

Physical properties of anionic poly(ϵ -caprolactam) synthesized in the presence of calcium chloride

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Salt-added poly(ϵ -caprolactam) (PCL), prepared by activated anionic polymerization in the presence of varying amounts of calcium chloride, has been fully characterized in terms of physical and mechanical properties. X-ray diffraction, melting and density data show that the salt progressively reduces polymer crystallinity; starting from ~ 5.5 mol% of calcium chloride, the resulting polyamide is completely amorphous. The salt, completely dissolved and confined in the amorphous regions, interacts strongly with the amide groups of PCL chains. Ion-dipole interactions induce stiffening of complexed C-N bonds and physical crosslinking, thus causing densification of the amorphous phase and a sharp increase in T_g . All data, compared with those pertaining to PCL-LiCl systems, reveal, even in wet conditions, a greater interaction effectiveness of Ca^{2+} , which seems to be associated with its higher coordination capability.

(Keywords: anionic poly(ϵ -caprolactam); calcium chloride; mixture; physical properties)

INTRODUCTION

Our previous research on ion-containing aliphatic polyamides has been mainly devoted to the preparation and characterization of poly(ϵ -caprolactam) (PCL) synthesized by activated anionic polymerization of its monomer (CL) in the presence of lithium chloride¹⁻⁴.

We have found that the addition of small amounts of the above salt to the polymerizing system modifies and/or improves many bulk properties of the resulting polyamide, but negatively affects both the maximum monomer conversion and the rate of polymerization^{2,4}. Polymer properties that are greatly influenced include the increase of density, glass transition temperature, melt viscosity, Young's modulus, yield and tensile strength, as well as the decrease of melting temperature, degree of crystallinity and crystallization rate³.

It should be underlined that the above modifications of PCL properties are only present in samples tested in dry conditions; indeed, the high hygroscopic character of the PCL-LiCl system causes a significant moisture uptake in the usual environmental media, thus cancelling almost all the beneficial effects.

In order to overcome the negative role of lithium chloride on both the polymerization process and the water sorption of PCL, but on the other hand to retain the relevant improvements of the other polymer properties, several salts have been considered as potential additives to the polyamide via direct synthesis.

As previously reported⁵, after some preliminary tests on salt solubility and their role on polymerizability of CL, calcium chloride has been selected for a detailed study of its influence upon both the anionic polymerization of CL and the physical properties of salt-polymer mixtures. We have already shown that CaCl_2 does not greatly affect the free energy of polymerization and causes only a slight retardation of both the initial and the overall reaction rate⁵. Indeed, the presence of CaCl_2 in the polymerizing medium decreases the high polymer yield much less than does LiCl ^{2,5}.

In this paper we report on the physical and mechanical properties of the resulting PCL- CaCl_2 mixtures. The aim of this work is two-fold: (a) to prepare polymer mixtures with properties very similar to those of the PCL-LiCl system, but with a much stronger resistance to water sorption; (b) to obtain a better knowledge of the specific interactions between polymer and dissolved salt and to compare the effectiveness of Li^+ and Ca^{2+} ions in this respect.

EXPERIMENTAL

Materials

PCL- CaCl_2 mixtures were prepared by activated anionic polymerization of CL in an adiabatic reactor in the presence of varying amounts of ultra-dried calcium chloride. Polymerization procedures and apparatus were as previously described^{2,5}.

The as-polymerized material was finely ground under liquid nitrogen, demonomerized by thermal treatment at 110°C under vacuum for 72 h, and compression-moulded

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into 150 μm thick films in a Laboratory Carver Press at 170–200°C between poly(tetrafluoroethylene) sheets. Films were slowly cooled to room temperature and stored in a vacuum desiccator over anhydrous phosphorus pentoxide.

Mechanical properties were tested on both anhydrous samples, kept for six days in a vacuum desiccator over P₂O₅, and wet samples, conditioned at room temperature and 65% r.h. for the time necessary to reach constant weight. All other physical properties were tested only on anhydrous samples.

