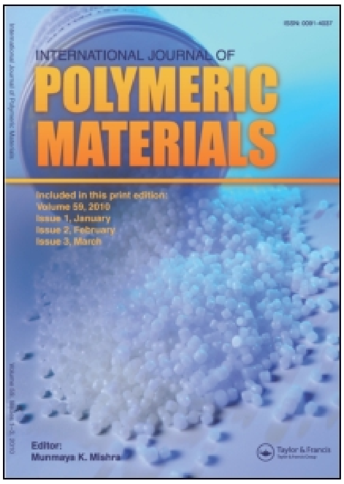

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Siegmann, A. and Baraam, Z.(1980) 'Nylon-6 Containing Metal Halides I: Melting and Crystallization', International Journal of Polymeric Materials, 8: 4, 243 — 253

To link to this Article: DOI: 10.1080/00914038008077952

URL: http://dx.doi.org/10.1080/00914038008077952

Intern. J. Polymeric Mater., 1980, Vol. 8, pp. 243–253
0091–4037/80/0804–0243 $06.50/0

Printed in Great Britain

Nylon-6 Containing Metal Halides I: Melting and Crystallization

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(*Received January 1, 1980*)

The melting and crystallization of nylon-6 containing copper chloride, copper bromide and iron chloride has been studied by differential scanning calorimetry. The incorporation of these metal halides results in a substantial melting temperature depression, above the expected in a polymer–diluent mixture, and a strong retardation of the crystallization rate. The strong binding, probably through a complex formation, between the salt and the polymer chain results in the formation of a copolymer structure differing in its properties from the pure polymer.

1. INTRODUCTION

We have recently reported the effect of copper chloride on the melting and crystallization of bulk nylon-6.[1] It was shown that $CuCl_2$ can be absorbed from aqueous solutions by nylon-6, resulting in a substantial suppression of the polymer melting temperature, above the expected in a polymer–diluent mixture, and a large reduction in the crystallization rate and final crystallinity of the pure polymer crystallized from a mixture in the molten state. Furthermore, the incorporation of $CuCl_2$ causes a large elevation of the glass transition temperature, Tg, compared to the one of the pure polymer.[2] The latter differ from systems in which low molecular weight additives either, when compatible, lower the Tg[3] or, when dispersed as a second phase, slightly affect the Tg (e.g., Ref. 4) of the polymer. It has been suggested that this behavior of nylon-6–$CuCl_2$ system results from a direct strong interaction, through the formation of a copolymer-like structure, between the salt ionic molecules and the polar groups of the disordered polymer chains.

Inorganic salts such as LiCl, LiBr, $MgCl_2$ and $CaCl_2$ were reported [5–8] to substantially suppress the melting temperature, Tm, of nylon-6, to markedly slow the crystallization rate, to lower the final degree of crystallinity and at high enough concentration of some of these salts to even prevent crystallization. Moreover, it has been reported that the Tg of nylon-6[8,9] and other polar polymers[10–13] is significantly affected by incorporation of inorganic salts such as mentioned above. Also, the melt viscosity of nylon-6 is considerably increased in the presence of such salts (e.g., Ref. 7). In addition, the specific volume of nylon-6–LiCl mixtures above the melting temperature is considerably lower than that expected on the basis of simple additivity.[14] This information indicates the existence of strong interaction between the polar nylon-6 and some inorganic salts, so called, salting-in agents.

Previously, polymer–salt mixtures were prepared by either mixing polymer and salt solutions followed by the solvent evaporation[7] or by keeping a dry mixture of the two at temperature above the polymer melting temperature, allowing diffusion of the salt into the polymer (e.g., Ref. 5). In the present study, to prevent such rough thermal history and to use a more practical approach, the salts were absorbed from solutions into the polymer bulk. $CuCl_2$, $CuBr_2$, $FeCl_3$ and KCl were chosen as the metal halides for several reasons: they are very active on stressed nylon-6;[15] they represent various valent metals and will enable to study the effect of the anion and cations on the nylon behavior.

The aim of this work is to study the effect of various metal halides on the melting and crystallization of nylon-6 and to better understanding of the activity of these halides in the nylon-6 system.

