FIRST-ORDER PHASE TRANSITIONS IN THERMOTROPIC LIQUID CRYSTALLINE POLYMERS-POLYESTERAMIDES

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Abstract

Thermotropic mesomorphic behaviour of two liquid crystalline polymers (polyesteramides) was studied using differential scanning calorimetry (DSC). The polymers were found to melt in stages, multiple first-order transitions, indicating the possibility of existing one or two mesomorphic phases. This has been observed clearly in one of the polymers as reproducible minor exotherms appeared above the uppermost major endotherm. The total heats of transitions and entropies were found to be in good agreement with group additivity calculations if one assumes a level of crystallinity in the range of 24 to 32 %.
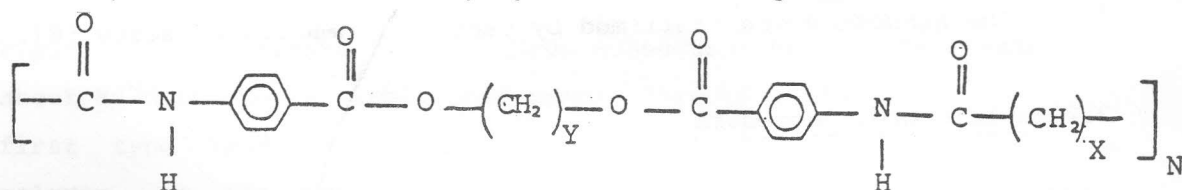
1. Introduction

Liquid crystalline (LC) materials are those which have the tendency above the melting temperature (T_m) of simultaneously combining the features of a liquid (i.e., flow properties) and a crystalline character (i.e., optical anisotropy) [1]. The liquid crystalline phase is often called the mesophase, and a substance having such a character a mesogen. Polymeric materials exhibit mesomorphic behaviour whose degree of molecular order either in solution (termed lyotropic), or in the melt (termed thermotropic) is intermediate between those of solid crystals (perfect long-range order), and those of isotropic liquids (statistical order) [2,3]. Polymeric liquid crystals (PLC) have opened a new and exciting channel in the technological use of polymers because of the thermal stability, chemical resistance, and high mechanical properties of commerically available materials. In addition to their technological potential in areas ranging from microelectronics to biotechnology, they are great substrates for new discoveries in the chemistry and physics of condensed matter [4].

There has been an increase in interest in liquid crystal polymers in recent years, especially after the development of high modulus fibers based on lyotropic aromatic polyamides: Kevlar and X-500, both of which have excellent mechanical properties [5]. Thermotropic liquid crystalline polymers are classified on the basis of their molecular layers arrangement [3,6 and 7]. In nematic liquid crystals, molecules are orientationally ordered along an average direction known as the "director" axis but their centers of mass lack positional order. In smectic phases, molecules are not only orientationally ordered but are also arranged in layers that produce a density wave [6]. Positional order within the layers of smectic phases varies and in some cases the

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gradually in space in a helical pattern [3,7]. Polymeric liquid
crystals (PLC) are catogerized in two major groups: one is specified
by its backbone, or main-chain, mesomorphicity and the other exihibits
liquid crystallinity due to the nature of its side groups.

Aharoni [8] has synthesized and made an initial characterization of a
new family of alternating polyesteramides which belong to the
main-chain polymeric liquid crystal group (MCPLC) but whose
mesomorphicity is dependent on intermolecular hydrogen-bonds directed
about normally to the main-chain direction. There are four common
experimental procedures used in the study of the phase transitions of
thermotropic liquid crystals and the nature of these phase [9]: (1)
differential scanning calorimetry (DSC) scans; (2) studies of textures
using cross-polarized light; (3) studies of the structures by means of
X-rays diffraction patterns; and (4) miscibility relations of liquid-
crystalline modifications in binary mixtures. The last technique is
not possible to be performed with the polyesteramides because there
exist no analogues monomeric or low molecular weight liquid crystals
to be used in the miscibility study [9,10].