Extensive Soxhlet extractions by water (48 h) were performed for u.v. absorption measurements and comparative melting temperature data.

X-ray diffraction

Wide-angle X-ray diffraction (WAXD) measurements (Ni-filtered Cu K α radiation) were performed in a dry argon atmosphere, with a Tenno diffractometer. WAXD patterns were recorded on flat photographic films; the sample-to-film distance was 0.05 m.

Density

Density measurements were carried out using a carbon tetrachloride/n-heptane gradient density column at room temperature.

Transition temperatures

The glass transition (T_g) and melting (T_m) temperatures were measured with a Perkin–Elmer DSC-7 differential scanning calorimeter, at a heating rate of 20°C min⁻¹ in a dry nitrogen atmosphere. The shape of the d.s.c. curves around T_g varies in the presence of the salt and shows a more or less sharp endothermic peak. According to the criterion used in the previous work³, the temperature corresponding to the maximum was adopted as T_g . Analogously, T_m values were taken at the maximum of the melting peak.

Mechanical properties

The Young's modulus M was determined on thin strips (1.5 $\times 10^{-4}$ m thick, 2.5 $\times 10^{-3}$ m wide) of anhydrous and wet samples at room temperature. Measurements were performed with an Instron model 1122 tensile machine, operating at 5 $\times 10^{-2}$ m min⁻¹ crosshead speed with 5 $\times 10^{-2}$ m gauge length.

RESULTS AND DISCUSSION

X-ray diffraction

The WAXD patterns of PCL samples, containing different amounts of calcium chloride, are shown in *Figure 1*. The lack of diffraction lines typical of salt crystals is evidence for the complete solubility of the inorganic salt in the bulk polymer. The crystal structure of the polyamide appears to be strongly affected by the presence of the salt: whereas the sample containing 1.5 mol% of CaCl₂ shows the two characteristic diffraction lines of the α -form (*Figure 1b*), typical of unsalted polymer slowly cooled from the melt (*Figure 1a*)⁶, on increasing the salt amount up to 5.1 mol% (*Figure 1c*) only one diffraction line, caused by γ -form crystals⁷, appears. At higher salt content (7.1 mol%), no diffraction line is recorded and the polymer can be considered completely amorphous (*Figure 1d*).

The effect of calcium chloride on the WAXD patterns of PCL is analogous to that of lithium chloride, as previously discussed³: the dissolved salt is fully dissociated in the polyamide matrix and Ca²⁺ (as well as Li⁺) ions strongly interact with oxygen atoms of the amide group, which are the main electron-donor sites in the macromolecule. Moreover, the enhanced delocalization of the nitrogen non-bonding electron pair weakens the N–H bond and allows the partial positive charge of the hydrogen to interact with the chlorine ion. Ion–dipole interactions with multiple amide groups of different chains are likely (see later), so that the overall effect of the salt results in physical crosslinking of the polymer chains, with decreasing segmental mobility on increasing the amount of salt. This implies an increase of melt viscosity of the salt-added PCL and a sharp reduction of its crystallization rate up to complete hindering of the crystallization process.

Density

The values of density as a function of CaCl₂ content in PCL samples are quoted in *Table 1*. The data do not reveal any appreciable variation, while the degree of crystallinity, as indicated in *Figure 1*, rapidly decreases on increasing the salt content, showing zero crystallinity for 7.1 mol% of salt.

As discussed in the previous work on the PCL–LiCl system³, the density values can be the result of at least two counteracting effects of the salt^{3,8,9}: the contribution of its high density to the specific volume of the mixture and the aforementioned decrease of PCL crystallinity. However, by assuming ideal additivity of volumes, the calculated density of a completely amorphous mixture containing 7.1 mol% calcium chloride is appreciably lower than the experimental value given in *Table 1*. The further contraction of specific volume in the glassy state supports the idea that strong intermolecular interactions between the two components of the mixture are present. On this basis it is possible to calculate an interaction coefficient α between the amorphous polyamide and the salt, through the following relationship:

$$\rho = \frac{\rho_p}{1 - X_0(1 - \rho_p/\rho_s + \alpha)} \quad (1)$$

where ρ is the density of the fully amorphous mixture, experimentally measured; ρ_p is the density of fully amorphous PCL (1084 kg m⁻³)¹⁰; ρ_s is the salt density (2150 kg m⁻³ for CaCl₂); and X_0 is the weight fraction of salt.

