Translated from *Uspekhi Khimii*, 48, 722-748 (1979) U.D.C. 541.64 : 539.199

The Influence of Hydrogen Bonds and Ionic Interactions on the Properties of Carboxyl-containing Copolymers and Ionomers Based on Them

M.G.Marina, Yu.B.Monakov, and S.R.Rafikov

The changes in the properties of copolymers as a function of the introduction of units with carboxy- and salt groups into the macrochain are examined. Attention is concentrated on the analysis of the results of the study of copolymers in the acid and ionomeric forms in solutions. The decisive influence of ionic interactions on the properties of ionomers in bulk and on their hydrodynamic and conformational characteristics is demonstrated. The difference between hydrogen and ionic bonds in the sense of their effects both on the primary ordering of macromolecules within the chains in copolymers of the types indicated and on the interchain interaction processes is emphasised.
The bibliography includes 163 references.

CONTENTS

I. Introduction 389
II. The influence of hydrogen bonds on certain properties of carboxyl-containing copolymers in bulk 389
III. Manifestation of the specific interaction between carboxy-groups of copolymers in solutions 390
IV. The influence of ionic interactions on the properties of monomers in bulk 393
V. The properties of solutions of copolymers with ionogenic salt groups 394

I. INTRODUCTION

One of the achievements in the regulation of the properties of polymers by the modification of their structure is the synthesis of ionomers. The term "ionomers" was first ascribed to ternary copolymers of ethylene with acrylic acids and their salts[1-6]; at the present time it is also used for other copolymers with ionogenic salt groups. The effective operational and technical properties of ionomers were already reported in the first studies, which attracted to them the continuous attention of specialists in many countries. The results of large-scale studies indicate some common features of ionomers of a wide variety of classes due primarily to the ionic and polar interactions in the macromolecular matrix.

Apart from the dispersion of dipole type interactions usual for all polymers, in the solid state ionomer macromolecules are also linked by ionic bonds, which are the strongest among those known; account must also be taken of the presence of hydrogen bonds between COOH groups. In dilute solutions the conformational characteristics of ionomers are in many respects determined by the same types of specific interactions, but this time at an intramolecular level. The differential approach to the assessment of these interactions and the determination of the dominant ones will permit a comparison of the properties of carboxyl-containing copolymers (CCC) in an acid form and copolymers with partial or complete neutralisation of the carboxy-groups by metal ions (ionomers). Since the properties of ionomers in the solid state are being investigated very vigorously at the present time and a number of reviews[7-16] deal very completely with the situation in this field, in the present review attention is concentrated on the result of the study of the CCC and ionomers in solution.

II. THE INFLUENCE OF HYDROGEN BONDS ON CERTAIN PROPERTIES OF CARBOXYL-CONTAINING COPOLYMERS IN BULK

The specific properties of solid carboxyl-containing copolymers and their solutions are to a large extent determined by the ability of the CCC to form hydrogen bonds which give rise to additional stronger contacts at intramolecular and intermolecular levels. The presence of an extensive system of such contacts leads to the appearance in solid CCC of a series of clear-cut effects. The characteristics of the formation and function of hydrogen bonds and the effects induced by them are being investigated by infrared spectroscopic[17-31] and calorimetric[18-20,23,25,31] methods; valuable information is provided by the study of the thermomechanical[18-20,23], viscoelastic[32,33], sorption[28,34,35], and other properties of the CCC.

The vast majority of the carboxy-groups in CCC are linked via hydrogen bonds to the dimeric complexes; the stretching vibration bands of the $>C=O$ groups at 1695 to 1705 cm^{-1} [17,20,21,23,25,29] and the 940 cm^{-1} band, attributed to the migrations of the out-of-plane OH group in the dimer[19,20], correspond to them. Below the glass point T_g, where there is no segmental motion of the chains, the intensity of the bands due to free carboxy-groups (1740 to 1750 cm^{-1}) is extremely insignificant[17,20,21,23,25,29], which indicates a low concentration of such groups in CCC. However, with increase in temperature there is some increase of the intensity of the free carboxyl band, which is particularly noteable near T_g.[17,23,28,29] The dissociation of hydrogen bonds in the styrene–methacrylic acid (MAA) copolymer (85 : 15) at 120°C leads to the appearance of an inflection in the curves describing the temperature variation of the intensity of the 1745 and 1700 cm^{-1} bands; this inflection corresponds to the glass point, which has been recorded at 120°C also by differential thermal analysis and by dynamic mechanical measurements[23].

The intial fraction of free COOH groups (α) in CCC is appreciably lower than after the heating–cooling cycle: in the range of temperatures above T_g the parameter α assumes its equilibrium value, which persists when the specimen is cooled[29]. The quenching of the structure thus formed leads to a closer packing of the macromolecules (an increase of density) of the hydrogen-bonded copolymer compared with the unannealed specimen[34,36].

The rupture of the main bulk of hydrogen bonds after the attainment of T_g can hardly be regarded solely as a consequence of the thermal lability of the corresponding cross links, since in this case one would have observed a steady shift of T_g towards higher temperatures with increasing content of COOH groups in the copolymer[17-20,23,29,37]. The

dissociation of hydrogen bridge bonds is apparently promoted, apart from temperature as such, also by the increased thermal motion of the chains. This apparently explains the dependence of the equilibrium constant for the formation of hydrogen bonds on the concentration of carboxyl-containing units in the copolymer[29]. The hypothesis that hydrogen bonds can be broken as a result of the active motion of macrochains is consistent with experimental data[25,28] concerning the stabilisation of the network of hydrogen bonds between carboxy-groups in partly neutralised CCC specimens (ionomers), because the appearance of strong hydrogen bonds increases the mobility of the chains. The fixed position of carboxylate ions in ionomers makes the relative intensity of the 1723 cm^{-1} absorption band (stretching vibrations of carboxy-groups involved in hydrogen bonds with carboxylate ions) unchanged even at temperatures above T_g.[28]

The observed changes in the T_g of CCC as a function of the number and type of hydrogen bonds are consistent with the view according to which certain transitions (of the T_g type) are interpreted[38] simply as a consequence of the disappearance of the different types of intermolecular (secondary) bonds in the solid polymer specimen.

Hydrogen bonds make an appreciable contribution to the enthalpy of the vitreous state, which is proportional to the content of carboxyl-containing units in the polymer[18]. The heat of dimerisation of carboxy-groups found for various CCC varies from 7.32 to 11.6 kcal $mole^{-1}$, [17,19-21,23,29], i.e. is very close to the value characteristic of low-molecular-weight compounds with COOH groups in non-polar solvents[39]. With increase of the degree of neutralisation of carboxy-groups in CCC, the enthalpy of the residual intermolecular hydrogen bonds increases[25] as a result of their strengthening.

The degree of crystallinity of polyethylene decreases after the introduction of acrylic acid units in consequence of the formation of hydrogen bridge bonds[19,20,21,40]. The crystallinity of such copolymers decreases linearly with increasing content of the acid and reaches zero when the content of acid unit is more than 8–9 mole %.[4,31] The dimerisation of carboxy-groups proceeds only in amorphous parts of the copolymer and the bulky acid groups are thereby excluded from the crystal lattice of the polyethylene[19,20,31]. This is also promoted by the tendency towards spontaneous aggregation of COOH groups in systems of this kind[32]. A certain incompatibility of hydrocarbon units and acrylic acid units, due to thermodynamic factors which is intensified owing to the presence of hydrogen bonds, is manifested to the greatest extent in graft copolymers. This has been shown for polypropylene with grafted polyacrylic acid chains in a study[41] where the presence of two phases was detected with the aid of transmission and scanning electron microscopy, indicating the microheterogeneity of the copolymer structure.

The presence of an extensive network of hydrogen bonds hinders the diffusion of solvent vapour into the bulk of the methyl methacrylate (MMA)–MAA copolymer, such hindrance to diffusion increasing with increase of the content of MAA units in the copolymer, i.e. with increasing density of the hydrogen bond network[34,35]. Analysis of the solvent sorption and desorption pattern and the observed distinct hysteresis demonstrate a redistribution of hydrogen bonds, an appreciable rearrangement of the steric structure of the network, and a change in the polymer–solvent interaction after the attainment of a certain degree of swelling of the polymer. Annealing of the specimens decreases the sorption capacity and causes the disappearance of a whole kinetic region of the sorption isotherms, which is regarded[34] as a critcal effect. The sorption characteristics of CCC depend significantly on the type of solvent–on its ability to compete in the formation of hydrogen bonds[28].

The decrease of swelling in benzene of the graft copolymers of natural rubber with acrylic polymers of methacrylic acid with increasing degree of grafting can apparently also be regarded as evidence for the formation in such copolymers of additional interchain contacts via hydrogen bonds; this tendency towards a decrease of swelling is most pronounced in copolymers with methacrylic acid[42]. The different contributions of COOH groups to the formation of hydrogen bonds as a function of the nature of the acid has also been observed (by infrared spectroscopy) in graft copolymers of starch with acrylic and methacrylic acids[27]. The difference between these acids is also manifested by the fact that the increase of T_g is more pronounced in the graft copolymer of cellulose with methacrylic acid compared with the copolymer with acrylic acid[43].

Although both intramolecular and intermolecular hydrogen bonds can be formed simultaneously in solid CCC, in some cases the interpretation of experimental data leads to the conclusion that interchain cross links are formed preferentially[19,21,23], while in others account is taken mainly of the presence of intramolecular dimeric complexes[17,24].

III. MANIFESTATION OF THE SPECIFIC INTERACTION BETWEEN THE CARBOXY-GROUPS OF COPOLYMERS IN SOLUTION

When we proceed from the consideration of solid carboxyl-containing copolymers to their dilute solution, it is possible to estimate the properties of an isolated macromolecule due to the presence of hydrogen bonds within a given chain only. These bonds can be formed between the carboxy-groups of the same macrochain, between a carboxy-group and another monomeric chain containing a hydrogen bond acceptor (for example in MMA copolymers with MAA), and also between a carboxy-group in the chain and a solvent molecule. However, interchain interactions also begin to be manifested in concentrated solutions.