In this paper, our attention is restricted to the thermotropic
mesomorphic behaviour of two polyesteramides of general structure:

$$\left[-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-\bigcirc-\overset{\overset{O}{\|}}{C}-O-\left(CH_2\right)_Y-O-\overset{\overset{O}{\|}}{C}-\bigcirc-\underset{\underset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-\left(CH_2\right)_X-\right]_N$$

where X and Y are the numbers of methylene groups between the amide
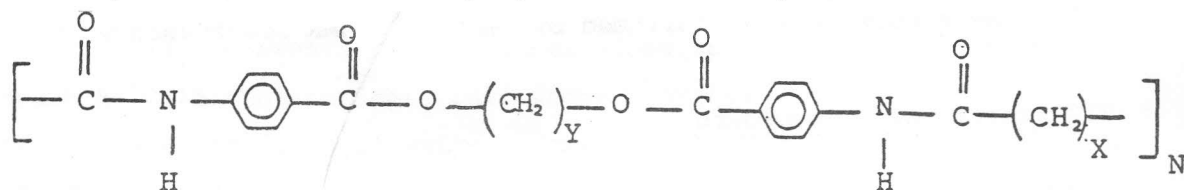
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molecules tilt relative to the layer's normal (tilted smectic C phase) Cholestric liquid crystals are normally formed by chiral molecules, and in these mesophases, the director of nematic layers rotates gradually in space in a helical pattern [3,7]. Polymeric liquid crystals (PLC) are catogerized in two major groups: one is specified by its backbone, or main-chain, mesomorphicity and the other exihibits liquid crystallinity due to the nature of its side groups.

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In this paper, our attention is restricted to the thermotropic mesomorphic behaviour of two polyesteramides of general structure:

$$\left[-\overset{\overset{O}{\|}}{C} - \overset{\underset{|}{H}}{N} - \bigcirc - \overset{\overset{O}{\|}}{C} - O - (CH_2)_Y - O - \overset{\overset{O}{\|}}{C} - \bigcirc - \overset{\underset{|}{H}}{N} - \overset{\overset{O}{\|}}{C} - (CH_2)_X - \right]_N$$

where X and Y are the numbers of methylene groups between the amide

residues and between the ester moieties respectively and N is the number of repeat units in the molecule. The two polyesteramides under investigation are: Y=3, X=8, and Y=3, X=12, with molecular weights per repeat unit of 480 and 536 respectively. As Aharoni [8] has pointed out, the unique structural features of this new family of PLC are their high regularity and strict alteration of two amide groups and two ester groups and the substitution of each aromatic ring in the para position by one amide and one ester group. Also the fact that these reactive groups are pairwise connected by alkylene chains, and all amide residues are intermolecularly interacted with each other by hydrogen bonds (H-bonds) between adjacent chains. In the present study, only the results of the caloric study will be given and discussed.

2. Experimental

2.1 Samples

Two batches of polyesteramides: the first has the trade name A1462-23C; Y=3, X=8, the other has the trade name A1702-40; Y=3, X=12, were supplied by the Allied-Signal Corporation, Engineered Materials, Morristown, N.J., U.S.A., to the Dept. of Materials Science and Metallurgy, Cambridge University, U.K. It was stated that the polymers were prepared from the acides and aromatic amines in the presence of triphenyl phosphite and pyridine according to the Yamazaki procedure [11]. The structure was confirmed by carbon-13 NMR spectroscopy [8].

2.2 Experimental Procedure

Thermal studies were conducted by using a DSC 7 Perkin-Elmer

Differential Scanning Calorimeter which is computer controlled with the 3700-Data Station [12]. The system belongs to Materials Science and Metallurgy Department, University of Cambridge. The theory of operation of the DSC 7 is based on the Perkin-Elmer power compensated "nullbalance" DSC principle in which energy absorbed or evolved by the sample is compensated by adding or substracting an equivalent amount of electrical energy to a heater located in the sample holder. The cell consists of independent dual furnaces constructed of platinum-iridium alloy with independent platinum heaters. The temperature sensors are distributed platinum resistance thermometers.

The sample sizes were in the range of 3-5 mg. The heating and cooling rates were 10 K/minute. The samples were always in a dry nitrogen atmosphere during the thermal scans. Six complete scanning cycles (heating, cooling, and reheating) were taken, for each polymer, using different samples of each type, with nearly similar weights. For each run the sample was heated at a rate of about 10 K/minute to the desired temperature and allowed to equilibrate for at least 10 minutes before the scan was started. Also experimental runs were taken for one sample (second type) which was subjected to isothermal annealing at 210°C for one and two hours. The system was calibrated using Tin and Zinc standard samples. Calorimetric precision is better than + 0.1 % and temperature accuracy is + 0.1°C.

