Translated from *Uspekhi Khimii*, **57**, 856-870 (1988) U.D.C. 541.64:678.7-13:53.096

The Glass Points and Dielectric Relaxation of Carboxyl-containing Copolymers and Ionomers Based on Them

I.A.Ionova, Yu.B.Monakov, and S.R.Rafikov

The influence of the content and distribution of carboxy-groups along the polymer chain, the amount and nature of the cations introduced, and the dielectric constant of the polymer matrix on the dielectric relaxation and the glass points of carboxyl-containing copolymers (CCC) and their ionomers is considered. It is shown that the specific features of the properties of the ionomers are determined by the formation of ionic aggregates: multiplets in the presence of a low content of ion clusters at a fairly high concentration of ions which depends on the structure of the initial copolymer. It is concluded that the type of distribution of the carboxy-groups and the dielectric constant of the polymer matrix have a decisive influence on the ion aggregation process.
The bibliography includes 85 references.

CONTENTS

I. Introduction 475
II. Contribution of hydrogen bonds to the intermolecular interaction of carboxyl-containing copolymers 475
III. Dielectric relaxation properties of certain carboxyl-containing copolymers 476
IV. Transition to the vitreous state in ionomers 477
V. Dielectric relaxation of ionomers 479

I. INTRODUCTION

The partial or complete neutralisation of the COOH groups in carboxyl-containing copolymers leads to the occurrence of ionic interactions, which imparts to the copolymers unique properties capable of being varied within wide limits.[1-4] In the majority of ionic copolymers, this interaction of the ions entails microphase separation caused by the incompatibility of the salt groups and the hydrocarbon units of the chain.[5] At a certain concentration of the ions, the phase separation leads to the coexistence of two types of ionic aggregates, namely multiplets and clusters.

The introduction of ions into polymers is reflected most notably in the rheological behaviour of the melts, the relaxation of stresses, the dynamic, mechanical, and dielectric properties, and the glass point.[6-12] The present reivew deals with questions concerning the dielectric relaxation and glass points of ionomers based on carboxyl-containing copolymers of different composition and structure. Thermomechanical and dielectric studies make it possible to obtain information about the molecular mobility and the character of the aggregation of the salt groups and about the influence of this aggregation on important technological characteristics of the ionomers.

II. CONTRIBUTION OF HYDROGEN BONDS TO THE INTERMOLECULAR INTERACTION IN CARBOXYL-CONTAINING COPOLYMERS

The properties of polymers containing carboxy-groups are determined to a large extent by their ability to form hydrogen bonds between the C-OH groups. In contrast to chemical cross-links, hydrogen bonds are unstable, dissociating and reforming anew under the influence of thermal motion. However, it is in fact the hydrogen bonds that have a decisive influence on the mechanism of the vitrification of polymers[13] and on their mechanical properties in the highly elastic and viscofluid states.[14]

The majority of the carboxy-groups in carboxyl-containing copolymers are linked by hydrogen bonds into dimeric complexes[15-17] whose heat of dissociation varies from 7 to 15 kcal mol^{-1},[18-21] which agrees well with data for low-molecular-weight carboxylic acids.

Spectroscopic studies make it possible to characterise quantitatively the formation of hydrogen bonds from the temperature variation of the absorption band maxima corresponding to the $\nu(C=O)$ vibrations of the free COOH groups and dimeric associated species (1740-1750 and 1695-1705 cm^{-1} respectively).[22-26] On heating to the glass point T_g, the relative intensities of these bands hardly change, while at higher temperatures the low-frequency band weakens and the intensity of the 1740 cm^{-1} band increases.[18,22] For the styrene-methacrylic acid (MAA) (85:15) copolymers, an inflection associated with the dissociation of the intermolecular hydrogen bonds appears on the curves for the temperature variation of the 1700 and 1745 cm^{-1} absorption band intensities at 120 °C, which corresponds to the glass point, also found to be 120 °C by other methods.[18,27]

Detailed study of the temperature variation of the intermolecular interaction energy in polystyrene (PS) and in the styrene-MAA copolymer (16 mole %) by differential IR spectroscopy[28,29] showed that appreciable disruption of the hydrogen bonds and weakening of the van der Waals intermolecular interaction (interaction mainly between benzene rings) begin already in the region of the temperature of the β-transition;† the first stage of this process occurs in the range of the glass points. The character of the temperature variation of the energy for intermolecular bonds of different types is different. Relatively weak van der Waals interaction changes stepwise, falling especially sharply after the attainment of the fluidity temperature. In the case of hydrogen bonds, the temperature variation of the energy shows breaks at characteristic temperatures.[28]

The main effect occurring when carboxy-groups are introduced into the copolymer—the formation of hydrogen bonds—intensifies the intermolecular interaction. However, the copolymerisation of styrene with MAA entails also a series of other effects: a weakening of the van der Waals interaction, an increase in mechanical losses in the region of the β-transition compared with PS; an increase in the

†The β-transition, which corresponds to the onset of the movement of short sequences of styrene units, is a precursor of the movement which occurs at T_g.[30,31]

degree of coiling of the chains.[29] It follows from the study of the conformational changes in the styrene–MAA copolymer that these effects are especially pronounced, starting from an MAA concentration of 10–15 mole %, in the copolymers, and the average distances between the hydrogen bond bridges become comparable to the increase in the size of Kuhn's kinetic segment in PS.[29]

In view of the small decrease in the intermolecular interaction energy on transition through the glass point,[28] the appreciable change in the mechanical properties of polymers in the region of T_g cannot be explained solely by the decrease in intermolecular interaction energy and is apparently induced by the appearance of cooperative segmental motion. This is confirmed by the shift of T_g towards higher temperatures with increase in the content of COOH groups in the copolymer. Thus the increase in the MAA content in the copolymer with methyl methacrylate (MMA) from zero to 15 and 28% is accompanied by an increase in the glass point from 103 °C to 109° and 137 °C respectively.[17] The shift of T_g towards higher temperatures with increase in the number of carboxy-groups is caused by the increased hydrogen bond network. In the butadiene–MAA copolymer, the increase in the number of hydrogen bonds with increase in the content of the acid also increases the dynamic modulus of elasticity and T_g.[32] The dependence of T_g on the content of the acid component is described most satisfactorily by the equation for cross-links.[20,32]

The majority of the experimental data lead to the conclusion that interchain cross-links are formed preferentially via hydrogen bonding.[15,18,23] The change in the thermodynamic parameters in the ethyl methacrylate–MAA copolymers with increase in the MAA content is also explained by the intensification of the interchain interaction as a consequence of the formation of hydrogen bonds:[33] a decrease in their heat capacity, entropy, and free energy and an increase in the equilibrium constant and the limiting copolymerisation temperature, which corresponds to an increase in the thermodynamic stability of the copolymers. The above changes in the thermodynamic parameters of the copolymers are much greater than might have been expected from the additivity of the properties of the copolymers relative to the corresponding homopolymers.

