Bulk Properties of Synthetic Polymer–Inorganic Salt Systems. II. Crystallization Kinetics of Salted Poly(caproamide)

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ABSTRACT: The kinetics of crystallization of mixtures of stabilized nylon 6 and LiCl or LiBr (composition range 0–4% w/w) was determined using dilatometric and optical microscopy techniques. The dilatometric technique, along with small-angle X-ray and calorimetric determinations, was also used in order to confirm the validity of previously reported data for the melting behavior of nylon 6–salt mixtures. Under the conditions adopted, good thermal stability of the mixtures was observed. The equilibrium melting temperature, determined using three independent techniques, is consistently depressed by increasing salt content, the effect of LiCl and LiBr being roughly the same. The determination of the degree of crystallinity is complicated by the coexistence of α and γ forms of nylon 6 when salt is present. When long crystallization times and appropriate supercoolings are adopted, the degree of crystallinity developed by the nylon 6–salt mixtures appears to approach the value observed for pure nylon 6. However, LiCl (and to a lesser extent LiBr) strongly reduces the rate of crystallization of nylon 6. The crystallization kinetics of the mixtures cannot be fitted to Avrami's equation. However, the essential morphological features of nylon 6 are not altered by the presence of salts. The specific volume of the nylon 6–LiCl mixtures above the melting temperature is considerably smaller than that expected on the basis of simple additivity of specific volumes of polymer and salt. The effect is indicative of strong intermolecular interactions occurring in the liquid state and is probably responsible for the reduction of crystallization rate and the increase of melt viscosity caused by LiCl.

We have recently shown[1] that a strong interaction between a synthetic polymer such as nylon 6 and inorganic salts such as LiCl and LiBr takes place in the absence of water or any conventional liquid diluent. This interaction is in some respects similar to that observed in aqueous solutions of biopolymers.

In the preceding paper[1] we reported the melting behavior of mixtures of nylon 6 with LiBr, LiCl, or KCl. The analysis was carried out through differential scanning calorimetry and was essentially directed toward the determination of the effect of salts on the equilibrium melting temperature, T_m, of the mixtures. Although a large depression of T_m due to addition of LiCl and LiBr was reported, the desirability of assessing the equilibrium melting behavior using alternative techniques was indicated. Preliminary data, previously obtained using differential scanning calorimetry,[1] also indicated a noticeable effect of LiBr and LiCl in reducing the rate of crystallization of nylon 6.

The present work is primarily directed toward a detailed determination of the effect of salts on the kinetics of crystallization of nylon 6, using dilatometric techniques. We have also obtained additional data for the equilibrium melting behavior using dilatometric, calorimetric, and small-angle X-ray techniques. As an improvement on our previous study,[1] we have used here stabilized nylon 6 to minimize complications due to thermal degradation.

Experimental Section

Materials. An unfractionated sample of nylon 6 (TiO_2 free) was used. The sample was monomer free and was stabilized with acetic acid. Its intrinsic viscosity in *m*-cresol at 25° was 1.37 dl/g (±0.01), corresponding to a molecular weight[2,3] of about 17,500. The sample was kindly supplied by Snia Viscosa. Salts used in this work were analytical grade LiBr and LiCl.

Polymer–salt mixtures were prepared by adding, in a glass tube, nylon 6 pellets to a salt solution in CH_3OH. The amount of the latter was adequate to wet the entire polymer and to give polymer samples containing 2 and 4% (w/w) of dry salt. Glass tubes were maintained at 50° for about 1 day to eliminate CH_3OH and then dried at 100° under vacuum for about 5 hr to remove last traces of solvent and any adsorbed water. All tubes were then allowed to stay at 260° (±1°) for about 5 hr while directly connected to a vacuum apparatus (10^{-3} mm). This procedure was designed to achieve fusion and optimum homogenization, as well as to remove any trace of monomer, or other volatile products, which could have upset the dilatometric measurement. (In our previous study[1] the polymer was not stabilized and the homogenization step was carried out at 260° in glass tubes sealed under vacuum. Moreover, the polymer was used as a powder obtained from a dissolution and reprecipitation step. The modification introduced in the present work proved to be mandatory in order to obtain reliable dilatometric data). The present thermal treatment was ended by subsequent cooling at room temperature. Samples were stored in a moisture-free atmosphere for lengths of time not exceeding a few days. Pure nylon 6 used was also subjected to the above indicated treatment. Four systems, thus prepared, have been used: pure nylon 6, nylon 6–2% LiCl, nylon 6–4% LiCl, nylon 6–4% LiBr (the nylon 6–KCl system was not investigated due to the poor compatibility of KCl and nylon 6[1]).

