aggregation of the complexes through hydrophobic interaction. Primary complexes are dispersed in the solution because of their cationic atmosphere immediately after reaction, but they are gradually rich in hydrophobicity in accordance with the progress of the reformation of intra-complex, and then because of moving equilibrium of electrostatic repulsion with hydrophobic attraction the complexes aggregate gradually and regularly to a fibrous structure. Such aggregation is influenced by many factors, for example, the structure of the component polyelectrolytes (chain length, hydrophobicity, rigidity, and so on) and the complexation conditions (solvent, ionic strength, temperature, etc.).

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Bulk Properties of Synthetic Polymer–Inorganic Salt Systems. IV. Role of the Polymeric Substrate

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ABSTRACT: The equilibrium melting behavior and the kinetics of crystallization of mixtures of a synthetic polymer with LiCl (composition range 0–10 w/w) were determined using differential scanning calorimetry. Polymers investigated were: nylon 4, nylon 6, nylon 66, nylon 11, poly(ethylene terephthalate) (PET), polyoxymethylene (POM), polyethylene (PE). Preparation of the mixtures was achieved by several methods, including polymerization in the presence of the salt. The choice of the most efficient method for mixing the two components is a crytical one when polymer–salt compatibility is poor. On increasing the number of CH_2 groups per polymer unit in the nylon series, the melting point depression due to LiCl decreases. The depression is almost a negligible one in the case of nylon 11 which is able to dissolve only about 1% LiCl. Simultaneously with the decrease of the melting temperature depression, an effect of LiCl in reducing crystallization rate is observed. In the case of PET, no melting point depression due to LiCl is observed, and the salt has a noticeable effect in increasing crystallization rate. Upon further decreasing the polarity of the chain, the effect of LiCl on increasing crystallization rate decreases until, for PE, all salt effects vanish. In a case in which the decomposition temperature of the polymer was close to its melting temperature, LiCl was able to depress the latter without affecting the former.

We have recently reported the effect of inorganic salts on the melting behavior[1] and on the crystallization kinetics[2] of nylon 6 in the absence of water or any conventional liquid diluent. It was shown that some salts, notably LiCl and LiBr, can intimately mix with nylon 6 causing a large reduction of the thermodynamic melting temperature and of the crystallization rate of the pure polymer. Other salts, notably KCl, are incompatible with nylon 6 and are unable to affect its melting temperature. The ranking of various salts for their ability to interact with undiluted nylon 6 is similar to the order of various ions for interacting with biopolymers in the presence of water.[3–5] A general mechanism for direct interaction (i.e., binding[6]) between ions such as Li^+ or Br^- and polar groups of the disordered polymer seems to be involved.[1–6]

In addition to the interest connected with the detailed mechanism of salt interaction, undiluted polymer–salt mixtures have now attracted attention for the possibility that they offer to control some processing parameters such as processing temperature, melt viscosity, and rate of crystallization.[7–10] Use of salt additives may, in principle, be advantageous for processing high melting or thermally unstable polymers.[8–10]

Although the effect of various salts for a given polymer substrate (nylon 6) was adequately investigated,[1,2,7] much less is known concerning the effect of a given salt on different polymers. In this work we analyze the melting and the crystallization behavior of several polymers mostly in the presence of LiCl. The purpose is that of establishing how the compatibility of LiCl is affected by an alteration of number and type of polar groups along the polymer chain. Polymers investigated include members of the nylon series: poly(pyrrolidone), poly(ϵ-caprolactam), poly(hexamethylene adipamide), and poly(ω-aminoundecanoic acid) (nylon 4, nylon 6, nylon 66, nylon 11) where the ratio of methylene to amide group can be analyzed, and polymers such as poly(ethylene terephthalate), polyoxymethylene, and, also, polyethylene.

Preliminary attempts to investigate the above systems revealed that the occurrence of polymer–salt interaction is dependent upon the manner in which the polymer–salt mixture is formed. Accordingly, the efficiency of various mixing processes, including direct polymerization in the presence of LiCl, was considered in detail.

Experimental Section

Materials. Preparation of Polymer–Salt Mixtures. Nylon 4. Sample Ny4, TiO_2 free, was kindly supplied by the ALRAC Corp.,