Consequently, the coefficient α is expressed in terms of weight fraction of the mixture. Considering the range of mixture compositions corresponding to fully amorphous materials (see later), a value of $\alpha = 0.24$ is obtained, whereas, by using the density values of amorphous

Table 1 Density (ρ') of poly(ϵ -caprolactam)–CaCl₂ systems

CaCl ₂ content (mol%)	ρ' (kg m ⁻³)
0	1140
1.5	1151
3.5	1141
5.1	1126
7.1	1142

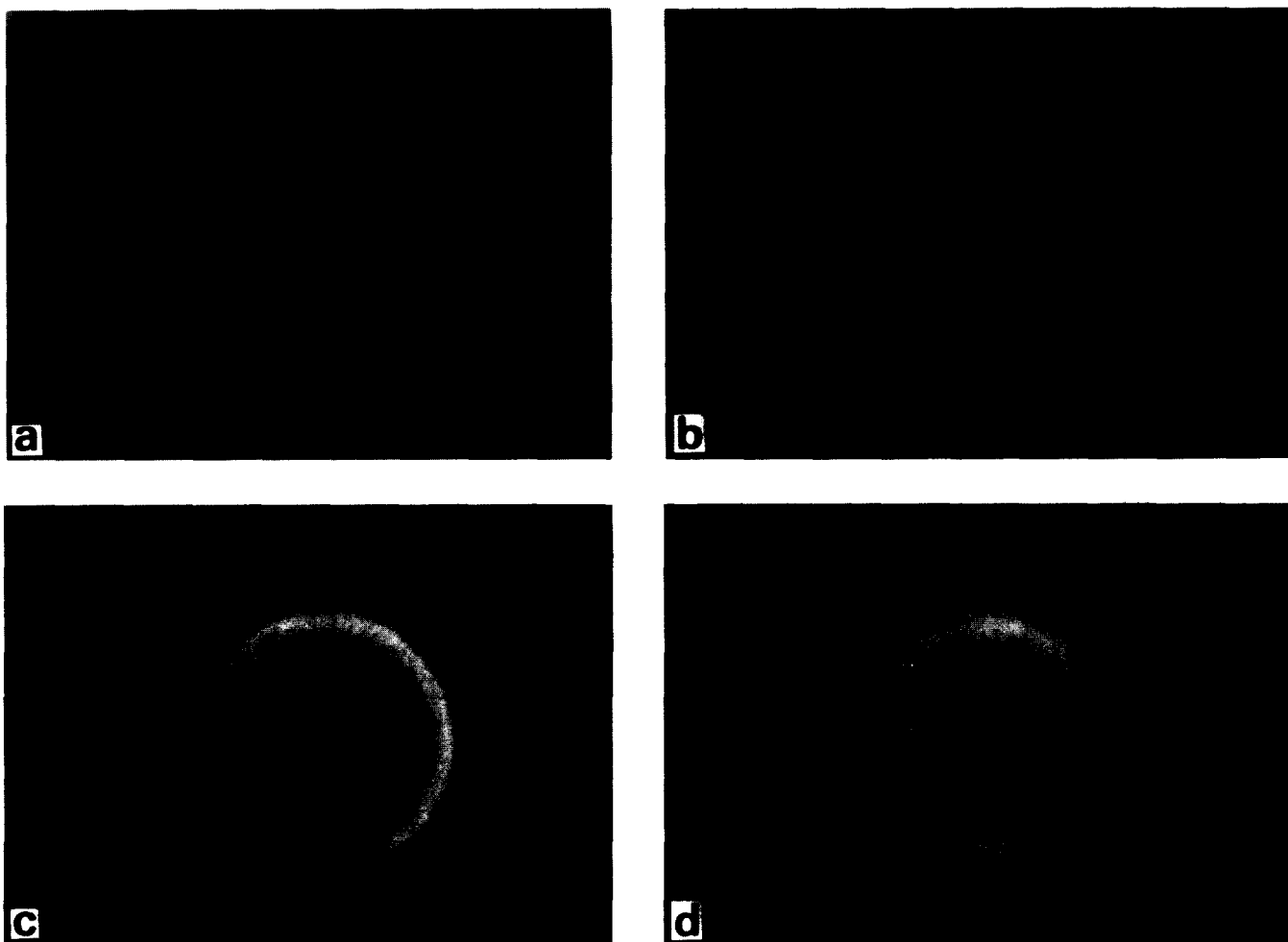


Figure 1 WAXD patterns of anhydrous PCL- CaCl_2 mixtures for various CaCl_2 contents: (a) 0; (b) 1.5; (c) 5.1; (d) 7.1 mol%

polyamide-LiCl systems of ref. 3 (for LiCl, $\rho_s = 2068 \text{ kg m}^{-3}$), $\alpha = 0.42$ is calculated.

In order to compare the interaction effectiveness of Li^+ and Ca^{2+} with amorphous PCL chains, a molar coefficient β has been considered. This latter can be easily evaluated from:

$$\beta \approx \alpha M_s / M_{\text{cru}} \quad (2)$$

where M_s is the molecular mass of the salt and M_{cru} is the molecular mass of PCL constitutional repeat unit.