Viscosity Measurements. Viscosity measurements were carried out in *m*-cresol at 25°, as previously described,[1,4] using Ubbelhode-type viscometers. Efflux time of solvent was never less than 200 sec. Reduced specific viscosity *vs.* polymer concentration plots were accurately linear; the indetermination on the extrapolation of the intrinsic viscosity was never greater than ±1%.

Thermal Analysis. The determination of fusion temperature, T_f, and of fusion enthalpy, ΔH_f, using a differential scanning calorimeter was executed as previously described[1] (Perkin-Elmer instrument DSC-1B, heating rates of 16°/min). The thermal treatment used corresponds to the treatment indicated as no. 2 in the preceding paper: premelting in the DSC instrument at 260° for 12 min, crystallization at temperature T_c for a length of time t_c (between 3 and 180 min), recording of the melting profile upon increasing the temperature above T_c.

Small-Angle X-Ray Analysis. The large spacing of nylon 6 and nylon 6–salt mixtures was determined using a Kratky camera[5] provided with accessories permitting the intensity pattern to be measured with a proportional counter. Samples were here prepared in the form of thin plates having a smooth surface. The X-ray data (intensity *vs.* 2θ) were first corrected for air scattering and sample adsorption (an estimated background was subtracted), and then for collimation error. The long period p was derived using Bragg's law.

Dilatometric Analysis. Conventional Bekkedahl-type Pyrex dilatometers were used (capillary radius and length, respectively, 0.5 mm and 25 cm; angle between dilatometer bulb and measuring capillary ~80°). Polymer samples (about 1 g) were confined in the dilatometer, the entire apparatus was evacuated and then filled with purified Hg under vacuum. Weights of glass dilatometer and Hg were determined at room temperature. Temperature control (Lauda NBS-8 thermostats with Italglas U.T. 250W oil) was precise within ±0.05°. The determination of densities of samples was carried out at 25° using a conventional pycnometer filled with purified toluene under vacuum.

For the determination of the temperature dependence of the specific volume, dilatometers were first allowed to stay at 261° in an oil bath for 30 min and then maintained in a second oil bath

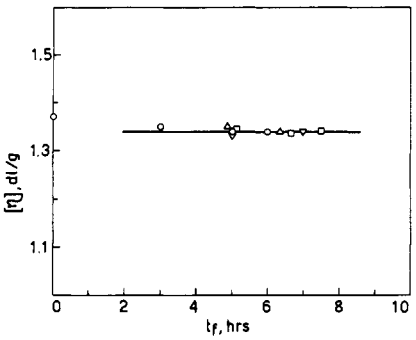

Figure 1. Intrinsic viscosity at 25° as a function of fusion time at 260° for pure (stabilized) nylon 6 and nylon 6-salt mixtures: (○) pure nylon 6; (□) nylon 6-2% LiCl; (▽) nylon 6-4% LiCl; (△) nylon 6-4% LiBr.

at a relatively high crystallization temperature for about 15 days in order to develop a large degree of crystallinity (T_c used: 210° for pure nylon 6; 199° for 2% LiCl and 4% LiBr mixtures; 182° for the nylon 6-4% LiCl mixture). Bath temperature was then increased using a rate of heating of about 1°/24 hr in the range from T_c to about 20° above the melting point. Independent measurements were performed in the temperature range between 20 and 80° (heating rate of about 5°/24 hr) in order to determine the relevant thermal expansion coefficient of pure nylon 6.

For the determination of the kinetics of crystallization, the dilatometers were first equilibrated at 261° for 30 min and then transferred to a second oil bath maintained at temperature T_c. A fresh sample was used for each determination. Duplicate and triplicate measurements were performed in order to assess reproducibility. Under the conditions adopted (*cf.* also Materials) all dilatometric data were accurately reproducible.

Optical Microscopy. The analysis was carried out with a Reichert Zetopan polarizing microscope equipped with a Mettler FP52 hot-stage controlled to ±0.3° (Mettler FP5 temperature control apparatus). Photographs were taken on Ilford FP4 films, using a Reichert Remica III camera, associated to a microphotographic system Reichert Kam-ES for exposure control. Magnifications of up to 400X were used.