Table I
Characteristics of Polymer–Salt Mixtures Investigated

Sample	Salt: w/w	Molar fraction	$[\eta]$, dl/g	Technique for preparing salt mixtures
Ny4			2.30	Solution (control)
Ny4-3	LiCl 3%	0.058	2.34	Solution
Ny4-4	LiCl 4%	0.077	2.34	Solution
Ny4-5	LiCl 5%	0.096	2.30	Solution
Ny4-8	LiCl 8%	0.149	2.30	Solution
Ny4-10	LiCl 10%	0.182	2.30	Solution
Ny4-6(Ca)	$CaCl_2$ 6%	0.047	2.30	Solution
Ny4-8(Ca)	$CaCl_2$ 8%	0.063	2.30	Solution
Ny4-10(Ca)	$CaCl_2$ 10%	0.079	2.30	Solution
Ny6A			1.50	Polymerization
Ny6A-2	LiCl 2%	0.052	1.50	Polymerization
Ny6B			1.10	Solution (control)
Ny6B-2	LiCl 2%	0.052	1.10	Solution
Ny6B-4	LiCl 4%	0.100	1.10	Solution
Ny66			0.86	Fusion (control)
Ny66-1	LiCl 1%	0.051	0.48	Fusion
Ny66-2	LiCl 2%	0.098	0.47	Fusion
Ny11A			0.95	Polymerization
Ny11A-1	LiCl 1%	0.042	0.68	Polymerization
Ny11A-2	LiCl 2%	0.081	0.47	Polymerization
Ny11B			1.24	Dispersion (control)
Ny11B			1.48	Fusion (control)
Ny11B-1	LiCl 1%	0.042	1.24	Dispersion
Ny11B-1	LiCl 1%	0.042	0.98	Fusion
PET			0.65	Dispersion (control)
PET 0.5	LiCl 0.5%	0.019	0.65	Dispersion
PET 1	LiCl 1%	0.037	0.65	Dispersion
PET 2	LiCl 2%	0.072	0.65	Dispersion
PET 2	LiCl 2%	0.072		Fusion
PET 4	LiCl 4%	0.136	0.65	Dispersion
POM				Dispersion (control)
POM 2	LiCl 2%	0.021		Dispersion
PE				Dispersion (control)
PE 2	LiCl 2%	0.013		Dispersion

Stamford, Conn. Its intrinsic viscosity in a methyl alcohol solution containing 20% LiCl at 40°C was 2.35 dl/g. In hexafluoro-2-propanol at 25° an inherent viscosity of 1.3–1.5 (0.5% polymer) was reported by the producer.[11]

For the preparation of nylon 4–salt mixtures, a concentrated solution of the polymer in 85% HCOOH containing a controlled amount of LiCl or $CaCl_2$ was prepared. The solvent was allowed to evaporate until a solid film was formed. Last traces of HCOOH were eliminated maintaining the films under vacuum at 100° for 2 days. Polymer–salt mixtures containing up to 10% LiCl or $CaCl_2$ were prepared. The intrinsic viscosity of the mixtures was essentially the same as that of the original polymer.

Nylon 6. Sample Ny6A (unstabilized) was obtained by anionic polymerization of caprolactam in bulk at low temperature, as described in more detail elsewhere.[9,10] Polymerization was carried out in the absence of LiCl (sample Ny6A) and in the presence of 2% LiCl (sample Ny6A-2). Intrinsic viscosity at 25° in *m*-cresol for both samples was 1.5 dl/g corresponding to a molecular weight[12,13] (mol wt) of ~20000.

Sample Ny6B is the same SNIA VISCOSA stabilized sample used in our previous work.[2] It was used here for the preparation of nylon 6–LiCl mixtures (Ny6B-2,4) using a solution technique (in previous work[2] nylon 6–salt mixtures were prepared by mixing the two undiluted components at a temperature above the melting point of pure nylon 6). A concentrated solution of the polymer in 85% HCOOH containing a controlled amount of LiCl was prepared. Solvent was then removed by evaporation at 80°. Films obtained were completely dried out under vacuum at 80° for 4 days. Intrinsic viscosity in *m*-cresol at 25° following HCOOH evaporation was 1.1 dl/g (mol wt ≃ 12000) for pure Ny6B (control) and its salt mixtures.

Nylon 66. Sample Ny66 was an unfractionated stabilized polymer (TiO_2 free) supplied by SNIA VISCOSA. Its intrinsic viscosity in *m*-cresol at 25° was 1.08 dl/g corresponding to a molecular weight[14] of ~25000. Polymer–LiCl mixtures were prepared following the same fusion technique previously used[2] for nylon 6 with the difference that the homogenization temperature was 285°, and the homogenization time was 2 hr. (higher temperature, or longer time, would result in a too extensive degradation of the polymer[15]). Following the thermal treatment, the intrinsic viscosity of the pure nylon 66 (control) sample was 0.86 dl/g (mol wt ≃ 18500), and that of nylon 66 containing 1% LiCl (sample Ny66-1) was 0.48 dl/g (mol wt ≃ 9000).