The formation of intramolecular hydrogen bonds of the polymer–polymer type is not characteristic of polymeric acids, because they dissolve mainly in protic solvents (water, alcohols, and their mixtures). All these solvents ionise the carboxy-groups of the macrochain and in addition they can themselves form hydrogen bonds of the polymer–solvent type. The presence of a single C=O stretching vibration band at 1710 cm^{-1} in the infrared spectrum of the initial polyacrylic acid solution indicates a single type of hydrogen bonds in this system, namely COOH–H_2O bonds[44]. However, in an aqueous alcoholic solution of polymethacrylic acid infrared spectroscopy reveals the appearance of hydrogen bonds within the chains[45].

For CCC, it is possible to use organic solvents with a wide range of polarities and donor–acceptor capacities. By varying the composition of the solvent and the concentration of the polymer in the latter, it is possible to convert hydrogen bonds of one type into another, and thereby achieve a specific influence on the structure of CCC in solution. The presence of hydrogen bonds of all types alters the hydrodynamic characteristics of the CCC; the intensity of their formation is therefore usually inferred from viscometric data, which, together with the results of the study of CCC in solution by other methods, can yield detailed

information about the mechanism of the formation and dissociation of these bonds and about the extent to which they influence the conformational characteristics of CCC macromolecules.

The problem of the possible cross-linking of an isolated macromolecule has been considered theoretically by Kuhn and Balmer[46], who concluded that, when the ring intramolecular bonds are formed, the size of the macrocoil should diminish. Experimental data for the hydrodynamic properties of CCC having hydrogen bonds within the chain confirms this conclusion. MMA–MAA copolymers in which the MAA units are capable of forming stronger contacts, by virtue of the formation of hydrogen bonds, with all other units are interesting in this respect[47-61]; it has proved possible to regulate the effective density of such contacts by altering either the solvent or the relative content of MAA units in the copolymer. It has been shown for MMA–MAA copolymers[47-61] that selective interactions within the chains occur in dilute solutions in consequence of the formation of hydrogen bonds of the polymer–polymer type, which lead to additional contraction of the polymer coil in "inert" solvents (hydrocarbons, halogenated hydrocarbons, and other solvents, which cannot break the hydrogen bonds in the copolymer or which exhibit a very weak capacity for their formation with the carboxy-groups of CCC). In such solvents the macromolecules of the MMA–MAA copolymer undergo internal "vulcanisation" owing to the formation of a network of hydrogen bonds; because of these bonds, the points of contact involving groups which are remote in terms of their positions along the chain proved to be rigidly fixed: the so-called "frozen" conformation arises.

The disruption of the system of such contacts and transition to the state of the usual flexible statistical coil occur when a small amount (several per cent) of a substance actively competing for hydrogen bonds, for example dimethylformamide (DMF), is introduced into the inert solvent–copolymer system. This transition is indicated by the sharp (abrupt) changes in the hydrodynamic characteristics and conformations of the copolymer macromolecules. Since the thermodynamic quality of the solvent at a low DMF concentration in the latter hardly changes, all the effects observed following the addition of DMF are due to a change in the nature of the hydrogen bonds (hydrogen bonds within the chain of the polymer–polymer type are fully converted into bonds of the polymer–solvent type). This indicates an unambiguous correlation between the experimental parameters {particularly $[\eta]$} and the probability of the formation of stable contacts within the chain via hydrogen bonds.

The study of dilute solutions of MMA–MAA copolymers under the conditions of maximum formation of hydrogen bonds of the polymer–polymer type within the chains and when these bonds are broken by the addition of competing substances has shown that the values of $[\eta]$ for the copolymers increase after the introduction of competing substances by a factor of 2–5 and reach the intrinsic viscosities of poly(methyl methacrylate) with the same degree of polymerisation[51-54] or approach the values of $[\eta]$ of the copolymer in solvents where the formation of hydrogen bonds of the polymer–polymer type is impossible[58,60]. The equality of the values of $[\eta]$ and of the Huggins constant for the MMA–MAA copolymer and poly(methyl methacrylate) in a dichloroethane–DMF mixture indicates the similarity of the conformations of the MMA homopolymer macromolecules and the macromolecules of its copolymer with a low MAA content when the internal macrorings in the latter are liquidated[54].

It is significant that, when the hydrogen bonds within the chains are broken, the type of hydrodynamic homology also changes. For the MMA–MAA copolymer (with 7.6% of MAA) in dichloroethane, $[\eta] \propto M^{0.66}$, whereas following the addition of 5% of DMF the power exponent a increases to 0.87, i.e. becomes almost equal to the power exponent in dioxan ($a = 0.86$).[58,60] The intrinsic viscosity of a copolymer with a high content of MAA units (34%) in acetone is almost independent of the molecular weight (a is close to zero).[55,56,58,59] It is suggested that the copolymer macromolecule in acetone has the conformation of a quasi continuous coil highly "cross-linked" by hydrogen bonds, whose rupture as a result of the addition of DMF leads to an increase of a to 0.26.[59] The results illustrate the marked dependence of the conformation of the coil on the nature of the hydrogen bonds.

The efficiency of the formation of contacts via hydrogen bonds is determined primarily by the number of MAA units in the copolymer macromolecule and depends thus both on the composition of the copolymer and on the degree of its polymerisation[62,63]. In consequence of this there is (for a given solvent) a progressive "contraction" of the MMA-MAA copolymer coils as the molecular weight and the MAA content increase[53]. The critical DMF concentration at which the rupture of the network of hydrogen bonds within the chain occurs and $[\eta]$ of the copolymer approaches the value for poly(methyl methacrylate) depends only on the MAA content in the copolymer and is independent of its molecular weight. The contraction of coils via hydrogen bonding is therefore proportional to the number of MAA units in the copolymer and inversely proportional to the DMF concentration in the solvent[57,61].

Other conditions being equal, the efficiency of the formation of hydrogen bonds is also determined by the way in which the units are distributed, i.e. by the microstructure of the copolymer chain[64]. An appreciable difference has been observed between MMA–MAA copolymers having the same composition but obtained in different ways: by the hydrolysis of poly(methyl methacrylate) (statistical distribution of MAA units) or by radical copolymerisation (deviation from a rigorous statistical distribution because MAA units are grouped into diads, triads, etc. to a large extent). In the former case the contraction of coils is more pronounced owing to the greater density of cross linking via hydrogen bonds[57,61,64].

Since the contraction of the CCC macrocoil depends on the degree of polymerisation, the shape of the coils is to a large extent determined by the molecular weight. Strictly speaking even fractions of CCC with a homogeneous composition cannot be regarded as a polymer-homologous series under the conditions of the manifestation of selective interactions within the chain, because the ratio of the dimeric and monomeric forms of the carboxy-groups is determined (other conditions being equal) by the molecular weight of the fraction. In other words one can assume that the fractions, as it were, differ in composition. In this case the more effective formation of hydrogen bonds with increasing molecular weight will promote an anomalous decrease of the power exponent a in the equation $[\eta] = KM^a$; the rupture of hydrogen bonds within the chain owing to the addition of small amounts of a proton acceptor restores the normal value of the exponent. The above changes in a cannot be accounted for by an improvement or impairment of the thermodynamic quality of the solvent. One must therefore take into account the conventional nature of the results of the estimation of the parameters of equations of the Mark–Kuhn–Houwink type (for any hydrodynamic properties) and the unperturbed dimensions

of the CCC obtained by the Stockmayer–Fixman method when selective interactions within the copolymer chain take place[57,61].

Apart from the MMA–MAA copolymers, the presence of cross-links within the chain via hydrogen bonding and their influence on the hydrodynamic characteristics have been established also for other CCC of different compositions based on acrylic[58,65-72] and methacrylic[71,73-75] acids as well as monobutyl itaconate[76-80]. Different inert solvents (toluene, xylene, chlorobenzene, dichloroethane, carbon tetrachloride, bromoform, etc.) were used in the investigation; apart from DMF, other compounds capable of forming hydrogen bonds of the type polymer–solvent (acetic and methacrylic acids, methanol, dioxan, tetrahydrofuran, dimethyl sulphoxide, amines etc.) can also be used as competing additives. The experimental data obtained do not conflict with relations established for MMA–MAA copolymers, although in each specific case particular features of the test system can be manifested. This is associated primarily with the proton-accepting activity of the second component of the solvent, i.e. with its ability to compete with the polymer units in the formation of hydrogen bonds. On the other hand, the mechanism of the dissociation of the hydrogen bonds within the chain is apparently in all cases similar and is determined mainly by the preferential solvation of the carboxy-group by the competing additives.

In contrast to MMA–MAA copolymers, a characteristic feature of which is the formation of two types of hydrogen bonds within the chains, the copolymers of styrene and acrylic acid make it possible to investigate in the "purest" form the hydrogen bonds between the carboxy-group, although the presence of a weak hydrogen bond between the COOH group and the π electrons of the benzene ring has also been observed for systems of this kind[71]. A study of the copolymers of 4-vinylbenzoic (I), acrylic (II), and methacrylic (III) acids with styrene (IV) in carbon tetrachloride has shown that under these conditions the number of bonds of this type increases in the sequence of copolymers (I) – (IV) < (II) – (IV) < (III) – (IV).[71]

Apart from the effect of competing additive properties a study was also made of the effect of temperature on the intramolecular cross-links due to hydrogen bonds in CCC in inert solvents. It has been established that the intrinsic viscosity (which in the given case can be regarded as a measure of the effectiveness of various contacts between carboxy-groups within the chain) remains virtually unchanged over a wide temperature range up to 70 to 110°C; [53,54,58,60,73,80] nor is there any change in the Huggins constant. The constancy of $[\eta]$ in the above temperature range has been explained by the high energy of the hydrogen bonds, which exceeds the energy of the thermal motion of the chain units; this fact indicates indirectly the occurrence of intramolecular structure formation[58,60]. Since a marked temperature variation of the degree of decomposition of hydrogen bonds is characteristic of a model low-molecular-weight analogue (isobutyric acid, i.e. hydrogenated MAA), [73] one may say that the chain structure of CCC macromolecules introduces specific features into the mechanism of the formation and decomposition of these bonds. It has been suggested[73] that the equilibrium between the free and bound COOH groups in CCC solutions is determined by the effective concentration of active groups within the macromolecular coil, and not by their overall concentration in solution, as for hydrogenated MAA. The data showing the independence of the number of hydrogen bonds within the chain of temperature in CCC solutions are consistent with the results of the study of these copolymers in the solid state; the entire set of data obtained confirm the conclusion that the energy of polymer–polymer hydrogen bonds is fairly high.

