Polyether-metal salt complexes: 1. The elevation of the glass transition temperature of polyethers by metal salts

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Various metal halides have been dispersed in high and low molecular weight, amorphous poly(propylene oxide), by solution blending techniques, to give single phase polymeric complexes which remained thermoplastic even at very high salt loadings. These complexes were amorphous and showed a single well-defined glass transition temperature (T_g) by differential thermal analysis with the T_g of the complex up to 140°C greater than the T_g of the parent polymer. The T_g elevation depended upon both the amount and the type of salt added and for a given salt the elevation followed a sigmoidal curve which levelled out at high salt concentrations. The T_g data have been interpreted in terms of a chelate ring model involving the co-ordination of two adjacent ether oxygen atoms in the polymer backbone to the salt. Using this model it was possible to consider the complex as a random copolymer consisting of complexed and uncomplexed monomer units. The contribution of crosslinking by metal salts to the elevation of T_g was assessed by studying poly(tetramethylene glycol)-zinc chloride complexes in which chelate formation is entropically unfavourable. Mechanical data are reported for $ZnCl_2$ complexes with high molecular weight poly(propylene oxide). The results indicate that $ZnCl_2$ increased the rubbery modulus and this has been interpreted in terms of $ZnCl_2$ forming a few, weak intermolecular crosslinks.

INTRODUCTION

The glass transition temperature, T_g, of a polymer is an important physical characteristic of that polymer and, although the depression of T_g by addition of low molecular weight compatible molecules to a polymer is well established[1], the reverse situation in which low molecular weight molecules elevate T_g has not been so extensively studied. In this paper it will be shown that with polyethers one method of elevating T_g is by the molecular dispersion of metal salts in the polymer such that the resulting polymer–metal salt complexes are single phase. It is important to note that the work described in this paper is not concerned with the addition of second phase fillers, such as carbon black or silica, which generally have very little effect on the value of T_g[2].

The effect of the incorporation of ions on the glass transition temperature of polymers has been recently reviewed by Eisenberg[3,4] and only the more pertinent papers are mentioned here. Moacanin and Cuddihy[5] produced large increases in the T_g of poly(propylene oxide) by dissolving lithium perchlorate in the polymer. The increase in T_g was interpreted in terms of strong ion-dipole interactions present in the system reducing the average segmental mobility of the polymer chain.

Hannon and Wissbrun[6] have elevated the T_g of the condensation polymer formed from 2,2-bis-4-hydroxyphenylpropane and 1-chloro-2, 3-epoxy-propane by dissolving calcium thiocyanate in the polymer. They suggested that the increase in T_g was due to the salt reducing the free volume of the polymer. These authors[7] have also investigated polymer–salt interactions in cellulose acetate, poly(vinyl acetate), poly(vinyl alcohol), poly(methyl acrylate) containing bivalent metal nitrates. In most cases the metal salt increased T_g but in some instances T_g was decreased by the presence of salt.

Several workers have studied the effects of various metal salts on the glass transition temperature and crystallinity of polyamides. Andrews[8] studied the dynamic mechanical behaviour of nylon-6 treated with zinc chloride and found that the α relaxation associated with the glass-rubber transition was shifted to higher temperatures with increasing $ZnCl_2$ content. Ciferri *et al.*[9–11] and Frasci *et al.*[12] found that alkali metal halides, especially LiCl and LiBr, continuously depressed the melting temperature of nylon-6 with increasing salt content. Furthermore, increasing salt content reduced the degree of crystallinity and the rate of crystallization of the polymer. These effects were interpreted in terms of strong interactions between the amide group in the amorphous regions of the polymer and the metal halides. In recent work Acierno *et al.*[13] found, somewhat surprisingly in view of the above observations, that the T_g of nylon-6 was not affected by the type and concentration of alkali metal salts in the polymer up to a salt concentration of 5 mole %.

Reich and co-workers[14–16] in their studies of mixtures of poly(acrylonitrile) and hydrated metal perchlorates found a decrease in T_g with increasing concentration of added salt. It appears that in this system the salt–water complex acted as a plasticizer.

In an earlier publication[17] we reported preliminary results on the elevation of the T_g of polyethers by zinc and cobalt

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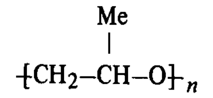
(II) chlorides. The results reported in this present paper are a continuation of this earlier work with more extensive data on the effects of a wide range of metal halides on the T_g and physical properties of polyethers.

The majority of work described in this paper involves the addition of metal halides to high and low molecular weight, non crystalline poly(propylene oxide)



$$-\!\!\left[CH_2-\underset{}{\overset{\overset{\displaystyle Me}{|}}{CH}}-O\right]\!\!-_n$$

This polyether has been studied more extensively than other polyethers because it is amorphous and, thus, the complicating effects of crystallinity have been avoided. The effects of the number of carbon atoms between oxygen atoms have also been briefly investigated by studying the interactions of zinc chloride with poly(tetramethylene glycol) $[(CH_2)_4-O]_n$. Mechanical data are also reported for high molecular weight poly(propylene oxide) – zinc chloride complexes.

EXPERIMENTAL

High molecular weight poly(propylene oxide) [PPO(H)], containing less than 5% co-units of alkyl glycidyl ether, (Parel 58, $\bar{M}_n = 3.5 \times 10^5$, $T_g = -64°C$, supplied by Hercules Inc.) was purified to remove residual traces of initiator. These were removed by high speed centrifuging, at 10 000 rpm for 1 h, of a 5 wt-vol % solution of the polymer in dry distilled acetone. The polymer was precipitated from the clear solution by slowly pouring it, with stirring, into a large volume of distilled water. The precipitated polymer was dried under vacuum at 60°C and then freeze-dried from benzene solution. The purified polymer contained no water and was completely amorphous, as evidenced by infrared analysis and X-ray scattering, respectively.

Amorphous, low molecular weight poly(propylene glycol) [PPO(L)], (PPG 2000, $\bar{M}_n = 1.6 \times 10^3$, $T_g = -66°C$, supplied by Shell Ltd.) and partially crystalline poly(tetramethylene glycol) [PTMG], (Polymeg 2010, $\bar{M}_n = 2000$, $T_g = -76°C$, $T_M = 24°C$, supplied by Quaker Oats Co.) were degassed at 50°C under vacuum and required no further purification.