Nylon 11. Sample Ny11A (unstabilized) was obtained by hydrolytic polymerization[16] of 11-aminoundecanoic acid at 215° under vacuum (10^{-1}–10^{-2} mm) for 3 hr. Intrinsic viscosity in *m*-cresol at 25° was 0.95 dl/g. Polymerization was also carried out in the presence of LiCl. The monomer was wetted with a LiCl solution in CH_3OH which was then removed by evaporation at 80°. LiCl was soluble in the monomer at 215° at a concentration of 1% but was insoluble in the case of the 2% mixture. Intrinsic viscosity of sample Ny11A-1 (containing 1% LiCl) in *m*-cresol at 25° was 0.68 dl/g.

Sample Ny11B was an unstabilized polymer supplied by SNIA VISCOSA having an intrinsic viscosity in *m*-cresol at 25° of 1.24 dl/g. This sample was used for the preparation of mixtures (Ny11B-1) containing 1% LiCl either by using a simple dispersion technique (similar to that described in detail below for PET) or a fusion technique similar to that previously used[2] for nylon 6. In the latter case, the pure (control) polymer and the salt mixtures were maintained in a glass tube sealed under vacuum at 226° for 5 hr. Intrinsic viscosity following the thermal treatment was 1.48 dl/g for sample Ny11B and 0.98 dl/g for sample Ny11B-1. No alteration of intrinsic viscosity was observed when the dispersion technique was used.

Poly(ethylene terephthalate). Sample PET (TiO_2 free) was supplied by SNIA VISCOSA. The polymer was supplied in the unrefined powder form, and had an intrinsic viscosity in a 60:40 phenol–tetrachloroethane solution at 20° of 0.65 dl/g, corresponding[17] to a molecular weight of 19000. Polymer mixtures containing up to 4% LiCl were prepared using the following dispersion technique. LiCl was homogeneously dispersed into the polymer by adding a solution of salt in CH_3OH to the polyester powder as to wet the entire polymer. Samples were allowed to stay at 50° for about 24 hr to remove CH_3OH and then dried at 100° under vacuum for about 5 hr. The (control) pure polymer was treated with CH_3OH containing no salt. The intrinsic viscosity of the mixtures thus prepared was equal to that of the original polymer.

The salt mixture containing 2% LiCl (PET-2) was alternatively prepared according to a fusion technique in a tube sealed under vacuum and maintained at 295° for 5 hr. Significant postpolymerization was observed under the latter conditions.

Polyoxymethylene. Sample POM is a Du Pont product (Delrin 900) having a molecular weight (determined by GPC) of about 96000. The preparation of the polymer–salt mixture containing 2% LiCl was performed following the same dispersion technique used in the case of PET.

Polyethylene. Sample PE is a Solvay high density polymer (Eltex A/1050) having a reported molecular weight of 13800 (GPC) and $M_w/M_n \simeq 8$. The preparation of a salt mixture containing 2% LiCl was performed using the same dispersion technique described above in the case of PET.

All data pertaining to the preparation of the polymer–salt mixtures used in this investigation are collected in Table I. Analytical grade LiCl and $CaCl_2$ (only used for nylon 4) were employed. Compositions are expressed on a weight basis (w/w) unless otherwise specified. Salt molar fractions are listed in Table I. Following the preparation of salt mixtures as indicated above, samples were stored at room temperature in a moisture-free atmosphere for lengths of time not exceeding a few days. Subsequent thermal treatments are described in the next section.

Viscosity Measurements. Viscosity measurements were carried out in the solvents and at the temperatures above indicated following the technique previously described.[1] Efflux time of solvent was never less than 200 sec. Linear plots of reduced specific viscosity vs. polymer concentration allowed an extrapolation of the intrinsic viscosity with an indetermination never greater than ±1%.

Thermal Analysis. A Perkin-Elmer differential scanning calorimeter Model 1-B was used to determine both the melting and the crystallization kinetics behavior of the polymer–salt mixtures.[1,2] The equilibrium melting temperatures T_m were generally determined, as previously described,[1,2] according to the method of Hoff-

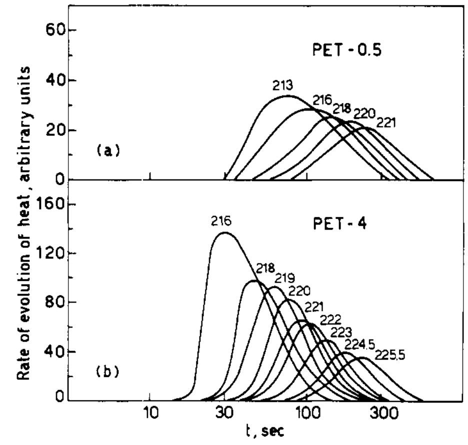

Figure 1. Typical DSC isotherms for poly(ethylene terephthalate)–LiCl systems: (a) 0.5% w/w LiCl; (b) 4% w/w LiCl. Isothermal crystallization temperatures T_c are indicated.

