

ON THE STRUCTURE AND PROPERTIES OF POLYAMIDES. XXXII.*
INFLUENCE OF NON-CRYSTALLIZABLE UNITS
ON THE CRYSTALLIZATION OF POLYCAPROLACTAM

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The induction periods of crystallization were measured for anionic copolymers of caprolactam with γ -methyl- ϵ -caprolactam or ϵ -methyl- ϵ -caprolactam and a mixture of C-methylcaprolactams. The induction period increases with increasing content of C-methyl- ϵ -caprolactam units and the prolongation is almost exclusively due to the depression of the melting temperature.

Activated anionic polymerization of ϵ -caprolactam enabled the study of crystallization of thermal-history free polycaprolactam, *i.e.* a polymer which is formed immediately from the monomer in the form of an undercooled amorphous melt^{1,2}. It followed from a study of the side reactions of the catalytic system, that a number of substances are formed in the polymerizing system, some of which may form non-crystallizable units incorporated into polymer molecules, or they may form cross-links between macromolecules³.

In order to verify separately the influence of non-crystallizable units on the crystallization of polycaprolactam without thermal history we studied the induction period of crystallization of copolymerization products of ϵ -caprolactam with C-methyl- ϵ -caprolactam in which the substituted lactam molecules incorporated into the polymer represent the non-crystallizable units.

EXPERIMENTAL

ϵ -Caprolactam⁴, γ -methyl- ϵ -caprolactam⁵, ϵ -methyl- ϵ -caprolactam⁶, and the mixture of C-methyl- ϵ -caprolactam isomers were distilled immediately before polymerization. C-Methylcaprolactam isomer mixtures were obtained by purifying the technical mixture⁷; their composition (Table I) was determined by gas-chromatography⁸. Polymerization was carried out in the same apparatus and with the same amounts of substances as described elsewhere¹; sodium ϵ -caprolactam was used for initiation, the activator was N,N,N',N'-tetraacetylhexamethylenediamine. The induction periods were determined by a procedure described earlier¹.

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Characterization of polymers. The polymers and copolymers were characterized by intrinsic viscosity in tricresol⁹. In agreement with the literature⁹ it was found that for selected copolymers the Huggins' constant has the same value as in the case of polycaprolactam. The degree of polymerization of polycaprolactam samples was calculated from the relation¹⁰ $P = 102[\eta]^{1.34}$. The melting points of the polymerizates were determined by means of a microscope with heated stage (Boetius) at a heating rate of 1 to 2°C/min (precision $\pm 1^\circ\text{C}$).

RESULTS AND DISCUSSION

Induction Period and Undercooling

The prolongation of the induction period of copolymerizates was expressed as an equivalent decrease of the degree of undercooling W with respect to a reference ϵ -caprolactam polymer of the same molecular weight, prepared with 0.10 mol % of sodium ϵ -caprolactam and 0.05 mol % of N,N,N',N'-tetraacetylhexamethylenediamine. The term polymerizate is used for the equilibrium mixture of a polymer with the corresponding monomer and oligomers. Similarly, the term copolymerizate will be used.

The dependence of the induction periods of reference polymerizates (τ_r , min) on the degree of polymerization (P_r) and temperature (T_r) is expressed as follows (Eq. (6), ref.¹)

$$\log \tau_r = a - b \log (T_m^0 - T_r) + c \log P_r, \quad (1)$$

where $a = 10.67$, $b = 8.45$, and $c = 1.33$ (Table II, ref.¹). The equilibrium melting temperature $T_m^0 = 232^\circ\text{C}$ (ref.¹¹).

For the investigated copolymerizate with a degree of polymerization P , the induction period τ was found at the temperature T . Let us now calculate the temperature T_r at which the reference polymerizate having $P_r = P$ will crystallize with an induction period $\tau_r = \tau$. The difference between this calculated value T_r and the actual crystallization temperature T expresses the decrease of undercooling compared to the reference polymerizate, so that

$$W = T_r - T. \quad (2)$$

Inserting $\tau_r = \tau$ and $P_r = P$ there follows from Eqs (1) and (2)

$$W = T_m^0 - T - 10^{a/b} \tau^{-1/b} P^{c/b}. \quad (3)$$

Substituting $P = 102[\eta]^{1.34}$ (ref.¹⁰, $[\eta]$ is the intrinsic viscosity in tricresol, dl/g) and the mentioned values a , b , and c into (3) we obtain

$$W = T_m^0 - T - 37.84[\eta]^{0.210} \tau^{-0.118}. \quad (4)$$

It has to be mentioned that this manner of expressing the increase of the induction periods is only adequate if the crystallization temperatures lie within a narrow temperature interval.

Separation of the Effects Increasing the Induction Periods of Copolymerizates

The observed prolongation of induction periods of copolymerizates as compared to the induction periods of reference polymerizates is caused: a) by non-crystallizable C-methylactam units in the chain, b) by an increase of the low-molecular components, c) by an increase of the concentration of components of the catalytic system¹² (the concentrations of both components were increased with respect to the lower rate of polymerization of substituted lactams). To separate the individual influences, we assumed for simplicity that the contributions of the individual influences are additive and mutually independent. Under this assumption,

$$W = W_c + W_e + W_n, \quad (5)$$

where W_c is a contribution caused by the change of concentration of the catalytic system, W_e is a contribution corresponding to the increased content of low-molecular components, and W_n is a contribution corresponding to non-crystallizable units in the chain.