Dry sample chips, mounted between cleaned microscope slides, were melted for 15 min at 261° in the hot stage. Crystallization was carried out by rapidly cooling the sample maintained in the hot stage from 261° to the appropriate crystallization temperature; zero time of crystallization was assumed to be indicated by illumination of the temperature control light. Crystallization was carried out at 210.9, 212.0, and 214.0° for pure nylon 6; at 192.0, 194.1, and 197.1° for nylon 6-4% LiBr mixtures.

During isothermal crystallization, photographs were taken at different time intervals in order to determine radial growth rate of the spherulites and to observe morphological structure of the specimens.

Results

Sample Characterization. The intrinsic viscosity in *m*-cresol of pure nylon 6 and of nylon 6-salt mixtures is plotted in Figure 1 as a function of the fusion time t_f. For all samples investigated, $[\eta]$ is 1.34 dl/g (±0.01), corresponding to a molecular weight[2,3] of about 17,000. The initial increase of intrinsic viscosity with t_f, which was observed in our previous work,[1] is absent in the present instance due to the stabilization of the sample which prevents postpolymerization of unreacted ends.

It is also noteworthy that the presently investigated samples contained no low molecular weight volatile products (eliminated during the fusion step). In fact, no weight loss (apart from that due to the salt) was observed after extraction of the mixtures with hot water.

Melting Temperature. Using the DSC data the equilibrium melting temperature, T_m, was determined, according to Hoffman and Weeks,[6] from the intercept of the experimentally determined T_f *vs.* T_c line with the $T_f = T_c$ line.[1] Occurrence of multiple peaks was similar to that previously reported; the low-temperature peak,[1] T_f^b, is the one which corresponds to the fusion temperature of crystals formed at the relevant T_c. Other characteristics of DSC data were also similar to those already described.[1] Least-squares T_m values obtained for the present samples are reported in Table I.

Table I
DSC Data for (Stabilized) Nylon 6 and Nylon 6-Salt Systems

Sample	T_c (°C)	T_f (°C)	T_m (°C)
Pure nylon 6	185	212	240 (±2°)
	188	214	
	192	216	
	195	218	
	198	219	
	202	221	
	205	222	
	209	224	
Nylon 6 + 2% LiCl	170	202	225
	173	202	
	176	203	
	180	205	
	183	206	
	185	208	
	187	209	
	190	210	
	195	212	
Nylon 6 + 4% LiCl	150	193	206
	160	195	
	165	197	
	170	198	
Nylon 6 + 4% LiBr	175	202	225
	180	204	
	185	206	
	188	208	
	190	209	

Detailed X-ray data are collected in Table II. For the determination of the thickness of crystalline lamellae, l, the following formula was used[7]

$$l = Xp/[(\rho_c/\rho_a)(1 - X) + X] \quad (1)$$

where X is the degree of crystallinity, and ρ_a and ρ_c are the densities of amorphous and crystalline phases, respectively. ρ_a was determined using the specific volume *vs.* temperature plot determined dilatometrically. For ρ_c, a value of 1.23 g/cm^3 was taken[8] for pure nylon 6 (corresponding to the crystal density of pure α nylon 6) and a value of 1.21 g/cm^3 was taken for nylon 6-salt mixtures. The latter value is an average of the densities of pure α and pure γ nylon 6 which have been shown to coexist when salt is present.[1] The density of pure γ nylon 6, in line with a recent discussion by Illers *et al.*,[9] was taken equal to 1.19 g/cm^3 (small alterations of the ratio ρ_c/ρ_a (*cf. seq.*) had no significant effect on l). The value of X used in conjunction with eq 1 was determined from the ratio of the fusion enthalpy ΔH_f, determined in the DSC apparatus, and the enthalpy of fusion of pure crystalline nylon 6 which, according to several authors,[10] is equal to 45 cal/g. Assumption of the latter value implies the neglect of any salt effect, and equal values of melting enthalpies of α and γ nylon 6. The latter assumption appears in contrast with recent conclusions by Illers *et al.*[9,11] who suggested values of 55-64, and 51 cal per g for the melting enthalpy of pure α and pure γ nylon 6, respectively. However, it was found that while the above refinements could substantially affect the value of the degree of crystallinity, the absolute value of T_m, calculated according to eq 2 (*cf. seq.*), was not greatly affected (±5°).