3. Results and Discussion

Figure (1) represents typical three subsequent heating DSC scans from about 80°C to the isotropic melt temperature ($T_i \sim 250^\circ$C) of the first type (X=8, Y=3) polyesteramide(A1462-23C). As can be seen the polymer, on its way from the crystalline state to the isotropic
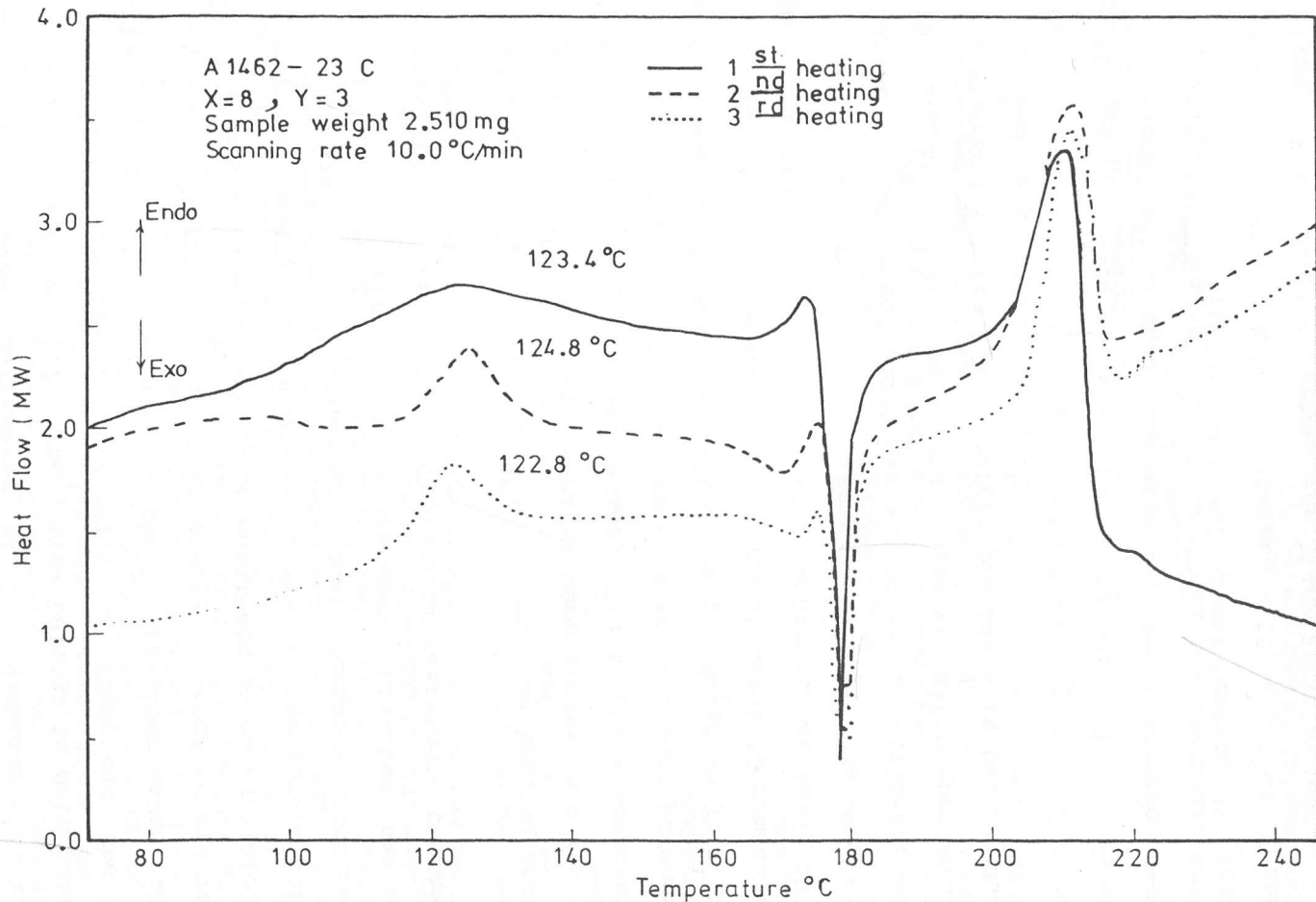
Fig (1) Heating cycles of DSC scans of polyesteramide X = 8 , Y= 3.

(clear) melt, is melting in stages; a case which was previously observed and discussed [13]. The first transition that occurs at about $123^{\circ}C$, observable as a small and shallow endotherm, corresponds to a softening transition T_s. It is reproducible in the three heating cycles within a maximum shift in the peak position of 2 C. A partial melting of one crystalline form (most probably smectic C_1 phase) can be seen at about $176^{\circ}C$. It is followed directly by a sharp exotherm with a peak temperature of $179^{\circ}C$ which might be a crystallization of a smectic C_2 mesophase [8]. The polymer stays for about $30^{\circ}C$ temperature range in this crystalline phase and then melts completely at about $T_m = 210^{\circ}C$. It was shown, from thermodynamic aspects, that the transition from a crystalline state to an ordered liquid phase is discontinuous, i.e, of first-order type [13].