The intramolecular bonds probably begin to appear in the presence of a fairly high content of carboxy-groups. In a study[34] of the physicomechanical properties of MAA and butyl acrylate copolymers, a maximum was observed on the curves for the dependence of the stability on composition. The presence of the maximum has been explained by the fact that initially an increase in the MAA content entails an increase in the number of intermolecular hydrogen bonds and hence the stability of the copolymer increases. On further increase in the MAA fraction in the copolymer, intramolecular bonds begin to appear, which leads to the coiling of the macromolecules into globules; as a result, the stability of the copolymer diminishes owing to the decrease in the energy of cohesion. In polyacrylic acid, dimerisation takes place mainly via the carboxy-groups belonging to the same hydrocarbon chain.[35]

III. DIELECTRIC RELAXATION PROPERTIES OF CERTAIN CARBOXYL-CONTAINING COPOLYMERS

The study of the dielectric properties of CCC provides important information about the role of hydrogen bonds in molecular relaxation proceses. The results of the investigation of the dielectric relaxation processes in copolymers of ethylene with methacrylic and acrylic acids have shown that α- and β-relaxation processes predominate in these copolymers.[36,40] The relaxation α-transition is associated with vitrification processes in the copolymer. The number of dipoles participating in the α-process can be calculated from the experimental data by the Onsager equation

$$N = \frac{9kT}{4\pi\mu^2} \frac{(2\varepsilon_0 + \varepsilon_\infty)(\varepsilon_0 - \varepsilon_\infty)}{\varepsilon_0 (\varepsilon_\infty + 2)^2}$$

where N is the number of dipoles, T the absolute temperature, μ the electric dipole moment of the COOH groups amounting to 1.75 D,[37] and ε_0 and ε_∞ are the relaxation and non-relaxation dielectric constants respectively. The number of free COOH groups determines the intensity of the observed α-relaxation. The α-process is in fact associated with their mobility and reorientation in the external electric field.[38,39] The low-temperature β-process is determined in both copolymers by the low mobility of the main chains of the copolymer.[36]

The β-relaxation observed in the copolymers of MAA and the polar methyl methacrylate at temperatures below T_g is essentially due to the movement of the ester side groups.[41] This is confirmed by the finding that any change in the MAA content does not shift the β-relaxation peak along the temperature axis (Fig.1), while the intensity of the dielectric relaxation $\Delta\varepsilon_\beta$ diminishes linearly with increase in the MAA fraction in the copolymer. The activation energy for the β-process has been estimated as 19 kcal mol^{-1}.[41] The sharp peak in the region of high temperatures (Fig.1) corresponds to the α-process, which is determined by the segmental thermal motion of the chain. With increase in the MAA content in the specimen, the temperature at which α-relaxation is observed shifts towards higher values and at the same time the activation energy for the α-process increases, which means that the segmental motion of the main chain of the copolymer is limited by the MAA units.

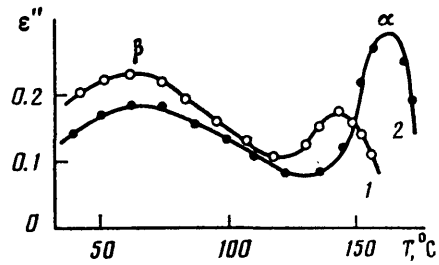


Figure 1. Temperature variation of the dielectric losses coefficient ε'' for the MMA–MAA copolymers at 30 Hz; MAA content (mole %): 1) 15; 2) 28.[41]

For the α-process, the increase in the relaxation intensity with temperature is caused by the increase in the number of mobile units as a result of the dissociation of the hydrogen bonds and the number of mobile units is assumed to be proportional to the dissociation constant. The dissociation energy of the hydrogen-bonded MAA dimer in the highly elastic state has been determined from the temperature variation of the relaxation intensity for α-processes ($\Delta\varepsilon_\alpha$). It proved to be 13 kcal mol^{-1}, which agrees with the dissociation energy determined from IR studies[17] for the MAA dimer in the MMA–MAA copolymer and with data for the dimers of other acids. However, the dissociation energy of the dimeric complex in the vitreous state is much lower than in the highly elastic state (0.7 kcal mol^{-1}). This has been attributed to differences between the supermolecular structures of the vitreous and highly elastic states. Although it follows from IR studies that the most intense

dissociation of hydrogen bonds occurs in the highly elastic state, a large number of the hydrogen-bonded dimeric complexes remain stable even at temperatures above T_g, as shown by the low value of the dissociation constant (4.27×10^{-5} mol cm^{-3}) and by the character of the dependence of the dielectric relaxation intensity on the number of cross-links.[17] Hence it follows that, even in the highly elastic state of the CCC, the hydrogen bonds act as fluctuating intermolecular bonds, although their energy is lower by a factor of 10 than the energy of covalent cross-links.

The replacement of methacrylic acid by acrylic acid (AA), i.e. the absence of α-methyl groups, influences the molecular mobility of the MMA–AA copolymer. In the study of the dielectric properties of these copolymers, two relaxation transitions were also observed: the high-temperature α-transition associated with segmental mobility and the low-temperature β-transition due to the mobility of the side groups.[42] In the case of the α-process, the relaxation intensity Δε, calculated from the area under the curve describing the variation of the dielectric losses coefficient ε″ with $1/T$ in accordance with the Williams equation, increases with increase in temperature (in contrast to the methacrylate homopolymer for which Δε is almost independent of temperature). The dissociation energy of the AA dimers, determined from the temperature variation of Δε, agrees well with the calculation based on the IR spectra. The activation energy ΔH^* and the temperature of the maximum T_{max} for the α-process decrease with increase in the content of the AA dimer in contrast to the MMA–MAA copolymer, for which both ΔH^* and T_{max} increase with increase in the MAA fraction.[41] On the other hand, the dissociation constants of the dimers of both copolymers, found from the IR spectra, are the same. Evidently, in the absence of the α-methyl group, the acrylic fragments play an important role in the increased segmental mobility in the copolymer at temperatures exceeding the glass point when the AA dimers decompose. The characteristics of the β-process depend little on the AA content, as in the case of the MMA–MAA copolymer.

In the case of the styrene–MAA copolymer,[43] a single peak, whose position and height increase with increase in the MAA content, is observed in the temperature variation of the dielectric losses coefficient ε″ in the region of the glass point. This is associated with the fact that an increase in the MAA fraction in the copolymer increases the number of cross-links formed by the acid dimers, which increase T_g and hence shift the α-relaxation to the region of higher temperatures. Calculations based on the monomer–dimer equilibrium have shown that 20% of the COOH groups are in a free state at T_g; they in fact contribute to ε″. With increase in temperature, the dimers ⇄ free COOH groups equilibrium is displaced to the right. Therefore, the higher the temperature corresponding to the ε″ peak, the greater its intensity. The initial sharp rise on the curve describing the variation of the temperature of the α-relaxation maximum ε″ with the content of carboxy-groups[43] is explained by the fact that, at low concentrations of the dimeric complexes, cross-links can suppress molecular motion more effectively that at high concentrations. This is also indicated by the minimal electrical conductivity σ (COOH groups make the main contribution to σ) at a concentration of 5 mole %, which is associated with the influence on σ not only by the properties of the charge carriers but also by the molecular mobility of the polymer matrix.