For the systems under study, equation (2) holds to a good approximation up to at least 10 wt % of the salt. For PCL- CaCl_2 systems, as the molecular mass of the salt is very close to that of the PCL monomer unit, $\alpha \approx \beta$; for PCL-LiCl mixtures, $\beta \approx 0.16$. By comparing β values, it appears that Ca^{2+} exerts a greater effect on the densification of PCL-salt systems compared to Li^+ . It is relevant to note that the β value for Ca^{2+} is ~ 1.5 times higher than that for Li^+ , a value coincident with the ratio between the coordination numbers (6 and 4) that these ions usually have in their low-molecular-mass complexes.

Degree of crystallinity

The degree of crystallinity χ_c has been calculated from density data (Figure 2, open circles) using the well known relationship:

$$\chi_c = (\rho' - \rho) / (\rho_c - \rho) \quad (3)$$

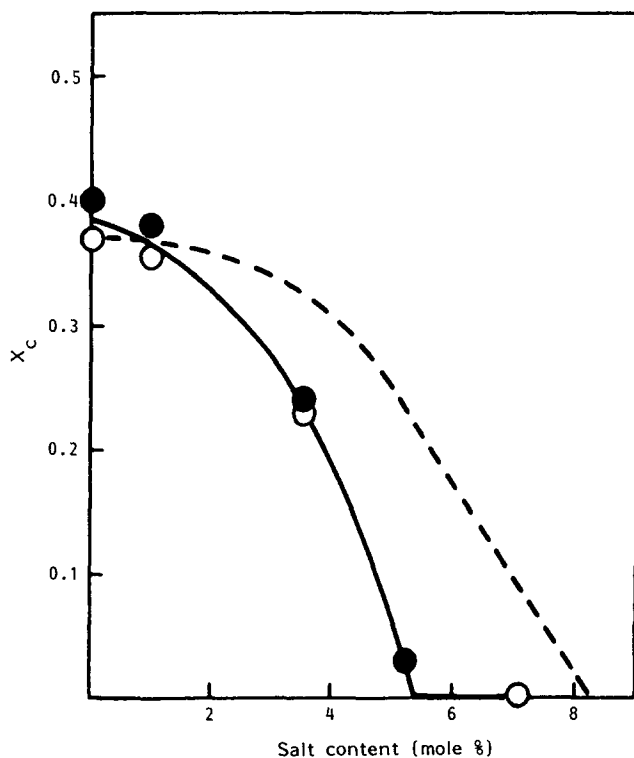


Figure 2 Degree of crystallinity χ_c vs. salt content in PCL: experimental points, CaCl_2 , from density (○) and d.s.c. (●); broken curve, LiCl (ref. 3)