Figure (2) shows a cooling DSC scan for the same sample. While cooling from the isotropic melt, there appears one major transition (exotherm at $192^{\circ}C$) which is substantially supercooled relative to the upermost major endotherm (at $210^{\circ}C$). In addition, a shallow exotherm is observed at about $136^{\circ}C$ which is superheated by $12^{\circ}C$ above the corresponding softening transition at T_s (during heating cycles). Its heat of transition (ΔH) accounts for $\sim$ 20 % of that of the major exotherm during cooling. The main feature of the above results is the presence of multiple reproducible first order transitions (endotherms) in the heating cycles of DSC scans. This may indicate the presence of thermotropic liquid crystallinity as defined by Noel [9] and verified very recently by Aharoni [8] and by Cheng et. al [14].

Figure (3) shows heating, cooling, and reheating cycles in DSC scans of the second type (X=12, Y=3). It can be noticed that these scans are similar to those of first type (X=8, Y=3). There appears clearly two
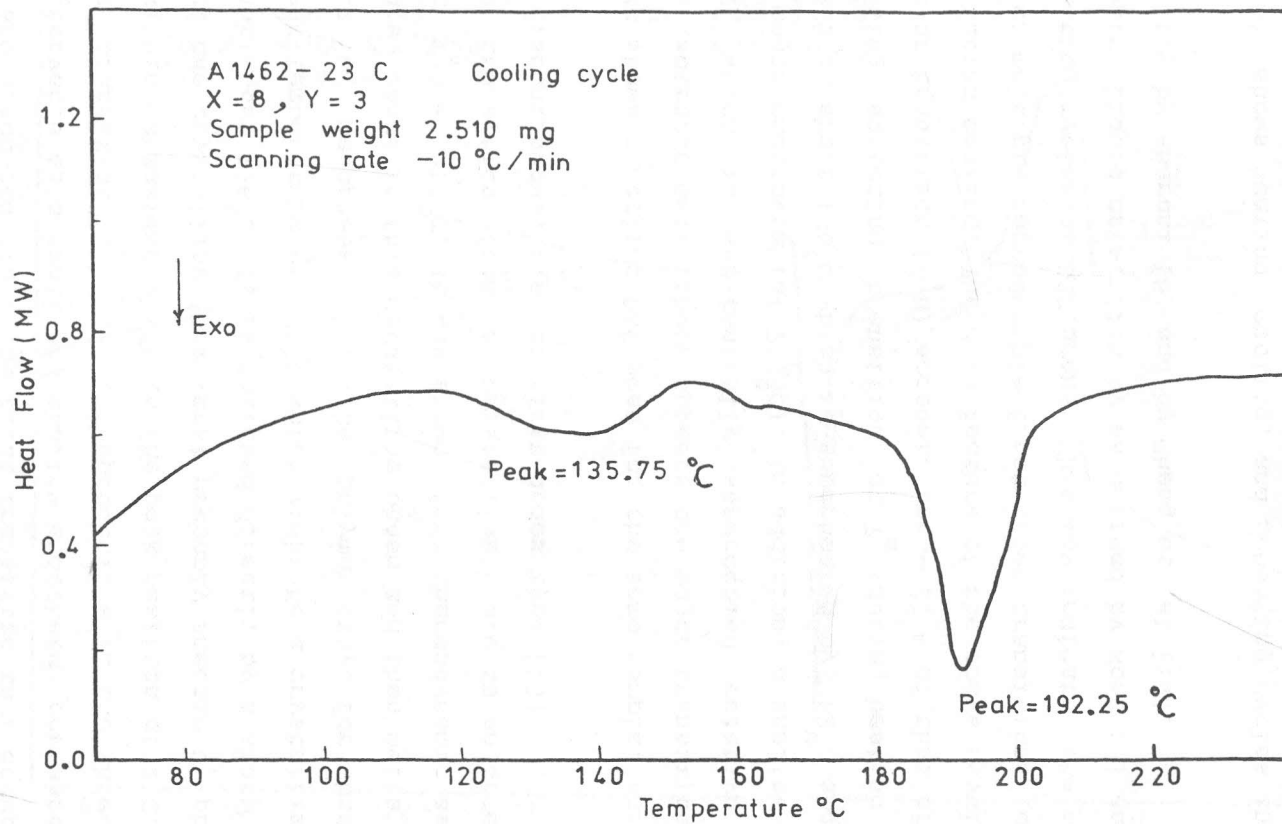
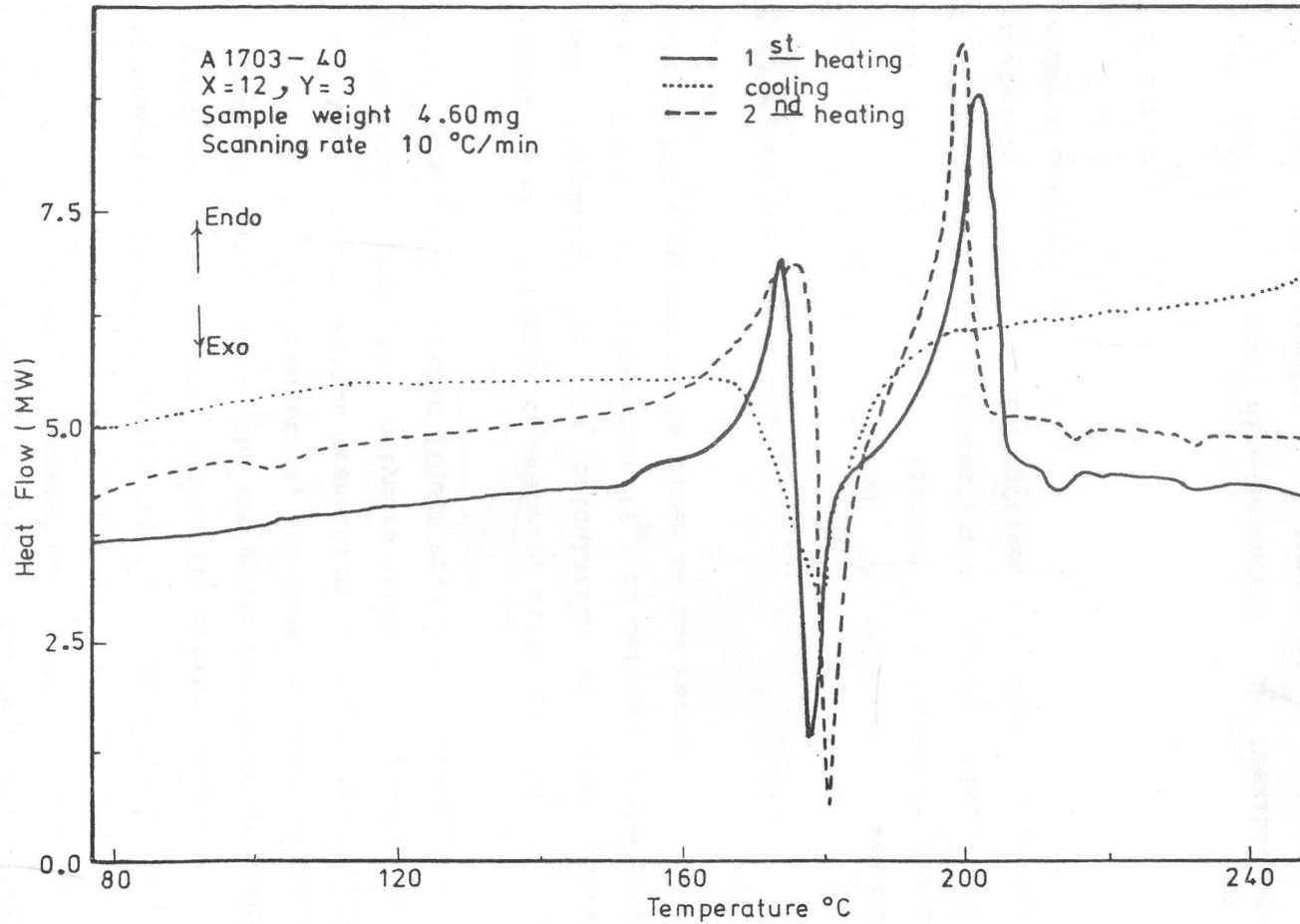Fig.(2) Cooling cycle of DSC scan of polyesteramide X = 8 , Y = 3.

Fig.(3) Heating , cooling , reheating DSC cycles for polyesteramide X = 12 , Y = 3.

minor and nearly reproducible transitions (exotherms) between T_m ($\sim 202^0C$) and the clearing temperature $T_i \sim (200^0C)$. The natural sequence of mesomorphic phases suggests that these minor transitions are of nematic type [13]. In Fig. (4) is given a magnified portion of two subsequent heating DSC scans for another sample of the second type. There appears again the two minor exotherms at about 215 and 233^0C with a heat of transition, for each, or approximately 7% of that of the crystallization transition (exotherm at $\sim 180^0C$). This may prove again that the polymers under study exhibity multiple mesophases, i.e., thermotropic liquid crystalline states.