Table II
Effect of Storage Time t_c at the Crystallization Temperature T_c (Melting Behavior of PET + 4% LiCl)

T_c, °C	t_c, min	T_f, °C
225	10	250.0
	30	251.5
	180	252.0
235	15	252.0
	30	253.5
	75	254.5
	120	256.0
	240	257.0
240	90	256.0
	180	258.0
	300	259.0

man and Weeks.[18] Samples were premelted in the calorimeter at 226° for nylon 11; 285° for nylon 66; 260° for nylon 6; 290° for PET; 200° for POM; 170° for PE, for a length of time of 10 min (PET, POM, PE, nylon 66) or 12 min (nylon 11, nylon 6). Samples were then quickly cooled by manual operation of the instrument to a crystallization temperature T_c, at which they were kept for a length of time t_c adequate to assure a reliable determination of the fusion temperature, T_f. Typical data for the effect of the permanence at the crystallization temperature are illustrated in Table II. t_c was generally between 1 and 8 hr unless otherwise specified. The fusion profile was registered using heating rates[1] of 32°/min (16°/min only in the case of nylon 4). The fusion temperature and the fusion enthalpy ΔH_f were determined from the position and area of the endothermal peak of fusion.[1] No premelting was generally done in the case of nylon 4 and nylon 6 mixtures prepared using the polymerization or the solution technique. In the latter cases, annealing at a temperature T_a, for a length of time t_a, was sometimes performed.

For the determination of the kinetics of crystallization, the calorimeter was used to register the isothermal rate of evolution of heat as a function of time at the crystallization temperature T_c. Before determination of crystallization isotherms, samples were premelted in the calorimeter (temperature and time as indicated above). Some PET samples were, however, premelted in a oven (same temperature and time as above), quenched to the glassy amorphous state in liquid nitrogen, dried, and finally placed in the DSC instrument set at the required annealing temperature T_a. A fresh sample of constant weight was used for each determination. Weights of sample of about 16 mg for PET, and of about 7 mg for the other polymers, were used. Illumination of the average temperature control light was used to indicate isothermal conditions.

DSC isotherms, such as illustrated in Figure 1, were processed by integration according to the equation

$$x_t = \int_0^t (\mathrm{d}H_t/\mathrm{d}t)\mathrm{d}t \Big/ \int_0^\infty (\mathrm{d}H_t/\mathrm{d}t)\mathrm{d}t \qquad (1)$$

where x_t is the weight fraction of converted (crystallized) material at time t. The parameter $t_{1/2}$, used to characterize the crystallization behavior, is the time necessary to obtain a conversion of 50%.

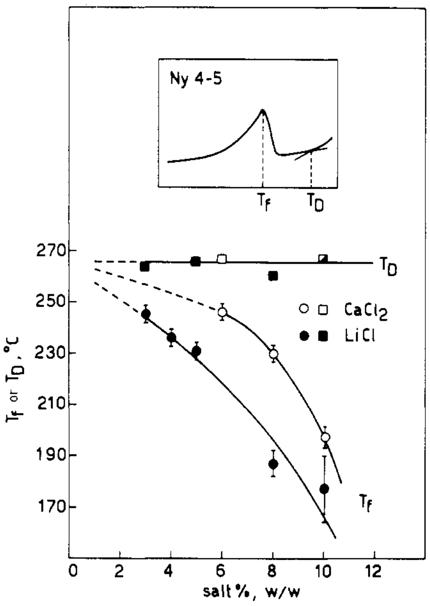

Figure 2. Variation of the fusion temperature (●, ○) and of the decomposition temperature (■, □) of nylon 4–salt systems with salt content. Black points, LiCl; open points, $CaCl_2$. Samples prepared using the solution method (cf. Table I) and annealing at T_a between 150 and 180°C.

The usefulness and the limitation of the DSC technique in obtaining crystallization parameters have been adequately discussed.[19-21] The fundamental advantage of the technique consists in requiring microsamples. Limitations of the method, which is less accurate than dilatometry, arise in errors in temperature settings. However, if crystallization is sufficiently rapid, kinetic isotherms can be satisfactorily and quantitatively determined.

Optical Microscopy. The analysis was performed using a Reichert Zetopan polarizing microscope as described before.[2] The spherulite radial growth rate $\dot{G}$ was determined from linear plots of spherulite radius vs. time.

Results

Nylon 4. A typical fusion profile for nylon 4 is illustrated in the insert of Figure 2. The decomposition temperature, T_D, was taken as the temperature at which the baseline, after the fusion peak, begins to show an upward swing due to degradation. The fusion temperature, T_f, was found not to be affected by variation of the annealing temperature T_a between 150 and 180°, for t_a up to 2 weeks. Higher values of T_a had to be avoided due to the occurrence of degradative effects which resulted in a decrease of T_f with T_a. Thus, an extrapolation of T_m using the Hoffman and Weeks approach could not be performed.

