

## Melting Temperatures and Polymer-Solvent Interaction for Polycaprolactam

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### INTRODUCTION

It is known that the degree of crystallinity and the melting temperature of a polymer are depressed by adding a foreign substance; the latter can be either a diluent or can be incorporated in the polymer as comonomer or terminal unit.

In the case of diluents added to a crystalline polymer, the relation between the lowering of the melting point and the concentration and type of the diluent is<sup>1</sup>

$$1/T_m - 1/T_m^0 = (R/\Delta H_u)(V_u/V_1)\{v_1 - [\kappa_1 + (1/2 - \psi_1)]v_1^2\} \quad (1)$$

where,  $V_u$  and  $V_1$  are the molar volumes of the polymer repeating unit and of the diluent, respectively,  $\Delta H_u$  is the heat of fusion per repeating unit for a perfectly crystalline polymer, and  $v_1$  is the diluent volume fraction

According to the following relation:

$$\chi_1 = \kappa_1 + 1/2 - \psi_1 \quad (2)$$

the bracketed term of the right-hand side of eq. (1) is expressed as  $\chi_1$ , a thermodynamic interaction parameter which is, according to eq. (2), divided in the two entropic and enthalpic ( $\kappa_1$ ) components.  $\chi_1$  can also be expressed as

$$\chi_1 = BV_1/RT \quad (3)$$

where  $B$  is the interaction energy density, characteristic of the solvent-solute pair.

In the majority of cases<sup>2</sup> the ideal value of 0.5 is assigned to  $\psi_1$ ; this is to say that in eq. (2)  $\chi_1$  identifies only with the enthalpic term.

In this case eq. (1) reduces to the form:

$$1/T_m - 1/T_m^0 = (R/\Delta H_u)(V_u/V_1)(v_1 - \kappa_1 v_1^2) \quad (4)$$

However, an equation of this type is generally used:<sup>3</sup>

$$1/T_m - 1/T_m^0 = (R/\Delta H_u)(V_u/V_1)[v_1 - (BV_1/RT)v_1^2] \quad (5)$$

where it is assumed that the term  $B$  of eq. (5) contains effectively an entropic term, i.e., that  $B$  exceeds the pure heat of mixing term of a magnitude equal to  $RT(1/2 - \psi_1)/v_1$ ; however, from literature data on  $\psi_1$  obtained with other systems it can be seen<sup>4</sup> that the discrepancy probably does not exceed 1 cal./cc.<sup>5</sup> In the literature, eq. (5) is generally used. It is customary to plot  $1/T_m$  as a function of  $v_1$ , obtaining  $1/T_m^0$  from the intercept; this is particularly important if for some reasons  $T_m^0$  cannot directly be determined.  $\Delta H_u$  can be computed from the initial slope. In a plot of this type a straight line is obtained only if  $\chi_1 = 0$ , while a downward concavity indicates  $\chi_1 < 0$ . However, it is more convenient to plot  $(1/T_m - 1/T_m^0)/v_1$  as a function of  $v_1/T_m$ ; in this way  $\Delta H_u$  is more easily calculated from the intercept, and  $B$  from the slope and the intercept. In such a plot a straight line is obviously obtained only if  $\psi_1 = 1/2$ , i.e., if eq. (5) has been correctly applied. As a matter of fact, Krigbaum and Tokita,<sup>2</sup> for the pair polyacrylonitrile/dimethylformamide (exceptionally good solvent), find a sensible curvature; in this case eq. (5) is not applicable owing to a not negligible entropic contribution. Hence they plot eq. (1) in the form:

$$\begin{aligned} (1/v_1) - (1/v_1)^2 \{ (1/T_m - 1/T_m^0) / [R/\Delta H_u (V_u/V_1)] \} \\ = 1/2 - \psi_1 + \psi_1(\Theta/T_m) \end{aligned} \quad (6)$$

where  $\kappa_1 = \psi_1(\Theta/T)$ ,  $\Theta$  being the "ideal temperature."<sup>1</sup> For the solvent/solute pair as above, Krigbaum obtains a straight line in such a plot and a  $\psi_1$  different from 0.5.

