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THERMAL PROPERTIES OF NEMATIC MAIN-CHAIN POLYESTERS WITH AZOXYBENZENE MESOGEN

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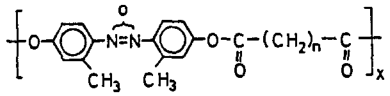
SUMMARY

The thermal properties of thermotropic polyesters with azoxybenzene mesogen were studied by using a differential scanning calorimeter and a high-pressure micro-DTA apparatus. Nematic glass transition, cold crystallization, crystal-nematic transition, and nematic-isotropic transition were measured as a function of pressure.

INTRODUCTION

Thermotropic liquid crystalline polymers with various mesophases have been intensively studied from both the theoretical and practical points of view. The study of thermal properties of thermotropic polymers gives a clear picture of structure-property correlation in liquid crystalline polymers. Blumstein et al(refs. 1-4) described the synthesis and thermal properties of main-chain nematic polyesters of regularly alternating 2,2'-dimethylazoxybenzene mesogen (mesogen 9) and alkanedioic acid ester as a flexible spacer. The general formula for the polyesters is given as follows.



On heating from the solid at low temperature, the polyesters can transit through a nematic mesophase before isotropization. It is known that a remarkable odd-even effect occurs regularly in persistent oscillation of the temperature and entropy of the nematic-isotropic transition for the materials. The object of this study is to investigate the thermal behaviors of nematic glass transition, cold crystallization, crystal(K) - nematic(N), and N - isotropic(I) transitions of the thermotropic polyesters under atmospheric and elevated pressures.

EXPERIMENTAL

The synthesis of the polymers is described elsewhere(ref.2). Two polyesters with different spacers of odd and even methylene groups were studied: one is

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based on dodecanedioic acid (DDA, n=10) and the other is based on nonanedioic (azelaic) acid (AZA, n=7). The unfractionated samples of the DDA-9 and AZA-9 polyesters used in this study have number-average molecular weight $\bar{M}n$ of 20,000 and 36,000, respectively. A low molecular weight sample of DDA-9 ($\bar{M}n$=4,000) was also studied.

Thermal analysis at atmospheric pressure was performed with a Perkin-Elmer DSC-II calorimeter. Glass transition T_g was determined as the temperature at which the heat capacity achieved one half of the entire change observed, ΔC_p. Other temperatures of cold crystallization, K - N, and N - I transitions were taken at the respective exothermic or endothermic peaks. The corresponding heats of transition were also determined. Temperature and heat of transition were calibrated with indium.

The high-pressure micro-DTA apparatus used in this study is designed to be operated in the temperature region from -40 °C to 400 °C under hydrostatic pressures up to 700 MPa (ref.5). The block diagram of the system is schematically illustrated in Fig. 1. A hand oil pump assembled with an intensifier is used to generate hydrostatic pressure in dimethylsilicone oil with low viscosity (10 cs). Pressure is fed to the container for manganin coil gauge, a compensating heater vessel, and a DTA vessel. DTA and heater assemblies are held inside the DTA vessel. Pressure is detected by a manganin coil gauge, in which each resistence is about 120 ohm. Pressure is displayed directly on a digital manometer with an accuracy of ±5 kg/cm^2. A compensating heater functions to hold the predetermined pressure during cooling and heating runs. Power output to the compensating heater is controlled proportional to the deviation from the predetermined value on a microvoltmeter. The zero-balancing function is performed automatically or manually by changing temperature in the compensating heater vessel. The DTA system uses a programmable temperature controller and a DTA circuit (PTC-10 and DTA 6, Rigaku Corp).