The variation of T_f and T_D with salt content is reported in Figure 2. It is seen that T_D is not affected by salt type and content, while T_f is considerably reduced by increasing salt content. On a weight basis, the effect of LiCl appears greater than that of $CaCl_2$. However, when salt molar fraction is considered, the efficiency of Ca^{2+} is greater than that of Li^+.

Nylon 6. The melting and the crystallization behavior of nylon 6–salt mixtures prepared using the fusion technique have already been thoroughly investigated.[1,2] For the scope of the present investigation, it was relevant to establish whether different methods for preparing the mixtures resulted in differences in physical properties. As discussed in more detail elsewhere,[10] when nylon 6 is polymerized in the presence of LiCl, the effect of the salt on the melting temperature is quite similar to the effect observed in the case of mixtures prepared using the fusion method. In particular, the direct fusion at the DSC instrument of samples

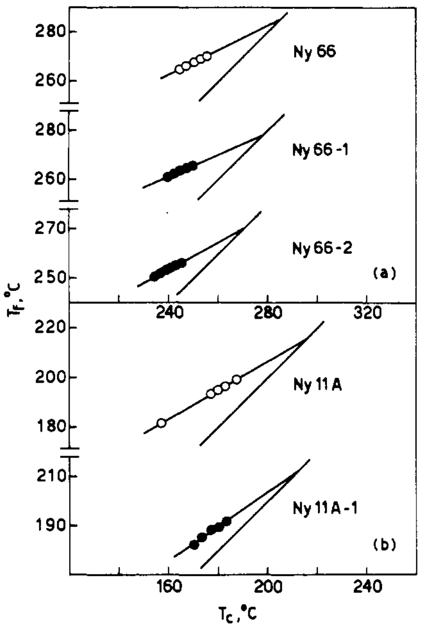

Figure 3. Variation of the fusion temperature with crystallization temperature for nylon 66–salt (a), and nylon 11–salt (b) systems. Open points, pure polymers; black points, LiCl mixtures.

Table III
Fusion Temperature Data for Nylon 6–Salt Mixtures (Solution Method)

Sample	Direct fusion	Annealing		Premelting	
	T_f, °C	T_a, °C[a]	T_f, °C	T_c, °C[a]	T_f, °C
Ny6B	212 (±2)	180	210	180	209
Ny6B-2	200	160	200	180	197
Ny6B-4	187	160	187	180	

[a] $t_a = t_c$ = 30 min.

Ny6A and Ny6A-2 yielded, respectively, T_f = 210° and T_f = 200°. The result is in line with previous data[1] obtained using the fusion method and $T_c \sim 180°$.

In the case of samples Ny6B, Ny6B-2, and Ny6B-4, prepared using the solution method, data for the fusion temperature are reported in Table III. The values of T_f observed in the case of direct fusion are about 20° lower that the corresponding thermodynamic temperatures which were determined in the case of samples prepared using the fusion method.[2] As observed in the case of nylon 4, annealing has no effect on T_f. The stability of crystals developed using the solution method corresponds to the stability observed when premelted nylon 6 is isothermally crystallized at $T_c \sim 180°$, as the data in Table III indicate.

The effect of salt on the depression of the fusion temperature of nylon 6 appears to be the same irrespective of the method used for preparing the mixtures.

Nylon 66. T_f was found to noticeably depend, at given T_c, upon t_c (lamellae thickening). Large t_c values (24–48 hr) had to be used in order to obtain reliable T_f values. Hoffman and Weeks plots of fusion temperature vs. crystallization temperature for nylon 66 are reported in Figure 3a. Least-squares T_m values obtained from these plots are collected in Table IV. The depression of T_m of pure nylon 66 due to the addition of 2% LiCl is in the order of 15°. A quite similar depression was observed[2] in the case of nylon 6 (cf. data shown for comparison in Table IV).

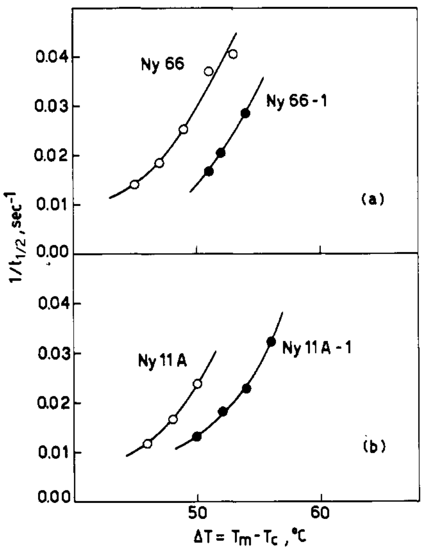

Figure 4. Reciprocal half-time of crystallization as a function of the difference between the equilibrium melting temperature T_m obtained from Figure 3 and the crystallization temperature T_c for nylon 66–salt (a) and nylon 11–salt systems. Open points, pure polymers; black points, LiCl mixtures.