## EXPERIMENTAL

Four samples of polycaprolactam (nylon 6) were used. The products were prepared in an autoclave (discontinuous hydrolytic process); their characteristics are reported in Table I. The polymers were used unfrac-

TABLE I  
Characteristics of Nylon 6 Samples Used in the  $T_m$  Determination

Sample	Amino groups, $\bar{M}_n$	Carboxylic groups, $\bar{M}_n$	Stabilizer, acetic acid/lactam/(m./m.)	$T_m^0$ , °C.
A	12.200*	11.600	0.001	228
B	7.200	6.700	—	226
C	31.000	29.000	—	228.5
D	14.000	14.500	—	227.5

\* Corrected for acetic acid.

tionated, and had been previously freed from residual monomer by prolonged hot water extraction. The average monomer content was negligible, max. 0.5%. The water content was <0.2% (Fisher titration). Their molecular weight distribution was regular (the most probable).

The solvents were all reagent grade and were redistilled before use. Their water content was lower than 0.01%. The finely cut product was introduced together with the solvent in a small glass tube, and the mixture (0.5–1.0 g.) was repeatedly deaerated with vacuum and pure dry nitrogen, and finally flame-sealed under slight vacuum.

The melting temperatures were determined in a silicone-oil bath thermostat. The following temperature cycle was used. The tubes were heated a few degrees above the mixture melting point and, after standing a few minutes at this temperature, were slowly cooled until the samples showed appreciable crystallinity. The temperature was then raised at the rate of 1°C./min.; in the vicinity of the  $T_m$  the rate was lower than 1°C./5 min.

$T_m$  (temperature at which the last traces of crystalline region disappear) was determined visually as the temperature at which the deep turbidity of the white crystalline polymer vanished.<sup>4</sup> This was also confirmed by observing the disappearance of light through crossed polaroids.<sup>6</sup> The two determinations are in full agreement. The  $T_m$  data are the average of various determinations which agree in general within  $\pm 0.5^\circ\text{C}$ .

The  $T_m^0$  value was determined by the hot-stage microscope, small polymer films being observed through crossed nicols.

In a few cases (nitrobenzene, nitrotoluenes, diphenyl ether) liquid-liquid phase separation was observed; however, the temperature of miscibility was in general not detected.

The density of the molten polymer was determined by the method of Flory<sup>7</sup> with the use of pycnometers of about 3 ml. capacity, immersed in an oil-bath thermostat. The following values were determined for sample A:  $d_4^{220} = 0.999$  g./cc.,  $d_4^{230.5} = 0.998$  g./cc.,  $d_4^{245} = 0.996$  g./cc. The densities of the diluents were taken from the literature; in a few cases they were determined directly.

As far as the calculation of  $v_1$  is concerned, the relation<sup>8</sup>  $M_0/M_1 = \rho_2/\rho_1$ , (where  $M^0$  and  $M_1$  are the molecular weights of the repeating unit and of the solvent,  $\rho_2$  and  $\rho_1$  are the densities of the polymer and the solvent, respectively) was never satisfied. In consequence we could not use the molar fractions to express  $v_1$ , but calculated it from the density of the polymer and of the diluents extrapolated at the melting temperature of the mixture, assuming no volume change with mixing.

## RESULTS AND DISCUSSION

In Table II the melting temperatures of polymer-diluent mixtures are given for the sample A type of polymer in various solvents. In Figure 1 three of them are plotted as an example.

As obtained from the intercept, all  $1/T_m^0$  are in full agreement with the value independently determined (hot-stage microscope). In such a plot the constant value of  $1/T_m$  as  $v_1$  increases indicates liquid-liquid phase separation according to the phase rule.