Data of T, ΔT, and P are recorded on a 3-pen recorder

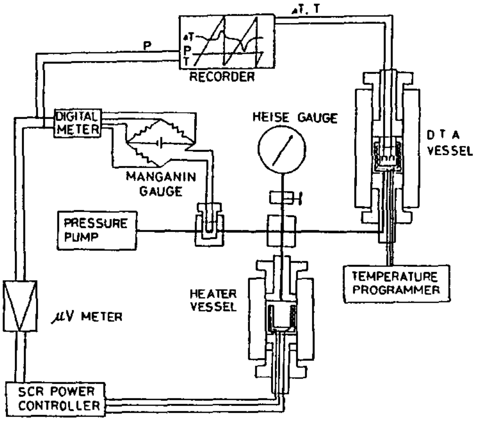

Fig. 1. Block diagram of a high-pressure micro-DTA apparatus.

and simultaneously stored in floppy disk of a data processor (PC-9801 RX2, NEC Corp.) to estimate transition temperature and heat of transition.

RESULTS and DISCUSSION

DSC measurements

Fig. 2 shows the typical DSC curves of two DDA-9 samples and a AZA-9 sample at 20 K/min. The thermal behaviors are considerably influenced by molecular weight(MW) in DDA-9 and by the well known odd-even effect. The DSC curves of the AZA-9(n=7) show T_g at 292 K and N - I transition at 419 K, besides a negligible transition at about 355 K. This indicates a transition of N-glass - N - I, which occurs normaly, independent of cooling rates. AZA-9 crystals are mainly grown by annealing at ambient temperatures for several days.

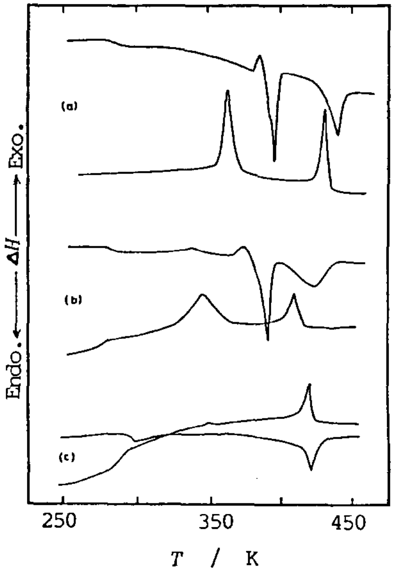

Fig. 2. DSC curves of thermotropic polyesters at 20 K/min: (a) DDA-9 ($\bar{M}n$=20,000), (b) DDA-9 ($\bar{M}n$=4,000), and (c) AZA-9 ($\bar{M}n$= 36,000).

Fig. 3 shows the effect of annealing of the nematic glass on the subsequent K - N transition of the AZA-9 sample. Annealing was performed isothermally at 70 ℃ in the DSC sample holder. The negligibly small peak of the K - N transition grows remarkably to multiple sharp peaks with increasing annealing time. The total enthalpy approaches to an equilibrium value of 7~8 kJ/mol, comparable to values of the DDA-9. The crystal formation of AZA-9 was ascertained by X-ray diffraction.

On the other hand, DDA-9 shows clearly an enantiotropic phase transition of K - N - I. The heating curves show the transitions of N-glass transition, cold crystallization, another exothermic peak,

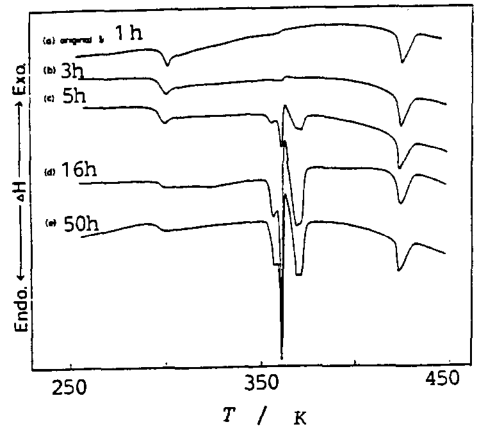

Fig. 3. Effect of annealing at 70°C of a nematic glass of AZA-9 on the growth and melting of the crystal.

K - N peak of melting, and N - I transition, typical of liquid crystalline polyesters.

Fig. 4 shows the scanning rate dependency of the thermal behaviors of the DDA-9 ($\bar{M}n$=4,000) sample. Crystallization from the N phase is greatly depressed with increasing cooling rate and it is entirely frozen into a glassy nematic phase at rates more than 80 K/min. The heating curves show Tg at about 291 K, and a large exothermic peak of cold crystallization at 340 K. Another exothermic peak appears at about 370 K, just below the K - N transition, as reported by Blumstein et al. It may be an exothermic peak of recrystallization to more stable crystals.