where ρ' is the experimental density of the semicrystalline mixture and ρ_c is the density of 100% crystalline polyamide. Density ρ_c has been assumed to be 1235 kg m⁻³ (ref. 10) for samples in which the α -form is present (0–1.5 mol% of CaCl₂) and 1210 kg m⁻³ for γ -form crystals of PCL¹⁰ induced by higher salt content.

The density of the salt-added amorphous polyamide, ρ , can be calculated from equation (1) by an iterative method, taking into account that the salt is entirely rejected from the polymer crystals. Thus, the actual weight fraction of the salt in the polymer amorphous phase, X_s , has been related to the nominal value X_0 by:

$$X_s = X_0 / [1 - \chi_c(1 - X_0)] \quad (4)$$

and introduced into equation (1).

Degrees of crystallinity have also been obtained by calorimetry (Figure 2, full circles), on the basis of the following relationship:

$$\chi_c = \Delta H_m^a / \Delta H_m^o \quad (5)$$

in which ΔH_m^a is the apparent enthalpy of melting of the samples examined and ΔH_m^o ($= 241 \text{ J g}^{-1}$)¹⁰ is the enthalpy of melting of fully crystalline PCL polymer. The crystallinity values obtained by the two techniques are in excellent agreement. The data for the PCL–LiCl system are also shown in Figure 2 (broken curve) for comparison. The general trend is characterized by a decreasing extent of crystallinity on increasing salt concentration; above a given salt concentration the polyamide cannot crystallize and a fully amorphous polymer is obtained. This concentration depends on the salt type, being about 5.5 mol% for CaCl₂ and about 8.5 mol% for LiCl. Taking the usual coordination numbers for Ca²⁺ and Li⁺, the average concentration of complexed amide groups necessary to produce completely amorphous PCL is almost the same ($\sim 1/3$ of total amide groups). Also on the basis of the aforementioned comparison between β values, it follows that calcium ions interact with a higher number of amide groups than Li⁺.

Glass transition temperature

The dependence of PCL glass transition temperature T_g on the content of CaCl₂ is given in Figure 3, where it is compared with the trend previously reported for the PCL–LiCl system³ (broken curve). In both cases T_g increases monotonically with salt content, the rate of increase depending on the type of salt. The increase in T_g is a consequence of both the crosslinking action of the salt and the stiffening of the amide bonds involved in the ion–dipole interactions. This latter phenomenon arises from the more pronounced double-bond nature of the C–N link, because of the strong interactions between calcium ion and carbonyl oxygen.

Applying the Fox rule¹¹, in terms of CaCl₂ concentration³, to our system one gets:

$$\frac{1}{T_g} = \frac{1}{T_{gu}} - \frac{ny_0}{1-y_0} \left(\frac{1}{T_{gu}} - \frac{1}{T_{gb}} \right) \quad (6)$$

where n is the number of amide groups interacting with a Ca²⁺ ion; y_0 is the mole fraction of the salt; and the suffixes u and b refer to the unbonded and bonded units, respectively. Taking the coordination number of the