2. EXPERIMENTAL

Nylon-6, manufactured by Hochst, W. Germany, with a viscosity average molecular weight of 25000, was used in the present work. The polymer was used without any further treatments. Analytical grade $CuCl_2$, $CuBr_2$, $FeCl_3$ and KCl were used as the metal halides.

At first, approximately 80μ thick nylon-6 films were prepared by compression molding of the raw material, using a laboratory Carver press, at 225°C, followed by a fast cooling with tap water passing through the press hot plates.

To incorporate homogeneously the salts at different levels into these films, the latter were immersed in saturated salt aqueous solutions at 90°C, for various periods of time (in the order of hrs). Control film was immersed in pure water at the same temperature. The resulting films were homogeneous brown, reddish-brown and yellow for $CuCl_2$, $CuBr_2$ and $FeCl_3$, respectively. Films immersed in KCl did not absorb the salt in any appreciable amount.

The maximum amounts of $CuCl_2$, $CuBr_2$ and $FeCl_3$ absorbed by the nylon films, under the present conditions, were 12, 18 and 27 mole percent, respectively. This method of incorporating such salts into nylon films is similar to the one reported by Mehta and Andrews[9] although, they have used a variety of solution concentrations to obtain different amounts of absorbed salt. The absorption method was chosen, at first, to prevent thermal degradation of the polymer during the rough thermal history required for mixing in the melt[5] and, secondly, to use a more practical method than mixing polymer and salt solutions, precipitation out and evaporation of residual solvents.[7] In the present method, the salts are being absorbed mainly by the disordered polymer chains, thus a complete mixture is actually not obtained. However, even in films prepared from polymer containing salt mixed in the melt, during crystallization (as occurs upon cooling the crystallizable polymer from the melt) segregation takes place, resulting in a pure crystalline nylon and a disordered nylon-salt mixture.[5]

Amount of salt absorbed by the nylon film was determined by weighing the samples prior and after immersion. Prior to weighing, samples were dried under vacuum at 90°C for at least 5 hrs (until a constant weight was attained). Since nylon-6 easily absorbs moisture and its properties are very moisture sensitive, all specimens were always kept dry in a desiccator at room temperature until used. Moisture in the polymer, if present, could be detected by thermal analysis, as an evaporation endotherm.

A du Pont 990 differential scanning calorimeter (DSC) was employed for thermal analysis. All specimens, carefully kept in the 9–13 mg range, were heated from ambient temperature, at a rate of 10°C/min, up to a temperature just beyond the completion of the melting process; then, the heater was turned off allowing the DSC cell to cool at its natural rate of Ca. 10°C/min. This heating cycle enables to follow both the melting process of nylon films absorbed with an inorganic salt and the crystallization from the melt of nylon–salt systems. The DSC was calibrated using standard materials having melting points in the temperature range of interest. Reported melting and crystallization temperatures are those at the endotherm and exotherm peak tips, respectively. Degree of supercooling is reported as the temperature difference between the actual melting and the onset of the crystallization exotherm.

The effect of absorbed salt on the polymer degree of crystallinity, crystal structure and the mode of salt dispersion in the films were determined using wide angle x-ray diffraction. A Phillips generator, equipped with a CoK_α radiation source and an iron filter, was used. The degree of crystallinity was determined by graphic separation of crystalline and amorphous contributions, as has been worked out for nylon-6 by Roldan *et al.*[16]

3. RESULTS AND DISCUSSION

The melting temperature, as determined directly from DSC, decreases continuously with increasing salt content. In the concentration range studied here, the addition of 10, 7 and 11 volume percent of $CuBr_2$, $CuCl_2$ and $FeCl_3$ results in maximum melting temperatures depression of 40, 35 and 40°C, respectively. Additional $CuBr_2$ does not result in any further depression of Tm. It should be noticed that the plot of Tm as a function of salt content (see Figure 1) is linear as long as "saturation" is not attained. In this concentration range there is no significant difference between the effects of copper chloride and bromide on Tm of nylon-6. This is in variance with the difference in salt activity reported for lithium bromide and chloride in depressing Tm of nylon-6;[5] the latter being the more effective. On the other hand, copper halides are significantly more effective than the iron halide. It should be also noted that Tm of control films and of films immersed in KCl solution did not change more than ± 1°C. The latter has been reported also when KCl was incorporated into nylon-6 by mixing in the melt,[5] forming a dispersed second phase.