TABLE II  
Melting Temperature of Mixtures of Nylon 6 (Type A) and Diluent

<i>m</i> -Cresol		<i>o</i> -Chlorophenol		Thymol		<i>p</i> -Nitrophenol		<i>p</i> -Methoxyphenol	
$v_1$	$10^3/T_m$	$v_1$	$10^3/T_m$	$v_1$	$10^3/T_m$	$v_1$	$10^3/T_m$	$v_1$	$10^3/T_m$
0.057	2.022	0.049	2.016	0.120	2.030	0.086	2.053	0.111	2.043
0.113	2.047	0.098	2.030	0.233	2.066	0.173	2.110	0.216	2.096
0.167	2.079	0.146	2.053	0.342	2.099	0.217	2.139	0.316	2.151
0.220	2.112	0.195	2.079	0.444	2.146	0.262	2.174	0.414	2.208
0.272	2.137	0.243	2.101	0.544	2.179	0.307	2.207	0.510	2.268
0.324	2.165	0.291	2.119	0.592	2.205	0.354	2.232		
0.370	2.208	0.338	2.155	0.611	2.215	0.449	2.307		
0.424	2.240	0.357	2.172	0.687	2.247				
0.522	2.309	0.386	2.181	0.733	2.268				
0.618	2.421								
Phenol		<i>o</i> -Nitrotoluene		<i>m</i> -Nitrotoluene		Nitrobenzene		Diphenyl ether	
$v_1$	$10^3/T_m$	$v_1$	$10^3/T_m$	$v_1$	$10^3/T_m$	$v_1$	$10^3/T_m$	$v_1$	$10^3/T_m$
0.110	2.049	0.052	2.022	0.050	2.014	0.099	2.047	0.055	2.008
0.215	2.110	0.072	2.028	0.103	2.028	0.148	2.062	0.110	2.015
0.317	2.174	0.103	2.037	0.205	2.049	0.197	2.075	0.163	2.018
0.420	2.232	0.154	2.047	0.306	2.060	0.296	2.092	0.216	2.022
0.515	2.304	0.204	2.053	0.406	2.070	0.394	2.103	0.269	2.026
		0.255	2.058	0.506	2.070	0.494	2.103	0.321	2.028
		0.342	2.064	0.606	2.070	0.552	2.101	0.526	2.028
		0.406	2.066			0.593	2.105	0.720	2.028
		0.506	2.066						
		0.557	2.066						
		0.606	2.066						
		0.655	2.066						
		0.705	2.066						
		0.751	2.068						

Figures 2 and 3 are plots of  $(1/T_m - 1/T_m^0)/v_1$  vs.  $v_1/T_m$  for A, B, C, and D polymers and diluents. The melting temperatures are given in Table III.

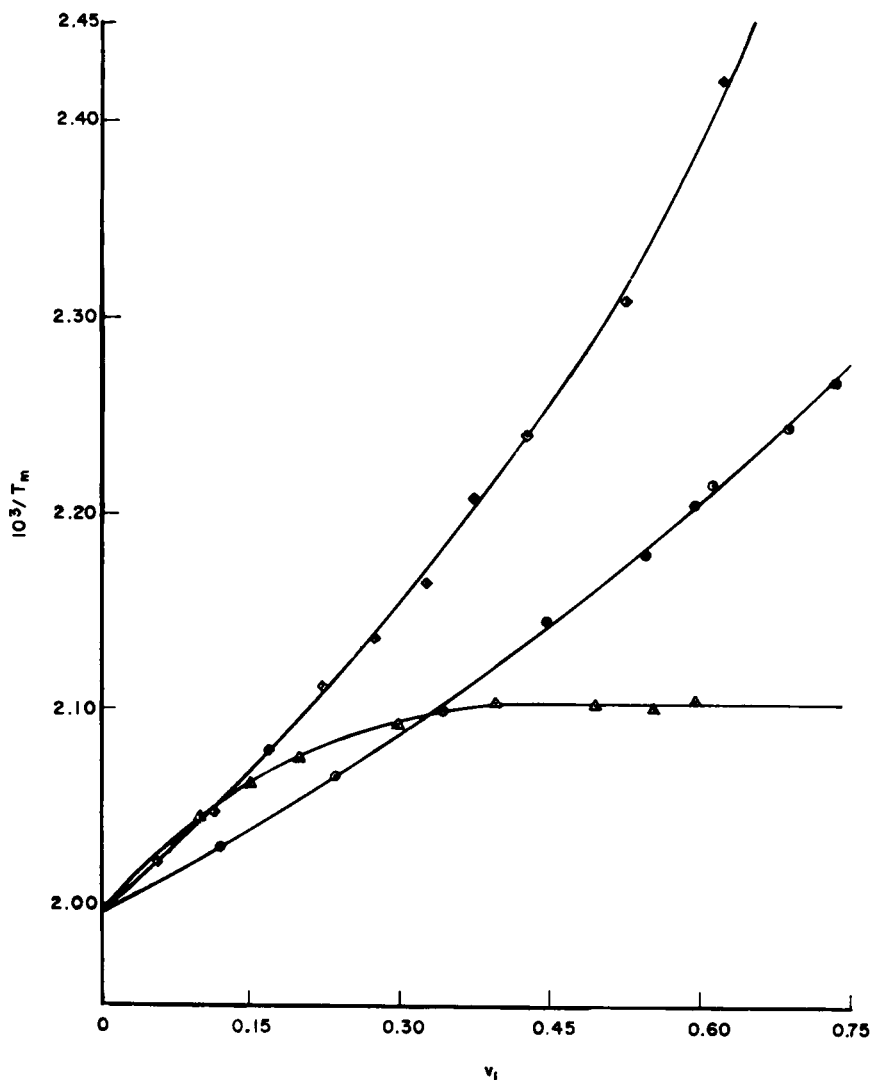


Fig. 1. Melting point data for polymer-diluent systems according to eq. (1). Polymer of type A ( $\odot$ ) thymol; ( $\triangle$ ) nitrobenzene; ( $\diamond$ ) *m*-cresol.