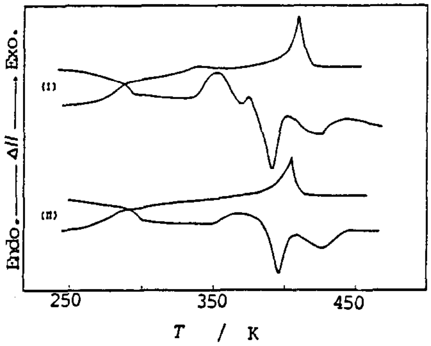

Fig. 4. DSC curves of the DDA-9 sample ($\bar{M}n$=4,000). Scanning rates: (I) 40 K/min and (II) 80 K/min.

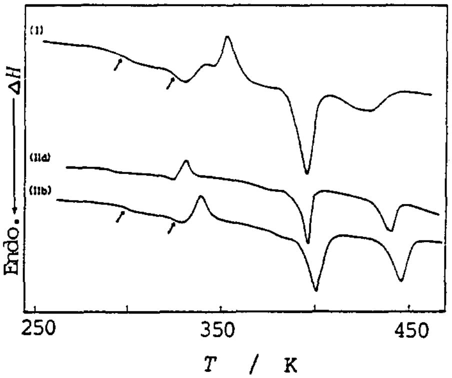

Fig. 5. DSC heating curves of the quenched samples aged at room temperature for overnight: (I) DDA-9 ($\bar{M}n$=4,000), 80 K/min, (IIa) and (IIb) DDA-9 ($\bar{M}n$=20,000), 20 and 80 K/min, respectively.

The effect of annealing or aging on both the quenched DDA-9 samples was studied. The DDA-9 samples were left for overnight after quenching the sample at about 200 K. The quenched samples are annealed spontaneously at room temperature for overnight. Fig. 5 shows the heating curves of these samples. In the low and high MW samples, glass transition occurs in two stages. New Tg can be observed at about 25~30 ℃ higher than the usual Tg. Cold crystallization is also observed as double peaks or an exothermic peak followed by ambiguous change in baseline toward higher temperature. These thermal behaviors suggest the two kinds of N-glass : one is a usual N-glass formed rapidly and the other may be a more stabilized glass relaxed by annealing of the former glass. The results are summarized in TABLEs 1 and 2. It is noted that the ΔH_{NI} values of the AZA-9 are between 1/3 and 1/4 of the values of the DDA-9.

TABLE 1

Transition temperatures of the thermotropic polyesters.

Sample	Heating rate	T / K				
	K/min	T_g	T_{cc}		T_{KN}	T_{NI}
DDA-9($\bar{M}n$=4,000)						
	20	283	334	368	388	422
	40	287	348	371	389	422
	80	292	362		391	423
Sample quenched followed by aging at room temp. for overnight						
	80	293 / 320	337 / 348		391	432
DDA-9 ($\bar{M}n$=20,000)						
	20	Yes	318	376	393	436
	40	283	320	376	394	438
	80	291	349		397	443
Sample quenched followed by aging at room temp. for overnight						
	20	286 / 317	327	378	392	436
	80	293 / 318	335	383	396	442
AZA-9 ($\bar{M}n$=36,000)						
	20	292			(355)	419
	80	297			(358)	422
Samples annealed at 70 °C for 50 h						
	20	291			357, 367	419

TABLE 2

Heats of transition of the thermotropic polyesters.