The determination of the melting temperature was performed using the Thompson[12] relation

Table II
Small-Angle X-Ray Data for (Stabilized) Nylon 6 and Nylon 6–Salt Systems

T_c (°C)[a]	T_f (°C)	p (Å)	ΔH_f (cal/g)	X	l (Å)	T_m (°C)	$\sigma_e/\Delta H$ (cm)
			Pure nylon 6				
180	211	113	15.6	0.346	37.2		
190	216	126	16.2	0.359	43.1	246 (±5°)	2.66×10^{-8}
200	220	130	18.0	0.399	49.5		
210	224	138	20.0	0.444	58.7		
			Nylon 6 + 2% LiCl				
180	205	113	14.0	0.311	33.9		
190	210	123	14.4	0.319	37.8	220	1.02×10^{-8}
200	213	232	14.0	0.311	69.5		
			Nylon 6 + 4% LiCl				
160	<195>	140	9.1	0.202	27.2	202	0.50×10^{-8}
170	198	210	11.6	0.257	52.1		
			Nylon 6 + 4% LiBR				
170	201	126	12.5	0.277	33.6		
180	204	142	13.0	0.288	39.4	225	1.80×10^{-8}
190	209	170	13.0	0.288	47.2		

[a] t_c is 48 hr; except for nylon 6 T_c = 210°, nylon 6 + 2% LiCl T_c = 200°, nylon 6 + 4% LiCl T_c = 170° when t_c is 96 hr.

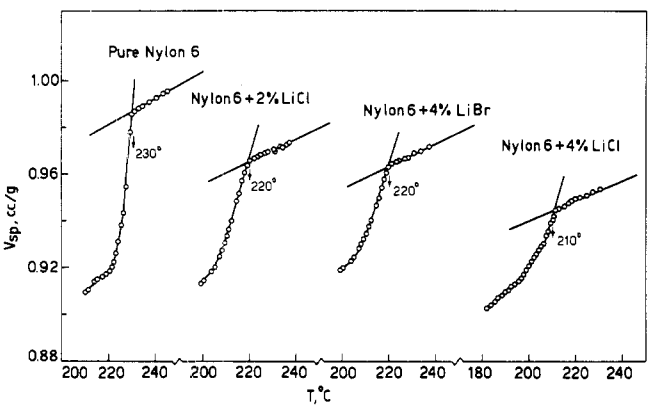

Figure 2. Variation of the specific volume with temperature for (stabilized) nylon 6 and nylon 6–salt mixtures. Heating rate 1°/24 hr. T_m is indicated.

$$T_f = T_m[1 - (2\sigma_e/\Delta Hl)] \quad (2)$$

where ΔH is the heat of fusion per unit volume of crystalline polymer and σ_e the fold surface free energy of the crystalline lamella. Plots of T_f *vs.* $1/l$ were linear. Results for T_m and $\sigma_e/\Delta H$ are collected in Table II.

Dilatometric data are reported in Figure 2. On increasing salt content the melting point is depressed, the specific volume of the liquid is decreased, and the transition appears to be less sharp. T_m values determined are collected in Table III along with a summary of melting point data using DSC and X-ray measurements.

Degree of Crystallinity. This section describes the determination of the degree of crystallinity using dilatometric data. From the data of the variation of the specific volume with temperature (*i.e.*, Figure 2), the degree of crystallinity X_T can be calculated, at any given temperature T, as the ratio $\Delta V_{sp}/\Delta V_{sp}{}^{tot}$. ΔV_{sp} is the difference between the specific volume of the liquid, $V_{sp}{}^a$, and that of semicrystalline material V_{sp}; while $\Delta V_{sp}{}^{tot}$ is the difference between the specific volume of the liquid and that of the completely crystalline material $V_{sp}{}^c$. The extrapolation of $V_{sp}{}^a$ and $V_{sp}{}^c$ at the relevant temperature T was performed using the specific volume and thermal expansion coefficients collected in Table IV. Included in Table IV are the results for the degree of crystallinity calculated for a supercooling of 20°.

The values of $V_{sp}{}^a$ and $dV_{sp}{}^a/dT$ were directly obtained using data such as those reported in Figure 2. For the determination of $V_{sp}{}^c$ for the nylon 6–salt mixtures, we have assumed (on the basis of our preceding results[1]) a 50% α–50% γ composition in the case of nylon 6–4% LiBr; a 70% α–30% γ composition for nylon 6–2% LiCl; and 70% γ–30% α composition in the case of nylon 6–4% LiCl. Accordingly, the $V_{sp}{}^c$ data listed in Table IV reflect the corresponding averages of the specific volumes of pure α (0.8130 cm³/g) and pure γ (0.8403 cm³/g) nylon 6.[9,11] For the thermal expansion coefficient of the pure crystalline (α or γ) phases we have taken the value of 2.41×10^{-4}°C^{-1} which was experimentally determined for our samples of pure nylon 6 below T_g. The latter value is in satisfactory agreement with the value 2.69×10^{-4}°C^{-1}, reported by Inoue.[13] The assumption of equal thermal expansion coefficients for both α and γ nylon 6 is probably incorrect. However, the calculated degree of crystallinity was not largely affected by reasonable alterations of the expansion coefficient. The largest source of error on the reported value of X arises from the relatively large density difference of pure α and pure γ nylon 6. The indicated limit of uncertainty (±10%) on X results by allowing a variation of ±20% α on the compositions used for calculating the values of $V_{sp}{}^c$ listed in Table IV.