For better understanding the polymer–salt relations, the observed Tm depression is compared with that predicted by Flor's equation[17] for a polymer–diluent mixture, in which only one of the components crystallizes over the complete composition range:

$$\frac{1}{Tm}-\frac{1}{Tm^{\circ}}=\frac{R}{\Delta H_u}\frac{Vu}{Vi}(v_1-\chi_1 v_1^2) \tag{1}$$

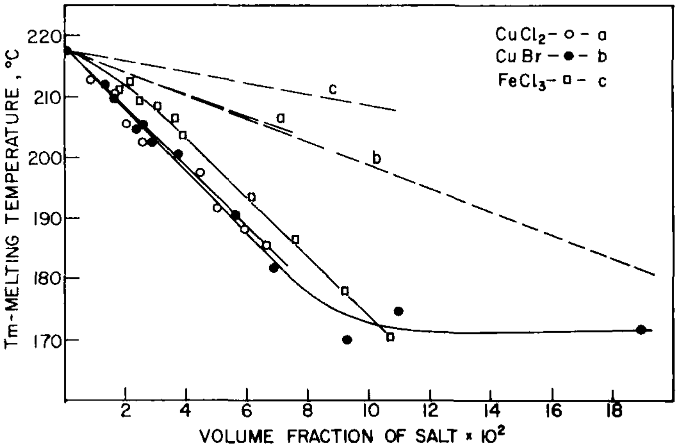

FIGURE 1 The dependence of nylon-6 melting temperature on salt concentration; measured values, ---- calculated according to Eq. 1.

Where, Tm° and Tm are the melting temperatures of pure and diluted polymer, respectively; Vu and Vi are the molar volumes of the repeating unit and diluent, respectively; ΔHu is the heat of fusion per mole of repeating unit, v_1 is the volume fraction of diluent and χ_1 is a polymer–diluent interaction parameter. This equation is plotted for the three types of polymer–salt systems in Figure 1, using a value of $\chi_1 = 0.2$ (a reasonable value for a "good" diluent[17]) and $\Delta Hu = 5100$ cal/mole.[18] It shows that the calculated values for $CuCl_2$ and $CuBr_2$ are very close and both are much lower than the values calculated for mixtures containing $FeCl_3$; this is qualitatively in good agreement with the experimental observations. However, the main observation in Figure 1 is the large difference between the calculated and measured values of Tm as a function of salt content; Eq (1) predicts a much smaller Tm depression than the measured values. Hence, the experimental data cannot be explained by this theory only, unless a high negative value of the interaction parameter is used. In other words, thermodynamic interactions between nylon-6 and metal halides, presented by χ_1, are not the only ones taking place in such systems; others have to be looked for.

Further depression of Tm will result if complexing between the salts and specific groups along the polymer chain could occur in the disordered regions. Therefore, an increase in the extent of complexing would shift the crystal–liquid equilibrium to lower temperatures. In such a case the melting point equation becomes the following:[19]

$$\frac{1}{Tm}-\frac{1}{Tm^\circ} = \frac{R}{\Delta Hu}\frac{Vu}{Vi}(v_1-\chi_1 v_1^2)+\frac{RNa}{\Delta Hu}\, ln(1+Ka_c) \qquad (2)$$

Where, Na is the number of reacting sites per repeat unit, K is a binding constant and a_c is the salt activity. The last term on the right in Eq. (2) represents the Tm depression, at a given composition, due to the polymer–salt complex formation. The free energy of binding, $\Delta F = NaRTln(1+Ka_c)$,[20] has been calculated in accordance with Eq. (2). Calculated values, using the experimental data presented in Figure 1, for the three nylon-6–salt systems, are summarized in Figure 2. The free energy of binding, so obtained, is linearly proportional to the salt concentration; above "saturation" ΔF levels off. Consequently, it appears that at salt contents lower than saturation, all salt molecules indeed form a complex with the polar groups along the nylon-6 chain in the disordered regions. Since the "saturation" concentration is much lower than predicted in accordance with stoichiometry, it is probably controlled by such factors as experimental procedures, polymer degree of crystallinity, diffusion processes, steric hindrances, etc. It should be also noted that the ΔF values show a considerable difference between the types of incorporated salts; $FeCl_3$ having the highest values and $CuCl_2$ the lowest