The problem of the influence of the CCC concentration in solution on the nature of hydrogen bonds formed is of interest. Infrared spectroscopic data have shown[73,74] that only hydrogen bonds within the chain are observed for the styrene–MAA (3.1 wt.% MAA) copolymer in toluene and carbond tetrachloride at CCC concentrations up to 5%; under these conditions, the proportion of free carboxy-groups is 11% and the remaining groups form dimers[74]. The low probability of intermolecular association of the macromolecules of a hydrogen-bonded copolymer of mono- and di-butyl itaconate is indicated by infrared spectroscopic and osmometric data in dilute solutions[80]. The linearity of the variation of the intrinsic viscosity with CCC concentration up to 2.5% is evidence for the absence of interchain association of styrene – MAA (2–5% MAA) copolymer macromolecules in benzene[81].

The absence of interchain association of CCC macromolecules in dilute solutions is significant in connection with the problem of the determination of the CCC molecular weight. One must take into account the range of molecular weights: it has been established[82] that the association of polystyrene molecules containing terminal carboxy-groups is observed in toluene for low-molecular-weight specimens (3×10^4); on the other hand, specimens with a higher molecular weight in dilute solutions do not form such associated species owing to the reduced probability of contacts between COOH groups belonging to different macromolecules. The situation changes with increase of the concentration of the CCC solution. On passing from a very dilute CCC solution in an inert solvent to a concentrated solution, three different concentration ranges were discovered[83]: (1) the system contains individual macromolecules and small associated species (dilute solutions); (2) an incomplete fluctuation network, made up of interchain hydrogen bonds with a finite lifetime, is in equilibrium with associated species and individual macromolecules (moderately concentrated solutions); (3) there exists a fluctuation network incorporating all the macromolecules present (concentrated solutions). The significant differences between the regions are manifested by the fact that the introduction of a proton acceptor into dilute solutions leads to a dissociation of the hydrogen bonds within the chain and to an increase of the reduced or characteristic [intrinsic] viscosity of the CCC solutions, whereas in the second and third concentration ranges a decrease of the viscosity of the CCC solution is observed after the addition of the proton acceptor[69], because the viscosity of these solutions is determined primarily by the interchain contacts and the proton acceptor disrupts those which are due to hydrogen bonds. Even gel formation is possible in the absence of a proton acceptor[84].

The study of the concentration dependence of the Newtonian viscosity of the styrene–acrylic acid (4% of acrylic acid) copolymer under the conditions of maximum (toluene) and minimum (toluene + 20% DMF) formation of hydrogen bonds made it possible to discover[69] the concentrations characterising the critical conditions for the transition from a dilute to a moderately concentrated (c'_{crit}) solution and from a moderately concentrated to a concentrated solution (c_{crit}). At the concentration c'_{crit} the formation of a three-dimensional hydrogen bond network in the CCC solution begins, while at the concentration c_{crit} its formation is completed. It has been found for the above copolymer (degree of polymerisation 2.5×10^3) that $c'_{crit} = 4.36$ and $c_{crit} = 6.9$ g dl^{-1} in toluene, whereas in toluene

containing 20% DMF, these concentrations are 2.08 and 12.9 g dl^{-1} respectively.

The data presented show that the transitional region in which the formation of the complete three-dimensional network begins and is completed throughout the bulk of the solution becomes significantly extended under conditions of the minimum formation of hydrogen bonds of the polymer–polymer type, whereas in toluene this process takes place over a fairly narrow concentration range. The maximum rupture of hydrogen bonds within the chains between carboxy-groups promotes the unravelling of the coil; as a result of this, the network of interchain bonds in the copolymer in the toluene + DMF mixture begins to be formed at lower concentrations c'_{crit} than in pure toluene owing to the greater probability of the formation of interchain contacts. The probability of the formation of such contacts increases also with increase of the molecular weight of the CCC, which promotes a decrease of both critical concentration[69]. Thus the formation of a hydrogen bond network in fact determines the conditions for the transition from one concentration range to the other.

The study of the rheological properties of solutions of MMA–MAA copolymers established that the ability to form interchain hydrogen bonds is the fundamental cause of a whole series of observed effects. Thus the fluctuation network of the interchain hydrogen bonds hinders the disruption of the structure of the CCC solution in an inert solvent and causes its antithixotropic stabilisation both under the conditions of simple shear and for complex (predominantly longitudinal) flow deformations[49,51,52,54,63,83]. When this type of three-dimensional network is created, the transition from one thermodynamic state of equilibrium to another is hindered and the relaxation time τ_0 increases significantly[63,85]. The appearance of an excess heat of activation for the viscous flow of the CCC solutions is also regarded as a result of the same structure-formation effect[62,69,83,85–88] and the increment in the heat of activation ΔU depends both on the content of carboxy-groups in the copolymer (U increases in proportion to the logarithm of the molar content of MAA units[83,87,88]) and on the presence of added proton acceptors in an inert solvent. Experimental data indicate an unambiguous correlation between the heat of activation for viscous flow and the density of effective interchain contacts due to hydrogen bonds, which makes it possible to regard U in the region of moderately concentrated CCC solutions as a measure of the density of the three-dimensional fluctuation network formed[62]. In fairly dilute solutions a sharp increase of U with concentration is observed, but the formation of a complete hydrogen bond network throughout the bulk of the concentrated solution causes an asymptotic approach of U to a constant (for a given molecular weight and a given composition of the copolymer) value, which is virtually independent of the concentration of the copolymer in the inert solvent for $c > c_{crit}$.[69,83,87,88] The higher the molecular weight of the copolymer and the higher the molar content of the MAA units in it, the lower the critical concentration after the attainment of which U becomes constant. It has been suggested[87] that the independence of U of c in this concentration range is consistent with the idea that, for a fairly large number of bond nodes (contacts), U is independent of the number of nodes for the given copolymer and depends solely on their nature[89].

As in dilute solutions, the introduction of a small amount of a proton acceptor into an inert solvent causes the rupture of the polymer–polymer hydrogen bonds in CCC and to a large extent weakens or completely eliminates the effects mentioned above, which confirms that they are due to the selective interchain interactions between groups capable of forming a hydrogen bond.

Analogous relations, due to the presence of stronger interchain contacts, have been discovered also in the study of the viscous and relaxation properties of poly(methacrylic acid) solutions in methanol, ethanol, and ethylene glycol in the concentration range 9–20%.[90] In this case the dihydric alcohol behaves as a cross-linking agent forming hydrogen bond bridges between the macrochains. As a result of this, the "relaxation viscosities" and durations of the initial period of the relaxation of strain in poly(methacrylic acid) solutions in ethylene glycol are greater by approximately three orders of magnitude than in monohydric alcohols at the same polymer concentration.

Data for the dependence of a whole series of characteristics of CCC solutions on concentration over a wide range of the latter showed that the concentration of a real CCC solution as such cannot serve as a criterion of its being dilute or concentrated, because the limits of the existence of solutions with and without strengthened interchain contact are not absolute, are mobile, and are determined primarily by the composition of the copolymer and its molecular weight as well as the ability of the solvent to compete with the polymer in the formation of hydrogen bonds. For CCC, with their ability to undergo selective interactions, only analysis of the properties of a specific system can provide an answer to the question whether the macromolecules in the given solution are isolated from one another, or whether there are contacts of a definite type between them up to the formation of a complete fluctuation network throughout the bulk of the system[88].

IV. THE INFLUENCE OF IONIC INTERACTIONS ON THE PROPERTIES OF MONOMERS IN BULK

The neutralisation of some of the carboxy-groups in CCC by metal ions of different valence leads to the enrichment of the spectrum of the possible types of selective interactions and hence to the appearance of a series of specific properties in such polymers (ionomers) in both the solid state and in solutions.

The hydrogen bond joins together only two functional groups ($n = 2$) of the macrochain, whereas electrostatic forces, which are in addition capable of acting over a long distance, can lead to the formation of very large ionic associated species ($n \geqslant 2$). The preferred interaction of solvent groups with one another in ionomers is also caused by their definite incompatibility with the hydrocarbon chain units. The existence of ionic accumulations (clusters and multiplets) in the bulk of the monomer has been justified theoretically[91]; the concept of cluster formation constitutes the basis of the interpretation of the majority of experimental data in recent years, obtained in the study of ionomers in the solid state. To a first approximation, one may assume that the decrease of segmental mobility in consequence of strong ionic interactions is the main cause of the increase of mechanical moduli and the decrease of the elasticity of ionomers compared with the corresponding carboxyl-containing copolymers[15,32,33,92].

The replacement of acid groups by salt groups significantly retards crystallisation up to its complete disappearance in copolymers of ethylene with acrylic acids[4,5,31,93], the influence of the neutralisation of carboxy-groups on the crystallisation kinetics being shown to the greatest extent for copolymers containing 1–7 mole % of the acid. Internal structural rearrangement due to ionic cross linking lead to an appreciable increase of T_g for ionomers (in a

particular ion concentration range) compared with CCC[7-9,11,12,14,15,25,94-101]; additional transitions are also observed in ionomers. In the discussion of problems concerning the influence of ionic cross links on the transition temperatures, the following factors must be taken into account. In contrast to covalent cross links, whose position in the specimen is rigorously fixed, ionic cross links in ionomers exhibit a definite mobility owing to the ability of cations to migrate in the bulk of the specimen. The results of a study of a mixture of an ethylene copolymer with acrylic acid and its ionomer in which the degree of neutralisation is 70%[92] showed that in mixtures of this kind regions rich in ions act as ion donors for the entire system, which becomes identical as regards its properties with an ionomeric specimen having a degree of neutralisation of 35%.

The inc rease of the segmental mobility of the chains with temperature also gives rise to greater possibilities for the redistribution of ionic cross links in the bulk of the specimen. It cannot be ruled out that, when T_g and T_y are reached, ionic associated species of one kind break down (otherwise the specimen would not have softened and would not have passed into a fluid state) and ionic accumulations of a new type are generated; the appearance of such ionic inhomogeneities is opposed by the entropy factor. Since the degree of Coulombic interaction is independent of temperature, particular types of ionic associated species will be manifested in the ionomer specimen at any temperature. Infrared spectroscopic data for ionomers of different structure suggest[102,103] the existence of a whole set of ionic associated species of different structure, whose relative content varies with temperature.