Table III
Summary of Equilibrium Melting Temperatures T_m for (Stabilized) Nylon 6–Salt Systems

Salt				
w/w	Molar Fraction	DSC Anal.	Small-Angle Anal.	Dilatometric Anal.
0	0.000	240 (±2°)	246 (±5°)	230 (±1°)
2% LiCl	0.052	225	220	220
4% LiCl	0.100	206	202	210
4% LiBr	0.052	225	225	220

Kinetics of Crystallization. The isothermal crystallization of samples at different temperatures T_c is illustrated in Figure 3 (although kinetics were followed up to a maximum crystallization time of about 8000 min, only the earlier, more interesting portion is reported here for convenience).

The quantity in ordinate, ΔV_{sp}, was derived from the difference between the height of the Hg meniscus, h_0, measured in the dilatometer at the temperature T_c before onset of crystallization (liquid state) and the corresponding height, h_t, measured as a function of time at the same T_c. Occurrence of a rather large induction time before onset of crystallization allowed a reliable determination of h_0. ΔV_{sp} increases with crystallization time, and the rate of increase generally increases on lowering T_c.

Table IV
Specific Volume, Coefficient of Thermal Expansion, and Degree of Crystallinity of (Stabilized) Nylon 6–Salt Systems

Sample	V_{sp}^a (240°), cm³ g⁻¹	dV_{sp}^a/dT, cm³ g⁻¹ °C⁻¹	V_{sp}^c (25°), cm³ g⁻¹	dV_{sp}^c/dT, cm³ g⁻¹ °C⁻¹	X % ΔT = 20
Pure nylon 6	0.9925	5.57×10^{-4}	0.8130	1.95×10^{-4}	52
Nylon 6 + 2% LiCl	0.9750	4.78×10^{-4}	0.8212	1.97×10^{-4}	43 ± 10
Nylon 6 + 4% LiCl	0.9570	4.22×10^{-4}	0.8321	1.99×10^{-4}	39 ± 10
Nylon 6 + 4% LiBr	0.9730	4.93×10^{-4}	0.8267	1.98×10^{-4}	38 ± 10

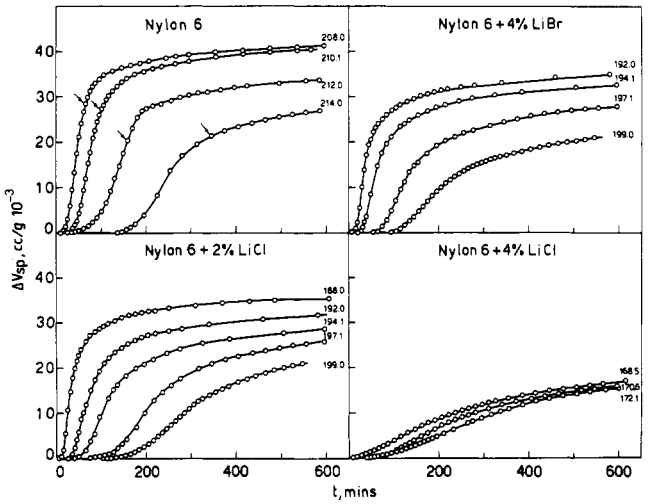

Figure 3. Isothermal variation of ΔV_{sp} with time for (stabilized) nylon 6 and nylon 6–salt mixtures at the indicated crystallization temperatures. Samples were premelted at 261° for 30 min.