With regard to the increased concentration of the catalytic system, the value of $W_c = 1.1^\circ\text{C}$ was taken into account¹².

It would be very difficult to investigate the crystallization of polycaprolactam and its copolymers without thermal history and with different contents of the respective lactams. Therefore, values of W_e were calculated with the use of data obtained from the study of the influence of N-methyl- ϵ -caprolactam additions on the induction period of polycaprolactam crystallization¹. It was found that an increase of the content of N-methylcaprolactam by 1% (wt.) is equivalent to a decrease of the undercooling value by $0.70 \pm 0.07^\circ\text{C}$. This value is substantially lower than the decrease of the melting temperature of the polymer due to monomers and oligomers (1.74°C : mol%, ref.¹³). This difference may be explained by the compensation of the influence of the depression of the melting temperature and the decrease of the viscosity of the system caused by the diluent¹. Assuming that the influence of low-molecular components is the same as the influence of N-methylcaprolactam, there applies

$$W_e = 70(E - E^*), \quad (6)$$

where E and E^* is the weight portion of low-molecular substances in the equilibrium copolymerizate and polymerizate, resp., at the given crystallization temperature.

The composition of the amorphous copolymerizate at the given crystallization temperature was calculated on the basis of published equilibrium data^{4-6,13}.

We assumed that copolymerization equilibrium is achieved when the bath temperature and that of the polymerizing mixture are equilibrated. This assumption need not be satisfied, especially with ϵ -methylcaprolactam copolymers⁶. However, at the moment of equilibration of the above mentioned temperature, the actual content of extractable low-molecular substances may differ from the equilibrium content by a fraction of per cent only. We believed this difference to be unimportant to the evaluation.

There holds for the equilibrium caprolactam content in the copolymerization mixture (A) that^{6,13}

$$A = A_0 A^*, \quad (7)$$

where A_0 is the caprolactam content in the initial reaction mixture and A^* is the equilibrium caprolactam content for the polymerization of caprolactam at the given temperature⁴. There holds for the equilibrium concentration of γ -methylcaprolactam in the copolymerization mixture (B) that⁶

$$B = B_0 B^* / q_B; \quad (8)$$

the values of B^* having been calculated with the use of published data^{5,6}. For copolymers of γ -methylcaprolactam¹³ $q_B = 1$ and for copolymers of ϵ -methylcaprolactam⁶ $q_B = 1.12$. The molar concentrations of water-extractable low-molecular components E_A and E_B were calculated under the assumption that the fraction of oligomers in the extract is the same in copolymerization as in homopolymerization. Since the extract contains a mean of 76% monomer⁴ in the case of caprolactam polymerization, $E_A = 1.32A$. For γ -methylcaprolactam $E_B = 1.1B$, and for ϵ -methylcaprolactam $E_B = 1.5B$ (ref.¹⁵). The values of the weight portion of extractable substances E were calculated from E_A and E_B values (Table I).

The concentrations of substituted units U_B in the copolymer chain (Table I) were calculated from

$$U_B = (B_0 - E_B) / (1 - E_B - E_A). \quad (9)$$

For practical assessment of the influence of additions of a substituted monomer into the initial reaction mixture, values of $(W - W_c) / B_0$ are given in Table I. From the results it follows that the ϵ -methylcaprolactam addition slows down crystallization slightly more than the γ -methylcaprolactam or a mixture of methylactams.

Relations (4), (5) and (6) were used to calculate the values of W_n . These values were compared with the melting temperature depressions ($T_m^0 - T_m$) caused by non-crystallizable units in the polymer chain. From the known relation r^{14}

$$1/T_m - 1/T_m^0 = - (R/\Delta H_u) \ln (1 - U_B) \quad (10)$$

it follows, from $(T_m^0 - T_m) \ll T_m$

$$T_m^0 - T_m \approx -(T_m^0)^2 (R/\Delta H_u) \ln(1 - U_B). \quad (11)$$

Now we define

$$F = W_n/(T_m^0 - T_m) \quad (12)$$

calculating the value of $(T_m^0 - T_m)$ with the use of relation (11) after substituting values of T_m^0 and ΔH_u (ref.¹³) and U_B calculated from relation (9). From the definition it follows that $F = 1$ when the prolongation of the induction period due to the influence of non-crystallizable C-methylactam units in the chain is caused by a depression of the melting temperature only. In the series of the C-methylactam copolymers studied, the calculated values of F (Table I) are higher by up to 37% than 1. This difference may be caused by a number of approximations used in the above method of evaluation.

Correction for the Effect of Viscosity

In the calculation of the value of F , the fact was disregarded that at a temperature of $(T + W_n)$ the viscosity of the polymer is in general different from that of the copolymer at a temperature of T . Therefore, we have attempted to determine a correction for the influence of the viscosity change, although the above calculation can only be a rough approximation with respect to the present state of our knowledge.