Preparation of polymer-metal salt complexes

All the complexes were prepared in essentially the same manner by dissolving both the polymer and the metal salt in a mutual solvent. Dry methanol was used to prepare the majority of the complexes but dry ethanol was used to prepare PPG(L)–cobalt (II) chloride complexes and PTMG–zinc chloride complexes because of the low solubilities of $Co(II)Cl_2$ and PTMG in methanol. All the metal salts used were rendered anhydrous and were stored under vacuum prior to use. It was often necessary to filter the metal salt solutions to remove the very small trace of metal oxide which was usually present in the salt. This was always less than 1% of the total weight of salt dissolved in the solvent.

The solutions of polymer and salt were added together and thoroughly mixed for several hours. The solution was then poured into a circular polytetrafluoroethylene mould and the bulk of the solvent was removed by blowing a stream of dry nitrogen over the solution at 50°C for 48 hours. Last traces of solvent were removed under vacuum, initially at 50°C for 24 h, and then at 100°C for several days. At every stage in the preparation of the complexes great care was taken to exclude water and, after preparation, the complexes were stored under vacuum.

Throughout this paper the concentration of salt in the polymer has been expressed in terms of the mole percentage of salt with respect to moles of monomer repeat unit in the polymer.

Glass transition temperature measurements

The T_g's of all the polymer–metal salt complexes prepared were determined using a DuPont Differential Thermal Analyser, equipped with the Differential Scanning Calorimetry Accessory (Catalogue Number 900600). The samples were scanned from −100° to +100°C at a heating rate of 15°C/min. Care was taken to keep the samples as dry as possible and the cell was evacuated for the most deliquescent complexes. The sample weights (5–10 mg) were measured in each case and it was possible to determine an approximate correlation between the sample weight and the magnitude of the T_g step as measured by the shift in baseline. This correlation will be discussed in the next section.

Mechanical relaxation measurements

Mechanical data were obtained for PPO(H)–$ZnCl_2$ complexes using a vibrating reed apparatus designed by Fielding-Russell and Wetton[18]. Each polymer sample, previously moulded into a rectangular bar of approximate dimensions $1.0 \times 0.2 \times 7$ cm^3, was clamped in the apparatus at its upper end so that it could be stressed as a cantilever. The bar was vibrated by energizing an electromagnetic coil adjacent to a small magnet glued to the free end of the specimen. The resultant movement of the sample was detected by a small piezoelectric strain transducer clamped against the upper end of the specimen. Resonant frequencies and half power points of the resonance curve were determined.

The vibrating reed apparatus fitted inside a vacuum tight circular brass container, and all measurements were made with the container evacuated to prevent air damping and absorption of moisture by the sample.

The complexes were rubbery at room temperature and could not be securely clamped into the apparatus. This problem was overcome by laminating the complexes with thin copper strips. The strips were used as central supports and the polymeric complexes were cast onto each side of the strips such that symmetrical arrangements were achieved.

The loss factor, $\tan \delta_p$, and Young's modulus E'_p, for a laminate comprising a metal strip sandwiched by polymer are given by equations derived by Nashif[19] and Fielding-Russell[20] such that

$$\tan \delta_p = \tan \delta_c [1 + E'_m / kE'_p]$$

and

$$E'_p = E'_m / k[(f_c/f_m)^2 (1 + 2h_p\rho_p / h_m\rho_m) - 1]$$

where f and E' are the respective resonant frequencies and Youngs' Moduli.

The suffix 'p' on the symbols refers to the polymer only, the suffix 'c' to the composite, and the suffix 'm' to the metal. Tan δ_c is given by reference 20:

$$\tan \delta_c = \frac{\Delta f}{f_c}$$

where f_c is the resonant frequency of the laminate and Δf

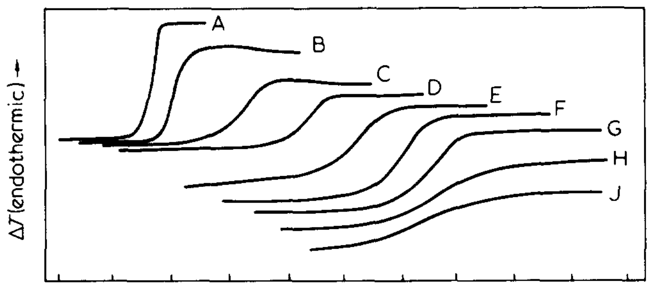


Figure 1 Some typical dsc traces of PPO (L)–$ZnCl_2$ complexes through the glass transition temperature. Mole % $ZnCl_2$ is A, 0; B, 5.4; C, 10.1; D, 14.5; E, 18.4; F, 22.2; G, 28.5; H, 38.9; J, 51.5

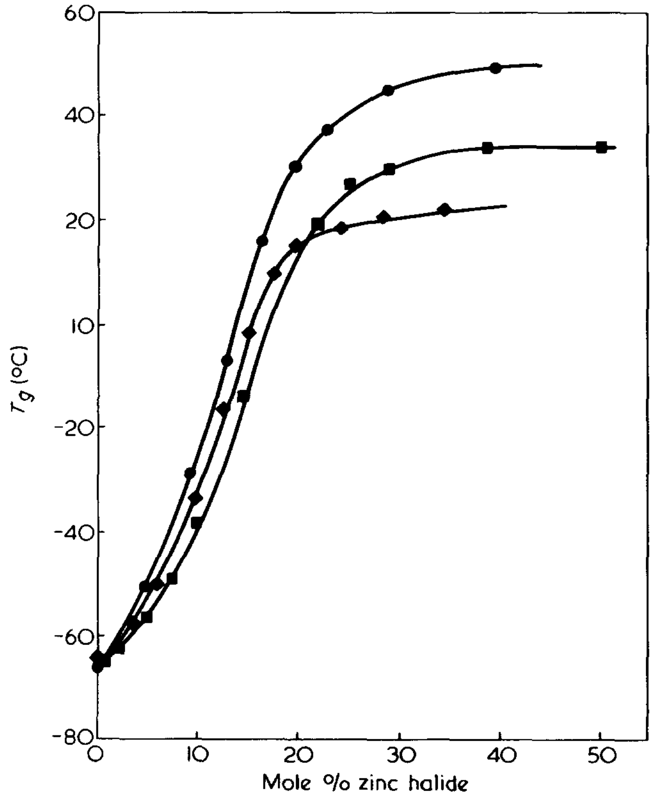


Figure 2 Glass transition temperatures of PPO(L)–Zinc Halide Complexes with respect to the amount of salt incorporated, concentrations are mole percentages with respect to monomer units. ■, $ZnCl_2$; ●, $ZnBr_2$; ◆, ZnI_2

is the half power width of the resonance curve. h is the thickness, ρ is the density and k is given by

$$k = 8[h_p/h_m]^3 + 12[h_p/h_m]^2 + 6[h_p/h_m]$$

The densities of the samples were calculated from a knowledge of the densities of amorphous $ZnCl_2$ and amorphous PPO(H) assuming additivity of volumes. This method assumed no interactions between the polymer and salt. Such interactions undoubtedly occurred and the theoretical densities are expected to be slightly less than the true sample densities. However, the errors involved in using the theoretical values for the densities are considerably less than the errors in geometrical parameters.

