# THERMODYNAMIC CHARACTERIZATION OF THE MELTING OF A SERIES OF POLYESTERAMIDES

G. MANZINI, V. CRESCENZI, A. CIANA, L. CICERI, G. DELLA FORTUNA and L. ZOTTERI

Istituto di Chimica, Università di Trieste, Trieste and Laboratori Ricerche SNAM-Progetti, Milan, Italy

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Abstract—The changes in enthalpy, entropy and volume upon melting have been determined by dilatometric and differential scanning calorimetry measurements for four polyesteramides of the type:

 $-[-CO-\phi-CO-NH-(CH_2)_n-NH-CO-\phi-CO-O-(CH_2)_n-O-]_x$ 

with the following values for n and m; 6-6, 12-2, 12-6 and 12-12. The changes in each state function vary quite regularly with the number of CH<sub>2</sub> groups/repeating unit. A comparison is made between experimental data on the entropy of fusion and theoretical predictions. There is emphasis on the influence on the thermodynamics of melting of the rigidity of the  $-OCO-\phi-CONH$  residues and, in particular, of the persistence in the molten state of many interchain hydrogen bonds.

# INTRODUCTION

A SERIES of crystalline copolymers of the type:



have been synthesized in our laboratories, with various combinations of n and m values. These polymers have both practical and scientific interest. They represent a new class of fibres of technological relevance built up of linear molecules each resulting from the regular enchainment of amide and ester groups.

As expected from their chemical composition, all the polymers exhibit high melting temperatures (in the approximate range: 200–250°C), are soluble only in phenols or stronger acids, and may be spun into fibres of high tensile strengths.

Detailed investigations on a number of physical and chemical properties of a variety of such polymers have been carried out in our laboratories. We report here a few results which appear of interest for a thermodynamic characterization of the melting behaviour for the polymers identified by the following pairs of n-m values: 6-6, 12-2, 12-6 and 12-12.

Differential scanning calorimetry (DSC), dilatometry and density measurements on partially crystalline, pure samples of the four particular copolymers and on their mixtures with a diluent have been performed. Isothermal compressibility data have also been collected for the molten polymers.

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The results of these measurements, together with X-ray density data, permit evaluation of the changes in enthalpy  $\Delta H_m^{\circ}$ , entropy  $\Delta S_m^{\circ}$  and volume  $\Delta V_m^{\circ}$  upon melting for all four polymers (100 per cent crystalline  $\xrightarrow{T_m^{\circ}}$  melt, transitions).

The changes in each state function may be correlated in a very regular although qualitative fashion with chemical composition of the repeating units.

The influence of the rigidity of the -O-CO-CO-NH- residues and,

in particular, of the ability of CO and NH groups to maintain in the melt an array of intermolecular hydrogen bonds on the thermodynamics of melting of the polymers is emphasized.

# **EXPERIMENTAL**

# (a) Preparation and purification of the polymers

### I. Preparation of the monomers<sup>(1)</sup>

(i) N,N'-p-carbobutoxybenzoyldodecamethylendiamine. 2780 g (10 moles) of di-n-butylterephthalate and 200·3 g (1 mole) of 1,12-dodecamethylenediamine were introduced in a flask with stirrer, nitrogen inlet, distillation column and thermometer. The temperature was raised within 1 hr to 200-210°C then, after 3 hr, to 220-225°C. This temperature was maintained for 1 hr while about 100 ml of n-butanol were distilled out. After cooling to 140-130°C, the column was replaced by a condenser, and 2 l. of n-butanol were added; after cooling to 100°C, the suspension was filtered off. From the filtered solution, the product precipitated on cooling; it was collected by filtration, washed twice with 1·5 l. acetone and dried at 80-90°C. The monomer was purified by dissolution in hot nbutanol (7,5 l.) in which oligomers are insoluble, and filtration at 100°C. On cooling, 432 g of purified monomer precipitated. The melting point was 168°C and the free amine groups were  $8.6 \times 10^{-6}$  eq/g. Elemental analysis: %C, 71.5 (theoretical 71.0); %H, 8.6 (theoretical 8.7); %N, 4.6 (theoretical 4.6).