The latent heat of fusion or enthalpy difference ΔH_m (T_m) is an important quantity for the calculation of other thermodynamic functions. The melting temperature (T_m) is defined by the peak of an endotherm in DSC scan and can be given as the ratio:

$$T_m = \Delta H_m / \Delta S_m ,\tag{1}$$

where ΔS_m is the entropy of melting. This relationship was found to be valid for other first order transitions observed in low molecular weight crystals [15] and in thermotropic liquid crystals [16]. It was demonstrated by Van Krevelen and Hoftyzer [17] that, in general, for a first-order transition j:

$$\Delta S_j = \Delta H_j / T_j ,\tag{2}$$

with ΔS_j and ΔH_j being size-dependent for flexible chain polymers. Since the formation of two or more solid phases is very common in meso-phase forming materials, it is necessary to use the total entropy:
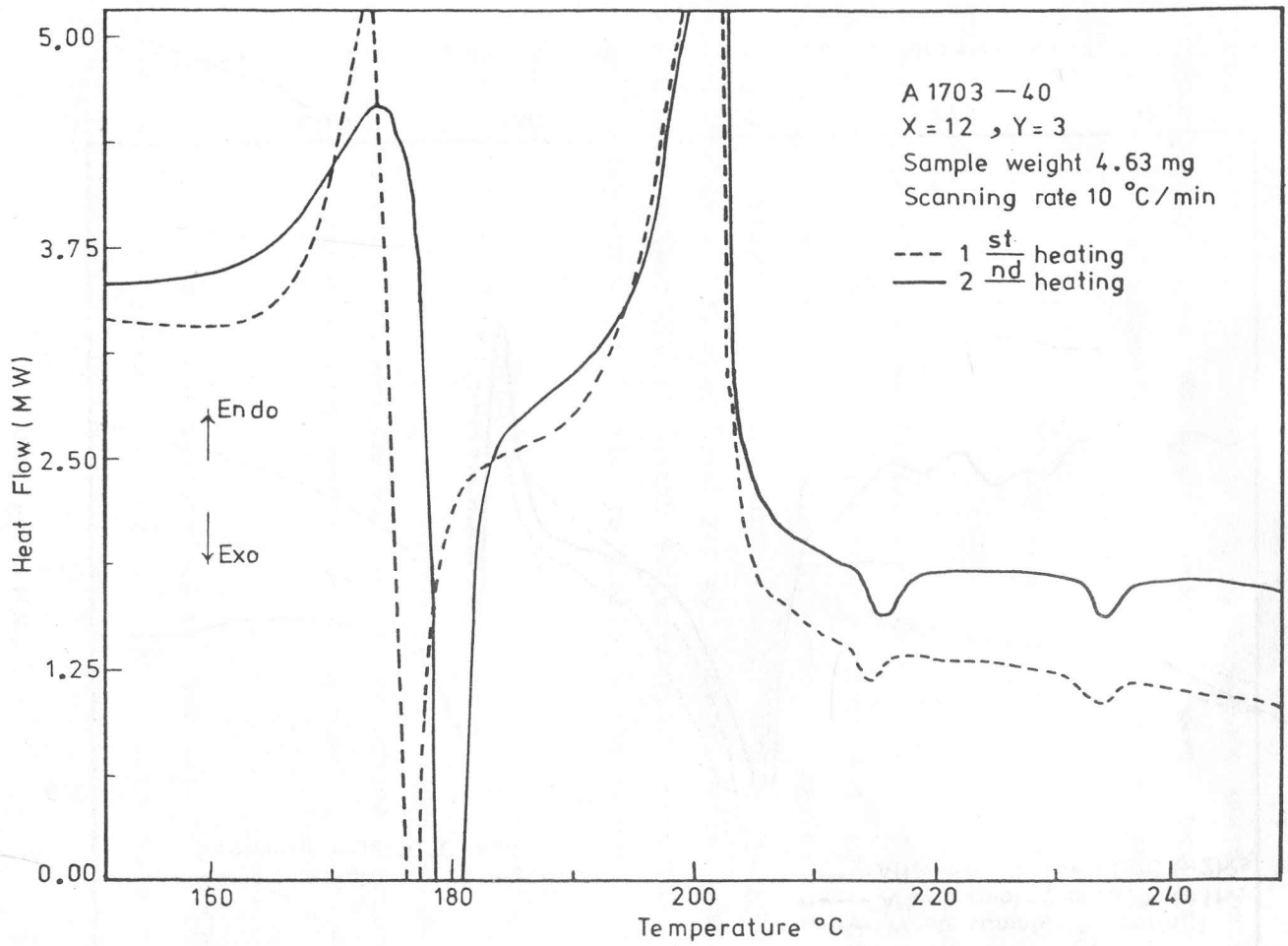
A 1703 — 40
X = 12 , Y = 3
Sample weight 4.63 mg
Scanning rate 10 °C / min