In the styrene–MAA block copolymers (with an MAA content of 5–30 mole %), two clear-cut α-processes are observed: at ~130 °C (α_1) and at 180 °C (α_2). The presence of two maxima, corresponding to the α-processes, not only confirms the block structure of the copolymers synthesised in emulsion but also indicates their microheterogeneity, i.e. the existence of two phases in the specimen.[44] One phase contains predominanatly polystyrene (PS) blocks and the other is enriched in poly-MAA blocks. The α_1-process at 130 °C is associated with the manifestation of segmental mobility of the PS blocks and its position depends only slightly on the ratio of the monomer units in the copolymer. The α_2-process at 180 °C is due to the molecular mobility in the region of the phase containing the poly-MAA blocks. With increase in the MAA content in the copolymer, the α_2-process shifts somewhat towards high temperatures and its intensity increases.

Thus the properties of CCC are mainly determined by their ability to form hydrogen bonds. Additional contacts at the intramolecular and intermolecular levels arise as a result of the hydrogen bonds, which increases the glass points and fluidity of the CCC. At low temperatures, the carboxy-groups exhibit a tendency to dimerise via hydrogen bonding, which renders them dielectrically inactive. With increase in temperature, the hydrogen-bonded carboxy-groups dissociate and exert the corresponding influence on the dielectric relaxation, for the behaviour of which free COOH groups are responsible.

IV. TRANSITION TO THE VITREOUS STATE IN IONOMERS

A partial or complete neutralisation of the carboxy-groups in the CCC leads to the appearance of a series of their specific properties, which are similar for different classes of ionomers. Thus the ability to adsorb water, the character of the variation of T_g with the concentration of ions, and the mechanical and dielectric properties of ethylenic and stryrene ionomers are very similar, while polystyrene and polyethylene differ markedly,[45] which is due to the characteristic features of the structures of the ionomers determined by the manifestation of ionic interactions.[46–53]

Neutralisation of carboxy-groups in CCC influences especially the glass point, which increases after the introduction of ionised groups into the polymer.[54–65] This increase in T_g is associated mainly with the decrease in segmental mobility as a consequence of ionic interactions and therefore depends on the nature of the cation.[5] Analysis of T_g data from the standpoint of the anion–cation interaction as a factor limiting segmental mobility led to the following general T_g relation[57] for fully neutralised silicates, phosphates, and acrylates:

$$T_g = Aq/a + B$$

where q is the charge on the cation, a the distance between the centres of the charges on the anion and the cation, and A and B are constants. Graphically the dependence of T_g on q/a for both polyphosphates and other fully ionised homopolymers is represented by straight lines having the same slope.[66] In partially neutralised polyphosphates T_g also varies linearly with q/a, but partly neutralised acrylate systems do not exhibit such a dependence. This may be caused by the presence of highly structured rigid associated species, which appreciably diminish the segmental mobility of the polymer.

In organic ionomers, a linear dependence of T_g on q/a is in general not observed, because the morphology of these materials is fairly complex and may vary with the concentration of ions. When the content of ions in the ionomers is low, the initial increase in T_g with the concentration of ions is in most cases linear (from 2 to 10 K per mole % of the ion-containing comonomer).[5,57,68] The glass points of sodium ionomers based on ethylene[69] obey satisfactorily the equation

$$T_g = n_1 T_{g1} + n_2 T_{g2},$$

where n_1 and n_2 are the mole fractions and T_{g1} and T_{g2} are the glass points of the two homopolymers. The study of different mechanisms of the increase in T_g for styrene ionomers[19] leads to the conclusion that the main mechanism of the rise of T_g in these ionomers involves the formation of cross-links between ionic domains and not a copolymerisation effect, as in ethylenic ionomers.[69] It is most likely that the regular increase in T_g with the concentration of ions

in both ionomers is caused by a superposition of two effects: the cross-linking and copolymerisation mechanisms with the influence of one of these mechanisms predominating in each type of ionomer.

The monotonic variation of T_g with the ion content of ethylenic ionomers and also the results obtained in the study of the relaxation of stresses, the absorption of water, and the dynamic, mechanical, and dielectric properties show that ionic aggregates are present in these ionomers even at very low concentrations of the ionic comonomer.[70] On the other hand, the study of the character of the variation of the glass points and of the fluidity of the ionomers based on styrene (20 mole % MAA) over a wide ion concentration range[65] reveals the breakdown of the linear dependence of the transition temperatures on the ion concentration for 30% neutralisation (~6 mole %).

Such breakdown of the monotonic variation with increase in the content of sodium methacrylate above 6 mole % has been observed for all the parameters of the styrene-based ionomers;[71] this is a result of the change in the morphology of the ionic aggregates, namely the transition from small multiplet formations to higher-order ionic accumulations—clusters. The existence of clusters is due to the equilibrium between the electrostatic forces arising between individual multiplets‡ and the elastic forces of the macromolecular chains, which resist the attraction of the multiplets.[72] One of the necessary conditions for the formation of clusters is that the interactions of the hydrocarbon chains with one another and with ions should be different,[73] which ensures an effective attraction between the ions and tends to stabilise the clusters. High ion concentrations and low dielectric constants of the polymer matrix are also necessary for the formation of clusters; on heating above a critical temperature, the clusters decompose.[73]

The unusual dependence of T_g on the content of the acrylic acid salt in ethyl acrylate copolymers is also associated with the formation of ionic clusters.[5,56] A single general curve is obtained for all the ions investigated (Na^+, Cs^+, Li^+, K^+, Ca^{2+}, Ba^{2+}) when the function $T_g = f(Cq/a)$ is plotted. Here C is the content of salt groups, q the charge on the cation, and a the distance between the centres of the charges on the anion and cation (Fig.2). The non-linear section corresponds to the deviation from the principle of the temperature–time superposition in the relaxation of stress for the ethyle acrylate–sodium acrylate copolymer (12 mole % of the ion-containing comonomer) and reflects the formation of clusters. Evidently in the region of low values of Cq/a, to which corresponds the linear section of the curve, the multiplets exert the dominant influence, while the clusters determine the behaviour of the ethyl acrylate ionomers for higher values of Cq/a. It follows from the data of Matsuura and Eisenberg[56] that the "cluster formation" principle, determining the rheological behaviour of ionomers, depends both on the ion concentration and on q/a; the character of the dependence of T_g on q/a, illustrated in Fig.2, is encountered only in materials in which fairly intense cluster formation takes place.[5] The effect involving the increase in T_g almost by a factor of two when the ion content in ethyl acrylate ionomers varies from 10 to 25% can be understood if it is supposed that the clusters ensure a more effective cross-linking than simple multiplets.

An important factor influencing T_g for ionomers is the amount of water which they have absorbed; water, whose content increases with ion concentration, lowers T_g. It has been shown that T_g for the sodium salt of polyacrylic acid decreases by ~8 K each time the water content is raised by 10%.[66] In ethyl acrylate-based ionomers in the presence of a definite amount of water (≥20 wt.%), T_g varies linearly with the water content regardless of the ion concentration (in the region of 20–50 mole % of sodium acrylate).