(ii) N,N'-p-carbomethoxybenzoylhexamethylenediamine. 305 g (1.57 moles) of dimethylterephthalate, 18.2 g (0.157 moles) of 1,6-hexamethylenediamine, 1084 ml of anhydrous toluene, 361 ml of anhydrous methanol and 40 ml of CH<sub>3</sub>OLi (1.27 M in methanol) were introduced in a flask with stirrer, condenser and nitrogen inlet. The flask was heated to reflux for 6.5 hr; during this time the reaction product precipitated from the initially clear solution. The solid was separated by filtration at 65°C, washed twice with 200 ml hot toluene (65°C), twice with 200 ml of hot methanol and dried under vacuum (final yield: 64.2 g). The melting point was 233–234°C. Elemental analysis: %C, 65.7 (theoretical 65.5); %H, 6.5 (theoretical 6.36); %N, 6.4 (theoretical 6.36).

#### II. Preparation of the polymers

The polymers were obtained by transesterification (in bulk at high temperature and under vacuum, of the monomers described above with the desired diols (ethylene glycol, 1,6-hexamethylene diol-1,12-dodecamethylenediol) using soluble titanium alcoholates as catalysts (titanium tetraiso) propylate or titanium tetrabutylate).

A typical synthesis was carried out as follows: 262 g (0.43 moles) of N,N'-*p*-carbobutoxibenzoyldodecamethylenediamine were introduced in a 1-l. flask with stirrer and outgassed under vacuum for 1 hr. Then 217 g (1.075 moles) of 1,12 dodecamethylenediol and 0.43 ml of titanium tetrabutylate 0.2 M in butanol were added. The flask was plunged in a bath at 200°C with stirring and nitrogen flow for 3 hr; then the temperature was raised to 220°C and maintained for 3.5 hr. After distillation of 77 ml of butanol, the Vigreux column was removed and vacuum slowly (100 min) applied while the temperature was raised from 220° to 250°C. Then, under vacuum, the temperature was raised to 270°C and after 1 hr, the polycondensation was interrupted.

A colourless polymer was obtained (relative viscosity: 2.52 at 25°C in phenol-tetrachloroethane equimolar mixture, concentration 1 g/dl). The polymer was purified by precipitation with excess water from a 10 per cent solution in trifluoroacetic acid.

The solid obtained was washed first with water to neutrality, then with acetone and finally dried at  $60^{\circ}$ C under vacuum.

The results of the elemental analyses were, for all four polymers, in excellent agreement with expectations.

#### (b) Density and dilatometric measurements

The densities at  $20 \pm 0.5^{\circ}$ C of the pure 6-6, 12-2, 12-6 and 12-12 polymer samples, previously outgassed and annealed at 150°C for 2 hr were determined by measuring the densities of acetone

and symdichloro-ethane mixtures of the same density of the samples, using 20-ml pycnometers (see Table 1).

The dependence of the specific volume upon temperature has been studied for each polymer using mercury dilatometers over the range from 20°C up to several degrees above the melting points. The original purified but unfractionated samples [the same as used for the density and DSC determinations (see section c)] were used for these experiments.

To avoid annealing phenomena during the measurements (as well as difficulties in maintaining for prolonged times the thermostatic bath at high temperatures) rather high heating rates were used (about  $10-15^{\circ}C/hr$ ).

With the usual corrections for the expansion of mercury (stem correction included) and of the pyrex dilatometer having as reference point the value of the molar volume of the partially crystalline sample at 20°C, the thermal expansion coefficients,  $\alpha$ , were calculated in each case directly from the experimental points of the molten polymers spanning a range of approximately 50°C (see Table 1). The values of the volume changes on melting,  $\Delta V_m^{\circ}$ , were estimated from the experimental dilatometric curves (Fig. 1) as  $\Delta V_x/C_W$  where  $C_W$  is the crystallinity content of the sample [see section (c)].