RESULTS

Glass transition temperature data

PPO(L)–metal salt complexes exhibited single glass transitions which normally occurred at considerably higher temperatures than the T_g of the parent polymer. This is illustrated in *Figure 1* for complexes formed between PPO(L) and zinc chloride. Although T_g was still well-defined at very high loadings of $ZnCl_2$, some broadening of the transition did occur especially at $ZnCl_2$ loadings of greater than 30 mole %. The other PPO(L)–metal salt complexes studied also exhibited similar well-defined, single glass transitions.

Figures 2 and *3* show the T_g data for the PPO(L)–metal salt complexes studied as a function of the mole % of metal salt in the complex. In *Figure 2* the effects of varying the anion on the elevation of T_g have been studied for a series of zinc halide complexes and in *Figure 3* the effects of varying the cation on the elevation of T_g have been studied for a series of metal chlorides. From these figures it can be seen that the elevation of T_g followed a sigmoidally shaped curve which levelled out at high salt concentration to give a limiting value of T_g which depended on the metal salt added.

Figure 3 also contains data for copper chloride and lithium chloride. It can be seen that T_g was completely independent of the concentration of LiCl present and that $CuCl_2$ only increased T_g by a few degrees. The results indicate that these salts were behaving very differently from salts such as $ZnCl_2$ which elevated T_g by up to 100°C.

PPO(L)–metal salt systems, with the exception of lithium and copper chlorides, were transparent viscous liquids above their T_g with the viscosity increasing as the concentration of metal salt increased. Below their T_g they were hard, brittle, transparent glasses. The colour of the complexes depended

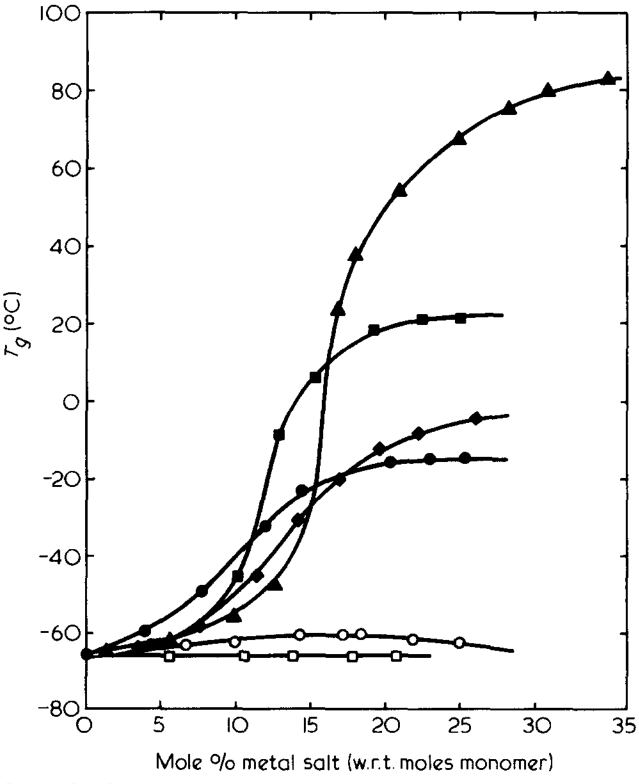


Figure 3 Glass transition temperatures of PPO(L)–Metal salt complexes as a function of salt concentration. △, $CoCl_2$; ■, $FeCl_3$; ◆, $SnCl_2$; ●, $HgCl_2$, ○, $CuCl_2$; □, LiCl

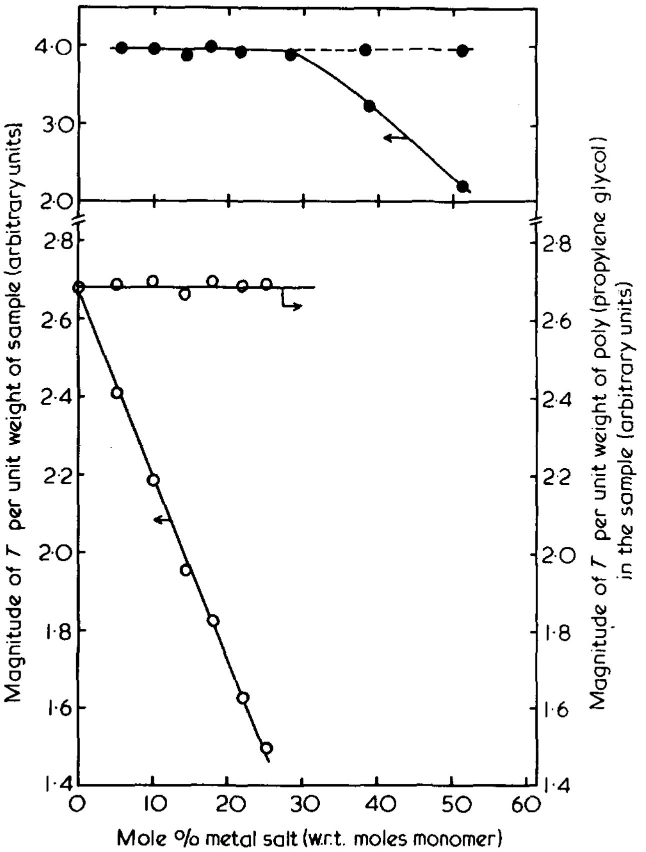


Figure 4 Magnitude of the glass transition of PPO(L)–Metal salt complexes as a function of salt concentration. ●, $ZnCl_2$, – – – – corrected assuming that there is $ZnCl_2$ present in the sample as a 2nd phase above 30 mole % $ZnCl_2$; ○, $CuCl_2$

on the metal salt such that cobalt (II) chloride complexes were blue, iron (III) chloride complexes reddish brown, mercury (II) chloride complexes pink and the remaining complexes slightly brown in colour. In all these complexes T_g was greater than the T_g of the parent polymer and the complexes, although slightly water sensitive, were not deliquescent like the parent metal salts.

Complexes of PPO(L) with $CuCl_2$ and LiCl had significantly different physical properties from the complexes discussed in the previous paragraph. $CuCl_2$ and LiCl complexes were optically opaque and as water sensitive as the original salts and slurries at room temperature. In these systems the salts were definitely present as second phase fillers not as complexed structures.