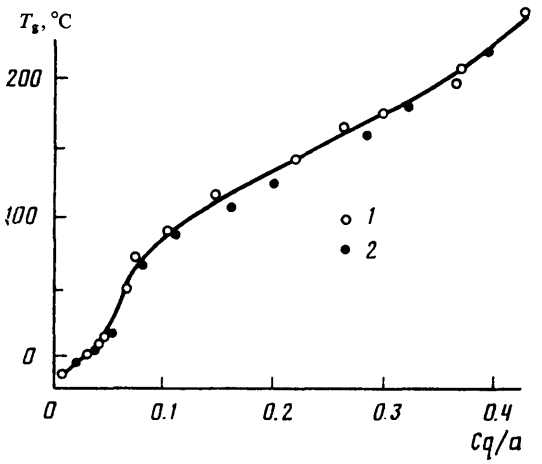


Figure 2. Dependence of T_g for ionomers based on the ethyl acrylate–acrylic acid copolymer on Cq/a for different ions: 1) Na^+, Li^+, Ca^{2+}, and Ba^{2+}; 2) K^+ and Cs^+.[56]

These data are qualitatively similar to the attainment of a plateau on the plot of T_g against ion concentration, which is observed for ionomers based on styrene–n-butyl methacrylate copolymers.[74] The glass points of these ionomers increase with increase in the ion content to 1.5 mole %. The limiting value of T_g is higher by 5–20 K that the T_g for the initial copolymer and depends on the molecular weight of the copolymer. The plateau on the relation between T_g and ion concentration can be accounted for by the balance between the influence of the ions, which increases the rigidity of the chain, and the plasticising action of water. In ionomers based on copolymers of acrylic acid and methyl methacrylate, T_g increases with increase in ion concentration in the range $0-1.5 \times 10^{-3}$ equiv. cm^{-3}.[75] Above the critical concentration (1.5×10^{-3} equiv. cm^{-3}), which is independent of the content of acrylic acid in the initial copolymer, T_g does not change. This can be explained by the for-mation of clusters of ionised groups which do not influence T_g. It has been suggested by Matsuura and Eisenberg[56] that the contradictions between the results of their studies of T_g for ethyl acrylate-based ionomers and the data of Tsutsui et al.[75] may be due to a number of causes. It may be that the character of the dependence of T_g on the ion content in these ionomers reflects the differences between the structures of the copolymers or clusters. Furthermore, the high degree of conversion of ionomers based on MMA–AA copolymers (36.5–48.7%), which is much higher than the degree of conversion of ethyl acrylate ionomers (7.2–14.5%), may lead to a high compositional inhomogeneity in the polymer and as a consequence to the separation of the specimen into different phases. Another possible cause of the disagreements is the presence of water, remaining in the specimens investigated by Tsutsui et al. after drying under mild conditions, which decreases T_g.

The nature of the cation should evidently exert an appreciable influence on the T_g of the ionomers via the parameter q/a. It follows from the study of a series of ionic copolymers based on butadiene that the univalent cations Na^+ and Li^+ have a greater influence on T_g than the univalent anion I^-.[76,77] There are indications

‡Multiplets are small compact ionic aggregates.

that Mg^{2+} ions in the ionised ethylene–acrylic acid copolymers are more effective from the standpoint of the increase in T_g than Na^+ ions. The dependence of the glass point and fluidity of the ionomers on the nature of the cation introduced can be traced satisfactorily in ionomers based on statistical styrene–methacrylic acid (20 mole %) copolymers.[64]

Under identical neutralisation conditions, the glass points and fluidities of the ionomers containing Na^+ ions exceed the corresponding values for the copolymers neutralised by Rb^+ ions.[64]. The reason is apparently that, as a result of the aggregtion of the salt groups of the ionomers in the hydrocarbon matrix, there is a possibility of a distribution of the ionised carboxy-groups in which they find themselves opposite one another, so that an electrostatic interaction takes place between them. If account is taken of the fact that the strength of interaction between ions is inversely proportional to the distance between them, which is determined by the radii of the ions, then "ionic cross-linking" with the Na^+ cation, which has a greater radius than the Rb^+ cation, is more stable. For this reason, specimens of ionomers containing Na^+ have higher transition temperatures than the corresponding Rb^+.

Another picture is observed if bivalent metal acetates have been used for the neutralisation of the carboxy-groups of the styrene–MAA statistical copolymer. Neutralisation by Zn^{2+} and Ca^{2+} ions alters very slightly the glass points and fluidities of the ionomers. This phenomenon can be explained by the fact that the neutralising agents in this case are not the doubly charged metal ions M^{2+} but singly charged ions of the type $M(CH_3COO)^+$ formed via the reaction[78]

$$M(CH_3COO)_2 \rightleftarrows M(CH_3COO)^+ + CH_3COO^-$$

The acetate groups in such singly charged ions shield the ionic charges by virtue of their large size, diminishing thereby the stability of the ionic cross-linking, i.e. they manifest a kind of plasticising effect. This is confirmed by the finding that the thermomechanical curves for ionomers with different contents of both Zn^{2+} and Ca^{2+} are identical and exhibit all the temperature-dependent transitions characteristic of thermoplastics. Furthermore, ionomers with 30% substitution by Ca^{2+} and Zn^{2+} ions are readily soluble in dioxan and dimethylformamide, which also confirms the absence of "cross-links".[64]

For the same content of salt groups, the mode of their distribution along the copolymer chain has a great influence on the glass points of ionomers.[64,65] Thus, whereas in statistical styrene–methacrylic acid copolymers a complex type of dependence of T_g on the ion concentration is observed, the introduction of MAA into the polystyrene chain in the form of a block leads to the absence of such dependence of T_g on the degree of neutralisation. This is caused by the characteristic features of the structure of these polymers: the ionomers formed are block copolymers having the composition (MA-Na–MAA)–(styrene–MAA–MA-Na)$_m$. Statistical copolymers are formed within the limits of the blocks and the distribution of the monomers in them is as follows: in the first block, there is more sodium methacrylate (MA-Na) than methacrylic acid, while in the second block the styrene–MAA content greatly exceeds the content of sodium methacrylate. Since the size of the styrene–MAA–MA-Na blocks is comparable to the size of the kinetic segment, ionic cross-links have little influence on T_g,[65] which is confirmed by the insignificant displacement of the maximum of the tangent of the dielectric losses angle for the α_1-process towards higher temperatures with increase in the degree of neutralisation.

The properties of ionomers based on graft copolymers are determined by the length of the blocks containing the ionogenic groups. They are similar to those of the ionomers of block-copolymers provided that the chain length of the grafted polyacid is sufficiently large. Thus the thermomechanical curves for ionomers based on graft ethylene–maleic anhydride copolymers,[64] in which the length of the side sections containing carboxy-groups is fairly considerable, showed the appearance of additional transition temperatures due to the manifestiation of the presence of ionic cross-links; these temperatures depend on the content of the acid and the degree of its neutralisation. The T_g for the monomers investigated are independent of the degree of neutralisation and are close to the melting point of polyethylene (100 °C). However, if the sections of the grafted polyacids are short (several monomer units), then the variation of the glass point with ion concentration in the ionomers of graft copolymers will resemble that for the ionomers of statistical copolymers. Such behaviour has been observed for ionomers based on graft styrene–MAA copolymers in which the short chains of the grafted poly-MAA are distributed statistically along the polystyrene chain.[44]

Thus the mode of distribution of the carboxy-groups (statistical block and graft copolymers) leads to different types of aggregation of the salt groups in the corresponding ionomers, which is distinctly manifested by the behaviour of the T_g of the ionomers. However, ion aggregation is difficult in a medium with a high dielectric constant,[5,73] which is reflected by the absence of a dependence of T_g for such ionomers (ionomers based on MAA–MAA copolymers) on the nature and amount of the cations and by the weak dependence of the maximum in the tangent of the dielectric losses angle for α-relaxation on the degree of neutralisation.