FIG. 1. Plot of molar volume of the polymers versus T (from dilatometry and density measurements).

#### (c) Differential Scanning Calorimetry (DSC) measurements

Melting endotherms of the same samples as used for density and dilatometric measurements were recorded by means of a DSC-1B Perkin Elmer differential scanning calorimetry.

The DSC-1B apparatus was employed also for investigating the melting behaviour of the polymers as a function of annealing time and/or temperature. The melting thermogram of a sample rapidly cooled from the melt is characterized by a unique endothermic peak at the temperature  $T_m$ .

In each case, annealing first results in a second smaller endotherm whose peak temperature (lower than  $T_m$ ) is a nearly linear function of  $T_c$  (annealing temperature) while  $T_m$  remains nearly constant. Prolonged annealing finally leads to a single endothermic peak centred at  $T_m \simeq T_m^\circ$  where  $T_m^\circ$  is the true, equilibrium melting temperature of the polymer (see below, Fig. 2). From the total areas of the endotherms, a set of enthalpy of melting values,  $\Delta H_x$ , for the partially crystalline samples were determined.

The heat of fusion per mole of repeating unit,  $\Delta H_m^{\circ}$  (kcal/mole) for the 100 per cent crystalline polymers considered, at their respective equilibrium melting temperatures  $(T_m^{\circ})$  have been evaluated

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FIG. 2. DSC endotherms of melting for the polymers at various annealing temperatures: 6-6 (1a) without annealing; (1b) 20' at 475°K;

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	(1c) 20' at 495°K;	(1d) 20' at 505°K.
122	(2a) without annealing;	(2b) 15' at 460°K;
	(2c) 15' at 480°K;	(2d) 15' at 490°K.
126	(3a) without annealing;	(3b) 15' at 450°K;
	(3c) 15' at 460°K;	(3d) 15' at 470°K.
12-12	(4a) without annealing;	(4b) 15' at 415°K;
	(4c) 15' at 440°K;	(4d) 15' at 450°K.
	• • •	

on the basis of DSC melting temperature  $T_m^*$  data for a number of polymer-dilution mixtures<sup>(1)</sup> (Fig. 3). In each case, the diluent was tricresylphosphate and the mixtures were prepared directly in the DSC aluminium volatile-sample holders (to avoid loss of diluent by evaporation), weighed and the thermograms recorded. Reproducibility of the  $T_m^*$  values was confirmed by repeated use of the same capsule.

The  $T_m^*$  values where introduced in the well-known Eqn. (1):

$$\left(\frac{1}{T_{m}^{*}} - \frac{1}{T_{m}^{\circ}}\right)\frac{1}{\phi_{1}} = \frac{RV_{a}}{\Delta H_{m}^{\circ}V_{1}}(1 - \chi\phi_{1}).$$
(2)

Polymer density data, as well as polymer thermal expansion coefficient (a) data, necessary for the calculation of diluent volumes fractions,  $\phi_1$ , at different  $T_m^*$  temperatures were obtained as explained in (b). Density and thermal expansion coefficient values for tricresylphosphate over a useful range of temperatures were determined with the aid of pycnometers and by dilatometry. The results are  $\rho_d^{20} = 1.159$  g/cm<sup>3</sup> and  $\alpha_d = 0.57 \times 10^{-3}$  cm<sup>3</sup>/g/degree.

The  $V_a$  value in Eqn. (2) was introduced in each case as the value of the volume/mole of repeating unit, at  $T_m^{\circ}$ , obtained by dilatometry. The molar volume of the diluent,  $V_1$ , was similarly computed. The crystallinity content,  $C_W$ , is here defined as:

$$C_W = \Delta H_x / \Delta H_m^{\circ}.$$



FIG. 3. Plot of  $(1/T_m - 1/T_m^\circ) 1/\phi_1$  vs  $\phi_1/T_m$  (melting point depression of polymer-diluent mixtures).