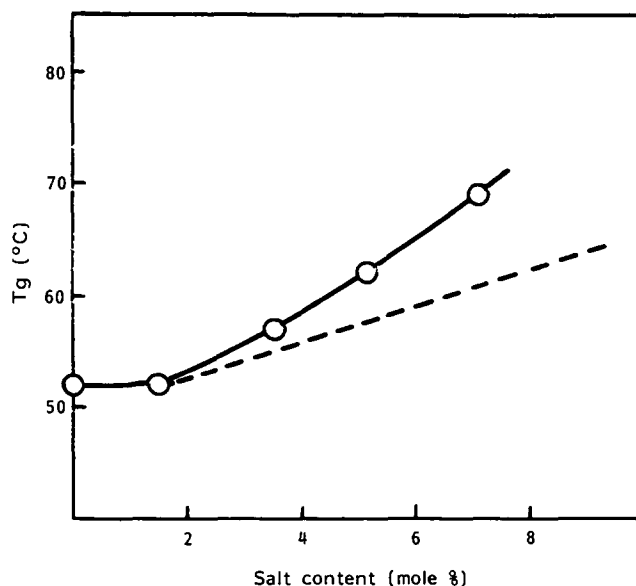


Figure 3 Glass transition temperature T_g vs. salt content in PCL: experimental points, CaCl₂; broken curve, LiCl (ref. 3)

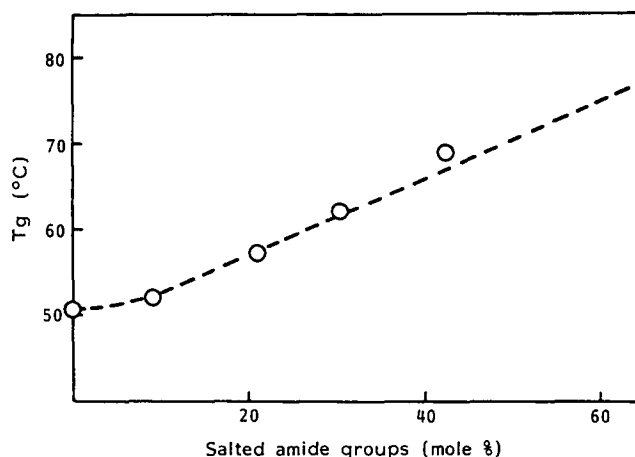


Figure 4 T_g vs. concentration of complexed amide groups: experimental points, CaCl₂; broken curve, LiCl (ref. 3)

calcium ion to be 6, a T_g value of 92°C for the fully bonded PCL is calculated. This result is in very good agreement with the values obtained by extrapolation of T_g data for the PCL–LiCl system by dilatometry and calorimetry³, taking a coordination number of 4 for Li⁺. In Figure 4, T_g is plotted against the molar concentration of amide groups coordinated to CaCl₂ and LiCl, whose coordination numbers are assumed to be 6 and 4, respectively. It is worth noting that a single curve is obtained, suggesting that the glass transition temperature of both systems depends only on the number of complexed amide groups of PCL chains.

Melting point

The melting temperature T_m of PCL–CaCl₂ mixtures decreases regularly with salt content, as shown in Figure 5. This result agrees with the findings previously reported for mechanical mixtures of the two components^{8,9}. As already mentioned, the strong increase of polymer melt viscosity, because of the crosslinking action of the salt, opposes the structural organization of chain segments, thus leading to a crystal phase less and less extended and

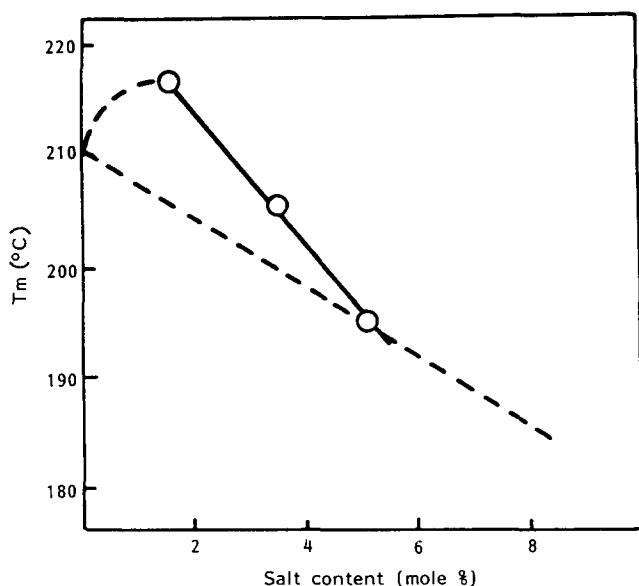


Figure 5 Melting temperature T_m vs. salt content in PCL: experimental points, CaCl_2 ; broken curve, LiCl (ref. 3)