Further evidence for this conclusion comes from an observation of the magnitude of the T_g process for PPO(L)–$CuCl_2$ systems as measured by the shift in baseline accompanying the T_g step. The results, shown in *Figure 4* indicate that the T_g process was due solely to the PPO(L) in the sample and that $CuCl_2$ was not involved in the transition. However, it can also be seen in *Figure 4* that a similar analysis with PPO (L)–$ZnCl_2$ complexes indicates that, at least up to 30 mole % $ZnCl_2$, the whole sample including the $ZnCl_2$ present was responsible for the T_g process. Above about 30 mole % $ZnCl_2$ the results indicate that $ZnCl_2$ in excess of this concentration was present as a second phase. However, if correction is made for this, the original constancy of the magnitude of the T_g step per unit weight was achieved up to 50 mole % $ZnCl_2$.

The interpretation of the results shown in *Figure 4* is based on the assumption that the specific heat difference between the glassy and rubbery states, as estimated from the step height, was independent of the concentration of metal salt present in the polymer. The consistency of the results indicates that for these complexes this is a valid procedure.

Complexes were also prepared between zinc halides and PPO(H). The elevation of T_g of the high molecular weight polymer by these salts was similar to the behaviour observed with PPO(L). The similarities are illustrated in *Figure 5* for the case of $ZnCl_2$. At low salt concentrations PPO(H)–zinc halide complexes were transparent, leathery compounds at room temperature and were tougher than the parent polymer. At higher salt concentrations T_g was elevated to above room temperature and the complexes were transparant, glassy plastics at this temperature. The water sensitivity of the PPO(H) complexes was comparable to that exhibited by the corresponding PPO(L) complexes. Both PPO(H) and PPO(L) complexes were plasticized by atmospheric moisture and great care was taken to keep the samples dry at all times. For example, the T_g of a PPO(H) complex containing 27.1 mole % $ZnCl_2$ was lowered from 32°C to 6°C by 4 days exposure to the atmosphere. Small amounts of water could be reversibly absorbed and desorbed without apparent damage to the structure of the complex since after drying the original T_g was regained. Both PPO(H) and PPO(L) complexes were thermoplastic even at very high salt loadings and they could be easily moulded above their T_g using conventional moulding techniques. There was no evidence for crystallinity in metal salt complexes formed from either PPO(H) or PPO(L), but it might be remembered that the present polyethers were also amorphous at ambient temperatures.

Figure 5 also contains data for the elevation of the T_g of PTMG by $ZnCl_2$. These data have been previously reported in an earlier publication[17] together with the effect of $ZnCl_2$ on the melting temperature of PTMG and are included for comparison purposes. The T_g data have been repeated in *Figure 5* for completeness and for subsequent comparison with the T_g data of PPO(L)–$ZnCl_2$ complexes.

Mechanical relaxation data

The results for the PPO(H)–$ZnCl_2$ complex at approximately 100 Hz are shown in *Figure 6* in terms of E' and

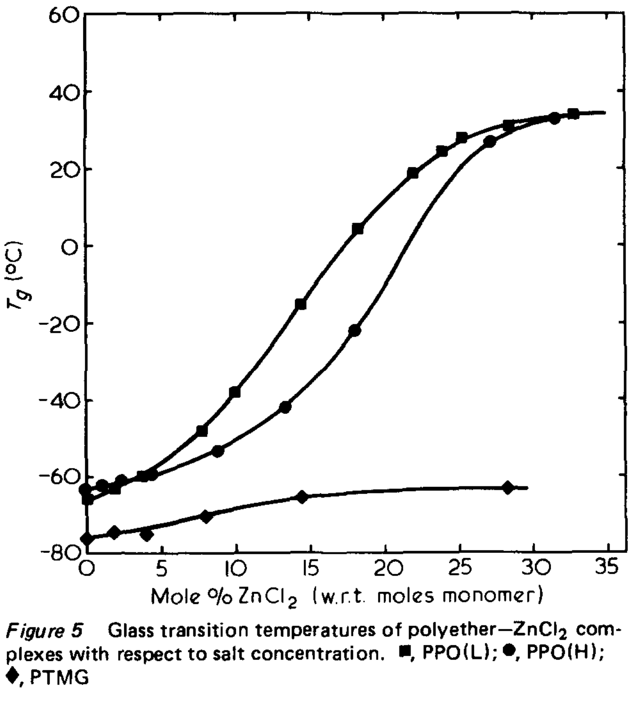


Figure 5 Glass transition temperatures of polyether–$ZnCl_2$ complexes with respect to salt concentration. ■, PPO(L); ●, PPO(H); ◆, PTMG

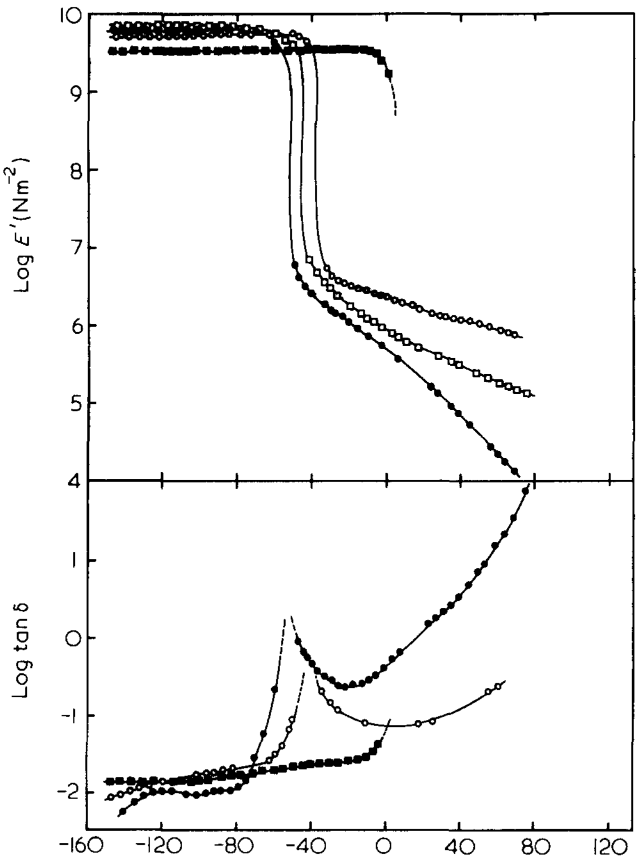


Figure 6 Mechanical data of laminated PPO(H)–$ZnCl_2$ complexes at 100 Hz versus temperature. ●, 0 mole % $ZnCl_2$; ○, 8.72 mole % $ZnCl_2$; □, 4.40 mole % $ZnCl_2$; ■, 18.0 mole % $ZnCl_2$

tan δ as a function of temperature. It can be seen that the complexes underwent a rapid drop in modulus over a narrow temperature range. This drop is associated with the glass to rubber transition. It is important to note that the complexes exhibited only a single modulus step which moved to higher temperatures with increasing concentration of $ZnCl_2$. This increase in the mechanical relaxation temperature paralleled the increase in the calorimetric T_g shown previously in *Figure 5*.