## (d) Isothermal compressibility measurements

The experimental equipment was an Instron rheometer consisting of a heated  $\frac{3}{8}$  in. (diam.)  $\times 15\frac{1}{16}$  in. (l.) barrel, a plug to close off one end of the barrel, a plunger to compress the polymer melt in the barrel and a compression load cell (up to 2000 kg). The cell was charged with the sample in such a way as to obtain an air-free highly packed polymer column. Leakage of the polymer melt past the plunger and the plug was not important as can be seen from the reproducibility of successive measurements on the same sample.

The measurements were performed up to 1000 kg (1360 atm) and the values of  $\beta$  were determined for the range of pressures which seemed most reliable, i.e. from 1000 to 500 kg. These values were linearly extrapolated to ambient pressure. The results thus obtained are reported in Table 1.

The temperatures of the measurements were  $230^{\circ}$ C for 12–12 and 12–6, and 270°C for 12–2 and 6–6.

# **RESULTS AND DISCUSSION**

A series of thermograms recorded using pure polymer samples annealed at different temperatures are reported in Fig. 2. In each case, it is seen that prolonged annealing promotes merging of the two initially more or less distinct endotherms. From the total area under each of the double or single peaked curves of Fig. 1, a set of enthalpy of melting values,  $\Delta H_x$ , have been evaluated for the four partially crystalline polymers. The  $\Delta H_x$  values obtained after 2 hr annealing at 430°K are listed in Table 1.

The enthalpy changes upon melting for 100 per cent crystalline samples  $(\Delta H_m^{\circ})$  have been obtained by the measurement (DSC) of melting temperatures  $T_m^*$  of polymer-diluent (tricresylphosphate) mixtures (see Experimental).

The results of the DSC measurements are plotted in Fig. 3 according to Eqn. (2) and the  $\Delta H_m^{\circ}$ ,  $T_m^{\circ}$  and  $\Delta S_m^{\circ} = \Delta H_m^{\circ}/T_m^{\circ}$  values derived are listed in Table 1.

T <sub>m</sub> °		T <sub>m</sub> °	$\Delta H_m^{\circ}$		$\Delta S_{m}^{\circ}$		$\Delta H_{\star}$	
Polymer	Mu	(°Ř)	(kcal/mole)	(cal/g)	(cal/deg·mole)	(cal/deg·bond)	(kcal/mole)	
6-6	494.60	526	. 22.2	45.0	42.2	2.11	6.5	
12-2	522.65	517	24.5	46.5	47.4	2.15	6.4	
12-12	662.92	407	33.5	50.5	71.3	2.19	8.4	

TABLE 1. RESUME OF EXPERIMENTAL THERMODYNAMIC

The results of the dilatometric experiments are illustrated in Fig. 1.

Thermal expansion coefficients,  $\alpha$ , together with  $V_a^{200^{\circ}}$  and  $\Delta V_m^{\circ}$  (volume change on melting) data directly derived from these experiments and crystallinity content data,  $C_W$  [for the calculation of  $C_W$  and  $\Delta V_m^{\circ}$  see sections (b) and (c) of the Experimental Part], are also reported in Table 1.

From Table 1, it appears that many properties of the class of polymers studied depend in a regular fashion on their chemical constitution. This fact is better indicated by the plots of Fig. 4.