V. DIELECTRIC RELAXATION OF IONOMERS

The neutralisation of the carboxy-groups in the CCC alters the dielectric relaxation of the copolymers, owing to its sensitivity to the presence of the polar groups of acids and salts directly involved in the formation of clusters. Dielectric studies can yield valuable information about the structure and character of the molecular motion of ionomers.[40,43,55,79–84]

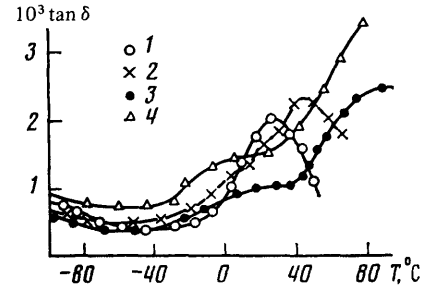


Figure 3. Temperature variation of tan δ for the sodium salts of the ethylene–MAA copolymer (4.1 mole %) at 1 kHz; degree of neutralisation (%): 1) 0; 2) 19; 3) 41; 4) 72.[79]

The intensity of α-relaxation in ethylene–MAA copolymers diminishes with increase in the extent of neutralisation and α_1- and α_2-relaxations appear (Fig.3).[79] The α_1-relaxation is associated with the T_g of the ionic phase of the ionomer; this is confirmed by the absence of α_1-relaxation in the copolymer and by the increase in its intensity and its shift towards higher temperatures with increase in the degree of neutralisation and by the bend in the curve describing the frequency and temperature variation for the α_1-process. The bend in the frequency-temperature variation for the α_2-process shows that this relaxation characterises the T_g of the hydrocarbon phase,

which becomes dielectrically active by virtue of the presence of free carboxy- or salt groups linked to the segments of this phase. The water absorbed by the ionomers shifts the α_1-peak towards lower temperatures, which is associated with the plasticising effect of water on the ionic phase. At a temperature of about –43 °C, an additional peak appears, whose height is approximately proportional to the water content and whose position depends slightly on its amount.[79] Modern calculations of the relaxation intensity have shown that the mobility of the water molecules themselves is responsible for this peak.

In the sodium salts of the ethylene–acrylic acid copolymer (9.3 mole %), the temperature of the α-relaxation maximum does not change and the height of the peak increases with increase in the degree of neutralisation W to 20%; for $W > 30\%$, the temperature of the α-maximum rises and the height of the peak diminishes following the appearance of α_1-relaxation.[40] Simultaneously with the change in the character of the temperature variation of the maximum and height of the relaxation peak as a function of the degree of neutralisation, the character of the temperature variation of the relaxation time also changes: for low extents of neutralisation, it is described by the Williams–Lundell–Ferry equation, whilst for high extents of neutralisation it is described by the Arrhenius equation. The dielectric increment $\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$, calculated from the Cole–Cole diagram for the α-relaxation, increases in proportion to the degree of neutralisation up to 20% ($\Delta\varepsilon = 0.119$ for $W = 0$ and 0.826 for $W = 20\%$), diminishing rapidly with increase in the degree of neutralisation above 30%. The influence of the degree of neutralisation on all the relaxation properties of the ethylene–AA copolymer indicated can be explained by the formation of ionic clusters for $W > 30\%$.[40] Since Δε at 30% neutralisation is higher than for the copolymer, it is concluded that not all the COONa groups are combined into clusters and it is suggested that these groups are dielectrically active in the α-relaxation process.

Detailed study of β-relaxation has thrown defnite light on the investigation of the structure and molecular motion in ionomers, because its extent is associated with the polar COONa groups which have not entered the clusters. Indeed, for the sodium salts of the copolymer, the position of the β-peak along the temperature scale is independent of the degree of neutralisation W, but the peak height increases with increase in W.[40,57] The dielectric increment for β-relaxation increases in proportion to the degree of neutralisation up to 20% and diminishes for $W > 30\%$. Since at low ion concentrations aggregation is not observed, the number of polar COONa groups responsible for β-relaxation increases with increase in the ion content. As a result of the formation of ionic clusters at a higher ion concentration, the number of polar groups involved in β-relaxation diminishes. Consequently the dielectric β-relaxation provides new evidence for the existence of clusters in ionomers.

The formation of ionic aggregates in copper(II) salts of the ethylene–acrylic acid copolymer proceeds with more difficulty than in the sodium salts owing to the complex structure of the copper(II) salts.[84] The temperature dependence of the dielectric losses coefficient ε″ for the copper salt of the ethylene–AA copolymer, which has in the main the dimeric structure of hydrated copper acetate,[85] is characterised by two maxima located at 50 °C (α-relaxation) and –100 °C (β-relaxation) for 20% neutralisation. The first maximum is due to the molecular Brownian movement at temperatures above T_g and the second is associated with the local molecular mobility below T_g, as in the sodium salts of these copolymers. In the region of α-relaxation the temperature T_{max}, corresponding to the maximum value of ε″, increases with increased extent of neutralisation and a diminution of ε″ is observed simultaneously up to $W = 34\%$. The α-relaxation process at $W = 71\%$ has a complex character and consists of α_2-relaxation at 0°C and α_1-relaxation at 60 °C. The dependence of the logarithm of the frequency of the ε″ maximum on $1/T_{max}$ satisfies the Williams–Lundell–Ferry equation for $W < 5\%$ and the Arrhenius equation for $W > 20\%$,[84] which indicates the retardation of the Brownian movement as a consequence of the interaction of the ionic groups with increase in the extent of neutralisation from 5 to 20%. The dependence of the dilelectric increment Δε on the extent of neutralisation passes through a maximum at $W = 5\%$, but at $W > 20\%$ the quantity Δε gradually diminishes, while T_{max} increases, owing to the onset of ionic aggregation at $W > 20\%$ (Fig.4). The increase in Δε and the decrease in T_{max} in the specimen neutralised to the extent of 71% indicate that, in the highly neutralised polymer, many Cu^{2+} ions can remain outside the ionic aggregates. This has also been observed for β-relaxation. The α_2-relaxation, appearing in the 71% neutralised specimen, refers, according to the authors,[84] to the molecular motion of short segments, incorporating copper(II) salts, between ionic aggregates. This is confirmed by the low activation energy for α_2-relaxation (~ 18 kcal mol^{-1}).[84]

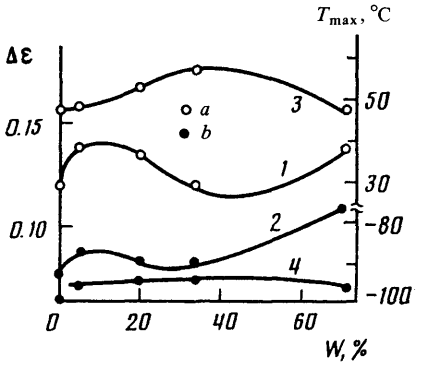


Figure 4. Dependence of the dielectric increment Δε (curves *1* and *2*) and of the position of the relaxation maximum T_{max} (curves *3* and *4*) on the degree of neutralisation W for the α- and β-relaxation in the copper(II) salts of the ethylene–AA copolymer (9 mole %): *a*) α-relaxation; *b*) β-relaxation.[84]

α_2-Relaxation has also been observed in the copper(II) salts of the styrene–methacrylic acid copolymer.[84,85] These salts have three types of structure: I—monomeric, II—monohydrated copper acetate, and III—pseudo-anhydrous copper formate, the fraction of each depending on the method used to prepare the copper carboxylate. These structures influence the molecular motion of the polymer; however, ionic aggregation in all the copper(II) salts of the styrene–MAA copolymer could not be observed either by the low-angle X-ray diffraction method or by electron microscopy.