In the rubbery state above T_g the dynamic modulus continued to decrease with increasing temperature. However, the decrease became less severe as the concentration of $ZnCl_2$ in the polymer increased. The errors involved in calculating the rubbery modulus from measurements on a laminated sample are considerable and the results for the rubbery modulus must be considered more qualitative than quantitative. *Figure 6* also shows that, within experimental error, the glassy modulus was unaffected by the addition of $ZnCl_2$ to the polymer.

The large maxima observed in the tan δ curves of *Figure 6* correspond to the glass to rubber α relaxation in each case. The only other peak observed was a small, broad peak at −120°C in the tan δ curve of the original polymer.

DISCUSSION

In the previous section it was shown that polyether–metal salt complexes exhibit well defined, single glass transitions which often occurred at considerably higher temperatures than the T_g of the parent polymer. It is well known[21] that block and graft copolymers, and many polymer blends exhibit two T_g's as a consequence of microphase separation into two individual polymer phase domains. Since polyether–metal salt complexes exhibited a single T_g and a single mechanical relaxation process the presence of a single polymeric phase is strongly indicated.

The existence of a single glass transition in these complexes does not exclude the possibility that the salt was acting as a filler, since filled polymers will still exhibit a single T_g[2], but such an explanation is not capable of explaining the very large elevations of T_g observed for the majority of polyether–salt systems. The T_g data of PPO(L)–$CuCl_2$ systems shown in *Figure 3* and the subsequent analysis of the magnitude of the T_g process shown in *Figure 4* are typical data for a filled rather than complexed system. The optical opaqueness of $CuCl_2$ systems further supports the presence of $CuCl_2$ in the polymer as a second phase in this case.

This paper is concerned with those systems comprising polymer–metal salt complexes which are optically transparent and in which T_g is elevated. Optical transparency indicates that this type of complex was either single phase or two phase with the heterogeneities smaller than about 200 nm. and certainly more finely dispersed than in filled systems. As discussed in the previous section an analysis of the magnitude of the T_g processes (*Figure 4*) for the complexes indicates that, up to 30 mole % $ZnCl_2$, the complexes comprised a single polymeric phase with the $ZnCl_2$ incorporated into that phase. Although results of this type are only reported here for PPO(L)–$ZnCl_2$ complexes a similar analysis has been undertaken for all polyether–metal salt complexes in which T_g was appreciably elevated by the metal salt and leads to the conclusion that in these cases a single phase is formed.

The T_g's of all the polyether–salt complexes reached limiting values at high salt concentrations. It is apparent that these values are achieved when the limit of 'solubility' of the salt in the polymer has been attained. Above this limit further salt exists as a second phase and produces no further elevation of T_g. Below this limit the salt is believed to be molecularly dispersed in the polymer. This statement is substantiated by small and wide angle X-ray evidence which will be presented in a later publication[22].

An estimate of the degree of molecular homogeneity of the polymer and the salt is given by the breadth of the glass transition. This method of estimating molecular homogeneity has been used in the field of polymer blends by several workers[2,23–25]. It has been commonly found that compatible polymer blends such as poly(2,6-dimethyl-1, 4-phenylene oxide)-polystyrene exhibited a single T_g but that the transition was broader than the glass transitions of the two constituent homopolymers[23,25]. If the two polymers had mixed with complete molecular homogeneity than the T_g of the blend would have been of the same breadth as the T_g's of the component polymers. The single well defined glass transitions of PPO(L)–salt complexes indicates molecular compatibility. Some broadening of the transition by metal salts was observed, particularly at the higher concentrations of metal salt. This indicates a greater variety of local relaxing environments and less genuine homogeneity at high salt concentrations.

From the large elevations of T_g observed it is apparent that strong interactions of a chemical nature must exist between the polymer and the salt. This assertion is supported by infrared, X-ray and swelling data which will form the subject of a separate publication[22]. The most probable chemical interactions to occur in polyether–salt complexes are

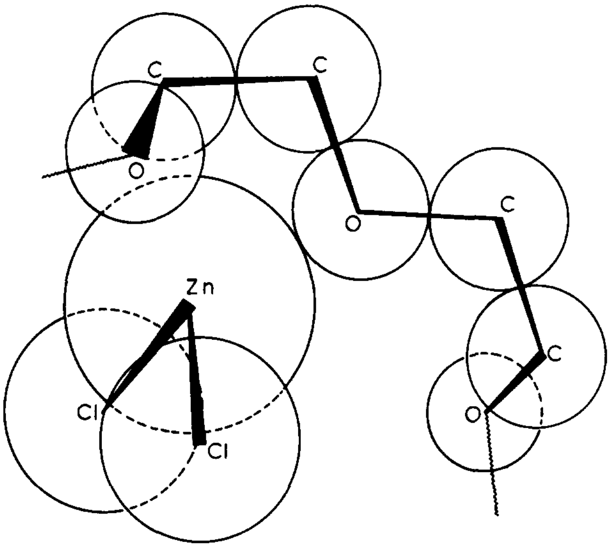


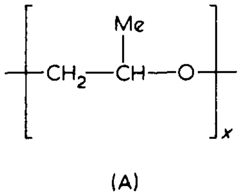
Figure 7 Molecular scale model of poly(propylene oxide)–zinc chloride chelate. (Methyl groups have been omitted)

those between the lone electron pairs on the ether oxygen atoms with the metal cation of the salt. Such interactions would result in the formation of coordinate bonds between the polymer chain and the metal salt. Since many metal cations are able to accept more than one lone pair of electrons the possibility exists for several oxygen atoms to coordinate to the same cation.

It is reasonable to assume that the limit of solubility of the salt in the polyether is reached when all the oxygen atoms that are able to coordinate to the salt have achieved this state. The mole percentage of salt at which this occurs will depend on the oxygen coordination number of the cation. Experimentally, the T_g elevation of PPO(L) by $ZnCl_2$, as seen in *Figure 2*, levelled out at about 30 mole % from which simple calculation indicates that on average about 2 oxygen atoms were coordinated to each $ZnCl_2$ molecule. Subsequent discussion will indicate that an oxygen coordination number of two forms the basis of a good working hypothesis and allows the possibility of intra- and intermolecular coordination to occur.