For example, it is easily verified that the molar volumes of the amorphous polymers can be expressed as additive of the volumes of the -O-CO--NH-groups and methylene groups. For instance at 200°C:

$$(V_a^{200^\circ})_{n,m} = 235 + 18.5 (n + m), \text{ cm}^3/\text{mole.}$$

The value of  $18.5 \text{ cm}^3$ /methylene groups is in good agreement with the value determined for polymethylene at the same temperature.<sup>(3)</sup>

More important, it may be deduced from the data of Table 1 that the regularly decreasing value of  $T_m^{\circ}$  on going from the 6-6 to the 12-12 polymer must be ascribed to the substantially lower entropy of melting of the former as compared with the latter. The  $\Delta H_m^{\circ}$  values increase regularly in the series 6-6, 12-2, 12-6 and 12-12. These figures, furthermore, can be correlated by the empirical equation:

$$\Delta H_m^{\circ} = 11 + (n + m) 0.93$$
, kcal/mole,

according to which the contribution of the -O-C-V and U groups and U according to which the contribution of the -O-C-V and U are the second secon

of the methylene groups to the enthalpy of melting, 5.5 kcal/group and 0.93 kcal/ methylene, respectively, may be taken as simply additive within experimental error. The latter figure happens to be very close to the enthalpy of melting of polymethylene, if the difference in melting temperatures are approximately allowed for.<sup>(4)</sup> In any case, the increase in enthalpy is more than counterbalanced by the increase in entropy of melting in the series of polymers studied in this work.

A possible rationalization of the trend of the  $\Delta S_m^{\circ}$  values with the number of methylene groups per repeating unit may be attempted by invoking two main factors: (1) the relative rigidity of the  $-O-CO-\sqrt{O}$ -CO-NH- residues, and (2) the ability of the -CO- and -NH- groups to form intermolecular hydrogen bonds also in the melt.

In this connection, expressing the total entropy of polymer melting in terms of an entropy change due to volume expansion of the melt,  $\Delta S_v$ , and of a configurational

C <sub>w</sub>	ρ <sub>x</sub> <sup>20°</sup>	$V_a^{200^\circ}$ (cm <sup>3</sup> /mole)	$a \times 10^3$ (cm <sup>3</sup> /g°)	Mean value between (°C)	$eta  imes 10^4$ (cm <sup>3</sup> /g atm) Experimental	$\Delta V_m^{\circ}$ (cm <sup>3</sup> /mole)
0·29	1·239	457	0.64	(230-280)	0.80 (at 270°)	75
0·26	1·213	493	0.65	(230-280)	0.86 (at 270°)	89
0·29	1·178	568	0.69	(200-250)	0.87 (at 230°)	98
0·25	1·140	679	0.75	(200-250)	0.99 (at 230°)	124

VALUES FOR THE FOUR POLYMERS CONSIDERED



FIG. 4. Resumé of some thermodynamic properties of the polymers as functions of the number of methylene groups per repeating unit.

entropy  $\Delta S_c$ , i.e.:  $\Delta S_m^{\circ} = \Delta S_v + \Delta S_c$ , it appears relevant to consider the values of both terms for the homologous polymers studied by us. The  $\Delta S_v = (\alpha/\beta) \Delta V_m^{\circ}$  values were calculated using the  $\alpha$  and  $\Delta V_m^{\circ}$  data reported in Table 1 and with the experimental  $\beta$  values (Table 1) referred to the melting temperature,  $T_m^{\circ}$ , for each polymer with the aid of the equation:<sup>(5)</sup>

$$\frac{\partial \ln \beta}{\partial T} = \frac{1}{T} + 2a,$$

assuming that  $\alpha$  is constant over the limited range of temperatures considered. The set of entropic terms and  $\beta$  values estimated thus are listed in Table 2.

Let us now proceed to compare the  $\Delta S_c$  values with those which may be evaluated following the mathematical procedures already described in detail for different chains.<sup>(6)</sup> For these calculations as applied to the chains of interest here, the geometrical parameters specified in Table 3 and the statistical weights given in Table 4 have been used.