Ionic aggregation with formation of clusters occurs in ionomers based on styrene with MA-Na (fully neutralised specimens containing between 2 and 9 mole % of sodium methacrylate).[80] The temperature variation of the tangent of the dielectric losses angle (tan δ) shows, after the subtraction of the losses due to conduction, two readily distinguishable overlapping maxima for all the ion concentrations except 2 mole %. Both peaks shift towards high temperatures with increase in the ion content. The low-temperature peak is due to regions with a low ion concentration, while the high-temperature peak is associated with large aggregates which have a higher T_g. The overall area under the peaks for the variation of tan δ with the reciprocal of temperature is correlated very satisfactorily with the overall ion concentration in the ionomers (correlation coefficient

0.975). The area under the low-temperature peak (α_2-relaxation) increases with increase in the salt content up to 5 mole % and then remains constant at higher concentrations.[5,57] This is evidence for the saturation of the hydrocarbon matrix by ionic groups at this ion concentration; at the higher ion concentration, all the additional ions are combined into clusters. On the other hand, the area under the high-temperature peak (α_1-relaxation) increases continuously with increasing concentration of the salt groups; at an ion concentration > 5 mole %, the increase accelerates.

With increase in temperature, the concentration of ionic groups in the hydrocarbon phase grows at the expense of the ion-rich region, i.e. the clusters decompose at high temperatures. This is indicated by the change in the relative sizes of the two relaxation peaks with increase in frequency. When the frequency is raised, which shifts both relaxation peaks towards higher temperatures, the height of the α_2-peak increases compared with the high-temperature α_1-peak.[57,80]

Thus it follows from the dielectric studies of the fully neutralised sodium ionomers based on the styrene–MAA copolymer[80] that clusters and multiplets coexist starting with an ion concentration of 2 mole %; the hydrocarbon matrix is saturated by ionic groups at 5–6 mole % of sodium methacrylate; the clusters dissociate at elevated temperatures. In the partly neutralised styrene–MAA polymers (9 mole %) two dielectric relaxation peaks appear at relatively low degrees of neutralisation (starting with 25%) in the region of the transition to the vitreous state, indicating the simultaneous presence of both multiplets and clusters in the ionomers.[43]

The temperature of the maximum T_{max} and the intensity ($T\Delta\varepsilon$) of the peak depend on the degree of neutralisation (Fig.5). Both peaks shift towards higher temperatures with increase in the extent of neutralisation W. However, at $W > 65\%$ (which corresponds to 5.85 mole % of the salt in the ionomer)[43] the increase in the extent of neutralisation leads to a faster shift of T_{max} for the high-temperature peak; on the other hand, T_{max} for the low-temperature peak increases very slowly, which is due to the saturation effect. Thus, as in fully neutralised styrene–MAA copolymers, in the partly neutralised copolymers containing ~6 mole % of ions the matrix is saturated by multiplets, while on further increase in the ion concentration the ionic groups begin to combine into clusters.

In the fully neutralised polymers, only 2% of the COO^-Na^+ groups are in a "free" state (are present as simple ion pairs), while in the remaining polymers they are combined into multiplets or clusters.[43] The presence of COO groups in partly neutralised copolymers increases the degree of dissolution of salt groups in the polymer matrix, such groups becoming dielectrically active.

While T_{max} for the low-temperature α_2-peak of the partly neutralised polymer is appreciably higher than for the pure salt containing the same number of ionic groups, in the case of the high-temperature peak the opposite situation obtains. Furthermore, the intensity of the α_2-peak of the partly neutralised polymer is much greater than that of the peak of the pure salt. The higher intensity of the low-temperature peak of the partly neutralised polymer is associated with the fact that the COONa groups combine with the COOH groups. Apart from giving rise to a considerable number of small clusters in the partly neutralised specimens (the clusters in the pure salt are more stable and larger), these additional interactions suppress the molecular motion in the matrix and shift the α_2-peak relative to the pure salt.

The different modes of distribution of the MAA units in the statistical block and graft copolymers lead to different characters of the aggregation of the salt groups in the corresponding monomers, which is clearly manifested in dielectric relaxation.[44] For the statistical styrene–MAA copolymers, the qualitative changes in the temperature variation of $\tan\delta$ for the sodium, rubidium, zinc, and cadmium ionomers with increase in the degree of neutralisation take place in the same manner. For all the ionomers, the intensity of the α-process increases with increase in the degree of neutralisation, which can be explained by the increase in dipole moment as the carboxy-groups are neutralised. The shift of the α-process to the high-temperature region is associated with the restriction of the segmental mobility with increase in the degree of neutralisation owing to ionic interactions. The high-temperature $\tan\delta$ maximum (above 200 °C) corresponding to molecular mobility in ionic clusters, whose presence might have been expected on the basis of earlier data,[43,80] could not be observed either because of the low fluidity temperatures of the ionomers investigated (below 200 °C) or as a consequence of the large dielectric losses associated with the increase in the electrical conductivity of the material in the region of the transition to the viscofluid state.

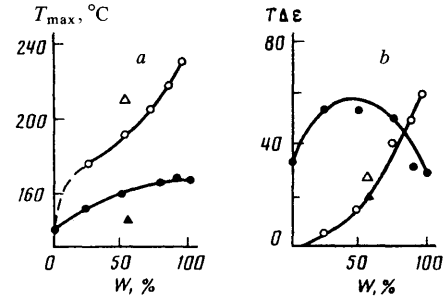


Figure 5. Dependence of T_{max} (*a*) and $\Delta\varepsilon$ (*b*) on the degree of neutralisation W for the high-temperature (1) and low-temperature (2) relaxation in the partly neutralised styrene–MAA copolymer (9 mole %); 3) and 4) the values of T_{max} and $T\Delta\varepsilon$ for the high- and low-temperature dielectric relaxation maxima respectively for the fully neutralised copolymer containing 5.06 mole % of the salt.[43] [The numbering of the symbols was omitted from the figure in the Russian text (Ed. of Translation).]