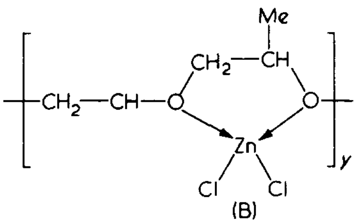
Intramolecular coordination

If two ether oxygen atoms in adjacent poly(propylene oxide) monomer units coordinated to the same $ZnCl_2$ molecule a five membered chelate ring would be formed as shown in *Figure 7*. It is already well documented[26] that $ZnCl_2$ forms chelate complexes with small molecules containing oxygen ligands such as acetylacetone. The formation of chelate rings randomly situated along the polymer chain would greatly stiffen the chain and hence increase T_g. If the polymer chain is considered to be composed of uncoordinated and coordinated monomer units as shown below, it is possible to interpret the elevation of T_g using conventional random copolymer relationships.



$$\left[-CH_2-\overset{\displaystyle Me}{\overset{|}{CH}}-O-\right]_x$$

(A)



(B)

The T_g data of PPO(L)–$ZnCl_2$ complexes shown in *Figure 2* may then be replotted in terms of the weight fraction of coordinated units as shown in *Figure 8*. The most general equation for the prediction of T_g of a random copolymer is given by the Gordon–Taylor–Wood equation[27–28]

$$T_g = \frac{T_{gA} + (kT_{gB} - T_{gA})W_B}{1-(1-k)W_B} \tag{1}$$

where T_g is the glass transition temperature of the copolymer containing weight fractions W_A and W_B of uncoordinated and coordinated units respectively, of glass transition temperatures T_{gA} and T_{gB} respectively. k is a constant only for the copolymer under consideration and has a value between 0 and 1.

By choosing $k = 0.3$ and $T_g = 370K$ it was possible to obtain a good fit between this equation (dashed line in *Figure 8*) and the experimental data up to a weight fraction of 0.7. Above a weight fraction of 0.7 the theoretical curve and the experimental points differed considerably with the experimental data reaching a limiting value of T_g.

Since the experimental points above a weight fraction of 0.7 were less than the theoretical values this suggests that the chain was not completely chelated. An estimate of the number of unchelated oxygen atoms arising from random ring formation may be obtained from the work of Flory[29] on intramolecular reactions between neighbouring substituents in vinyl polymers. Flory statistically analysed the condensation of pairs of consecutive substituents, X, in a high molecular weight polymer composed of $-CH_2CHX$ structural units. When these units were regularly arranged so

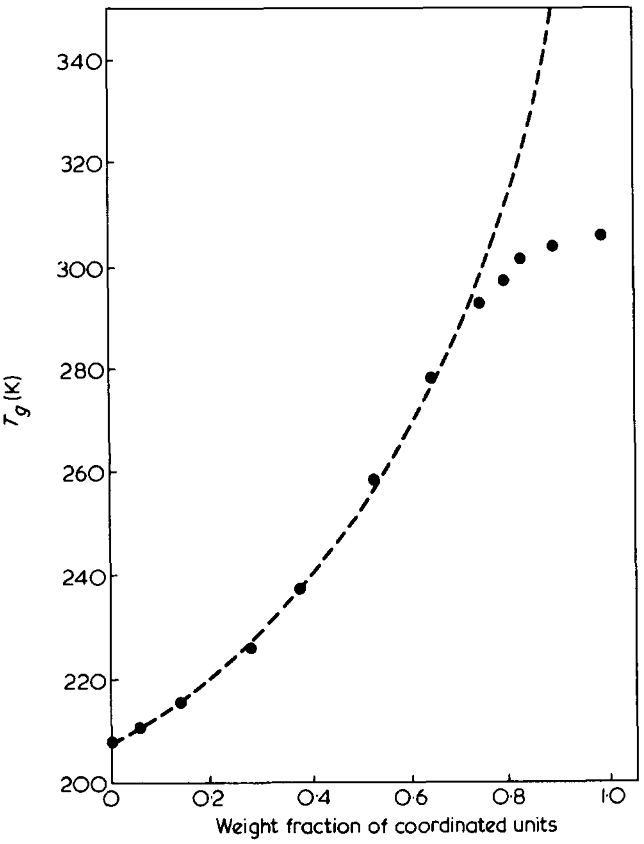


Figure 8 A comparison of the *Tg* data of PPO(L)–$ZnCl_2$ complexes with a copolymer model based on the Gordon–Taylor–Wood equation. (Equation 1). ●, Experimental; – – – – theoretical

Table 1 Polytetramethylene glycol/zinc chloride system. Comparison of experimental evaluation (ΔT_gexp) of T_g with that predicted by a fully crosslinking system from equation 2 ($\Delta T_{g\chi}$)

Mole % $ZnCl_2$	ΔT_gexp(°C)	$\Delta T_{g\chi}$(°C)
8	5	21
15	9	40
28	13	77

that the X's occurred on alternate atoms along the chain 13.5% of them were prevented from reacting due to isolation between reacted pairs. This sytem is analogous to the random formation of chelate rings along the chain. Thus from a purely statistical argument only 86.5% of the available oxygen atoms can form chelate rings. This corresponds to a maximum possible weight fraction of coordinated units of 0.94.

However, it is found experimentally that deviations from the theoretical curve occurred at weight fractions considerably less than 0.94. This implies that other factors such as unfavourable conformations limit the formation of chelate rings.

Intermolecular coordination

In intermolecular coordination the coordination of two oxygen atoms from neighbouring chains to the same metal cation will result in the formation of a crosslink between chains. It is well-known[30–31] that crosslinks increase the T_g of a polymer and Nielsen[30] has suggested the following empirical equation relating the molecular weight between crosslinks, M_C, to the elevation of T_g, ΔT_g, produced by these crosslinks.

$$\Delta T_g = \frac{3.9 \times 10^4}{M_C} \qquad (2)$$

It is pertinent at this point to discuss the T_g elevation of PTMG by $ZnCl_2$ shown in *Figure 5*, where chelate rings formed by adjacent chain oxygen coordination would contain 7 members. Generally, such large rings are entropically unstable and intermolecular coordination will be more likely than intramolecular coordination. Hence, from a study of a system in which ring formation is unlikely it is possible to assess the contribution of crosslinking to the elevation of T_g.