Calculations have been carried out first assuming the case of non-interacting chains, i.e. considering the limiting case of a melt in which no interchain hydrogen bonds are formed. The results are indicated as  $(\Delta S_c)_{0.0}$  in Table 2. The theoretical  $(\Delta S_c)_{0.0}$  values depend, of course, on the choice of an appropriate set of statistical weights for the different bonds along the repeating units. In our case such values were either those already employed in the case of polylactone chains,<sup>(6)</sup> (i.e. for the bonds within the

Polymer	$\beta \times 10^4$ (cm <sup>3</sup> /g atm) Corrected at $T_m^\circ$	$(cal/cm3°C) at T_m°$	$\Delta S_v$ (cal/deg·mole)	$\Delta S_n^{\circ} - \Delta S_v$ (cal/deg·mole)	(∆S <sub>c</sub> )₀.₀ (cal/deg mole)	$(\Delta S_e)_{1\cdot 0}$ (cal/deg·mole)
6-6	7.4	0-21	15.7	26.5	28.7*	21.7*
12-2	6-2	0.20	17.8	29-6	33-3	25.3
12-6	8.1	0.205	20-1	37-0	39-7	32.7
12–12	ŝ	0-205	25-6	45-7	50-7	43-7

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\* Virtual bond.

sequences  $-O-(CH_2)_m-O-$ ) or were evaluated from conformational energy maps (for bonds within the sequences  $-NH-CH_2-CH_2-$ ) using the potential energy functions of Giglio.<sup>(7)</sup>

Furthermore, the --NH-CO-O- moieties were considered rigid and planar.\*

From Table 2, it is seen that the theoretical  $(\Delta S_c)_{0.0}$  values are systematically higher than the  $\Delta S_c$  values from the experimental data.

Relying on our choice of the statistical weights and geometrical parameters used in the calculations, we think that much of this discrepancy might be ascribed to the fact that melting would reduce by a limited amount the number of interchain hydrogen bonds, as it is commonly in the case of polyamides.<sup>(7)</sup> Hydrogen bonding does, of course, impose constraints on the flexibility of the chains in the melt and thus must reduce the configurational terms with respect to those calculated for non-interacting chains  $(\Delta S_c)_{0.0}$ .

It is difficult to calculate  $\Delta S_c$  values applicable to the case of interacting chains, as considered in this study. To simplify the problem, the limiting case of a polymer melt in which no hydrogen bond is disrupted was considered with the assumption that this feature may be accounted for in the calculations by just the assumption of complete rigidity of the groups flanking either  $-CO_{-}$ ,  $-NH_{-}$  or  $-O_{-}$  groups. Accordingly, statistical weights for bonds 3, (3 + n), (7 + n) and (7 + n + m) (see Table 3) were considered as zero.

<sup>\*</sup> In the calculations, all statistical weights were referred to  $500^{\circ}$ K, mean value of the temperatures of melting of the polymers. Statistical weights are reported in Table 3. Correction to the exact  $T_m^{\circ}$  of the polymer was seen to be unimportant.

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The corresponding configurational entropy terms, indicated as  $(\Delta S_c)_{1.0}$ , are reported in Table 2. It appears that the experimental  $\Delta S_c$  values lie between the calculated  $(\Delta S_c)_{0.0}$  and  $(\Delta S_c)_{1.0}$  ones.

We cannot follow this argument too far in view of the crudeness of the model, of the unavoidable uncertainty in the statistical weights, and also of the accumulation

	12–12	126	6–6	12-2	σ	ψ	ω
Bond*	1	1	1	1	1.0		
	2	2	2	2			
	3	3	3	3	1.0		_
	4	4	4	4	1.0	1.0	0.5
	5	5	5	5	0.2	0.75	0.5
	6-13	6-13	6,7	6-13	0.6	1.0	0.12
	14	14	8	14	0.5	0.7	0.2
	15	15	9	15	1.0	1.1	0.6
	16	16	10	16	_	_	
	17	17	11	17	1.0		_
	18	18	12	18		_	—
	19	19	13	(19)	0.3(0.4)	-(-)	-(-)
	20	20	14	(20)	1.0(1.0)	1.0(1.0)	0.001(0.5)
	21	21	15	(21)	0.5(0.5)	0.8(1.0)	0.2(0.4)
	2229	22,23	16,17	(22)	0.6(-)	1.0(-)	0.15()
	30	24	18		0.9	0.75	0.2
	31	25	19		0.3	1.0	0.003
	32	26	20				

TABLE 4. ENUMERATION OF BONDS AND ASSOCIATED STATISTICAL WEIGHTS

\* See Table 3.