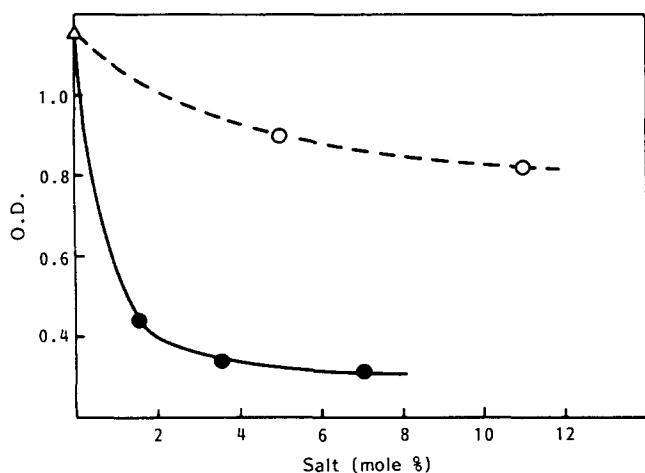


Figure 6 Optical density of neat PCL after salt extraction vs. salt content present during polymerization: full curve, CaCl_2 ; broken curve, LiCl

richer in defects. From the data of Figure 5, two peculiar effects can be noticed: (1) T_m values for PCL- CaCl_2 samples are higher than the corresponding ones for PCL- LiCl systems, at least up to 5 mol% of the salt; (2) the sample containing 1.5 mol% of CaCl_2 exhibits a melting temperature higher than that of neat demonomerized polyamide ($T_m \approx 212^\circ\text{C}$) prepared by anionic polymerization^{1,3}. It is well known that the anionic polymerization of CL, through a Claisen-type condensation reaction, can produce appreciable amounts of irregular structures¹, which could affect T_m . The u.v. absorption values (at 276 nm) of PCL solution in anhydrous formic acid can be used as a measure of these irregularities, being directly proportional to their concentration in the polymer chains. Indeed, as shown in Figure 6, both salts contribute to a sharp reduction of OD values as compared to neat PCL, CaCl_2 being much more effective than LiCl . Therefore, the aforementioned differences among T_m values could, in principle, be attributed to the synthesis of more regular PCL chains.

However, the same PCL samples as used for u.v. analysis, which were prepared by extensive Soxhlet extraction with water in order to remove completely salt, monomer, higher oligomers and low-molecular-mass side-products, do not exhibit any difference in T_m values (all close to 220°C), regardless of type and content of salt. Therefore, the above variations in the concentration of irregular structures in PCL chains, monitored by u.v., cannot be considered responsible for the T_m effects.

Indeed, for neat PCL, a T_m value of 221°C , corresponding to the water-extracted sample, matches with $\sim 214^\circ\text{C}$ for only demonomerized PCL. This sharp reduction (of $\sim 9^\circ\text{C}$) is undoubtedly due to residual higher oligomers, which are entirely soluble in molten PCL¹² and contribute strongly to T_m lowering.

On these grounds, the whole set of T_m data can be explained if one takes into account previously reported data^{4,5} on oligomer content. Only $\sim 0.8\%$ of higher oligomers are present in the sample synthesized in the presence of 1.5 mol% of CaCl_2 , whereas they represent $\sim 1.5\%$ for neat PCL and $\sim 2\%$ for the corresponding molar concentration of LiCl . A similar correlation can be found for samples with higher salt concentration. Therefore, T_m vs. salt content data reflect the rather complex influence of the experimental systems: on the one hand, different concentrations of residual higher oligomers are responsible for the gap between actual and maximum T_m values (water-extracted samples); on the other hand, salt-polymer interactions cause the expected T_m decrease as a function of salt content. Variations of irregular structure concentration due to the salt, evidenced by u.v. measurements, are not large enough to affect T_m data.