- - - 1 $\frac{st}{}$ heating
——— 2 $\frac{nd}{}$ heating

↑Endo

↓Exo

Heat Flow (M W)

Temperature °C

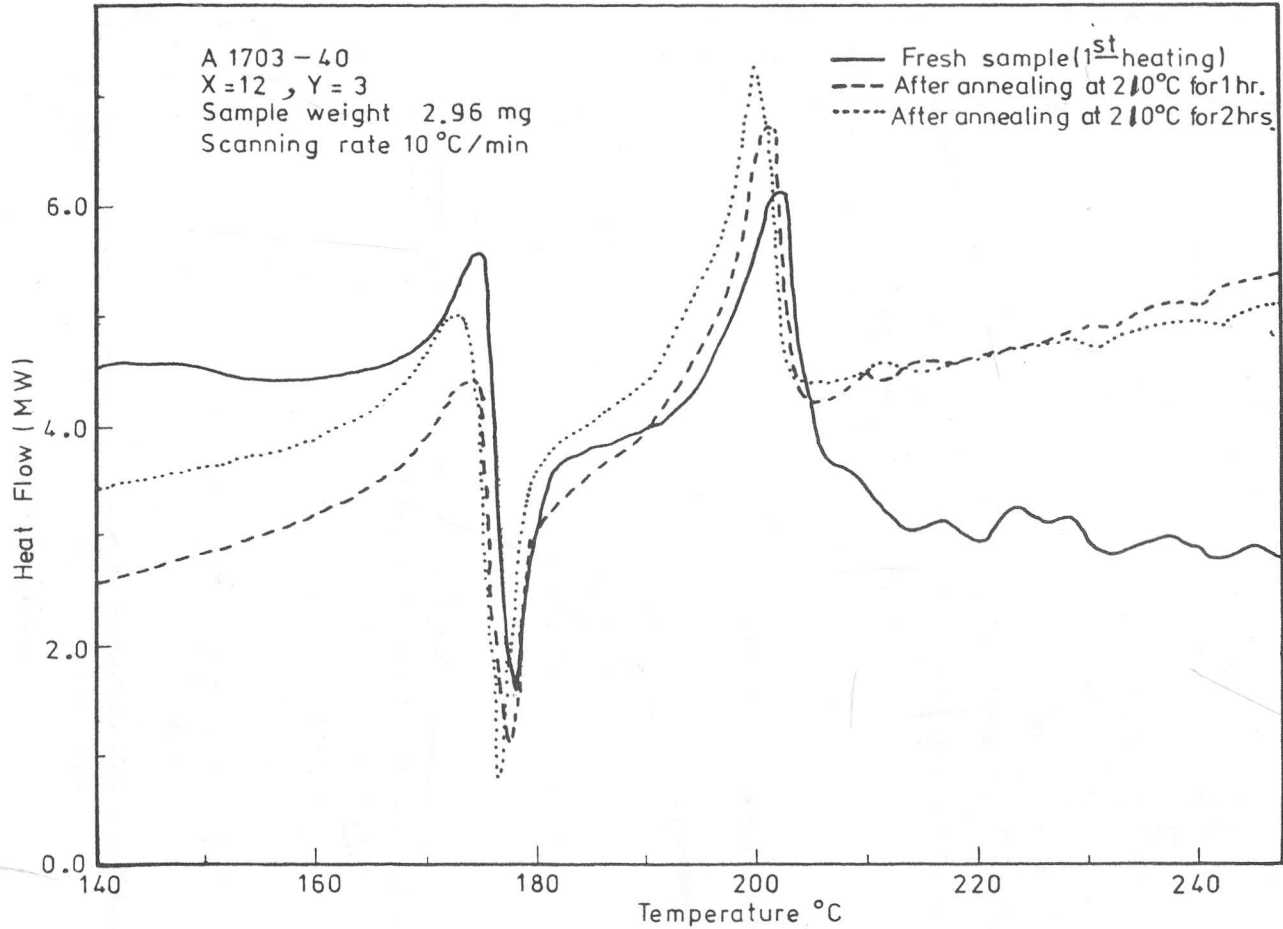Fig.(4) Magnified portion of two DSC heating scans of polyesteramide sample X=12 , Y= 3 .