The transition temperatures in ionomers are to a large extent determined by the content of acid groups in the copolymer and by the degree of their neutralisation[97]; in certain cases ionic cross links are so strong that they do not break even on heating to approximately 400°C (ionomers with a high degree of neutralisation based on graft ethylene–maleic anhydride copolymers). It was shown in the above study that[97] the nature of the cation also affects the transition temperatures: for the same degree of neutralisation, the softening and yield temperatures (T_S and T_y) for sodium ionomers based on statistical styrene–MAA (8 : 2) copolymers are greater than T_S and T_y for copolymers neutralised by rubidium ions. Thus the transition temperatures in sodium ionomers correspond to stronger ionic cross links formed by the Na^+ cation, which has a smaller radius than the Rb^+ cation.

It has been established for poly(acrylic acid) salts[104] and $T_g = 730\ (q/r) - 67$, where q is the charge of the cation and r the average distance between the centres of the charges of the cation and anion. This type of correlation between T_g and q/r id common to ionogenic polymers and is confirms the dependence of the transition temperatures of the electrostatic interactions in ionomers. Analysis of the available data shows[11] that one cannot rule out the possibility that the observed changes in the transition temperatures are caused by the possible operation in ionomers of a completely different flow mechanism than the segmental displacement occurring in the usual hydrocarbon polymers. The unusual nature of ionic cross links causes ionomers to behave at low temperatures as cross-linked polymeric materials, while at high temperatures they can melt[15].

The presence of additional stronger contacts between the ionomer macrochains owing to ionic interactions leads to a change of the kinetics and thermodynamic parameters of the sorption of solvent vapours. Neutralised CCC specimens, cross-linked by divinylbenzene, have appreciably lower swelling coefficients than the same copolymer in an acid form[105] and the introduction of urea into the system—an agent which actively breaks hydrogen bonds—entails an increase of the degree of swelling of the specimen also in a partly neutralised form. With increase of the degree of neutralisation of carboxy-groups in the ionomer, there is an increase in the resistance of the system to the action of a solvent capable of competing with the polymer in the formation of hydrogen bonds, as shown by the decrease of the rate of attainment of sorption equilibrium, the decrease of the diffusion coefficient of the solvent, and the corresponding increase of the activation energy for this process[28,106]. On passing to a significantly neutral solvent (toluene), it was observed[28] that the amount of sorbed solvent (in a state of equilibrium) in the styrene–acrylic acid (3.9% of acrylic acid) copolymer passes through a minimum and maximum when the degree of neutralisation (α) is 5–15% and 50% respectively. The authors[28] suggest that the increase of the resistance of the structure to the action of the solvent in the region of α = 5–15% is due to the strengthening of the existing fluctuation network of hydrogen bonds owing to additional interactions of the salt group. However, in the region α = 25–50% there is an "inversion of networks": a transition from hydrogen bonds to a lattice of ionic clusters. The imperfection of the network in this transitional region leads to the weakening of the interchain interactions in the ionomer, which is reflected in the experiment by an increase of the degree of sorption of toluene. For $\alpha > 50\%$, a kind of framework of clusters made up of metal ions, which significantly stabilises the ionomer structure, is formed.

Thus comparison of certain characteristics of CCC and their ionomers shows that the effects caused by the introduction of units with carboxy-groups into the hydrocarbon polymer chain change appreciable on partial neutralisation of these groups by metal ions. The characteristics of the properties of complex polymeric formations such as ionomers are in many respects caused by the superposition of the influences of hydrogen bonds and ionic interactions, the proportions of which are determined by the degree of neutralisation.

V. THE PROPERTIES OF SOLUTIONS OF COPOLYMERS WITH IONOGENIC SALT GROUPS

Whereas the physicochemical properties of ionomers in the condensed state are being investigated fairly vigorously, the number of studies on the conformation and transformations and behaviour of ionomers in solutions is not so great. Nevertheless certain common features in the variation of the conformational parameters of isolated CCC molecules on replacement of the protons of the carboxy-groups by various metal ions have been quite clearly demonstrated. The appearance of salt groups leads to sharp changes in interactions within the chains, the intensity of which in dilute solutions is inferred mainly from the intrinsic (characteristic of reduced) viscosity. The polarity of the solvent, its capacity to induce the dissociation of salt groups, exerts the primary influence on these interactions.

It is significant that, in contrast to neutralised homopolymeric acids, ionomers can be investigated (as a function of their composition) in solvents with a wide range of dielectric constants, although an organic solvent cannot be selected for some of them. The poor solubility of ionomers is caused by the extreme diphilic properties of their

macromolecules — the combination in one chain of a non-polar (hydrocarbon) unit and units with salt groups. It is therefore impossible to select for ionomers a solvent which will have the same or at least similar thermodynamic affinities for units of both types. The presence of inter-chain bond nodes in the form of ionic multiplets and clusters imparts to ionomers a high resistance to oil and motor fuel, because the action of organic products with a low dielectric constant cannot lead to the rupture of inter-chain ionic bonds.

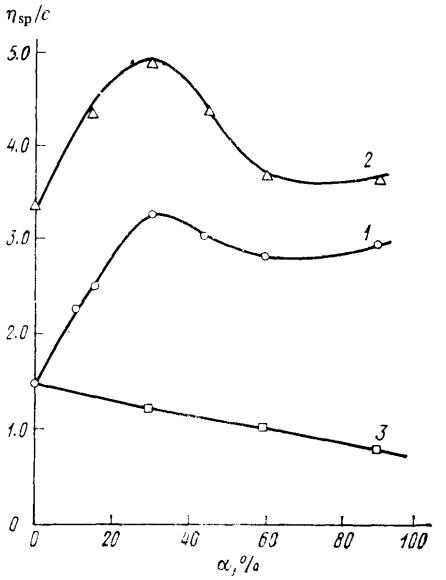


Figure 1. Dependence of the intrinsic viscosity ($c = 0.3\%$) on the degree of neutralisation of ionomers based on the styrene–methacrylic acid copolymer: *1*) Na-ionomers in DMF; *2*) Na-ionomers in DMF + 2% of water; *3*) Zn-ionomers in DMF. [75]

However, the same factors which ensure the notable physicomechanical properties of ionomers (including resistance to the action of solvents) complicate their study in solutions. In the first place the choice of solvent is made much more difficult and, what is most significant, in the study of a given ionomer it is usually impossible to use a wide range of different solvents. Another complication concerning the interpretation of data obtained in the study of the properties of ionomer solutions is due to the fact that, whereas hydrogen bonds of the polymer–polymer type can be completely destroyed by selecting a special solvent, electrostatic interactions in ionomer solutions always occur. By altering the nature of the solvent as a result of the introduction of various additives, it is possible to alter only the intensity of these interactions (both by changing the dielectric constant of the medium and by the solvation of ionic species). In solutions of ionomers a wide variety of intramolecular and intermolecular interactions (dipole–dipole, dipole–ionic, ionic, hydrogen bonds) can be manifested in principle. The real possibility of the manifestation and the intensities of particular interactions are determined by the specific nature of the ionomer and the solvent.

In a viscometric study in DMF ($\epsilon = 36$) the manifestation of polyelectrolyte swelling in the macromolecules of sodium ionomers, based on methacrylic acid copolymers, was noted[75,107–110]. The replacement of acid groups by salt groups, results in an increase of the ionogenic capacity in the region of dilute solutions. However, with increase of the concentration of the solution (up to 6%), the degree of ionisation falls appreciable[108]. The almost complete dissociation of salt groups with a univalent cation in ionomers based on the MMA–MAA copolymer (in DMF as the solvent) has been demonstrated also by electrochemical methods[111–113]. Bivalent metal ions interact with carboxylate groups of the ionomer chains so vigorously that the polyelectrolyte effect is as a rule not observed even in solvents with a fairly high polarity[75,114,115]. The study of electrolyte transfer in such systems also confirms the virtually complete absence of the dissociation of the salt groups of the macrochain, whereas the monomeric alkaline earth metal salts of methacrylic acid dissociate in DMF[111,116].

The macromolecules of ionomers based on acrylic acids containing univalent metal ions undergo a conformational transition in the course of ionisation in polar solvents[75,117]. The initial increase of intrinsic viscosity (Fig. 1) indicates a successive unravelling of the polyelectrolyte coil with increase of the number of ionogenic salt groups; the subsequent decrease of η_{sp}/c is due to the intense binding of sodium counterions and the consequent decrease of the effective number of charges on the chain. The onset of the conformational transition is determined by the content of the unsaturated acid in the copolymer. The occurrence of the conformational transition is confirmed also by potentiometric titration data[117]. Comparison of the viscometric behaviour of Na and Zn-ionomers based on the styrene–MAA (8:2) copolymer in the same solvent shows (Fig. 1) that there is no conformational transition in Zn-ionomers. This serves as yet another piece of evidence for the difference between the ionisation-dissociative processes in the methacrylate salt groups of ionomers in a polar solvent as a function of the nature of the metal.

When a highly polar solvent such as formamide ($\epsilon = 109$) is used, a sharp increase of the intrinsic viscosity of the sodium ionomer (degree of neutralisation $\alpha = 0.8$) is observed compared with the corresponding copolymer of ethyl acrylate and acrylic acid in an acid form[118]. Thus, in a medium with a fairly high dielectric constant, the macromolecules of ionomers with univalent cations exhibit the characteristic hydrodynamic and electrochemical features of polyelectrolytes.

However, the study of solutions of ionomers in weakly polar solvents is of great interest. A medium with a low dielectric constant imitates to a definite extent the environment of the ionomer macromolecule in bulk; furthermore, non-polar solvents in the majority of cases solvate ionic species very weakly. For this reason, in media of this kind the conditions for electrostatic interactions, which occur in solid ionomers and lead to the formation of ionic associated species, are established to the maximum extent. This ensures a direct relation between the results of a study of ionomers in weakly polar solutions and the results of their study in the condensed state. The transition to significantly non-polar solvents implies primarily an impairment of the solubility of the ionomer salt units and an intensification of electrostatic interactions. Such solvents exhibit a weak dissociating capacity; for $\epsilon < 10$ to 15, the dissociation of the solute hardly occurs and free ions are absent from the solution. Media with a low dielectric constant exhibit a characteristic tendency towards the formation of complex ionic species, such as

ion pairs, ion triplets, quadrupoles, and other higher-order aggregates[119]. The less polar the solvent the greater probability of the existence in the latter of contact ion pairs. All these factors, acting together, lead to a number of characteristics of the hydrodynamic properties and conformations of ionomer macromolecules in such solvents.