Sample	Heating rate	ΔH / kJ mol^{-1}			
	K/min	ΔH_{cc}		ΔH_{KN}	ΔH_{NI}
DDA-9 ($\bar{M}n$=4,000)					
	20	4.4		9.4	5.9
	40	7.0		9.5	5.8
	80		1.9	6.4	4.0
Samples quenched followed by aging at room temp. for overnight					
	80	3.5 - 4.2		9.2	4.2
DDA-9 ($\bar{M}n$=20,000)					
	20			10.4	7.4
	40			10.2	7.2
	80		1.1	7.5	8.1
Sample quenched followed by aging at room temp. for overnight					
	20	2.6	2.2	9.3	6.4
	80	2.7	2.4	10.0	6.5
AZA-9 ($\bar{M}n$=36,000)					
	20			Negligible	1.8
	80			Negligible	1.9
Sample annealed at 70 °C for 50 h					
	20			4.7 / 3.2	1.7

Thermal Behaviors under Pressures

DTA measurements under hydrostatic pressures were performed at a heating rate of 10 K/min. Fig. 6 shows the high-pressure DTA curves of the DDA-9 ($\bar{M}n$=4,000) sample cooled at 10 K/min under elevated pressures. The heating curves show clearly the same pattern as those observed in the DSC curves: glass transition, cold crystallization, an exothermic peak, K - N, and N - I transitions, etc. These thermal behaviors give a clear relation between transition temperature and pressure. Fig. 7 illustrates the T vs. P curves of N-glass transition, K - N, and N - I transitions of the sample. It can be seen that the temperature region between K - N and N - I transitions is almost constant in the low MW sample of DDA-9. The DTA measurements were done in the same way for the highly crystalline samples of DDA-9 ($\bar{M}n$=20,000) annealed at 100 °C for 2 h, an amorphous AZA-9 sample, a crystalline AZA-9 sample annealed at 70 °C for 20 h. The DTA curves of the annealed DDA-9 show the double endothermic peaks of K - N transition under pressures up to 500 MPa. But the N - I transition could be observed only at pressures up to 200 MPa because the sample decomposes at high temperatures in the nematic phase. Fig. 8 shows the *T* vs. P phase diagram of the highly crystalline sample of DDA-9.

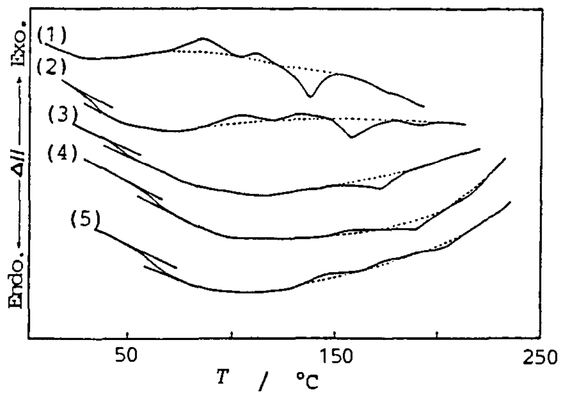

Fig. 6. DTA heating curves of the DDA-9 ($\bar{M}n$ = 4,000) polyester cooled under pressures. DTA runs show the 2nd heating at each pressure: (1) 100 MPa, (2) 200 MPa, (3) 300 MPa, (4) 400 MPa, and (5) 500 MPa.

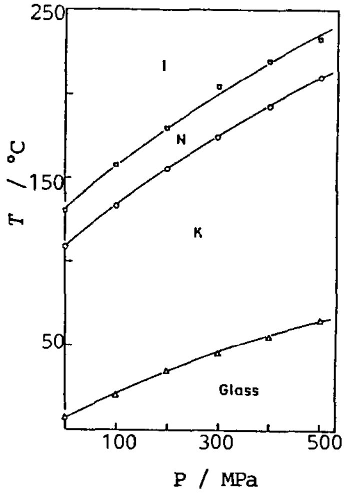

Fig. 7. *T* vs. P curve of the DDA-9 ($\bar{M}n$ = 4,000) polyester.

The temperature region of the N phase on the high MW DDA-9 becomes broad with increasing pressure like other liquid crystals.

This can be shown quantitatively by calculating each transition line, i.e., glass transition, K - N and N - I transitions for both the samples. A least-square fit to the data points was tried with 2nd-order polynomials in pressure. The equation , $T = a + b P + c P^2$, were estimated with the standard deviation less than 1.0 °C.