Fig.(5) Effect of annealing on DSC heating scans of polyesteramide X = 12, Y = 3.

$$\Delta S_{tot} = \Sigma \ \Delta S_j, \tag{3}$$

i.e., the summed entropy of all crystal forms which are stable, Table 1. gives representative sets of thermal transitions at T_j with their ΔH_j and ΔS_j for thr two polyesteramides (X=8, Y=3 and X=12, Y=3).

In order to compare the experimental total entropy S_{tot} with the theoretically estimated values one may use the group additivity rule [17] assuming 100 % crystallinity:

$$\Delta S_c = \Sigma \ n_i \Delta S_i, \tag{4}$$

where n_i is the number of groups of type 1 in the polymer and ΔS_i is the entropy contribution per group. It was assumed that the ester groups and amide groups do not contribute to the entropy of fusion while each methylene group contributes 8.4 J/mole K and for each phenyl it is 29.3 J/mole K. The total enthalpy difference ΔH_c calculated by the group additivity procedure of Van Krevelen and Hoftyzer [17], for 100 % crystallinity, can be given by the empirical relationship:

$$\Delta H_c \ (kJ/mole) = 41.8 + 3.76 \ (X+Y) \tag{5}$$

Table 2. gives representative sets of experimental ΔH_{tot} and ΔS_{tot} for the two polymers under investigations together with the calculated values according to the group additivity rules (equations 4 and 5). It is clear that agreement is likely only if one assumes a level of crystallinity in the present samples of the order of 24 % in the first type and about 32 % in the second type. These figures are

Table 1. Thermal Transition During Heating Cycles of
         Polyesteramides (X=8,Y=3 & X=12, Y=3) with
         Representative Sets of T, Δ H, and Δ S.
         (T : Kelvin, ΔH:kJ/mole, ΔS:J/mole°K)

Type of Transition		X=8, Y=3 M. W.=480	X=12, Y=3 M. W.= 536
Endo	T	397.80	
	Δ H	4.32	
	Δ S	10.86	
Endo	T	449.00	448.50
	Δ H	2.40	8.02
	Δ S	5.35	17.85
Exo	T	453.10	451.10
	Δ H	- 5.11	- 12.96
	Δ S	- 11.29	- 28.73
Endo	T	483.90	474.00
	Δ H	11.73	19.65
	Δ S	24.24	41.67
Exo	T	489.90*	488.20
	Δ H	- 0.55	- 0.91
	Δ S	- 1.12	- 1.86
Exo	T	516.00*	506.30
	Δ H	- 0.24	- 0.72
	Δ S	- 0.46	- 1.49

* not reproducible on subsequent heating.

Table 2. Total Heats ΔH_{tot} and Entropies ΔS_{tot}
         Averaged Over 6 Runs for Each Polymer, Together
         with ΔH_c and ΔS_c Calculated According
         to Group Additivity Procedures (ΔH in kJ/mole
         and ΔS in J/mole°K).

Polymer	ΔH_{tot}	ΔH_c	ΔS_{tot}	ΔS_c
X=8 , Y=3	20.65	83.16	40.45	151.00
X=12, Y=3	27.67	98.20	59.52	184.60

obtained by normalizing ΔH_{tot} and ΔS_{tot} to 100 % **crystallinity.**

The effect of annealing the polyesteramide (second type) for one and two hours at a temperature of $210^{\circ}C$ ($> T_m$) is shown in Fig. (5). It is clear that annealing makes the two major endotherms more sharper and shifts most of the transitions by only one to two degrees towards the low temperature side. The main features remain essentially the same and the minor exotherms (between T_m and T_i) are to some extent reproducible. This has been discussed by Runt and Harrison [18] as the molecular orientations and alignments are retained during annealing. It must be mentioned that the total heats of transitions and entropies for the annealed sample are within the average of the corresponding values in case of no annealing. This may reflect that the whole or a major fraction of the polymeric sample is participating in the thermal transitions and not a small fraction of it.

4. Conclusions

Thermotropic mesomorphicity, as defined by multiple first-order phase transitions, exists in the polyesteramides under investigations. The minor transitions above T_m are more clear and reproducible in the second type rather than the first one. The nature of these mesophases can not be specified completely by using DSC only. So firm assignment of the specific transitions requires optical microscopy and variable temperature X-ray diffraction studies which are still under investigation.

Acknoweldgment

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