phase.

For the reduction of the above mentioned problem we attempted the introduction of a long alkyl chain between amide linkages and that of the ethyl groups in the ortho position of phenyl ring adjacent to the amide linkage. From this we synthesized a series of new poly(3,3',5,5'-tetraethyldiphenylmethane-1, m-alkanedicarboxamides) (poly(TEDPM-ADA(m=8-18))) with aromatic diamine and aliphatic dicarboxylic acids by a condensation polymerization .(4) Their phase transitions and mesogenicity are studied by DSC and polarizing microscope observation.

EXPERIMENTAL

Synthesis

Poly(TEDPM-ADA(m=8-18)) was synthesized by direct polycondensation from 4,4'-diamino-3,3',5,5'-tetraethyldiphenylmethane(TEDPM) and 1,m-alkanedicarboxylic acids with different length methylene spacers(ADA(m=8-18)) in N-methylpyrrolidone/pyridine solution(4:1) in the presence of triphenylphosphite at 373 K for 3 h.(4) TEDPM (supplied from Nippon Kayaku Co., Ltd.) was recrystallized from methylethylketone and ADA(m=8-18) (supplied from The Nisshin Oil Mills, Ltd.) was from methanol before use. The synthetic route is shown in Fig. 1. The obtained polymers were washed

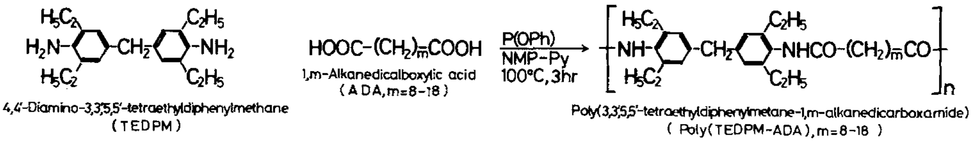

Figure 1. Synthetic route of polyamides(poly(TEDPM-ADA(m=8-18)).

by methanol. Identification was done by IR spectrum using an IR spectrophotometer, JASCO A 302. The limiting viscosity of the polymer was measured in sulfuric acids by use of an Ubbelohde's viscometer at 303 K.

Measurements of Physical Properties

Thermal properties of the polyamides were measured by use of a Perkin Elmer DSC 1B with a heating/cooling rate of 10 K min^{-1} from room temperature to over the melting point. The texture of the mesomorphic state was observed by use of a polarizing microscope, a Nikon Optiphot-pol XTP-11 equipped with a Mettler FP-82 hot stage with a heating/cooling rate of 10 K min^{-1} under crossed polarizers.

RESULTS AND DISCUSSION

Characterization

In the IR spectra, C=O and N-H streching was shown around 1650 and 3260 cm^{-1}. This result suggests the preesence of amide linkage. The relatively large limiting viscosity of polyamides indicates the formation of polymers as shown in Table 1.

DSC Measurements and Polarizing Microscope Observation

The DSC curves of poly(TEDPM-ADA(m=8-18)) are shown in Fig. 2 and the thermodynamic parameters are listed in Table 1. The m=13 was explained as being representative of the series of polyamides. In the first heating process, two endothermic peaks are observed and only one exothermic peak is found in the first cooling process. In the polarizing microscope observation a schlielen texture was observed between the two endothermic peaks in the first heating and below the temperature of exothermic peak in the first cooling. In Fig. 3, the polarizing microscope photograph of the m=13 at 492 K on