Judging from the experimental data[66,67,70,72,75,81,115,120-124] obtained using non-polar solvents or under the conditions of suppressed dissociation, in all cases a high degree of neutralisation of the carboxy-groups in CCC via metal ions is accompanied by the contraction of the macromolecular coil, as shown by the decrease of the intrinsic viscosity (or the specific or reduced viscosity at a low concentration) and by the increase of the diffusion coefficients of the ionomers compared with the corresponding copolymers in an acid form. The polyelectrolyte swelling in ionomers is not observed in this case. The contraction of the coil increases with increasing number of ionogenic salt groups in the macrochain (Figs. 2–4). The Huggins constant varies in opposition to $[\eta]$ with increase of the degree of neutralisation of carboxy-groups[66]. Although the conformation of the ionomer macromolecules in dilute solution is determined by the competing effects of forces of different kinds, experiment showed that forces drawing together the macromolecular coil predominate in this instance. The problem of their nature arises.

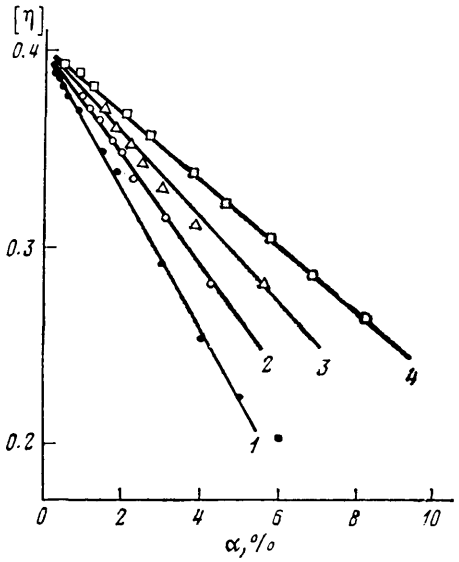


Figure 2. Dependence of the intrinsic viscosity in 1-octanol on the degree of neutralisation of Na-ionomers (line *1*), K-ionomers (line *2*), Cs-ionomers (line *3*), and Ca-ionomers (line *4*) based on the alternating maleic acid–hexadecyl vinyl ether copolymer[122].

The decrease in the size of the coil as a result of its contraction is associated primarily with the impairment of the thermodynamic quality of the solvent (non-polar solvents do not dissolve acrylate salts). This is also indicated by the increase of the Huggins constant on passing from the copolymer in an acid form to the ionomer. The thermodynamic factor promoting the aggregation of the ionomer salt groups within the chain is strengthened by electrostatic interaction forces between the ion pairs formed (here it is extremely significant that the Coulombic forces act over a long distance). The viscometric characteristics of the ionomers containing various metal ions constitute the most convincing evidence for the primary influence of ionic interactions on the conformational characteristics of their macromolecules. If the decrease of $[\eta]$ were caused solely by the impairment of the thermodynamic quality of the solvent, a clear cut dependence of $[\eta]$ on the nature of the cation introduced into the polymer would not have occurred (see Figs. 4–5 and literature data[81,107,110,112,115,121]). An increase of the radius of the cation leads to a weakening of the ionic interactions favouring the contraction of the coil. Accordingly, ionomers with a larger radius of the cation, introduced for the same charge of the latter, have a higher intrinsic viscosity.

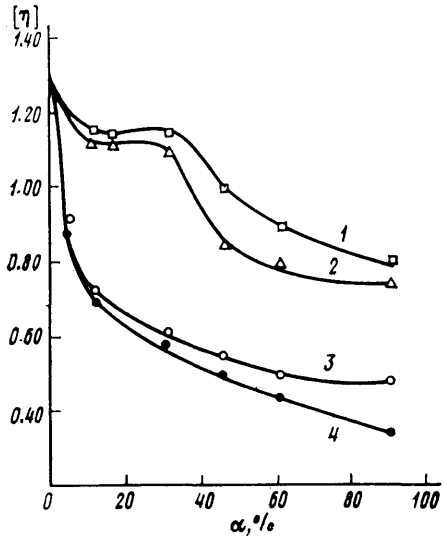


Figure 3. Dependence of the intrinsic viscosity in DMF + 0.05 M NaI on the degree of neutralisation of the Rb-ionomers (curve *1*), Na-ionomers (curve *2*), Ca-ionomers (curve *3*), and Zn-ionomers (curve *4*) based on the styrene–methacrylic acid copolymer[75].

The joint action of the thermodynamic factor and electrostatic interaction forces leads to the formation and stabilisation of ionic associated species of different degree of complexity, which can be regarded as stable bond nodes within the chains of ionomers in dilute solutions (the absence of interchain ionic interactions under these conditions has been confirmed by the equality of the molecular weights of the CCC before and after neutralisation[75,81,123]). An ionic quadrupole is formed in the simplest case under these conditions[81].

$$2\left\{\text{—COO}^{-}+\text{M}\right\} \rightleftarrows \begin{matrix}\left\{\text{—COO}^{-}+\text{M}\right\} \\ \left\{\text{M}^{+}-\text{OOC—}\right\}\end{matrix}$$

Such "cross linking" within the chain as a result of the interaction of two ion pairs does not differ in principle, as regards its effect on the size of the coil, from cross linking due to the formation of a dimeric hydrogen bond between carboxy-groups. However, experimental data show that the interaction between the salt groups of ionomers in non-polar solvents has a more effective influence on the contraction of the isolated coil than hydrogen bonds[70,72,81]. In the case of hydrogen bonds the number of cross-linked units is two. It has been found by infrared spectroscopy and viscometry for the sodium ionomer based on the styrene–acrylic acid (1.74% of acrylic acid) copolymer that the average number of ion pairs in ionic associated species is four[70,72].

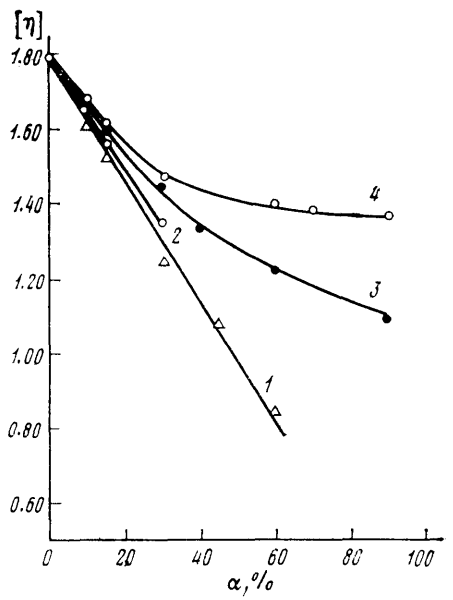


Figure 4. Dependence of the intrinsic viscosity in tetrahydrofuran on the degree of neutralisation of Na-ionomers (curve *1*), Rb-ionomers (curve *2*), Zn-ionomers (curve *3*), and Ca-ionomers (curve *4*) based on the styrene–methacrylic acid copolymer[75].

The set of data obtained for dilute solutions of sodium ionomers based on statistical styrene–MAA copolymers of different compositions suggests that the characteristics of the hydrodynamic behaviour and conformations of the ionomer macromolecules are determined by the formation of fairly large ionic associated species, which can behave as a disperse intramolecular microphase[124,125]. This type of microprecipitation phenomenon with all its consequence is characteristic only of block copolymers in selective solvents[126–130]. The observed specific feature of ionomers with a statistical distribution of units in the chain makes it possible to regard them as pseudo-block copolymers in solution. The intramolecular aggregation of ion pairs is not accompanied by the dissociation of interatomic bonds and a change in the sequence of units, i.e. the primary structure of the statistical copolymer chain is maintained. The secondary structure arising under these conditions imparts to the ionomer macromolecules a conformation more complex than that of the statistical coil.

One must bear in mind that the increased concentration of units with salt groups in the separate regions within the ionomer macrochain is a factor promoting an increase of the local electrostatic potential, enhanced binding of the metal cations, and the formation of ionic associated species with a size such that they begin to behave as a heterogeneous microphase. As an example of the influence of the mode of distribution of salt groups in the chain on the strength of the binding of counterions, one may refer to a study[131] where it has been shown that, for the same monomer ratio, aqueous solutions of sodium salts of the methyl acrylate–acrylic acid copolymer with salt units arranged in groups along the chain have a lower viscosity than solutions of the copolymer with a uniform (statistical) distribution of sodium acrylate units. Thus, even in aqueous solution, the arrangement of salt units in groups promotes an enhanced binding of counterions and the contraction of the coil; in a non-polar medium all these processes are additionally enhanced by the incompatibility of the salt groups and the solvent.

In this respect the hydrogen bonds in CCC are manifested in the opposite way[57,61,64]. The considerable concentration of unsaturated acid (or its salt) units in groups along the macrochain leads to a weakening of the influence of the hydrogen bonds and an enhancement of the influence of ionic interactions on the size and structure of the macrocoil in an inert non-polar solvent. Hydrogen and ionic bonds may prove to be comparable as regards the strength of their influence on the internal structure of the coil when the copolymer chain contains a small amount of statistically distributed units of the unsaturated acid or its salt; in this case both interactions are mainly pair interactions (the formation of large ionic associated species is unlikely) and the intrinsic viscosities of solutions of such copolymers in the acid and ionomeric forms are virtually the same[66,67,69].

It can be assumed that the selective interactions of the salt groups with one another, the formation of ionic associated species, and their segregation as a microphase occur in ionomer solutions for the same reasons as in the bulk of the ionomer (the incompatibility of the salt groups with the hydrocarbon part of the chain and electrostatic interactions). However, in solutions the formation of ionic associated species is also promoted by the thermodynamic incompatibility of the salt units with the weakly polar solvents usually employed for ionomers. The presence of a microphase in the form of ionic associated species determines the specific features of the behaviour of ionomers not only in the condensed state but also in dilute solutions.