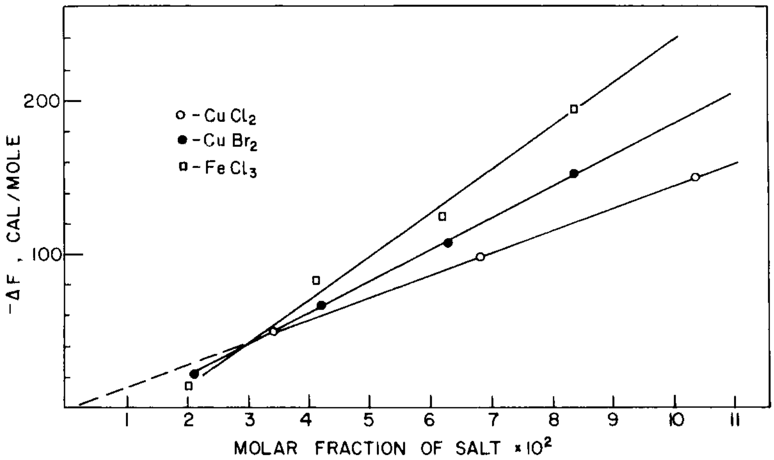

FIGURE 2 Free energy of binding in nylon-6–salt mixtures.

ones. Thus, the type of both anions and cations plays an important role in the binding process.

The x-ray diffraction patterns of nylon-6 films absorbed with the metal halides reveal the absence of any diffraction due to the incorporated salts. Hence, the salts studied here are not dispersed as a second phase in the polymer matrix, which is probably the system of KCl mixed with nylon-6 in the melt.[5] Also, the incorporation of these salts did not alter the typical nylon-6 diffraction pattern, which included the characteristic reflections of both the α and γ forms. In addition, there is no clear effect of these salts on the α to γ form ratio in the absorbed films. Thus, the salts do not diffuse into the crystalline lattice of the polymer and hence, enter mainly the disordered regions. Determination of the degree of crystallinity in films absorbed with $CuCl_2$ and $CuBr_2$ show some small changes with salt content; first an increase followed by a decrease with increasing salt concentration. However, in films absorbed with $FeCl_3$ the decrease is significant and the crystallinity drops by up to 20% upon the addition of 11 mole percent salt. It incidates that in the $FeCl_3$ case some kind of "melting" occurs. It should be noted here that the degree of crystallinity in pure nylon films, which have undergone the same history, is not changed.

Related to these findings are the DSC data, which show for all three systems that upon increasing salt concentration, in addition to the gradual *Tm* depression, the area of the melting endotherms is reduced. This observation should imply decreasing of either polymer crystallinity or apparent enthalpy of fusion. The former has been observed when the polymer crystallizes out of nylon–salt molten mixtures; crystallization is even prevented in the presence of high LiCl content (e.g., Ref. 8). However, in the present work, all films are semi-crystalline (Ca 50% crystallinity) to begin with, the maximum temperature they were treated at was 90°C (far below *Tm*) and in spite of it the x-ray diffraction patterns show a significant reduction in crystallinity in the nylon-6–$FeCl_3$ systems only. This inconsistency is beyond our present understanding. Nevertheless, one can speculate that saturated aqueous solution of $FeCl_3$ at 90°C (the absorption temperature) partially dissolves the crystalline polymer, followed by binding the salt molecules to these polymer chains and preventing them from recrystallization in the dry state. Hence, crystallinity as determined by both, x-ray diffraction and calorimetry is reduced compared to the pure nylon-6. In the presence of the other two salts, the polymer crystals are not affected by the salts solution however, early partial melting may occur upon heating the samples in the DSC cell. More of this pre-melting should occur with increasing salt content.