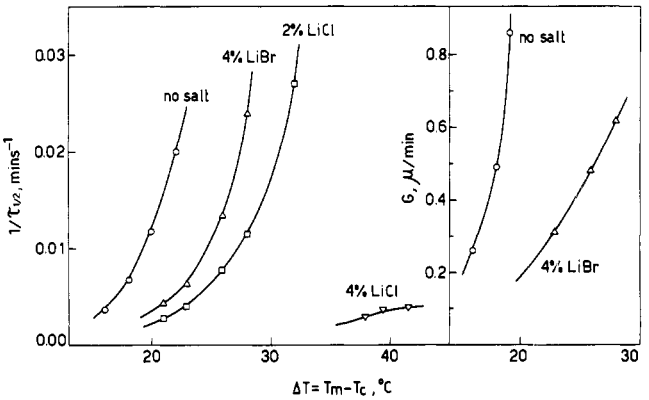

Figure 4. Reciprocal half-time of crystallization and radial growth rate G as a function of the difference between the equilibrium melting temperature and the crystallization temperature for (stabilized) nylon 6 and nylon 6–salt mixtures. Half-time was calculated with the reference to a total time of isothermal crystallization at T_c of 1400 min.

The reciprocal half-time of crystallization (reciprocal of the time necessary to reach half the value of ΔV_{sp} observed at 1400 min) is plotted in Figure 4 as a function of $\Delta T = T_m - T_c$ (T_m determined dilatometrically) in order to compare the rate of crystallization of different samples at the same degree of supercooling (for the sample containing 4% LiCl a higher degree of supercooling was necessary due to the slow rate of crystallization).

The isothermal crystallization data were also analyzed in terms of the well known Avrami equation[14-16]

$$\theta = (h_t - h_\infty)/(h_0 - h_\infty) = \exp(-kt^n) \qquad (3)$$

where h_t and h_0 have been defined above, θ is the weight fraction of unconverted liquid polymer, k a rate constant, n the Avrami exponent, and h_∞ is the height of the Hg meniscus at the end of the "primary" crystallization process. The latter was determined, according to Banks *et al.*,[17] by adjusting h_∞ until values of n, calculated from the differentiated Avrami equation, remain constant for the maximum range of time. The determination of our best h_∞ value was executed with a computer. Plots of log ($-\log \theta$) *vs.* log t for pure nylon 6 and nylon 6–salt mixtures are reported in Figure 5. Only in the case of pure nylon 6 was it possible to determine h_∞ values allowing representation of the significant part of the $h_0 - h_t$ *vs.* time curve (*cf.* Figure 3) in terms of Avrami equation. n values obtained are included in Figure 5. (We have indicated with an arrow in Figure 3 the time corresponding to the end of "primary" stage of crystallization thus defined.) In the case of nylon 6–salt mixtures, however, no h_∞ values yielding a constant value of n could be determined, casting serious doubt about the separability of "primary" and "secondary" crystallization stages. Data included in Figure 5 for nylon 6–salt mixtures have been obtained by arbitrarily assuming for h_∞ the height corresponding to 1400 min.

The optical microscopy data indicated that the crystallization of pure and salted nylon 6 is characterized by an initial induction period followed by the appearance of small birefrangent sheaf-like arrangements. Some of these arrangements grew into larger spherulites,[18] others increased in size but always showed a sheaf-like habit. No particular effect of the salt on the essential morphological features was detected. It was also observed that in the temperature range investigated, the number of spherulites and sheaf-like entities increased with time, indicating sporadic nucleation. For all systems investigated the spherulite radius increased linearly with time. The slope of this linear plot corresponds to the spherulite radial growth rate G. G data are included in Figure 4 as a function of supercooling ΔT. The presence of LiBr reduces the growth rate of nylon 6; the behavior may be compared to that observed in terms of the dilatometric results plotted in Figure 4, which correspond to the overall crystallization rate.

Discussion

Considering the values of intrinsic viscosity, 1.37 and 1.34 dl per g of the original nylon 6 sample (before any thermal treatment) and of the nylon 6–salt mixtures, respectively, it appears that under the experimental conditions adopted very little degradation took place. The invariance of molecular weight with fusion time and salt content is particularly useful for simplifying the analysis of kinetic results, as difference in molecular weight could cause different rates of crystallization. Moreover, the absence of low molecular weight degradation products removes a possible source of uncertainty in the thermodynamic melting temperatures. This is a significant advantage with respect to the experiments previously reported,[1] when some degradative effects were observed.