Mechanical properties

Values of Young's modulus M , determined for anhydrous and wet samples of PCL- CaCl_2 mixtures, are plotted in Figure 7 (full curves). As expected, the moduli of wet samples are much lower than those of anhydrous samples. In both cases, the modulus first increases on increasing the amount of salt and then decreases down to

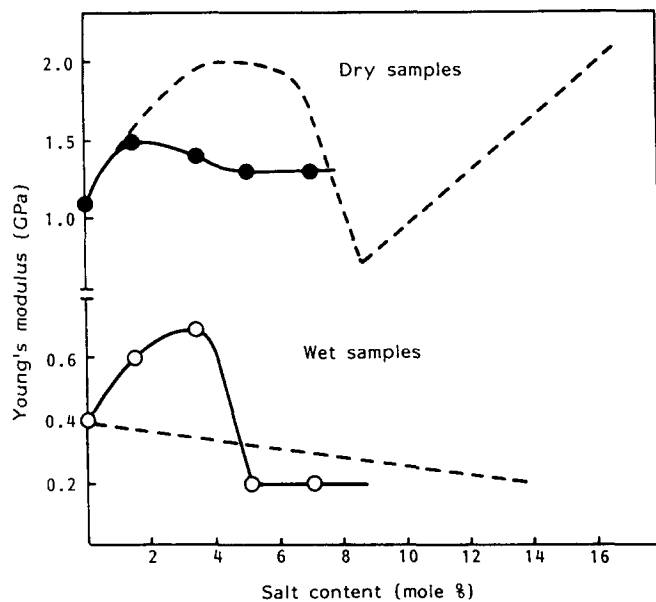


Figure 7 Young's modulus vs. salt content in PCL: experimental points, CaCl_2 ; broken curves, LiCl (ref. 3)

a constant value, for salt concentrations between 5 and 7 mol % (amorphous materials). All amorphous and dry samples with added CaCl₂ exhibit a Young's modulus higher than that of the neat polyamide, because the crosslinking action of the salt overcomes the crystal zone contribution. In contrast, above ~ 5 mol % of CaCl₂, the wet sample moduli are about half that of the pure polymer, because the water behaves as a physical crosslink breaker as well as a plasticizing agent of polyamide.

Compared to the PCL–LiCl mixture (Figure 7, broken curves), the differences between the moduli of anhydrous samples of the two systems could be predicted on the basis of a higher degree of crystallinity (see Figure 2) of PCL doped with lithium chloride. Very surprising results are obtained for wet samples. These, up to about 4 mol % of CaCl₂, are characterized by higher tensile moduli than the unsalted polyamide. This means that, contrary to the trend for PCL–LiCl mixtures, CaCl₂ preserves the interactions with amide groups, even in the presence of water, as recently suggested by Wizgoski *et al.*¹³.

CONCLUSIONS

On the one hand, the aforementioned results support the picture, already put forward for the PCL–LiCl system, that these salts easily dissolved in CL monomer are dissociated into ions and form strong ion–dipole complexes with CL molecules and growing chains, at the polymerization temperatures (150–200°C). On the basis of their concentration and coordinating capability, they interact with several amide groups belonging to different PCL chains, causing a decrease of crystallinity and melting temperature as well as an increase of melt viscosity, T_g and density of the amorphous phase. In this respect, if one takes coordination numbers of 6 and 4 for Ca²⁺ and Li⁺, respectively, a single set of data is often obtained. Namely, density, crystallinity and T_g values, expressed in terms of coordinated groups, not only reveal the common behaviour of LiCl and CaCl₂, but also show a rather excellent superposition.

On the other hand, CaCl₂ plays a very peculiar role, being able to minimize the formation of irregular structures in the polyamide chain and to retain the sharp increase in Young's modulus also in wet conditions. This valuable peculiarity may provide a range of suitable applications for the system under study. Direct synthesis of ion-containing PCL, as compared to the addition of the salt to the preformed polyamide, optimizes ion–dipole interactions and salt effectiveness, causing the largest modifications of polymer properties.

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