It can be noted that practically straight lines are obtained for diluents of the phenolic type. The resulting  $\Delta H$  values are in good agreement (see Table IV).

The case of *p*-nitrophenol is an exception; in fact, while a straight line is obtained, a  $\Delta H$  of 25.7 cal./g. is calculated. This is possibly due to the

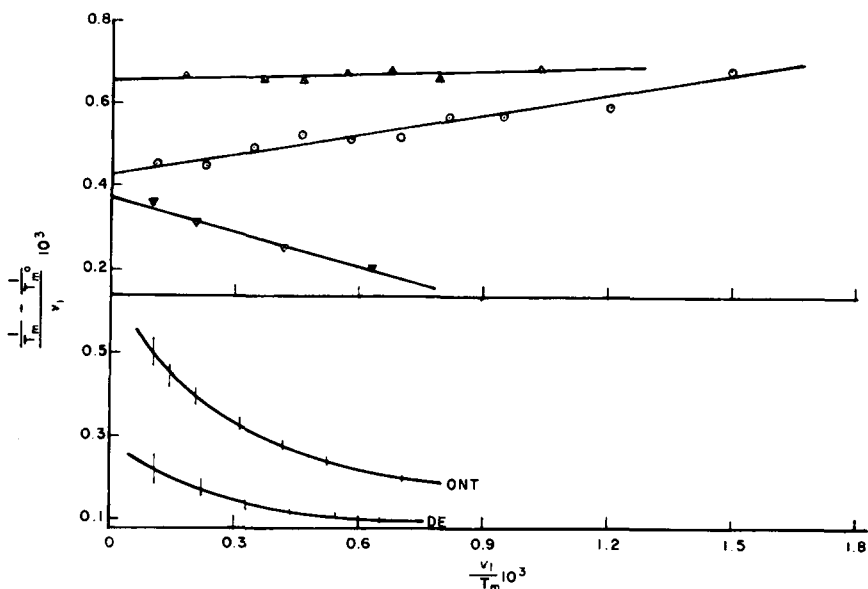


Fig. 2. Melting point data for polymer-diluent systems according to eq. (5). Lengths of vertical lines indicate error associated with a differential temperature uncertainty of  $\pm 0.5^\circ\text{C}$ . Polymer of type A in: ( $\Delta$ ) *p*-nitrophenol; ( $\circ$ ) *m*-cresol; ( $\nabla$ ) *m*-nitrotoluene; (ONT) *o*-nitrotoluene; (DE) diphenyl ether.