When the polymer–salt systems are heated above their melting, followed by cooling in the DSC cell, some crystallization kinetics information can be obtained. Figure 3 shows the dependence of the crystallization temperature, as determined from the exotherms observed upon cooling from the melt, on the salt content. It shows that the crystallization temperature, at an estimated cooling rate of 10°C/min, decreases markedly from 186°C for pure nylon-6 to 115, 120 and 130°C for nylon-6 containing 7, 10 and 13 volume percent of

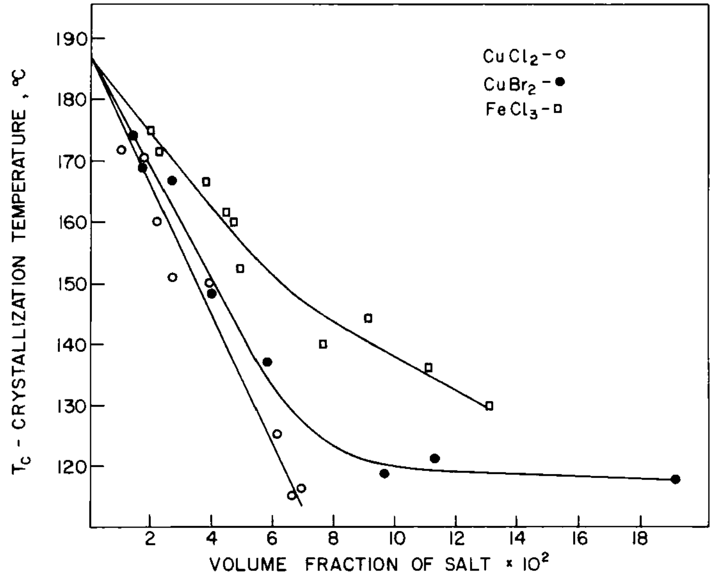

FIGURE 3 Crystallization temperature of nylon-6 as affected by salt concentration.

$CuCl_2$, $CuBr_2$ and $FeCl_3$, respectively. The supression of the crystallization temperature changes at first linearly with salt concentration and then, upon approaching the "saturation" composition mentioned above, levels off. The $CuCl_2$ is the most effective salt in supressing the crystallization temperature followed by $CuBr_2$ and $FeCl_3$. Secondly, the degree of supercooling, determined as the difference between the actual melting temperature of the polymer salt system and the onset temperature of the crystallization exotherm, is also affected by the added salt but to a lesser degree than the exotherm peak temperature. Figure 4 shows that the degree of supercooling, required for crystallization to occur at an estimated cooling rate of 10°C/min, increases from 25°C for pure nylon-6 to a maximum of 60, 40 and 40°C for nylon-6 containing 8, 7 and 6 volume percent of $CuCl_2$, $CuBr_2$ and $FeCl_3$, respectively. It is interesting to note that $CuCl_2$ continuously increases the degree of supercooling (in the studied concentration range) whereas the other two result in a maximum, followed by a gradual decrease; the maximum is attained at a relative low concentration.

The third characteristic of a crystallization process is the total heat evolved, which is expressed by the crystallization exotherm area. Figure 5 summarizes the relative exotherms area as affected by type and content of several metal halides. It shows that the relative area (taken as 100 for pure polymer) is substantially reduced by the incorporation of the salts, down to about 20% of that of the pure nylon-6, at concentration of about 11 volume percent of salt. Hence, there is probably a large reduction in crystallinity resulting of the presence of the salts. There is no significant difference between the effects of the various salts. Here also the phenomenon of "saturation" is observed.

The data presented above shows very clearly that the incorporation of such metal halides as $CuCl_2$, $CuBr_2$ and $FeCl_3$ into bulk nylon-6 affects both the crystallization kinetics of the polymer and its final degree of crystal-

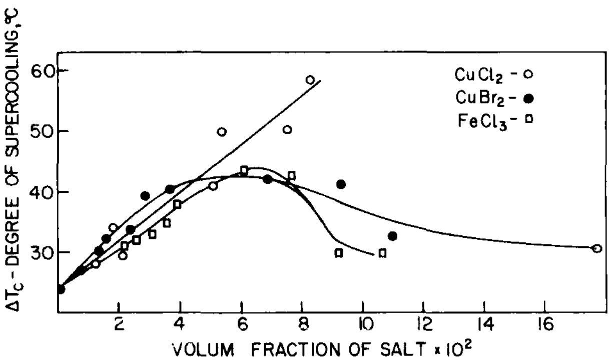

FIGURE 4 Degree of supercooling of nylon-6 as affected by salt concentration.