The validity of the idea of the dominant role of ionic interactions within the chain and intense intramolecular processes as the most characteristic feature of isolated ionomer macromolecules in solution is confirmed by experimental data. All the methods for altering the strength of electrostatic interactions lead to an appreciable alteration of the conformation of the coil, which is usually observed by measuring the intrinsic viscosity. The strength of ionic interaction within the chain may be regulated by changing the charge density on the chain (i.e. the degree of neutralisation), by altering the radius and charge of the cation introduced into the ionomer and the dielectric constant of the medium (solvent), or by introducing into the solution small amounts of substances capable of active solvation of the cations. The data quoted

above reflect the influence of the majority of these factors on the strength of ionic interactions.

The interesting possibility of a specific influence on the order of ionomer macromolecules within the chain and on their solubility can be realised by taking into account the nature of solvation phenomena. The fact that the solvent exerts a significant influence on the strength of ionic interactions within the chain in ionomers precisely by virtue of its solvating activity has been confirmed by the following experimental data. In a salt solution in DMF ($\epsilon = 37.6$) ionomers based on the styrene–MAA copolymer containing univalent metal ions have appreciably lower values of $[\eta]$ than ionomers based on the same copolymer but containing bivalent metal cations[75] (Fig. 3). Bivalent metal cations are bound by the polymeric ion more effectively than univalent cations. However in tetrahydrofuran (THF) ($\epsilon = 7.4$) the opposite behaviour has been observed for the same specimens[75] (Fig. 4): ionomers with univalent cations have a lower intrinsic viscosity. This is apparently due to the formation in this non-polar solvent of contact ion pairs for ionomers with univalent metals and solvate-separated ion pairs for the macromolecules of ionomers with bivalent metals. A similar dependence of $[\eta]$ on the charge of the counterion has been observed (Fig. 2) for neutralised specimens of the alternating maleic acid–hexadecyl vinyl ether copolymer in 1-octanol ($\epsilon = 10.3$); the calcium ionomer dissolves in this solvent even for $\alpha = 40\%$, while the sodium ionomer dissolves only up to $\alpha = 10\%$.[122] However, it must be emphasised that for ionomers the nature of the dependence of $[\eta]$ on the valence of the metal introduced into them is determined, apart from the nature of the solvent, also by the characteristics of the structure of the macro-chain. Thus in a salt solution in DMF ionomers based on the alternating maleic acid–hex-1-ene copolymer have a high value of $[\eta]$ when the chain contains bivalent metal cations[132], in contrast to ionomers based on the statistical methacrylic acid polymer[75].

When a non-polar solvent is treated with small amounts (several per cent) of other solvents capable of solvating metal cations more actively, an appreciable increase of the size of the macrocoil, i.e. of $[\eta]$ of the ionomer, is observed[66,67,70,72,75], although both the thermodynamic quality of the solvent and its polarity are hardly affected thereby on the macroscopic scale. The unravelling of the coil under these conditions is due to the weakening of the ionic interactions and the possible breakdown of large ionic associated species, because a weaker electrostatic field is generated around the solvated cation and the energy of the Coulombic interaction diminishes under these conditions. When solvents appreciably more polar than the main solvent are added, account must be taken of the significant increase of the local dielectric constant of the medium owing to the selective solvation of ion pairs by the more polar component of the solvent (this effect is manifested to a particularly large extent when water is added to an organic solvent, which is accompanied, as can be seen from Fig. 1, by the enhancement of the polyelectrolyte unravelling of the ionomer coil).

However, the influence of solvation processes on the intensity of ionic interactions can be followed in the "purest" form[75] (Fig. 5) in relation to sodium ionomers using pyridine (5 vol.%) as an additive to THF. In this case both components of the solvent have similar polarities and both pure THF and THF with additives contain no "cross links" within the chains due to hydrogen bonds. Fig. 5 shows that the addition of pyridine ($\epsilon = 12.3$) to THF ($\epsilon = 7.4$) increases the intrinsic viscosity of the ionomeric specimens, because pyridine solvates sodium cations more actively and diminished thereby the intensity of the electrostatic interactions and the contraction of the coil. The weakening of ionic interactions within the chain in sodium ionomers in the presence of pyridine is manifested most clearly for $\alpha > 30\%$, i.e. in the region of the concentration of salt groups, for which the probability of the formation of large associated species increases. It is instructive that the ionomer with $\alpha = 90\%$ does not dissolve in THF, whereas in the presence of pyridine it does so. A similar improvement of the stability of ionomers is achieved by adding acetic acid[75] and methanol[121] to THF. Ionomers based on ethylene dissolve only in mixed solvents consisting of an organic solvent having a solubility parameter $\delta = 8$–9 and acetic acid[22].

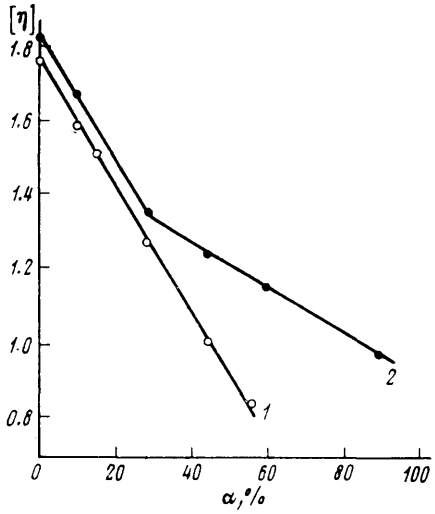


Figure 5. Dependence of the intrinsic viscosity on the degree of neutralisation of Na-ionomers based on the styrene-methacrylic acid copolymer; solvent: *1*) tetrahydrofuran; *2*) tetrahydrofuran + 5% of pyridine[75].

The choice of additives improving the solubility of ionomers is complicated by the fact that the main characteristics of the solvation of metal cations in non-aqueous media have still not been fully discovered, and comparative estimates of the solvating powers of solvents are not always correlated with their dielectric constants and dipole moments, because covalent σ and π interactions between the cation and the solvent molecule sometimes predominate over electrostatic (ion–dipole) interactions[133]. Significant changes in the solubility and hydrodynamic properties of ionomers can be expected when additives capable of forming complexes of the metal cations in the ionomeric are introduced into the inert solvent, particularly cations with *d* electron shells, whose high capacity of solvation is determined mainly by the donor–acceptor interactions with the solvent. This question still requires experimental tests.

In conformity with the concept of the dominant influence of ionic (electrostatic) interactions on the conformational characteristics of ionomer macromolecules, the size of the coil (for ionomers with univalent metal cations) is

independent of temperature in the range between -40° and +70°C, judging from viscometric data[107,120]. Furthermore, on passing to ionomers with bivalent metal cations, it has been noted[134] that the specific viscosity of their solutions decreases appreciably with increasing temperature. However, this finding not only does not conflict with the main concept but actually serves as one of its confirmations. The point is that an increase of temperature promotes the desolvation of cations, which is particularly pronounced for a bivalent metal cation, and this leads to an enhancement of their binding by the macrochain[135,136]. Under these conditions, the coil undergoes additional contraction, which is observed experimentally as a decrease of the viscosity of the ionomer solution[134]. In the discussion of the problem of the temperature dependence of the conformational parameters of the ionomer chain one must take into account the fact that the degree of desolvation is determined not only by the charge of the cation, but also by the nature of the solvent and the detailed mechanism of their interaction.

As shown above, the hydrodynamic properties of ionomers vary with the chemical nature of the cation introduced. The characteristics observed under these conditions are related in a definite manner to solvation phenomena and make it possible to determine the type of interaction between the counterion and the macrochain.

A definite view has now been formulated concerning the principal types of counterions in polyelectrolyte solutions. This problem has been dealt with in detail in reviews[137-145]. It is possible to distinguish three types of counterions: "free", "specifically bound", and "diffuse" or "atmospheric". Free counterions are not directly influenced by the electrostatic potential of the polymeric ion. The number of such counterions is fairly small even in aqueous polyelectrolyte solutions; their number in solutions with a reduced dielectric constant is even smaller, particularly in the case of bivalent counterions, as can be seen from the data presented at the beginning of this Section concerning the hydrodynamic and electrochemical properties of ionomer solutions.

The idea of the specific binding of counterions was first put forward in the study of aqueous solutions of polyacrylic acid salts[146,147]. Such counterions are associated with fixed ionic groups of the polymeric ion. As a result of this kind of binding in solution (even aqueous solutions), ion pairs and other more complex ionic formations and complex and chelate compounds are produced. The most important feature of the specific binding consists in the alteration of the solvent structure in the immediate vicinity of the polymeric ion and the counterion as a result of the desolvation or at least the reorganisation of the medium around the ion.

Diffuse or atmospheric counterions are subject to the influence of the electrostatic potential of polymeric ions, but they are not associated with the latter quite as strongly as specifically bound counterions. These ions form an ionic "atmosphere" around the polymeric ion and are retained in the vicinity of the latter exclusively by virtue of Coulombic interactions. Atmospheric counterions retain their solvation shells. The occurrence of specific binding does not eliminate the ionic atmosphere; the latter always exists to some extent around the polymeric ion.

The reversibility of the normal sequence of the binding of alkali metal ions by polycarboxylic acids in aqueous solutions can be regarded as direct evidence for occurrence of specific binding[148-157]. The normal binding sequence (from lithium to caesium) obeys the electrostatic interaction law, according to which the solvated ion with the minimum radius (Cs^+) is bound more strongly than the solvated ion with the maximum radius (Li^+). The opposite variation, observed for polycarboxylic acids, indicates the desolvation of counterions and hence their specific binding, which entails an increase of the viscosity of aqueous solutions of polycarboxylic acid salts in the sequence Li → Cs.

Water-soluble CCC salt exhibit a similar variation of the viscosities of the solutions as a function of the radius of the added cation: the intrinsic viscosity of such CCC salt solutions increases in the sequence Li < Na < K < Rb.[158,159]

As already mentioned above, the same type of variation of the viscosity for dilute solutions of ionomers is observed also when organic solvents are used[75,110,121,122]. Presumably the observed feature of carboxy-groups, which is manifested in the specific binding of the counterions and the formation of ion pairs in the macrochain of polycarboxylic acid salts even in an aqueous medium, should become still more pronounced for neutralised CCC in organic solvents with $\epsilon < 81$.