The comparison of the results for the thermodynamic melting temperature (*cf.* Table III) reveals a reasonable agreement among the data obtained using three independent approaches. According to theory,[6] T_m values ob-

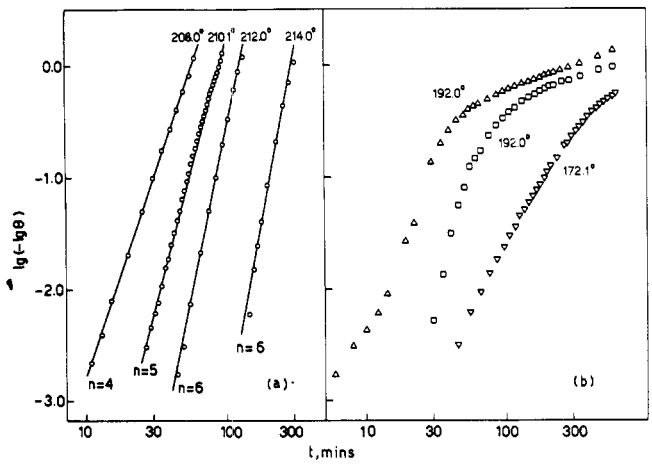

Figure 5. Avrami plots (*cf.* eq 3) for (stabilized) nylon 6 (a) and nylon 6–salt mixtures (b): (Δ) nylon 6–4% LiBr; (□) nylon 6–2% LiCl; (▽) nylon 6–4% LiCl. Crystallization temperature and Avrami exponents are indicated.

tained by extrapolating DSC and X-ray data represent the melting temperature of an ideal perfect crystal, while T_m obtained by dilatometry represents the melting temperature of the better real crystal formed during a slow (but not infinitively slow) heating process. The average depression of T_m due to the addition of 4% w/w of LiCl appears to be in order of 30°. This figure is somewhat smaller than the value (~50°) previously reported using unstabilized nylon 6. Part of the difference may be attributed to the occurrence of some degradation products in the samples previously used. However, it is clear that a significant part of the scatter between the results obtained using DSC, X-ray, and dilatometric analysis may be attributed to intrinsic indetermination of the various methods. In particular, the small-angle data are affected by the difficulty of an exact evaluation of l. A possible error of ±25% in the value of l does not seem to alter the occurrence of a linear relationship between T_f and $1/l$, confirming the existence of a structural periodicity which depends on crystallization condition. Moreover, the extrapolated values of T_m were not utterly sensitive to the indetermination on l. However, the latter indetermination significantly affected the $\sigma_e/\Delta H$ value derived from the plot of Thompson's equation. This fact prevents the attachment of more than a semiquantitative value to the $\sigma_e/\Delta H$ results.

In terms of the conventional melting point depression theory[19] the melting point depression due to the addition of a 4% diluent should be in order of 5°. The present results definitively confirm that LiCl and LiBr are able to cause a melting point depression which is significantly larger than expected in terms of the above theory. Moreover, when LiCl and LiBr are compared at the same molar fraction, the effects of the two salts appear to be about the same. A discussion of possible mechanisms for nylon 6–salt interaction was presented in our preceding paper.[1] The strong binding of salt to polymer in the amorphous state suggests that the bound polymer species may, in some respect, be regarded as a "copolymer." However, we believe that during the crystallization process salt may "unbind" from sites involved in the formation of a crystalline region.

The data reported in Table IV suggest than when suitable conditions are applied, *i.e.*, long crystallization time (15 days) and appropriate supercoolings, a large degree of crystallization can develop in nylon 6 irrespective of salt type and content. The main source of uncertainty in the determination of the degree of crystallinity of the nylon 6–salt mixtures derives from coexistence of α and γ forms, and the difficulty of determining the α–γ composition using the X-ray patterns of unoriented films.[1] Clearly, the method of determination of the degree of crystallinity based on the specific volume analysis is more accurate than the calorimetric method due to the indetermination of the melting enthalpies of pure α and pure γ nylon 6 reported in the literature.[9] Moreover, conceivable heat effect associated with salt binding with the amorphous polymer add additional doubts on the calorimetric determination of the degree of crystallinity.