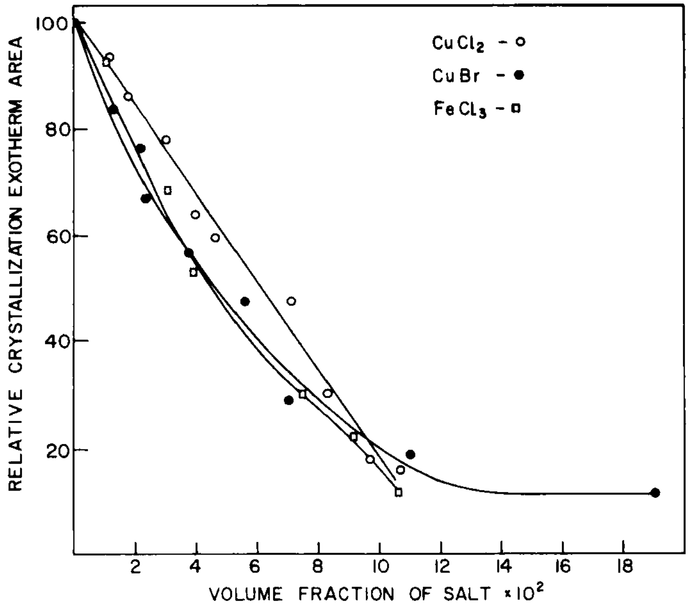

FIGURE 5 Relative crystallization exotherm area as affected by salt concentration.

linity. This effect resembles the crystallization hindrance reported in mixtures of nylon-6 and other halides (e.g., Refs. 8, 14). In nylon-6–LiCl mixtures the crystallization time had to be very prolonged and above a certain salt content no crystallization could even be detected. It should be mentioned that in regular polymer–diluent mixtures, in addition to the melting temperature depression, the supercooling is also lowered and an attenuation in the nucleation rate occurs, resulting in retardation of the overall rate of crystallization.[21]

The melting temperature depression and the crystallization retardation described above accompanied by the elevation of the glass transition temperature reported elsewhere,[2] strongly suggest the existence of high degree of binding between the metal halides and the nylon-6 chain. It is suggested that a copolymer-like structure is formed, consisting of pure nylon-6 segments and as a comonomer, segments with salt molecules bound to, similar to one of the description of ionomeric structure.[22] The possibility of some cross-linking of polymeric chains through salt molecules should not be excluded. The roll of the anions and cations in the formation of this bound structure and their effects on the properties of this new structure is not clear yet. Some of the properties seem to be affected by the type of salt and some do not.

The existence of this new structure is supported by several recent reports which describe the elevation of melt viscosity[6] and glass transition temperature[8] of nylon-6, upon the incorporation of various salts. It was also reported[7] that the density of the amide groups along the polymer chain determines the effectiveness of the salts in altering the polymer properties; the higher the density the larger the salt effects. Moreover, the glass transition of other polar polymers, such as poly(propylene oxide)[12,13] and poly(ethylene oxide),[23] is substantially affected by various complex forming salts. The existence of bound structure in polyamides has been shown by several authors, employing IR spectroscopy. However, even there, many inconsistencies still exist regarding the type of coordination complex formed and whether the nitrogen[15,24] or the oxygen[8,25] atoms of the amide groups is bound to the metal ion. In these works, no attention has been paid to the role of the anion.

The retardation in crystallization reported above may be due to either the marked increase in the viscosity of the mixture melt compared to that of pure nylon[14] and/or due to the formation of an irregular chain structure, only part of which can participate in the crystallization process; segments, with salt molecules attached to, remain in the disordered regions. It would be of great interest to study the effect of such salts on the morphology of such systems and the resulting mechanical properties. Such a preliminary study has been reported by Michailov *et al.*[26]

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