On passing from dilute solutions of ionomers to more concentrated solutions, there is a possibility of the formation of macromolecular associated species via interchain ionic cross links. Indeed ionomers (particularly ionomers with a bivalent metal) based on the styrene–MAA copolymer exhibit a sharp non-linear increase of the intrinsic viscosity in benzene ($\epsilon = 2.28$) with increase of the concentration above 1%, which is due to interchain association, whereas CCC itself (with MAA contents of 2 and 5%) in an acid form shows no deviations up to a concentration of 2.5%.[81] However, in dioxan ($\epsilon = 2.21$) the same monomers show no deviations from linearity up to a concentration of 2.25%. It is suggested that the relatively weak interaction between the ion pairs in this solvent can be a consequence of the solvation of the cations by dioxan. This example shows that, when solvents are compared from the standpoint of their influence on the intensity of electrostatic interactions within the chain and between different chains of ionomers, it is insufficient to take into account only the dielectric constants; one must also consider their solvating power.

In this connection one must emphasise that the selection of the solvent is particularly important in the determination of the molecular weights of ionomers. It has been found that the molecular weights of CCC and their sodium and barium ionomers with the same degree of polymerisation prove to be the same, when they are determined by light scattering in dioxan, whereas in benzene (working concentrations not in excess of 1%) the formation of interchain associated species in barium ionomers leads to an appreciable increase of the measured molecular weights[81].

The occurrence of interchain ionic interactions with increasing concentration causes such ionomer solutions (in the absence of dissociation in the given solvent) to have a higher viscosity than solutions with the corresponding copolymers in the acid form, wheras in dilute solutions ($c < 1\%$) the opposite relation is observed[75,81,121]. Similarly an increase in the degree of neutralisation (α) of carboxy-groups is accompanied by a decrease of $[\eta]$ and the viscosity of solutions of ionomers with a concentration of several per cent increases with increasing α.[75,121]

Whereas intramolecular and intermolecular association of the ionomer molecules in the presence of univalent cations takes place as a result of the ion pair interaction,

bivalent metal cations can give rise to ionic triplets of the type

$$\}\text{—COO}^-M^{2+}{}^-\text{OOC—}\{,$$

which are much more stable than a quadrupole made up of two ion pairs, The interchain association processes of macromolecules with salt groups are therefore most instructive for solutions of ionomers containing bivalent metal cations[75,81,114,134,160]. The nature of the bivalent metal also plays an important role under these conditions: judging from measurements of the dynamic double refraction, the calcium ionomers based on the styrene–MAA (8 : 2) copolymer form in TMF rod-like aggregates containing several thousand macromolecules, while zinc ionomers give rise to molecularly disperse solutions under these conditions[115].

The interchain interactions in solutions of ionomers containing univalent and bivalent metal cations lead to structure formation and gel formation[69,114,115,120,134,160,161], the nature of the structures produced being determined (other conditions being equal) by the polymer concentration and, depending on this factor, there is a transition from the gel state to a true solution on high dilution, i.e. reversible gels are formed. The occurrence of such a transition, which is impossible in polymeric gel systems with covalent cross links, is a characteristic feature of polymers with ionogenic groups where interchain ionic cross links have a finite lifetime and exhibit a definite mobility, i.e. they can break down and reform. Similar reversible gels are produced by poly(methacrylic acid)[162] and its salts[163] in water.

The nodes of the network structure of ionomer gels in organic solvents with a low polarity consist of concentrations of salt groups (ionic associated species, ionic swarms), which leads to microlayer formation in the system[120]. The energetic non-equivalence of the nodes of the network structure of an ionomer gel has been established; this is due to the heterogeneity of the ionic associated species produced, the energy of which is between 2 and 11 kcal mole^{-1}.[120] Since the structural order in the gel state is to a large extent predetermined by the conformational characteristics of isolated macromolecules, presumably the conclusion that ionic associated species of different composition are formed and undergo microprecipitation applies equally to ionomer macromolecules in dilute solutions.

The mobility of ionic bonds in gels increases with temperature: the gel of a strontium ionomer, which is fully elastic at 20°C and is based on the MMA–MAA copolymer, passes to the viscoelastic state with increase of temperature in cyclohexanone (ϵ = 18) and at 100°C the specimen (α = 10%) acquires viscofluid properties[161]. Similar transitions have also been observed for gels of sodium monomers based on the same copolymer[120]. The transition of these systems to the viscofluid state is displaced towards higher temperatures with increasing degree of neutralisation of carboxy-groups; there is a corresponding increase also of the range of viscoelasticity and the maximum deformation in the viscoelastic state diminishes under these conditions[120,161]. In this case one may speak of a close analogy between the behaviour of ionomers in bulk and their gels under the influence of temperature, which is probably due to similar processes involving the decomposition and reorganisation of ionic associated species.

Continuing the consecutive comparison of ionic interactions and hydrogen bonds in terms of the strength of their influence on the properties of CCC and ionomers, we may note that the greatest strength of ionic bonds, compared with hydrogen bonds, is manifested most clearly in the range of concentrated solutions of the corresponding copolymers. The entire set of experimental data obtained confirm this. The results of a study[69] of the copolymer of styrene with 4 mole % of acrylic acid and its sodium ionomer (α = 25%) are very instructive in this respect. Although the intrinsic viscosities of the CCC and its ionomer in toluene are virtually the same, the transition to concentrated solutions made it possible to discover the following differences between these types of copolymers: (1) the critical concentration for the formation of a complete three-dimensional network of strengthened interchain contacts diminishes almost by a factor of two on passing from the CCC to its ionomer; (2) a high heat of activation for viscous flow has been observed in ionomer solutions; (3) in contrast to its neutralised specimen, the copolymer in the acid form does not form gels in toluene.

With increase of the ionomer concentration; even for a low content of salt groups in the macrochain, there is apparently an increase of the probability of the formation of large ionic associated species at the intermolecular level, and in such solutions there is a corresponding onset of segregation phenomena, i.e. a microphase appears. In contrast to this, in a dilute solution of an ionomer with a low content of salt groups (of the order of 1%) in the macrochain, mainly ionic quadrupoles are formed, which do not differ from the dimeric hydrogen bonds in CCC as regards their influence on the conformational characteristics of the coil.

* * *

Analysis of the results of the study of ionomers shows that the formation of ionic associated species (multiplets and clusters) is the key factor which determines the specific features of the properties of these complex polymeric structures in bulk and in solution. The results obtained suggest a particular sensitivity of the conformational parameters of ionomer macromolecules and of the internal structure of their coils to any types of influence on the intensity of ionic (electrostatic) interactions, because the latter predominate as regards the strength of their influence on the above characteristics of ionomers. However, one cannot fail to take into account also the strong selective interactions between the carboxy-groups of the copolymers. The understanding of the mechanism of the primary ordering processes within the chain (with allowance for the formation of ionic and hydrogen bonds) can lead to the discovery of methods for the specific regulation of these processes, which in many respects determine the structure and properties of the ionomeric specimen in the condensed state.

REFERENCES

1. Chem. Process (Engl.), 10, 106 (1964).
2. Brit. Plast., 38, 262 (1965).
3. R. Torriani, Poliplasti, 13, 31 (1965).
4. R. W. Rees and D. J. Vaughan, Amer. Chem. Soc. Polymer Prepr., 6, 287 (1965).
5. R. W. Rees and D. J. Vaughan, Amer. Chem. Soc., Polymer Prepr., 6, 296 (1965).
6. S. Bonotto and C. L. Purcel, Rev. Plast. Mod., 16, 415 (1965).
7. A. Eisenberg, Adv. Polymer Sci., 5, 59 (1967).
8. A. Eisenberg, Macromolecules, 4, 125 (1971).