If all the $ZnCl_2$ molecules are assumed to act as crosslinks, then the elevation of T_g may be calculated from the mole % of $ZnCl_2$ in the polymer using equation (2). The T_g elevation predicted by this mechanism is shown in *Table 1* for PTMG–$ZnCl_2$ complexes. The use of this equation assumes that the crosslinks are thermally stable. The experimental T_g data for PTMG–$ZnCl_2$ complexes taken from *Figure 5* are also included in *Table 1*. The discrepancies between the theoretical predictions and experiment indicate that the crosslinks were either very weak with dissociation below T_g or that there were only a few crosslinks formed. These conclusions also agree with the fact that the complexes could be easily compression moulded above T_g. Although the data in *Table 1* are for PTMG–$ZnCl_2$ complexes it is reasonable to conclude that there will only be weak crosslinks in PPO(L)–$ZnCl_2$ (or PPO(H)–$ZnCl_2$) complexes and this conclusion is supported by mechanical data of PPO(H)–$ZnCl_2$ complexes discussed later in this section. Therefore the results indicate that in poly(propylene oxide)–$ZnCl_2$ complexes intra- rather than intermolecular coordination is the major factor responsible for the observed T_g elevations.

Monodentate complexation

Apart from intra- and intermolecular coordination a third possibility exists to explain the small elevations of the T_g of PTMG by $ZnCl_2$. This alternative involves the coordination of a single oxygen atom to a $ZnCl_2$ molecule. Such a molecule may then be considered to act as a side group on the main chain with consequent elevation of T_g[21].

This monodentate complex concept may also be incorporated into structure associated with PPO(L)–$ZnCl_2$ complexes described earlier. Since this model predicts that at least 13.5% of the oxygen atoms will be unchelated, it may be envisaged that these coordinate in a similar manner to the oxygen atoms of the PTMG chain. In *Figure 8*, above a weight fraction of 0.7, the experimental points deviated from the theoretical curve but T_g still increased slightly. This increase may well be attributed to single oxygen coordination as described above.

Ultimately all available oxygen atoms are coordinated and further addition of $ZnCl_2$ will form a second phase as previously mentioned.

Other factors affecting the elevation of T_g

The above discussion has been confined to the elevation of T_g of PPO(L) and PTMG by $ZnCl_2$. From the data shown in *Figures 2, 3* and *5* it is apparent that the elevation of T_g was a function not only of the polymer but also of the metal salt and discussion will now focus on factors which arise principally from the salt rather than from the polymer.

In *Figure 2* it can be clearly seen that $ZnBr_2$ produced the greatest elevation of T_g and that ZnI_2 produced the smallest elevation. The curves for $ZnBr_2$ and ZnI_2 were similar in shape to the curve for $ZnCl_2$ and it is reasonable to assume that the chelate ring model for PPO(L)–$ZnCl_2$ complexes is also valid for complexes of PPO(L) with $ZnBr_2$ and ZnI_2. However, this model must be capable of explaining the different elevation of T_g by different salts and also, as will be discussed later, the slightly different shapes of the sigmoidal curves for other metal chlorides, where the metal is not zinc.

In order to fit equation (1) to the experimental data it was necessary to adjust k and T_{gB}, where T_{gB}, the glass transition of a totally chelated chain, depends on the metal salt coordinated to the polymer chain. Although T_{gB} could not be measured directly its value is reflected in the limiting value of T_g extrapolated from plots such as shown in *Figure 8* to a weight fraction of unity.

Both the polarity and the size of the metal salt molecule will affect T_{gB}, since the former influences intermolecular forces and the latter affects chain flexibility. *Table 2* gives some covalent and ionic bond lengths and also the electronegativity differences between the atoms associated with the bonds in PPO(L)–zinc halide complexes. The data were taken from Pauling[32] and bond percentage ionic characters, Z, were calculated using an equation derived by Pauling[32].

Table 2 Some parameters of zinc halide bonds

Bond	Covalent Bond Length (nm)	Ionic Bond Length (nm)	$x_A - x_B$	I
Zn–Cl	0.23	0.26	1.4	39
Zn–Br	0.24	0.28	1.2	30
Zn–I	0.26	0.29	0.9	18

$$I = 100[1 - \exp(-\tfrac{1}{4}(\chi_A - \chi_B)^2)] \quad (3)$$

where $\chi_A - \chi_B$ is the Pauling electronegativity difference for the bond A–B.

In the complexation of PPO(L) with zinc halides, if size is the controlling parameter then ZnI_2 will produce the greatest elevation of T_g. Conversely, if polarity, as reflected in the ionic character of the zinc–halide bond, is the controlling parameter then $ZnCl_2$ should produce the greatest elevation of T_g. In fact $ZnBr_2$ produces the maximum elevation of T_g at any given mole fraction of salt and this suggests that a fine balance of both these effects is involved, as indeed it is in influencing the T_g of normal organic polymers.

A further complication arises with increasing size of anion or cation, assuming the same basic geometry (tetrahedral in the Zn salt case) of the complex. Increasing steric hindrance may make it more difficult to achieve a high degree of chelated structure of the chain and T_g will reach a limiting value at lower salt concentrations. Experimentally, as shown in *Figures 2* and *3*, the limiting value of T_g was observed at 30 mole % for $ZnCl_2$ complexes, 20 mole % for ZnI_2 and 18 mole % for $HgCl_2$ complexes.

An important factor in complex formation is the electronic configuration of the cation and this is particularly important in terms of the number and spatial arrangement of ligands around the cation, governed by the hybridization of the electronic orbitals. Thus complexation of the ether units can only occur in a conformation which satisfies the hybridization geometry of the central cation[33]. For example, zinc prefers a coordination number of 4 and normally forms tetrahedral complexes[26]. Molecular models indicate that neighbouring oxygens in the PPO chain can coordinate at these tetrahedral sites with a minimum of bond distortion.

Copper also prefers a coordination number of 4 in many of its complexes but these are often square planar rather than tetrahedral[34]. A possible explanation for the inability of $CuCl_2$ to elevate the T_g of PPO(L) is that it required the conformation of the polymer chain to satisfy the geometric requirements of a square planar complex. The polymer chain cannot satisfy these requirements without bond distortion and steric clashes.

Cations such as Co(II) prefer octahedral symmetry with a coordination number of 6 (34) and these cations would be capable of coordinating with more oxygen atoms than Zn(II). Thus more complicated interactions could occur in PPO(L)–$CoCl_2$ complexes than in $ZnCl_2$ complexes. For example, in $CoCl_2$ complexes it would be possible for tetradentate coordination from the chain. This bulky structure would greatly elevate T_g and may be responsible for the large elevation of T_g observed in PPO(L)–$CoCl_2$ complexes as seen in *Figure 3*. These complexes could still be compression moulded above T_g which suggests that any intermolecular coordination is either absent or that these crosslinks are thermally labile above T_g.