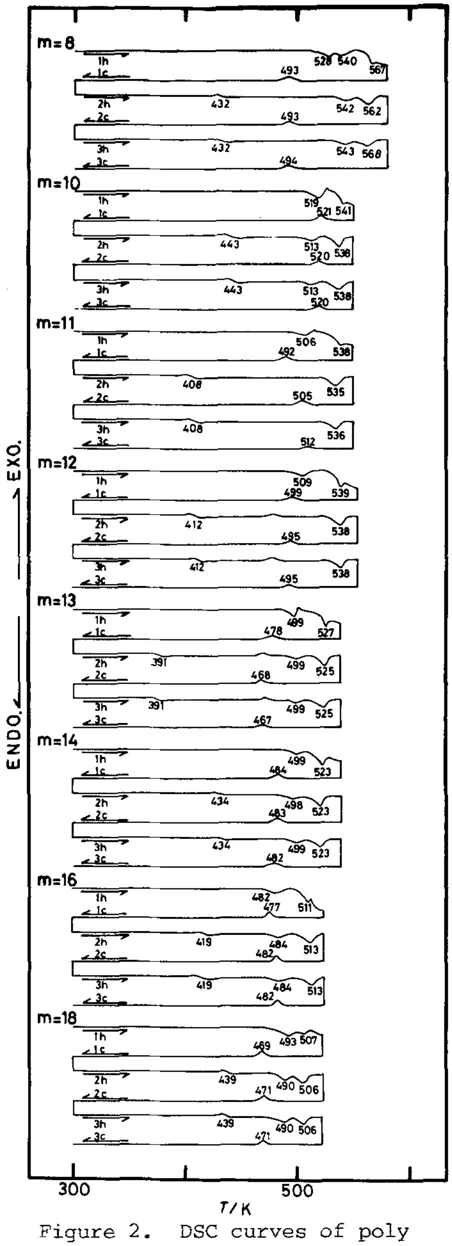

Figure 2. DSC curves of poly (TEDPM-ADA(m=8-18)).

Table 1. Physical Properties of Poly(TEDPM-ADA)

		1st heating												1st cooling			
	m	T_t / K	ΔH_t / Jg^{-1}	ΔS_t / $JK^{-1}g^{-1}$	T_t / K	ΔH_t / Jg^{-1}	ΔS_t / $JK^{-1}g^{-1}$	T_m / K	ΔH_m / Jg^{-1}	ΔS_m / $JK^{-1}g^{-1}$	T_{N-I} / K	ΔH_{N-I} / Jg^{-1}	ΔS_{N-I} / $JK^{-1}g^{-1}$	T_{I-N} / K	ΔH_{I-N} / Jg^{-1}	ΔS_{I-N} / $JK^{-1}g^{-1}$	[η] / dlg^{-1}
Poly(TEDPM-ADA)	8	528	3.3	0.006	540	6.6	0.012	567	9.9	0.018				493	5.5	0.013	0.09
	10				519	32.2	0.065	541	4.1	0.008				521	14.5	0.035	0.13
	11				506	14.8	0.041	538	4.6	0.009				492	18.1	0.043	0.15
	12							509	15.7	0.034	539	9.3	0.017	499	19.3	0.040	0.09
	13							499	20.2	0.050	527	9.0	0.018	478	10.8	0.023	0.18
	14							499	1.4	0.089	523	13.1	0.025	484	16.6	0.045	0.22
	16							482	18.9	0.041	511	3.8	0.009	477	20.8	0.050	0.09
	18							493	13.1	0.028	507	1.5	0.003	469	15.3	0.061	0.14

T_t: phase transition temperature, ΔH_t: phase transition enthalpy, ΔS_t: phase transition entropy, T_m: melting point, ΔH_m: phase transition enthalpy of melting, ΔS_m: phase transition entropy of melting, T_{N-I}: temperature of N-I phase transition, ΔH_{N-I}: enthalpy of N-I phase transition, ΔS_{N-I}: entropy of N-I phase transition, T_{I-N}: temperature of I-N phase transition, ΔH_{I-N}: enthalpy of I-N phase transition, ΔS_{I-N}: entropy of I-N phase transition

cooling from melting is shown. The nematic schlielen texture is exhibited in the figure. In the second heating process, a small exothermic peak with subsequent endothermic peak is found around 391 K and this is the characteristic of glass transition. In the first cooling, below this glass transition region, the schlielen texture was still observed especially at room temperature and the m=13 became glassy nematic state. In the second heating at the higher temperature of glass transition, one exothermic peak, which corresponds to crystallization is observed at 472 K. Above this temperature two endothermic peaks are observed. They correspond to crystalline-mesomorphic phase transition and to mesomorphic-isotropic one. In the second cooling process the peaks observed are almost the same as those of the first cooling process. Similar curves as those of the second processes are obtained in third thermal processes. In the m=12-18, thermal behavior almost similar to the m=13 was observed although the crystallization was not clerarly observed. As shown in Fig. 2, in the polyamides of the m=8-11, similar thermal behavior as the m=12-18 was observed, but the mesomorphic state was not observed in the first heating process. In the polarizing microscope observation similar schlieren texture to the m=13 was shown in all the series of polyamides. The schlielen texture was also remained until room temperature in all polyamides in the cooling processes.

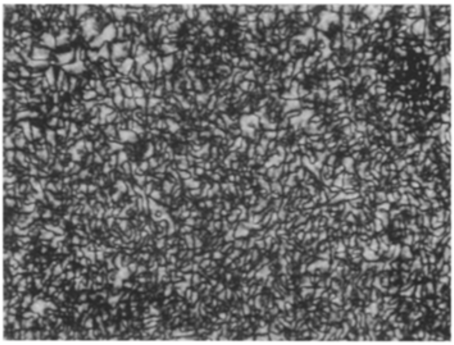

Figure 3. Polarizing microscope photograph of m=13 in poly(TEDPM-ADA) at 492 K.