Let us start from relation (4) in ref.¹

$$\tau = A\eta(T_m^0 - T)^{-b}, \quad (13)$$

expressing the local viscosity in the following form¹⁶,

$$\eta = f(P_w, P_n) \exp [4.12 \cdot 10^3/R(51.6 + T - T_g)], \quad (14)$$

T_g being the glass transition temperature. Let us assume that the function $f(P_w, P_n)$ in relation (14) is the same for the polymer and copolymer having equal intrinsic viscosity values. The glass transition temperatures of copolymers were calculated under the assumption that they are linear functions of their composition. In this case, the respective ratio of local viscosities Q may be expressed as follows:

$$Q = \exp \{ (4.12 \cdot 10^3/R) [(51.6 + T - T_g - \alpha U_B)^{-1} - (51.6 + T + W_n - T_g)^{-1}] \}. \quad (15)$$

The glass transition temperature of polycaprolactam² $T_g = 315$ K; the values of α were estimated on the basis of γ -relaxation processes¹⁷ (for γ -methylcaprolactam

copolymers $\alpha \approx -20$, for γ -methylcaprolactam copolymers⁶ $\alpha \approx +20$, where melting temperature for poly- ϵ -methylcaprolactam determined by the penetrometric method corresponds to the T_g value of this polymer). For comparison with the de-

TABLE I

Induction Periods (τ) of Copolymerization Products

The concentration of sodium ϵ -caprolactam was 0.30 mol %, the concentration of N,N,N',N'-tetraacetylhexamethylenediamine was 0.15 mol %; the time necessary for the equilibration of the bath temperature and that of the polymer was 13 minutes. T the crystallization temperature, B_0 the mol fraction of C-methyl- ϵ -caprolactam in the starting reaction mixture, $[\eta]$ the intrinsic viscosity in tricresol at 25°C, E the calculated weight fraction of the water-extractable compounds, U_B the mole fraction of C-methylcaprolactam units in polymer chains; for W , W_c , F , and F' see Eqs (4), (5), (12), (18).

T °C	B_0	$[\eta]$ dl/g	E	U_B	τ min	W °C	$(W - W_c)/B_0$ °C/mol	F	F'
γ -Methylcaprolactam									
190.0	0.096	1.80	0.080	0.080	36	14.0	134	1.15	0.97
190.0	0.136	1.72	0.088	0.114	196	19.3	134	1.12	0.98
195.0	0.065	1.92	0.077	0.054	37	8.7	116	1.00	0.86
200.0	0.056	1.77	0.079	0.046	168	8.7	136	1.21	1.07
200.0	0.063	1.68	0.080	0.051	156	8.8	123	1.08	0.95
<i>Mean value</i>							129	1.11	0.97
ϵ -Methylcaprolactam									
190.0	0.091	1.83	0.065	0.088	82	16.5	169	1.36	1.12
190.0	0.091	1.88	0.065	0.088	88	16.6	170	1.37	1.13
195.0	0.048	1.85	0.066	0.046	36	8.8	160	1.34	1.09
195.0	0.091	1.74	0.068	0.088	306	15.4	157	1.26	1.08
200.0	0.048	1.76	0.069	0.046	146	8.4	152	1.27	1.07
200.0	0.048	1.69	0.069	0.046	148	8.6	156	1.30	1.11
<i>Mean value</i>							161	1.32	1.10
Mixture of C-methylcaprolactams (7% α -, 57% (β - + δ -), 16% γ -, 20% ϵ -)									
195.0	0.083	1.80	—	—	104	12.3	136	—	—
200.0	0.044	1.82	—	—	72	6.1	115	—	—
Mixture of C-methylcaprolactams (3% α -, 76% (β - + δ -), 15% γ -, 6% ϵ -)									
195.0	0.089	1.83	—	—	111	12.4	128	—	—
200.0	0.046	1.82	—	—	75	6.2	111	—	—

pression of the melting temperature of the copolymer, the contribution of viscosity changes must be expressed in terms of the equivalent change of the degree of undercooling:

$$Q = \left[\frac{T_m^0 - T - W_n'}{T_m^0 - T - W_n} \right]^b \quad (16)$$

For the corrected value of W_n' we obtain

$$W_n' = T_m^0 - T - (T_m^0 - T - W_n) Q^{1/b}, \quad (17)$$

so that

$$F' = W_n' / (T_m^0 - T_m). \quad (18)$$

The calculated values of F' (Table I) are sufficiently close to 1. Therefore, if the correction for viscosity variations is justified, then the increase of the induction period of crystallization due to noncrystallizable C-methylcaprolactam units in the chain is caused by the melting temperature depression only. The differences in F' values for copolymerizates of γ -methylcaprolactam ($F' = 0.97$) and ϵ -methylcaprolactam ($F' = 1.10$) may be caused, besides approximation, by the fact that substitution in the immediate vicinity of the amide group will influence the crystallization more than substitution in the γ -position. This again agrees with results achieved by a study of the morphologic structure of copolymerizates^{1,8}.

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