Effect of the polymer molecular weight

Moacanin and Cuddihy[5] reported that $LiClO_4$ behaved differently in high and low molecular weight poly(propylene oxide). In the low molecular weight material a single T_g was observed which moved to higher temperatures with increasing salt concentration. However, in the high molecular weight polymer two T_g's were observed at −65°C and −10°C. The former was thought to arise from uncoordinated chain segments and the latter from polyether segments stabilized by $LiClO_4$.

In the work reported in this paper both high and low molecular weight poly(propylene oxide)–zinc halide complexes exhibited a single T_g which moved to higher temperatures with increasing salt concentration as shown in *Figure 5*. It can be seen that both the initial and final values of T_g, at zero and high salt concentrations, were practically independent of molecular weight, but that in the intervening region the T_g of the lower molecular weight polymer was always higher, reflecting perhaps more efficient kinetics of chelation at lower molecular weights.

Plasticization effects

It has been briefly mentioned that even small amounts of water greatly depressed the T_g of PPO–$ZnCl_2$ complexes. This effect was common to all the polyether–metal salt complexes studied, although some were more susceptible to moisture than others. Similar plasticization effects have been observed by several workers[35–38] in ionomeric systems. These effects have been explained in terms of water either destroying ionic clusters or changing the nature of these clusters[37]. However, X-ray data for PPO(H)–$ZnCl_2$ complexes, which will be reported in a later publication[22], indicate the absence of any ionic clusters in these materials. In the present materials it is believed that water plasticizes polyether–salt complexes by breaking the coordinate bonds between the ether oxygen atoms of the polymer chain and the metal salt. These salts are then simultaneously hydrated and the system transforms to the original uncomplexed polymer 'filled' with hydrated salt. Such a system will have a T_g equal or close to the T_g of the uncomplexed polyether. There is some evidence from dielectric studies that a single water molecule displaces a single oxygen at low water concentrations thus breaking the chelate ring structure but otherwise leaving the salts singly coordinated to the chain. This state is easily reverted to the fully chelated form by heat or vacuum.

Mechanical relaxation studies

Several workers[39–42] have studied independently the dynamic mechanical properties of poly(propylene-oxide) and the data for the original polymer shown in *Figure 6* are in agreement with their results. In the original polymer no rubbery plateau region was observed above T_g and the rubbery modulus decreased rapidly with increasing temperature indicating extensive translational motion of the polymer chains. This behaviour is not unexpected in an amorphous uncrosslinked polymer since above T_g only chain entanglements hinder viscous flow.

The temperature dependence of the rubber modulus of PPO(H)–$ZnCl_2$ complexes containing 4.4 and 8.7 mole % $ZnCl_2$ was very similar to that of a lightly crosslinked polymer[21]. Crosslinks prevent the chains from translating relative to one another and, thus, to a first approximation, the rubbery modulus remains constant for a crosslinked rubber up to temperatures at which chemical degradation begins to occur. Therefore, one possible explanation of the decreased temperature dependence of the rubbery modulus was that the $ZnCl_2$ molecules were acting as crosslinks. Since the rubbery modulus still decreased with increasing temperature, this suggests that they were labile at temperatures above T_g. It is probable that the salt molecule crosslinks will not be as strong as normal crosslinks consisting of primary chemical bonds and this would favour the idea that the crosslinks were labile above T_g. The presence of only a few weak crosslinks would agree with the T_g data since the majority of oxygen atoms in the chain will be involved in chelate formation as previously described.

A precedent for thermally labile ionic crosslinks comes from the work of Otocka and Eirich[43]. In their studies of ionic bonding in butadiene copolymers they found that salt groups increased the rubbery modulus of the polymer by forming intermolecular bridges. Furthermore, they found that these bridges were neither thermally nor mechanically very stable and, although stronger than Van der Waal or hydrogen bonds, they were nowhere near as strong as covalent crosslinks. In the butadiene-methyl(2-methyl-5-vinyl) pyridinum iodide copolymer they observed a new relaxation above T_g at a temperature T_ϵ. Below T_ϵ the copolymer behaved as a conventional crosslinked elastomer but above T_ϵ the crosslinks were thermally and mechanically labile. In the PPO(H)–$ZnCl_2$ complexes no new relaxations were observed above T_g by mechanical spectroscopy but they were observed very strongly in dielectric relaxation.

CONCLUSIONS

Novel complexes have been prepared between polyethers and a number of metal halides. These complexes were optically transparent, though coloured, and remained thermoplastic even at very high salt loadings. The complexes formed with PPO(H) were tough polymeric materials which could be readily moulded above T_g using conventional plastics technology. The experimental evidence indicates that the salts were forming a single phase system with the polymer and were not acting as conventional second phase fillers. $CuCl_2$ and LiCl were exceptional in that they did not form single phase molecular complexes with the polyethers studied.

The molecularly dispersed complexes were amorphous and by d.s.c. showed a well-defined glass transition with, in the case of $CoCl_2$ in PPO(L), the T_g of the complex up to 140°C greater than the T_g of the original polymer. The elevation of T_g depended upon the polyether and upon both the amount and type of salt added. A satisfactory model for the poly(propylene oxide) complexes has been postulated involving coordination of two adjacent ether oxygen atoms in the polymer backbone to the metal salt, thus creating five-membered rings. Using this model it is possible to consider the system as a copolymer consisting of complexed and uncomplexed monomer units. T_g elevation of zinc halide complexes can then be adequately described using conventional copolymer relationships, at least up to 20 mole % of salt. Above this concentration further chelate formation became impossible but further small elevations of T_g can be explained by single oxygen coordination together with small amounts of coordination crosslinks between chains. These latter two possibilities are believed to be responsible for the T_g elevation of PTMG by $ZnCl_2$ since ring formation is unlikely in this polymer. Other metal salts may be capable of higher oxygen coordination numbers and the large effects of $CoCl_2$ can thus be rationalized.

In the mechanical relaxation studies of PPO(H)–$ZnCl_2$ complexes it was found that the mechanical T_g data paralleled the calorimetric T_g data. The glassy modulus was unaffected by the addition of $ZnCl_2$ to the polymer but the rubbery modulus increased. This increase was explained in terms of some $ZnCl_2$ molecules forming a few weak crosslinks which were sufficiently thermally labile to allow moulding above T_g.

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