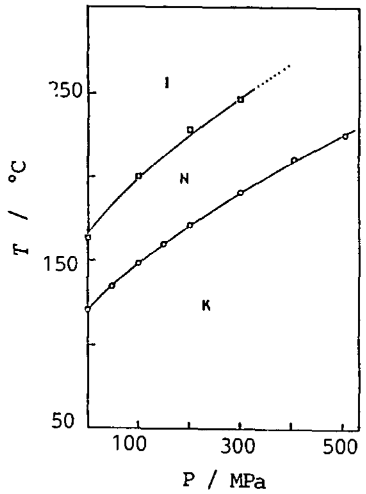

Fig. 8. T vs. P curve of the DDA-9($\bar{M}n \approx 20{,}000$) polyester.

DDA-9

N - I transition

High MW : $T = 163.5 + 0.397P - 0.000344P^2$

Low MW : $T = 130.6 + 0.304P - 0.000198P^2$

K - N transition

High MW : $T = 121.2 + 0.288P - 0.000162P^2$

Low MW : $T = 109.6 + 0.246P - 0.000092P^2$

Glass transition

High MW :

Low MW : $T_g = 8.0 + 0.136P - 0.000045P^2$

The T vs. P phase diagram of the AZA-9 sample is shown in Fig. 9. Glass transition and N - I transition are observed clearly under pressures up to 500 MPa. The multiple peaks of K - N transition were observed for the crystalline sample annealed at 70 °C for 20 h.

The highest melting point of K - N transition is shown as a dotted curve in Fig. 9. The 2nd-order polynomials were obtained as follows.

AZA-9

N - I transition

$T = 145.8 + 0.353P - 0.000238P^2$

K - N transition

$T = 95.0 + 0.280P - 0.000146P^2$

Glass transition

$T_g = 20.6 + 0.331P - 0.000222P^2$

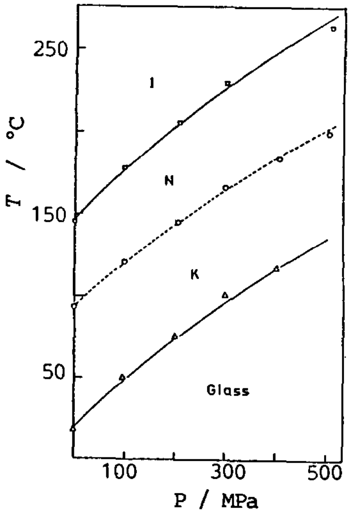

Fig. 9. T vs. P curve of the AZA-9 ($\bar{M}n \approx 36{,}000$) polyester.

TABLE 3

Thermodynamic data for the K - N and N - I transitions of DDA-9 and AZA-9 polyesters.

Sample	K - N transition				N - I transition			
	T K	$(dT/dP)_{p=0}$ K/MPa	ΔS J/K mol	ΔV cm^3/mol	T K	$(dT/dP)_{p=0}$ K/MPa	ΔS J/K mol	ΔV cm^3/mol
DDA-9 ($\bar{M}n$=20,000)	393	0.288	26.5	7.6	437	0.397	16.5	6.5
DDA-9 ($\bar{M}n$=4,000)	389	0.246	24.2	6.0	420	0.304	14.0	4.2
AZA-9 (amorphous)	355	—	Negligible	—	418	0.344	4.3	1.5
AZA-9 (crystalline)	367	0.280	21.2	5.9	419	0.343	4.0	1.4

According to the Clausius-Clapeylon equation $dT/dP = T(\Delta V/\Delta H)$, ΔV is estimated for both the K - N and N - I transitions. TABLE 3 lists the experimental results of the initial pressure coefficient $(dT/dP)_{p=0}$, and the ΔS data for both the transitions. It is noted that the entropy ΔS and volume ΔV on the K - N transition are comparative values for the DDA-9 and AZA-9 crystals, while in the N - I transition the values in DDA-9 are roughly 3~4 times larger than the values in AZA-9. This fact reflects the odd-even effect of volume of transition as well as entropy ΔS in the nematic polyesters. This corresponds with the existence of the two distinct molecular arrangements in the nematic phase: highly ordered nematic structure in DDA-9 and an ordinary nematic structure in AZA-9.

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