Table IV
Equilibrium Melting Temperature T_m for Nylon 66–Salt and Nylon 11–Salt Systems

Sample	LiCl (w/w), %	T_m, °C
Ny66	0	285 (±2)
Ny66-1	1	278
Ny66-2	2	270
Ny11A	0	215 (±1)
Ny11A-1	1	213
Nylon 6[a]	0	240 (±2)
Nylon 6[a]	2	225
Nylon 6[a]	4	206

[a] Data (shown for comparison) from ref 2.

Crystallization kinetics was investigated at T_c = 232, 234, 236, 238, and 240° for pure nylon 66, and at T_c = 224, 226, 227° for the Ny66-1 sample. Results are reported in Figure 4a in terms of the reciprocal time $t_{1/2}$ necessary to obtain a conversion of 50% plotted vs. supercooling $\Delta T = T_m - T_c$. As in the case of nylon 6,[2] the presence of LiCl reduces the crystallization rate of nylon 66 (allowing for the decreased viscosity of sample Ny66-1 with respect to sample Ny66 an even greater difference in crystallization rates in the absence of degradation is expected).

Nylon 11. Results obtained with samples Ny11B and Ny11B-1, when the dispersion method for preparing the mixture was used, showed no difference between the fusion temperature of the two samples, and between the corresponding kinetic parameter $t_{1/2}$. Likewise, when the fusion method for preparing the mixture was adopted, no alteration on the T_f value was observed (216° for both Ny11B and Ny11B-1) and only a small increase of crystallization rate was noticed. In particular, $t_{1/2}$ values at T_c = 155° for samples Ny11B and Ny11B-1 were respectively 42 and 41 sec using the dispersion method, and 51 and 27 sec using the fusion method.

Attempts to explore the possibility that a LiCl effect could be revealed using the best possible mixing method resulted in the synthesis of samples Ny11A, Ny11A-1, and Ny11A-2. Evidence of insolubilized LiCl was obtained for sample Ny11A-2. Results obtained using the well solubilized 1% sample are reported in Figures 3b and 4b. Considering the attempts to improve the precision of T_m, least-square T_m values reported in Table IV indicate a small depression due to 1% LiCl, barely greater than the experimental indetermination.

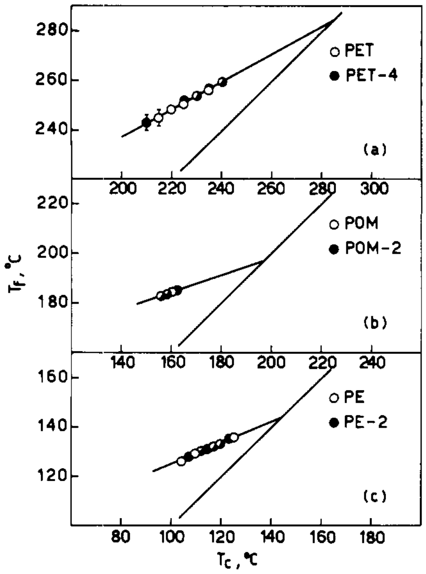

Figure 5. Variation of the fusion temperature with crystallization temperature for poly(ethylene terephthalate)–salt (a), polyoxymethylene–salt (b), and polyethylene–salt systems (c). Open points, pure polymers; black points, LiCl mixtures.

The kinetic data support the indication of some degree of interaction between LiCl and nylon 11. The rate of crystallization (T_c = 165, 167, 169° for Nyl1A, and 157, 159, 161, 163° for Nyl1A-1) is decreased by the addition of 1% LiCl. The effect reported in Figure 4b includes a contribution due to the reduction of molecular weight of sample Nyl1A-1 (cf. Table I).

Poly(ethylene terephthalate). Typical Hoffman and Weeks plots are reported in Figure 5a. It is seen that LiCl has no effect on the melting temperature of PET which is 284 ± 1°. The above results pertain to samples prepared using the simple dispersion method. A similar result was obtained for the sample prepared using the fusion method. Direct observation of molten sample PET-0.5 under the optical microscope revealed the occurrence of undissolved salt crystals.

Crystallization kinetics results are collected in Figure 6. Results obtained for the samples annealed at temperatures T_a are distinguished from the results obtained for samples crystallized directly from the melt at temperature T_c. In both cases, the crystallization rate of PET is increased by increasing the concentration of LiCl up to about 2%. Further increase of LiCl content has no effect on $t_{1/2}$. Owing to the occurrence of postpolymerization (cf. Experimental Section), sample PET-2 prepared using the fusion method was not used for obtaining crystallization data.