For the ionomers based on the styrene–MAA block copolymers, two distinct α-relaxation processes are observed, which makes it possible to infer their microheterogeneity.[44] The α_1-process is associated with the segmental mobility of the styrene–MAA–MA–Na blocks, while the α_2-process is determined by the segmental mobility of the phase enriched in MA–Na. With increase in the degree of neutralisation, the maxima in the tangent of the dielectric loss angle for the α_1- and α_2-processes become more intense, the α_2-process shifting markedly towards high temperatures (Fig.6). The small displacement of the process agrees with the small increase in the softening temperatures of the ionomers. The increasing intensity of the α_1-process shows that the PS blocks in these block copolymers do indeed contain statistically distributed MA–Na units which have a high dipole moment. The blocks enriched in MA–Na are segregated into a separate phase. The shift of the α_2-process to the temperature range above 250–300 °C (with a corresponding shift of the fluidity temperature) indicates intense ionic interactions within sections of this phase. Evidently the sizes of these sections are such that they incorporate blocks ranging from several macromolecules.

Therefore the viscous flow of the ionomer can begin only at a temperature where the energy of thermal motion is sufficient to dissociate the intermolecular ionic bonds to "deinhibit" the molecular mobility in these sections.

For the ionomers based on graft styrene–MAA copolymers, a single peak corresponding to the α-process is observed in the temperature variation of tan δ; its position and intensity vary with increasing degree of neutralisation similarly to the peak for the α-process involving ionomers based on statistical copolymers. Such similarity of the properties of the ionomers of graft and statistical copolymers shows that the short chains of graft poly-MAA [44] are distributed statistically along the chain of the PS macromolecule.

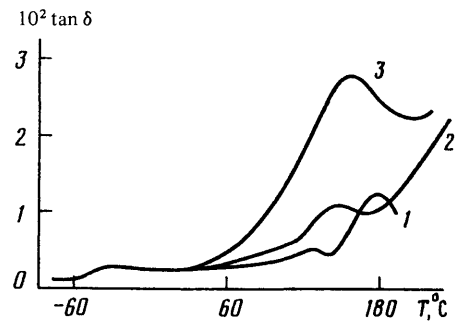


Figure 6. Temperature variation of tan δ for the styrene–MAA block copolymers (12 mole %) (curve *1*) and of its sodium ionomers (curves *2* and *3*); degree of neutralisation (mole %): 2) 10; 3) 40.[44]

Thus the dielectric behaviour of the ionomers can be most convincingly interpreted from the standpoint of microphase separation: whereas there is only one peak of the dielectric losses angle tangent for the initial copolymer, after neutralisation two such peaks with a fairly high intensity appear. This phenomenon reflects the existence of two glass points. The first of these is the T_g of the matrix, which contains a small amount of ionic groups, while the second is the T_g of the phase-separated ion-rich region. In other words, below a certain ion concentration the dielectric behaviour of the polymers is determined by small compact ionic aggregates (multiplets), which behave like cross-links, while above this critical concentration the larger ionic aggregates (clusters) influence the properties of the ionomers.

The dielectric relaxation and the character of the variation of T_g with ion concentrations for monomers based on vitreous and partly crystalline CCC are qualitatively similar despite the differences between the stabilities of the main chains and the dielectric constants of the hydrocarbon matrices. The nature of the neutralised groups determines the capacity of the salt groups for aggregation and therefore influences the physical properties of the ionomers. The mode of distribution of the salt groups along the polymer chain and the dielectric constant of the polymer matrix have a decisive influence on the aggregation of ions. The nature of the cation and its content influence the properties of the ionomers at specific concentrations of the carboxy-groups, which depend on the structure (type) of the initial copolymer.

REFERENCES

1. R.Rees, D.Vaughan, and A.Surlyn, Polym.Prepr., 1965, **6**, 287.
2. R.H.Kinsey, Appl.Polym.Symp., 1969(11), 77.
3. L.A.Sirota and V.M.Polyakova, "Khimicheskaya Tekhnologiya" (Chemical Engineering), Izd.Naukova Dumka, Kiev, 1978, No.3, p.21.
4. S.R.Rafikov and A.A.Andrusenko, "Sintez i Svoistva Polimerov" (The Synthesis and Properties of Polymers), Ufa, 1974, p.4.
5. C.Bazuin and A.Eisenberg, Ind.Eng.Chem.Prod.Res.Dev., 1981, **20**, 271.
6. S.Bonotto and E.F.Bonner, Macromolecules, 1968, **1**, 510.
7. M.Navratil and A.Eisenberg, Macromolecules, 1974, **7**, 84.
8. R.Longworth and D.Vaughan, Amer.Chem.Soc.Polym. Prepr., 1968, **9**, 525.
9. A.Eisenberg, H.Matsuura, and T.Tsutsui, J.Polym.Sci.Polym. Phys.Ed., 1980, **18**, 479.
10. M.Nagura, K.Hirabayashi, and H.Ishikawa, Angew.Macromol. Chem., 1975, **43**, 185.
11. D.G.Peiffer, Polymer, 1980, **21**, 1135.
12. A.Eisenberg and M.Navratil, J.Polym.Sci.Polym.Letters, 1972, **10**, 537.
13. A.A.Tager, "Fizikokhimiya Polimerov" (Physical Chemistry of Polymers), Izd.Khimiya, Moscow, 1978, p.159.
14. A.A.Askadskii, "Deformatsiya Polimerov" (Deformation of Polymers), Izd.Khimiya, Moscow, 1973, p.185.
15. W.J.Macknight, L.W.McKenna, B.E.Read, and R.S.Stein, J.Phys.Chem., 1968, **72**, 1122.
16. B.E.Read and R.S.Stein, Macromolecules, 1968, **1**, 116.
17. Y.Kihira, J.Sci.Hiroshima Univ., 1976, **40A**(2), 293.
18. K.Ogura and H.Sobue, Polymer J., 1972, **3**(2), 153.
19. K.Ogura, H.Sobue, and S.Nakamura, J.Polym.Sci.Polym.Phys. Ed., 1973, **11**, 2079.
20. E.P.Otocka and T.K.Kwei, Macromolecules, 1968, **1**, 49.
21. T.R.Earnest and W.J.Macknight, Macromolecules, 1980, **13**, 844.
22. A.G.Zak, N.A.Kuznetsov, I.S.Lishanskii, and A.L.Smolyanskii, Izv.Vys.Ucheb.Zaved., Khim.i Khim.Tekhnol., 1975, **18**, 951.
23. E.P.Otocka and T.K.Kwei, Amer.Chem.Soc.Polym.Prepr., 1968, **9**, 583.
24. L.M.Kalyuzhnaya, A.N.Krasovskii, Yu.N.Panov, et al., Vysokomol.Soed., 1975, **17A**, 993.
25. Y.Uemura, R.S.Stein, and W.J.Macknight, Macromolecules, 1971, **4**, 490.
26. E.Gruber, J.Mohammed, and J.Schurz, Kolloid Z. und Z.Polym., 1974, **252**, 278.
27. V.A.Bershtein, V.M.Egorov, L.G.Razgulyaeva, and V.A.Stepanov, Vysokomol.Soed., 1978, **20A**, 2278.
28. V.A.Bershtein, M.Z.Petkevich, L.G.Razgulyaeva, and V.A.Stepanov, Vysokomol.Soed., 1978, **20A**, 2681.
29. V.A.Bershtein, L.G.Razgulyaeva, V.M.Gal'perin, et al., Vysokomol.Soed., 1978, **20A**, 1885.
30. R.F.Boyer, Polymer, 1976, **17**, 996.
31. O.Yano and Y.Wada, J.Polym.Sci., A-2, 1971, **9**, 669.
32. E.P.Otocka and F.R.Eirich, J.Polym.Sci.,A-2, 1968, **6**, 395.
33. I.B.Rabinovich and L.I.Pavlinov, Vysokomol.Soed., 1968, **10A**, 416.
34. S.A.Ryabov, N.N.Slavnitskaya, L.A.Mitrofanova, and Yu.D.Semchikov, Fiziko-khimicheskie Osnovy Sinteza i Pererabotki Polimerov, 1977(2), 76.
35. V.N.Demishev, L.G.Sidorova, M.V.Shishkina, et al., Zhur. Prikl.Khim., 1972, 350.
36. E.A.Nicol, B.E.Read, and G.W.Chantry, Brit.Polym.J., 1973, **5**, 379.