A most interesting feature revealed by the data in Table IV and Figure 2 is the decrease of specific volume of the liquid mixtures on increasing salt concentration. Since the specific volume of the salt is smaller than that of the polymer, one can calculate the expected specific volume of the mixtures, assuming simple additivity. The International Critical Tables report that the temperature variations of the density of liquid LiCl and LiBr follow the equations $d = 1.762 - 0.000432T$, and $d = 2.930 - 0.000700T$, respectively. Using these equations, one can calculate that at 240° the presence of LiBr accounts for the entire contraction of specific volume in going from pure nylon 6 to the 4% LiBr mixture. However, in the case of the 2 and 4% LiCl mixtures, the additivity rule accounts for only about 50% of the contraction of specific volume observed. Since the total contraction of specific volumes in going from pure nylon 6 to the 2 and 4% LiCl mixtures is about 1.7 and 3.5%, respectively, about 0.8 and 1.6% contraction seems to result from strong intermolecular interactions occurring in the liquid state for the nylon 6–LiCl mixtures. This observation is qualitatively in line with the increase of melt viscosity of nylon 6 caused by LiCl which was preliminarily reported in our preceding communication,[1] but is in contrast with the absence of a large effect of salts on the glass transition temperature T_g, which was also observed in preliminary results.[20] We note, however, that the expansion coefficient of nylon 6 is decreased by addition of LiCl, apparently reducing the difference in the free volumes of nylon 6 and nylon 6–LiCl mixtures at temperatures near T_g. The problem shall receive more detailed consideration following completion of a current investigation of melt viscosity and T_g of nylon 6–salt mixtures.

Considering now the crystallization kinetics, we observe that, as shown by Turska and Gogolewski,[21] the thermal treatment we have used (melting for 30 min at 261°) is adequate for destroying the crystalline memory of nylon 6. The data reported (*cf.* Figure 4) indicate that crystallization rate (at a given supercooling) decreases in the order: pure nylon 6 > nylon 6–LiBr > nylon 6–LiCl, even when data at the same molar fraction of salt are considered. Thus, while LiCl and LiBr have about the same effect on the depression of T_m, the former salt has a larger effect on the reduction of crystallization rate.

The results of the application of Avrami equation to pure nylon 6 are in satisfactory agreement with results reported by other investigators[13,18,21] for samples of comparable molecular weight. On the other hand, deviations from Avrami treatment, such as those observed here for the nylon 6–salt mixtures, are not surprising. In fact, fractional and nonconstant n values, and general limitations of Avrami equation, have often been reported and discussed.[22-25] Several causes of deviations have been suggested,[23,25] particularly with respect to the nature and time dependence of nucleation and growth processes, which may be more complex than assumed in Avrami's simple treatment of the overall crystallization process.

The general equations[26,27] controlling both the nucleation and the growth processes have the form (written for

the steady rate of spherulite radial growth G)

$$\log G = \log G_0 - (\Delta F^*/2.3RT) - (\Delta\phi/2.3RT) \quad (4)$$

which includes a "transport" term causing an increase of G with increasing T at low temperature (ΔF^* is the free energy of activation of interfacial jump rate), and a "thermodynamic" term. When the rate-determining step in the growth process is the formation of a two-dimensional surface nucleus (as may be the case with nylon 6[18]), the thermodynamic term may be written in the form[27]

$$\Delta\phi/RT = 4b_0\sigma\sigma_e T_m^2/R\Delta HT^2\Delta T \quad (5)$$

which includes the monolayer thickness of the surface nucleus b_0 (4.2 Å[18]), the lateral surface free energy σ, the end (folded) surface free energy σ_e (appearing also in eq 2), and the supercooling ΔT (accounting for the decrease of G with increasing temperature toward T_m). Although our limited G data were not obtained in view of a detailed analysis of eq 4, we have attempted an evaluation of the slopes of a $\log G + \Delta H^*/2.3RT$ *vs.* $T_m^2/T^2\Delta T$ plot, as suggested by Hoffman and Weeks.[27] The values obtained, 56.1 and 46.3°K in the case of pure nylon 6 and nylon 6 + 4% LiBr, respectively, appear to suggest that the reduction of crystallization rate due to the salt is not determined by the thermodynamic term appearing in eq 4. The trend of the $\sigma_e/\Delta H$ data reported in Table II seems to add support to the latter conclusion. This conclusion must be taken with caution in view of the experimental imprecision of the surface energy terms determined from eq 2 and 4. Moreover, Hoffman *et al.*[28] have called attention to the possibility that surface energies determined from thermodynamic data may be different from those determined from kinetic results (*cf.* also Roe *et al.*[29]). However, if indeed salts cause a decrease of the surface free energy of nylon 6, the observed reduction of crystallization rate may well be controlled by the transport term. In fact, Hoffman and Weeks[27] have equated the activation free energy ΔF^* appearing in eq 4 with the free energy of activation for viscous flow ΔF_η^*. The above indicated salt effects on the contraction of specific volume, and on the increase of melt viscosity of nylon 6,[1] would then qualitatively justify the corresponding decrease of crystallization rates.

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