The phase transition temperature of poly(TEDPM-ADA(m=8-18)) versus the number of methylene spacers, m, is plotted in Fig. 4 in the first heating/cooling processes. The transition temperature from nematic to isotropic liquid state, T_{N-I}, lowers with an increase in the length of the alkyl chain and odd-even effects are observed. In Fig. 5, a phase diagram of the second heating/cooling processes of the polyamides is shown. The synbols except glass transition temperature, T_g, are the same as in Fig. 4. The second heating process is a little bit different from the first heating proces. The gass transition temperature is observed around 420 K. Above this temperature region, the main chain may be able to move freely and the polyamides change from nematic glass into nematic liquid crystals. In the m=8-10 and 13-18, at higher temperature region the crystallization from nematic to crystals occurs partially and they melt to liquid crystals at the similar temperature as the first heating process. In the m=11 and 12, no crystallization occurs and only nematic-isotropic phase transition is found around 540 K.

Liquid Crystalline State of Poly (TEDPM-ADA(m=8-18))

Consequently, enantiotropic nematic liquid crystal was observed in poly(TEPDM-ADA(m=12-18)) and monotropic nematic liquid crystal was obsereved in poly(TEDPM-ADA(m=8-11)). The longer alkyl spacer increases mesogenicity of the polyamides. This suggests that mesogen in the main chain takes the liquid crystalline arrangements more easily in relatively longer alkyl environments. The T_{N-I} decreases with an increase in the alkyl chain length. Usually, the ortho substitution of the benzene ring by alkyl group is considered to lower the stability of the liquid crystalline state because of the increase of lateral width of the mesogen. But in polyamides with no alkyl chain in the ortho position of the benzene ring adjacent to the amide linkage, the mesogenicity is decreased than poly(TEDPM-ADA).(5) The reason is the effect on the mesogenicity of the weakning of hydrogen bonding is superior to that of the increase of the lateral width.

Lastly, we will consider the molecular shape of diphenyl methane. The two benzene rings of the diphenylmethane are bent almost at tetrahedron angles in the carbon atom in between the two benzene rings because the carbon atom has sp^3 hybrid

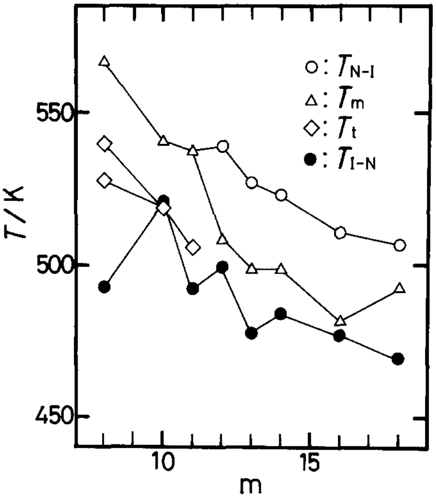

Figure 4. Plots of transition temperature versus m for poly(TEDPM-ADA(m=8-18)) in the first heating/ cooling processes. ○:temperature of N-I transition, T_{N-I}; △:melting point, T_m; ◇:transition temperature, T_t; ●:temperature of I-N transition, T_{I-N}.

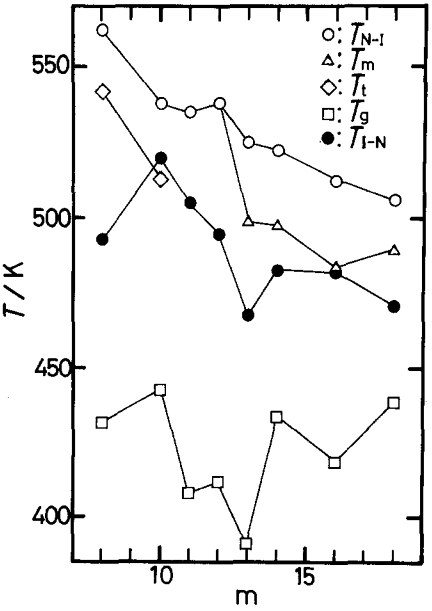

Figure 5. Plots of transition temperature versus m for poly(TEDPM-ADA(m=8-18)) in the first heating/ cooling processes. □:glass transition temperature, T_g.

and the two rings deform from lineality. This deformation may weaken the liquid crystallinity of the polyamides. The presence of liquid crystals in such series of polyamides seems to be interesting. The relationship between molecular shape and mesogenicity was solved by studying the liquid crystallinity of different polyamides with different rigid core of mesogen. The relation will be described elsewhere.

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