37. R.D.Nelson, D.R.Lide, and A.A.Maryott, "Selected Values of Electric Dipole Moments for Molecules in the Gas Phase", Acad.Press, New York, 1967, p.75.
38. R.M.Neumann and W.J.Macknight, J.Polym.Sci.Polym.Symp., 1978(63), 281.
39. W.J.Macknight and E.A.Emerson, "Symposium in Connection with Meeting of American Chemical Soceity, 1971", Plenum Press, New York, 1972, p.237.
40. S.Yano, Y.Fujimara, F.Kato, et al., Polym.J., 1981, p.283.
41. Y.Kihira, J.Sci.Hiroshima Univ., 1976, **40A**(2), 285.
42. Y.Kihira, J.Murakami, and H.Yamamura, Amer.Chem.Soc. Polym.Prepr., 1979, **20**, 674.
43. K.Arai and A.Eisenberg, J.Macromol.Sci.Phys., 1980, **17B**, 803.
44. I.A.Ionova, G.V.Leplyanin, and S.R.Rafikov, Vysokomol. Soed., 1980, **22B**, 311.
45. A.Eisenberg, Amer.Chem.Soc.Polym.Prepr., 1973, **14**, 871.
46. R.Longworth and D.Vaughan, Nature, 1968, **218**(5136), 85.
47. W.J.Macknight, W.P.Taggart, and R.S.Stein, J.Polym.Sci. Polym.Symp. 1974(45), 113.
48. C.L.Marx, D.F.Caulfield, and S.L.Cooper, Macromolecules, 1973, **6**, 344.
49. J.Kao, R.S.Stein, W.J.Macknight, et al., Macromolecules, 1974, **7**, 95.
50. E.D.Andreeva, V.N.Nikitin, and Yu.M.Boyartchuk, Macromolecules, 1976, **9**, 238.
51. E.D.Andreeva and Yu.M.Boyarchuk, Vysokomol.Soed., 1976, **18B**, 179.
52. Yu.M.Boyarchuk, E.D.Andreeva, L.V.Konovalov, and V.N.Nikitin, Zhur.Prikl.Spektrosk., 1975, **23**, 101.
53. E.D.Andreeva, V.N.Nikitin, and Yu.M.Boyarchuk, Vysokomol.Soed., 1975, **17B**, 773.
54. A.Eisenberg, Macromolecules, 1971, **4**, 125.
55. W.J.Macknight and T.R.Earnest, J.Polym.Sci.Macromol.Rev., 1981, **16**, 41.
56. H.Matsuura and A.Eisenberg, J.Polym.Sci.Polym.Phys.Ed., 1976, **14**, 1201.
57. L.Holliday, Ionic Polymers, New York. Applied Science, 1975, 416.
58. L.S.Bolotnikova, A.G.Zak, I.S.Lishanskii, et al., Vysokomol. Soed., 1975, **17B**, 98.
59. M.W.Williams, J.Polym.Sci.Polym.Symp., 1974(45), 129.
60. T.Tsutsui and T.Tanaka, Polymer, 1977, **18**, 817.
61. D.G.Peiffer, Polymer, 1980, **21**, 1135.
62. B.I.Utei, B.M.Zuev, L.Kh.Akhmetgaleeva, and E.V.Kuznetsov, Trudy Kazan Khim.-Tekhnol.Inst., 1975, Part 56, 130.
63. R.Becker, Z.Phys.Chem., 1976, **257**, 667.
64. S.R.Rafikov, Yu.B.Monakov, and I.A.Ionova, Vysokomol. Soed., 1973, **15A**, 1974.
65. L.F.Antonova, I.A.Ionova, G.V.Leplyanin, and S.R.Rafikov, Article Deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 9.07.75, No.3026-75.
66. A.Eisenberg, H.Matsura, and T.Yokoyama, J.Polym.Sci., A-2, **9**, 2131.
67. A.Eisenberg, Amer.Chem.Soc.Polym.Prepr., 1979, **20**, 286.
68. A.Eisenberg, J.Polym.Sci.Polym.Symp., 1974(45), 99.
69. E.P.Otocka and T.K.Kwei, Macromolecules, 1968, **1**, 401.
70. A.Eisenberg and M.King, "Ion-Containing Polymers—Physical Properties and Structure", Acad.Press, New York, 1977, p.47.
71. R.Longworth, "Ionic Polymers", Halstead Press, New York, 1975, p.69.
72. A.Eisenberg, Macromolecules, 1970, **3**, 147.
73. O.A.Ponomarev and I.A.Ionova, Vysokomol.Soed., 1974, **16A**, 1023.
74. M.W.Williams, Polym.Prepr.Amer.Chem.Soc., 1973, **14**, 896.
75. T.Tsutsui, T.Yakoyama, and T.Tanaka, Kobunshi ronbushu, 1974, **31**, 565; Ref.Zhur.Khim., 1975, 7S125.
76. E.P.Otocka and F.R.Eirich, J.Polym.Sci., A-2, 1968, **6**, 921.
77. E.P.Otocka and F.R.Eirich, J.Polym.Sci., A-2, 1968, **6**, 933.
78. J.Marinsky (Editor), "Ion Exchange" (Translated into Russian), Izd.Mir, Moscow, 1968, p.371.
79. P.J.Phillips and W.J.Macknight, J.Polym.Sci., A-2, 1970, **8**, 727.
80. J.M.Hodge and A.Eisenberg, Macromolecules, 1978, **11**, 283.
81. E.P.Otocka, J.Macromol.Sci.Revs.Macromol.Chem., 1971, **C5**, 275.
82. J.M.Hodge and A.Eisenberg, J.Non-Cryst.Solids, 1978, **27**, 441.
83. A.Eisenberg, Adv.Polym.Sci., 1967, **5**, 59.
84. S.Yano, Y.Fujiwara, K.Aoki, and J.Yamauchi, Colloid and Polym.Sci., 1980, **258**, 61.
85. J.Yamauchi and S.Yano, Macromol.Chem., 1978, **179**, 2799.

Institute of Chemistry
of the Bashkir Scientific
Centre, The Urals Branch
of the USSR Academy
of Sciences, Ufa