We recall that:

 $\Delta S_c = R[\ln Z + T/Z \cdot dZ/dT],$ 

where the configurational partition function, Z, is given by:

$$Z = [1 \ 0 \ 0 \ \dots \ 0] \left\{ \begin{array}{c} n \\ \pi \\ i = 1 \end{array} \right\} \left\{ \begin{array}{c} 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{array} \right\},$$

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with the matrix  $U_i$ , for bond *i*, having the general form:

$$U_i = \begin{bmatrix} 1 & \sigma_i & \sigma_i \\ 1 & \sigma_i \psi_i & \sigma_i \omega_i \\ 1 & \sigma_i \omega_i & \sigma_i \psi_i \end{bmatrix}.$$

of experimental errors in the estimate of  $\Delta S_c$ . At this stage, it is safe only to conclude that, in agreement with expectation as well as with direct experimental observations and as reflected in the results of the calculations, the polymer chains considered here exhibit quite a high degree of stiffness in the melt mostly to be ascribed to interchain hydrogen bonding.

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**Résumé**—On a déterminé les changements d'enthalpie d'entropie et de volume pendant la fusion, par dilatométrie et par calorimétrie différentielle, de quatre poly estéramides du type:

les valeurs de n et m étant: 6-6, 12-2, 12-6 et 12-12. Les changements dans chaque fonction d'état varient régulièrement avec le nombre de groupements CH<sub>2</sub> par unité se répétant. On fait une comparaison entre les données expérimentales sur l'entropie de fusion et les prévisions théoriques. Ceci montre l'influence de la rigidité des résidus --OCO--O--CONH-- sur la thermodynamique de fusion et, en particulier, de la persistance à l'état fondu de nombreuses liaisons hydrogène entre les chaînes.

Sommario—Tramite le tecniche sperimentali dilatometriche e calorimetriche (DSC) sono state determinate le variazioni di alcune grandezze termodinamiche relative alla fusione (volume, entalpia ed entropia) di una serie di poliesterammidi recentemente sintetizzate. Queste grandezze sono risultate dipendere in modo regolare dal numero di gruppi metilenici presenti nell'unità ripetitiva dei polimeri. E' stato fatto quindi un raffronto fra i dati sperimentali relativi all'entropia di fusione ed i valori calcolati secondo uno schema teorico già in precedenza messo a punto. E' risultata evidente l'importanza della conservazione allo stato fuso di buona parte dei legami idrogeno presenti nel cristallo.

Zusammenfassung-Für vier Polyesteramide des Typs

$$-[-CO-\phi-CO-NH-(CH_2)_n-NH-CO-\phi-CO-O-(CH_2)_n-O-]_x$$

mit *n* und m = 6-6, 12-2, 12-6 und 12-12 wurden die Änderungen der Enthalpie, Entropie und im Volumen beim Schmelzen durch dilatometrische und differantialcalorimetrische Messungen gemessen. In jeder Zustandsfunktion verlaufen diese Änderungen sehr regelmässig als Funktion der Anzahl der CH<sub>2</sub>-Gruppen für die wiederkehrende Einheit. Es wird ein Vergleich zwischen den experimentellen Daten der Bewegungsentropie und theoretischen Voraussagen getroffen. Es besteht ein deutlicher Einfluß der Steifheit der --OCO--O--CONH-Einheiten auf die Thermodynamik des Schmelzens und besonders auf das Vorhandensein intermolekularer Wasserstoffbrücken im geschmolzenen Zustand.

<sup>(4)</sup> Ref. (2), p. 119.