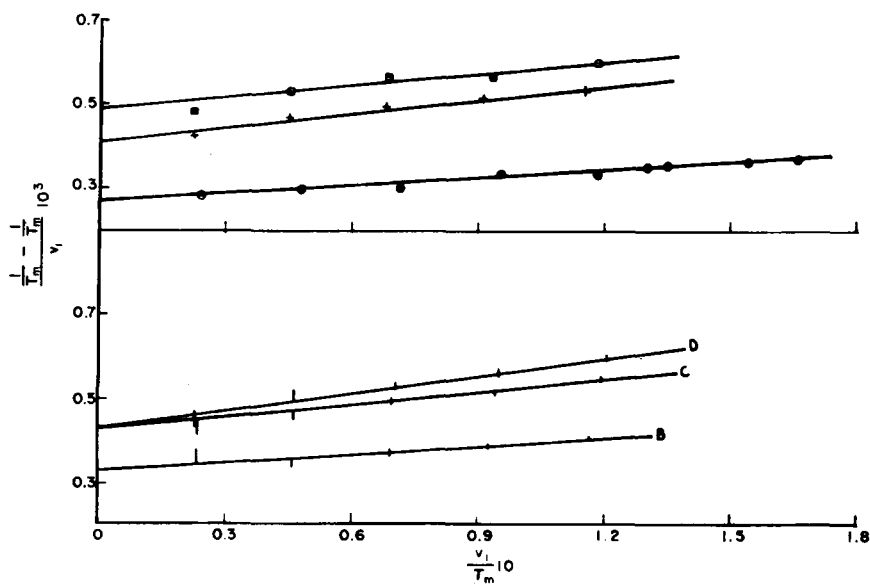


Fig. 3. Melting point data for polymer-diluent systems according to eq. (5). Lengths of vertical lines indicate error associated with a differential temperature uncertainty of  $\pm 0.5^\circ\text{C}$ .: ( $\square$ ) A-type polymer-phenol; ( $+$ ) A-type polymer-*p*-methoxyphenol; ( $\circ$ ) A-type polymer-thymol; (D) D-type polymer-*m*-cresol; (C) C-type polymer-*m*-cresol; (B) B-type polymer-*m*-cresol.

TABLE III  
Melting Temperature of Mixtures of Nylon 6 (Types B, C, D) and *m*-Cresol

Type B		Type C		Type D	
$v_1$	$10^3/T_m$	$v_1$	$10^3/T_m$	$v_1$	$10^3/T_m$
0.113	2.045	0.113	2.045	0.113	2.047
0.221	2.081	0.220	2.096	0.220	2.110
0.326	2.125	0.324	2.155	0.324	2.169
0.427	2.172	0.425	2.215	0.424	2.237
0.525	2.217	0.523	2.283	0.522	2.309

TABLE IV  
Heat of Fusion of A-Type Nylon and Interaction Constant with Various Diluents

Diluent	$\Delta H$ , cal./g.	$B$ , cal./cc.
<i>m</i> -Cresol	37.1	-5.6
<i>o</i> -Chlorophenol	41.3	-3.9
Phenol	38.4	-3.6
<i>p</i> -Methoxyphenol	34.0	-3.2
Thymol	39.7	-1.4
<i>m</i> -Nitrotoluene	37.1	8.2
<i>p</i> -Nitrophenol	25.7	—

elevated acidity of this phenol ( $K_a = 6.2 \times 10^{-8}$ ), which could cause poly-electrolyte effects and some hydrolysis of the polyamide.

For other diluents (i.e., diphenyl ether, *o*-nitrotoluene, nitrobenzene) a slight curvature was found, which cannot be caused only by experimental errors.

If we try to draw a straight line through these points, a  $\Delta H$  sensibly different from that given above is found.

If we plot the data according to eq. (6), using for the  $\Delta H_u$ 's the average obtained from the phenols (see Fig. 4) for these solvents (and even for *m*-nitrotoluene), a straight line is obtained; the intercept of this line can be assumed as practically zero within experimental error. This indicates for phenolic solvents a  $\psi_1$  value of 0.5 in agreement with the assumption made for eq. (5). A definite curvature is, on the contrary, obtained for the diluents nitrobenzene, *o*-nitrotoluene, and diphenyl ether; this indicates that eq. (5) possibly does not correctly represent the phenomenon for these solvents; therefore, the  $\Delta H_u$  values obtained from these diluents are probably incorrect and must be disregarded.

The average  $\Delta H$  (37.9 cal./g.) agrees with the average  $\Delta H$  found by Rybníkář<sup>9</sup> by various methods (38.2 cal./g.).

A value for  $\Delta S$  of  $37.9/501 = 7.56 \times 10^{-2}$  cal./g. deg. is obtained. In Figure 3 the values of  $(1/T_m - 1/T_m^0)/v_1$  vs.  $v_1/T_m$  are reported for the diluent *m*-cresol and three different polycaprolactams (see Table I). As can be seen from the coinciding intercepts in Figures 2 and 3, the A, C, and D types furnish practically coincident  $\Delta H$ 's; in the case of the *B* type

(degree of polymerization ca. 60) a different value is obtained (48.4 cal./g.). As a matter of fact, it is known that eq. (5) was obtained from:

$$\mu_u - \mu_u^0 = RT(V_u/V_1)[(\ln v_2)/X - (1 - 1/X)(1 - v_2) + \chi_1(1 - v_2)^2] \quad (7)$$

where  $\mu_u - \mu_u^0$  is the chemical potential difference for repeating unit and  $X$  the degree of polymerization, considering  $X$  infinite. For polymer B,  $X$  cannot be considered infinite, the simplifications introduced for obtaining eq. (5) therefore cannot be made, and hence eq. (5) does not correctly apply.