Polyoxymethylene. Direct observation of sample POM-2 under the optical microscope revealed the presence of undissolved LiCl in the molten state. (Against the possible contention that the simple dispersion method was not adequate to ensure proper mixing, we note that conditions for improved mixing existed during the premelting stage in the DSC apparatus due to the small size of the sample.) In any case, the Hoffman and Weeks plot for samples POM and POM-2 (Figure 5b) fails to reveal any effect of LiCl on the melting temperature which was found to be 197° for both samples.

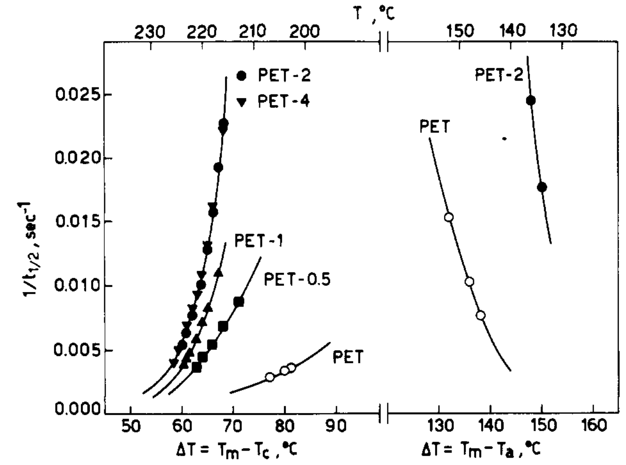

Figure 6. Reciprocal half-time of crystallization as a function of ΔT for poly(ethylene terephthalate)–salt systems. Open points, pure polymer; black points, LiCl mixtures. ΔT represents the difference $T_m - T_c$ for the curves on the left, and the difference $T_m - T_a$ for the two curves on the right. T_m (cf. Figure 5) is 284° in all cases.

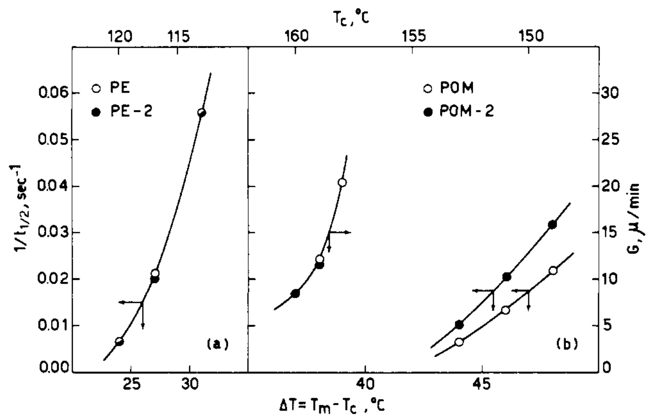

Figure 7. Reciprocal half-time of crystallization and radial growth rate as a function of the supercooling $T_m - T_c$ for polyethylene–salt (a) (T_m = 144°) and polyoxymethylene–salt (b) (T_m = 197°) systems. Open points, pure polymers; black points, LiCl mixtures.

Crystallization results are presented in Figure 7b. The data reveal a small increase of crystallization rate due to LiCl. The spherulite growth rate is not affected by the salt. This finding suggests that LiCl acts as an heterogeneous nucleating agent. The fusion enthalpy ΔH_f, determined at the end of the isothermal crystallization in DSC instrument, indicates that the degree of crystallinity of samples POM and POM-2 was roughly the same.

Polyethylene. The Hoffman and Weeks plot (Figure 5c) reveals no effect of LiCl on the melting temperature which is 144°. Undissolved salt was observed in the molten polymer.

Crystallization kinetics (Figure 7a) is also not affected by LiCl. ΔH_f at the end of the crystallization in the DSC instrument was the same for PE and PE-2.

Discussion

The depression of the melting temperature of pure nylons due to the addition of 5 mol % LiCl is reported in Figure 8 as a function of the number of CH_2 per repeating unit. Data are obtained from Table IV, taking average values for nylon 6 and nylon 66 on the basis of one amide group per residue. In the case of nylon 4, ΔT_m was evaluated from the initial linear region of the T_f vs. LiCl concentration plot taking $\Delta T_f \approx \Delta T_m$, a satisfactory approximation when fusion occurs within 20° from T_m. ΔT_m is seen to decrease when the polarity of the polymer, measured by the number of CH_2 per repeating unit, decreases. Simultaneously with the decrease of ΔT_m, the LiCl–polymer compatibility decreases. In fact, the solubility of LiCl in nylon 11 is so poor that only about 1% salt could be dissolved in