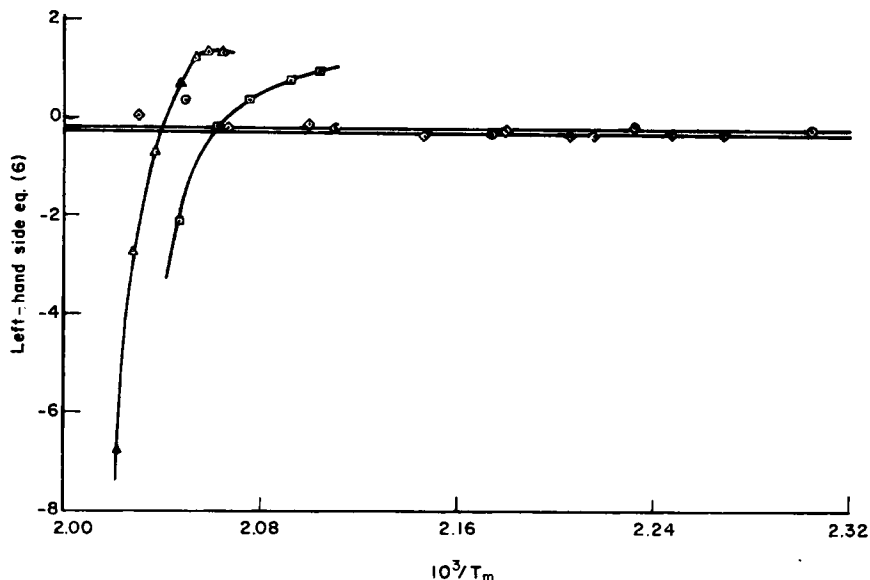


Fig. 4. Plot of left-hand side of eq. (6) vs.  $10^3/T_m$ . Polymer of type A in: (○) phenol; (◇) thymol; (□) nitrobenzene; (△) *o*-nitrotoluene.

The similarity of behavior of the lines for the A and D types, of similar molecular weight but different in respect to the presence of acetic acid stabilizer, agrees with Flory's theory.

In Table IV the B values obtained from the plots of Figures 2 and 3 are reported.

The solvent power of the various phenols with nylon 6 decreases in the order *m*-cresol > *o*-chlorophenol > phenol > *p*-methoxyphenol > thymol. From viscosimetric data Rybníkář<sup>10</sup> finds for *m*-cresol a better solvent power than phenol, with nylon 6. On the other hand, Valentine,<sup>11</sup> from swelling measurements for nylon 66, finds the following order (expressed as  $\chi_1$  at 50°C.): *p*-methoxyphenol > thymol > *m*-cresol > phenol > *o*-chlorophenol. The great differences in temperature of measurement are possibly responsible for the discrepancy.



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### Synopsis

Melting points of four polycaprolactam samples of different molecular weight and their mixtures with various diluents were determined. Heats of fusion and polymer-diluent energy of mixing parameters were calculated according to the theory of Flory. The heats of fusion were found to be about 38 cal./g. The experimental results (independence from molecular weight above a certain value, and from the nature of terminal groups, etc.) agree with the theory. However, in a few cases of poor solvents anomalous behavior can be suspected.

### Résumé

Les points de fusion de quatre échantillons de polycaprolactam de différent poids moléculaire et leurs mélanges avec plusieurs diluants ont été déterminés. Les chaleurs de fusion et les paramètres exprimants l'énergie de mélange polymère-diluant ont été calculés selon la théorie de Flory. On a trouvé pour la chaleur de fusion une valeur d'environ 38 cal./g. Les résultats (indépendance du poids moléculaire au delà d'une certaine valeur, de la nature des groupes terminaux, etc.) sont en accord avec la théorie. Toutefois on peut suspecter des déviations dans quelque cas de mauvais solvant.

### Zusammenfassung

Schmelzpunkte von vier Polycaprolactam Muster von verschiedenem Molekulargewicht und ihre Mischungen mit verschiedenen Verdünnungsmitteln wurden bestimmt. Schmelzwärmen und Parameter der Polymer-Verdünnungsmittelmischenergie wurden nach der Floryschen Theorie berechnet. Von unseren Messungen wurde eine Schmelzwärme von ungefähr 38 kal./g. berechnet. Die experimentelle Ergebnisse (Unabhängigkeit vom Molekulargewicht über einen bestimmten Wert, von der Natur der Endgruppen, u.s.w.) sind mit der Theorie im Einklang. Immernoch, in einigen Fällen von nicht guten Verdünnungsmitteln kann man an ein unregelmässiges Verhältnis denken.

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