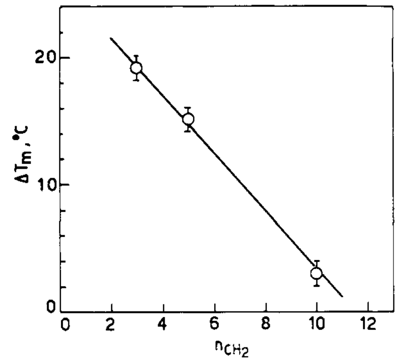

Figure 8. Difference between the melting temperature of pure polymer and the melting temperature of LiCl mixtures containing 0.05 salt molar fraction for nylon 4 (approximated), nylon 6 or nylon 66, nylon 11. In the abscissa is the number of CH_2 groups per repeating unit.

the polymer using the most efficient technique for preparing the mixtures. Comparison of the results obtained using different mixing methods for the members of the nylon family reveals that only in the case of low polymer–salt compatibility the depression of both T_m and $t_{1/2}$ is critically dependent upon the mixing technique. (For instance, three different mixing methods (fusion, solution, and polymerization) gave the same melting point depression in the case of nylon 6, while in the case of nylon 11 only by using the polymerization method could a small T_m depression be detected.)

The occurrence of a depression of T_m appears to be associated to a decrease of crystallization rate of the pure nylons. The correlation between the depression of T_m and $1/t_{1/2}$ can be made semiquantitative by estimating the effect of molecular weight alteration, due to partial degradation during the various mixing steps, on crystallization rate. Turska and Gogolewski[22] have determined the variation of crystallization rate with molecular weight in the case of nylon 6. Assuming that the reported dependence of $t_{1/2}$ vs. $[\eta]$ remains valid also for other members of the nylon series, we have estimated the contribution to $t_{1/2}$ of the alterations of intrinsic viscosity reported in Table I. For a supercooling of 50°, when the expected increase of crystallization rate due to the reduction of viscosity for samples Ny66 and Ny11A is added to the $t_{1/2}$ values actually reported in Figure 4, the crystallization rate of sample Ny66-1 is lower, by a factor of about 2, than for sample Ny11A-1. On a similar basis, the reported alterations of $t_{1/2}$ (cf. Results) for samples Ny11B and Ny11B-1, when no LiCl effect on T_m was observed, can be entirely attributed to the corresponding variations of intrinsic viscosities listed in Table I. Thus a reduction of the LiCl effect in depressing the melting temperature is paralleled by a reduction of the ability of the salt in decreasing the crystallization rate of pure nylons. The reduction of the latter, in cases in which strong polymer–salt interactions in the molten state[1–3] occur, may be attributed to a slow rate of unbinding,[2] and to the high melt viscosity[3] of the nylon–LiCl mixtures.

In the cases of PET, POM, and PE the absence of a LiCl solubility is evidenced by direct microscopic observations, and by the absence of a depression of T_m. The acceleration of the crystallization rate caused by the salt in the cases of PET and POM is also indicative of the lack of strong polymer–salt interactions. Since no alteration of intrinsic viscosity was generally observed with the particular mixing method adopted for these polymers, the increase of crystallization rate can unambiguously be related to an ability of undissolved LiCl to act as an heterogeneous nucleating agent. Comparison of data in Figures 6 and 7 clearly indicates that LiCl is a much more effective nucleating agent for PET than for POM. The extensive data obtained in the case of PET reveal that LiCl increases the crystallization rate both before and after the typical maximum occurring on the crystallization rate vs. supercooling curves.

Occurrence of a saturation at 2% LiCl (Figure 6) in the case of PET, lack of a salt effect on the rate of spherulite growth (Figure 7), and the microscopic observation of spherulites in the case of POM (greater in number and smaller in size when LiCl is present) are in line with established characteristics of heterogeneous nucleation.[23,24] Absence of a LiCl solubility is not, clearly, the only criterion on which the nucleating role of LiCl can be based. In fact, no accelerating effect was observed in the cases of Ny11B and PE. The efficiency of LiCl in promoting nucleation appears to be primarily related to the occurrence of a low crystallization rate for the pure polymer. Some residual (weak) polymer–salt interaction, or some specific surface characteristics of LiCl particles, must also be involved. (In fact, no nucleating effect was noticed for KCl.)

Some additional results of this investigation should be emphasized. The observation that LiCl is able to depress the melting point of nylon 4 without affecting its decomposition temperature may be used with advantage whenever the fusion and the melt properties of polar, high-melting polymers are investigated. Use of salt additives in these instances may be of particular interest in connection with polymer processing.[9] The good efficiency of mixing techniques such as the solution and the polymerization method (cf. nylon 6) is also of interest whenever premelting of the polymer has to be avoided. An additional advantage of the solution method is the possibility of obtaining, without specific thermal treatments, well stabilized high-melting crystals. Finally, the nucleating effect of salt additives may be of particular technological advantage in the case of slowly crystallizing polymers such as PET.

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