9. E. P. Otocka, J. Macromol. Sci. Rev. Macromol. Chem., C5, 275 (1971).
10. C. Andrei, Mater. Plast., 8, 287 (1971).
11. W. J. MacKnight, Amer. Chem. Soc. Polymer Prepr., 14, 813 (1973).
12. A. Eisenberg, Amer. Chem. Soc. Polymer Prepr., 14, 871 (1973).
13. M. F. Hoover and G. B. Butler, J. Polymer Sci.; Polymer Symp., 45, 1 (1974).
14. A. Eisenberg, J. Polymer Sci; Polymer Symp., 45, 99 (1974).
15. S. R. Rafikov and A. A. Andrusenko, Symposium, "Sintez i Svoistva Polimerov" (The Synthesis and Properties of Polymers), Ufa, 1974, p.4.
16. K. Czaja, M. Nowakowska, and J. Pacha, Polymery, 20, 113 (1975).
17. A. L. Smolyanskii, Trudy Vologodskogo Moloch. Inst., No. 49, 149 (1966).
18. E. P. Otocka and F. R. Eirich, J. Polymer Sci., A-2, 6, 895 (1968).
19. E. P. Otocka and T. K. Kwei, Amer. Chem. Soc., Polymer Prepr., 9, 583 (1968).
20. E. P. Otocka and T. K. Kwei, Macromolecules, 1, 244 (1968).
21. W. J. MacKnight, L. W. MacKenna, B. E. Read, and R. S. Stein, J. Phys. Chem., 72, 1122 (1968).
22. Y. Tachi, A. Takahashi, and I. Kagawa, Kogoyo Kagaku Zasshi, (J. Chem. Soc. Japan, Ind. Chem. Sect), 73, 398 (1970).
23. K. Ogura and H. Sobue, Polymer J., 3, 153 (1972).
24. V. N. Demishev, L. G. Sidorova, M. V. Shishkina, V. A. Barakova, and V. F. Naumov, Zhur. Prikl. Khim., 45, 350 (1972).
25. K. Ogura, H. Sobue, and S. Nakamura, J. Polymer Sci., Polymer Phys. Ed., 11, 2079 (1973).
26. A. G. Zak, N. A. Kuznetsov, I. S. Lishanskii, Z. A. Roganova, and A. L. Smolyanskii, Vysokomol. Soed., 16A, 886 (1974).
27. E. Gruber, J. Mohammed, and J. Schurz, Kolloid-Z. Z. Polymer, 252, 278 (1974).
28. L. M. Kalyuzhnaya, A. N. Krasovskii, Yu. N. Panov. A. G. Zak, I. S. Lishanksii, and S. Ya. Frenkel', Vysokomol. Soed., 17A, 993 (1975).
29. A. G. Zak, N. A. Kuznetsov, I. S. Lishanskii, and A. L. Smolyanskii, Izv. Vys. Ucheb. Zaved. Khim. i Khim. Tekhnol., 18, 951 (1975).
30. Y. Uemura, R. S. Stein, and W. J. MacKnight, Macromolecules, 4, 490 (1971).
31. W. J. MacKnight, W. P. Taggart, and L. W. MacKenna, J. Polymer Sci., Polymer Symp., 46, 83 (1974).
32. T. C. Ward and A. V. Tobolsky, J. Appl. Polymer Sci., 11, 2403 (1967).
33. A. V. Tobolsky, P. F. Lyons and N. Hata, Amer. Chem. Soc., Polymer Prepr., 9, 594 (1968).
34. L. M. Kalyuzhnaya, Yu. N Panov, and S. Ya. Frenkel', Vysokomol. Soed., 16A, 2036 (1974).
35. L. M. Kalyuzhnaya, Yu. N. Panov, and S. Ya. Frenkel', Vysokomol. Soed., 18A, 1568 (1976).
36. T. Hatakeyama and H. Kanetsuna, J. Polymer Sci., Polymer Phys. Ed., 11, 815 (1973).
37. Yu. N. Panov, A. M. Stalevich, V. G. Tiranov, L. K. Yakovenko, and S. Ya. Frenkel', Mekhanika Polimerov, 399 (1967).
38. R. D. Andrews, J. Polymer Sci., C14, 261 (1966).
39. N. D. Sokolov, Zhur. Vses. Khim. Obshch. im. Mendeleeva, 17, 299 (1972).
40. G. Kortleve, C. A. F. Tuijnman, and C. G. Vonk, J. Polymer Sci., A-2, 10, 123 (1972).
41. M. Pegoraro, A. Penati, G. Gianotti, and A. Capizzi, Chem. Zvesti, 26, 224 (1972).
42. Y. Kozai, Y. Ikeda, and S. Yamasaki, Nippon Gomu Kyokaishi (J. Soc. Rubber Ind., Japan), 44, 375 (1971).
43. Y. Ogiwara, H. Kubota, S. Hayashi, and K. Sekine, J. Appl. Polymer Sci., 16, 2197 (1972).
44. L. Bardet, G. Cassanas-Fabre, and M. Alain, J. Mol. Struct., 24, 153 (1975).
45. B. Z. Volchek, A. I. Kol'tsov, T. N. Nekrasova, and A. V. Purkina, Vysokomol. Soed., 12B, 754 (1970).
46. W. Kuhn and I. Balmer, J. Polymer Sci., 57, 311 (1962).
47. V. G. Aldoshin and S. Ya. Frenkel', Vysokomol. Soed., 4, 116 (1962).
48. V. A. Myagchenkov, E. V. Kuznetsov, and A. B. Myasnikova, Trudy Kazan. Khim. Tekhnol. Inst., No. 34, 325 (1965).
49. Yu. N. Panov, S. Ya. Frenkel', T. I. Samsonova, L. S. Bolotnikova, N. G. Bel'nikevich, and S. A. Agranova, Ukrain. Fiz. Zhur., 12, 276 (1967).
50. V. A. Myagchenkov, L. M. Ishutinova, E. V. Kuznetsov, and S. Ya. Frenkel', Vysokomol. Soed., 9A, 2559 (1967).
51. Yu. N. Panov, S. A. Agranova, and S. Ya. Frenkel', Kolloid. Zhur., 30, 269 (1968).
52. Yu. N. Panov, O. Quadrat, and M. Bohdanecky, Europ. Polymer J., 4, 661 (1968).
53. N. T. Kuralova, Yu. N. Panov, and S. Ya. Frenkel', Vysokomol. Soed., 11B, 428 (1969).
54. Yu. N. Panov, O. Quadrat, and N. Bohdanecky, Symposium, "Sintez, Struktura i Svoistva Polimerov" (The Synthesis, Structure, and Properties of Polymers), Izd. Nauka, Leningrad, 1970, p.91.
55. E. A. Bekturov and R. E. Legkunets, Vysokomol. Soed., 12A, 626 (1970).
56. E. A. Bekturov, R. E. Legkunets, and S. R. Rafikov, Izv. Akad. Nauk Kazakh SSR, Ser. Khim., No. 3, 31 (1971).
57. Yu. N. Panov and S. Ya. Frenkel', Europ. Polymer J., 8, 1067 (1972).
58. E. A. Bekturov, R. E. Legkunets, and S. R. Rafikov, Prepr. Int. Symp. Macromolecul., Helsinkii, 1972, Vol. 3, Sect. 2., p.25.
59. R. E. Legkunets, V. V. Roganov, and E. A. Bekturov, Izv. Akad. Nauk Kazakh SSR, Ser. Khim., No. 1, 74 (1972).
60. R. E. Legkunets, R. E. Khamzamulina, and E. A. Bekturov, Izv. Akad. Nauk Kazakh SSR, Ser. Khim., No. 2, 21 (1972).
61. Yu. N. Panov, N. T. Kuralova, and S. Ya. Frenkel', Vysokomol. Soed., 15B, 440 (1973).
62. Yu. N. Panov and S. Ya. Frenkel', Vysokomol. Soed., 9A, 937 (1967).
63. Yu. N. Panov, A. Ya. Malkin, and S. Ya. Frenkel', Vysokomol. Soed., 9A, 2381 (1967).
64. V. A. Myagchenkov and S. Ya. Frenkel', Uspekhi Khim., 42, 827 (1973) [Russ. Chem. Rev., No. 5 (1973)].
65. I. A. Baranovskaya and V. E. Eskin, Vysokomel. Soed., 15B, 794 (1973).
66. L. S. Bolotnikova, A. G. Zak, I. S. Lishanskii, D. A. Malyshev, Yu. N. Panov, and S. Ya. Frenkel', Vysokomel. Soed., 15A, 995 (1973).
67. L. S. Bolotnikova, A. G. Zak, I. S. Lishanskii, D. A. Malyshev, Yu. N Panov, and S. Ya. Frenkel', Vysokomel. Soed., 15A, 2296 (1973).

68. R. E. Legkunets, V. V. Roganov, E. A. Bekturov, and A. K. Akhmetova, Izv. Akad. Nauk Kazakh SSR, Ser. Khim., No. 1, 31 (1973).
69. L. S. Bolotnikova, A. G. Zak, I. S. Lishanskii, Sh. Mirkamilov, Yu. N. Panov, and S. Ya. Frenkel', Kolloid. Zhur., 36, 203 (1974).
70. A. G. Zak, N. A. Kuznetsov, I. S. Lishanskii, Z. A. Roganova, and A. I. Smolyanskii, Vysokomel. Soed., 16B, 829 (1974).
71. A. G. Zak, N. A. Kuznetsov, I. S. Lishanskii, Z. A. Roganova, and A. I. Smolyanskii, Vysokomol. Soed., 16A, 886 (1974).
72. A. G. Zak, N. A. Kuznetsov, I. S. Lishanskii, Z. A. Roganova, and A. I. Smolyanskii, Vysokomel. Soed., 17A, 275 (1975).
73. A. L. Smolyanskii, Vysokomel. Soed., 9B, 74 (1967).
74. V. M. Gal'perin, N. A. Kuznetsov, and A. L. Smolyanskii, Vysokomel Soed., 14A, 2684 (1972).
75. Yu. B. Monakov, S. R. Rafikov, N. V. Duvakina, V. P. Budtov, N. G. Marina, and Z. A. Sankina, Symposium, "Khimiya i Fiziko-Khimiya Vysokomolekulyarnykh Soedinenii" (The Chemistry and Physical Chemistry of Macromolecular Compounds), Ufa, 1975, p.183.
76. L. A. Bimendina, Symposium, "Materialy II Nauchnoi Konferentsii Molodykh Uchenykh Akademii Nauk Kazakh SSR" (Proceedings of the IInd Scientific Conference of Young Scientists of the Kazakh SSR Academy of Sciences), Alma-Ata, 1970, p.209.
77. E. A. Bekturov, L. A. Bimendina, and S. V. Bereza, Vysokomol. Soed., 12A, 2179 (1970).
78. E. A. Bekturov and L. A. Bimendina, Izv. Akad. Nauk Kazakh SSR, Ser. Khim., No. 1, 38 (1971).
79. E. A. Bekturov, L. A. Bimendina, and S. R. Rafikov, Izv. Akad. Nauk Kazakh SSR, Ser. Khim., No. 2, 44 (1971).
80. E. A. Bekturov, L. A. Bimendina, V. V. Roganov, and S. R. Rafikov, Vysokomol. Soed., 14A, 343 (1972).
81. N. Z. Erdi and H. Morawetz, J. Colloid Sci., 19, 708 (1964).
82. A. K. Banthia, H. K. Biswas, S. C. Guhaniyogi, and B. M. Mandel, J. Indian Chem. Soc., 49, 1271 (1972).
83. S. Y. Frenkel and Y. N. Panov, J. Polymer Sci., C30, 503 (1970).
84. P. Smeitek and S. Ya. Frenkel', Vysokomol. Soed., 4, 429 (1962).
85. Yu. N. Panov, K. E. Nordbek, and S. Ya. Frenkel', Vysokomol. Soed., 6, 47 (1964).
86. Yu. N. Panov and S. Ya. Frenkel', Symposium, "Teplovoe Dvizhenie Molekul i Mezhmolekulyarnoe Vzaimodeistvie v Zhidkostyakh i Rastvorakh" (Thermal Motion of Molecules and Intermolecular Interaction in Liquids and Solutions), Samarkand, 1969, p.361.
87. Yu. N. Panov, L. K. Yakovenko, and S. Ya. Frenkel', Kolloid. Zhur., 32, 573 (1970).
88. S. Ya. Frenkel', G. K. El'yashevich, and Yu. N. Panov, Symposium, "Uspekhi Khimii i Fiziki Polimerov" (Advances in the Chemistry and Physics of Polymers), Izd. Khimiya, Moscow, 1970, p.87.
89. G. M. Bartenev, Dokl. Akad. Nauk SSSR, 133, 88 (1960).
90. B. V. Myasnikov, A. V. Ryabov, and D. N. Emel'yanov, Trudy po Khim. i Khim. Tekhnol. (Gor'kii), No. 2 (18), 52 [1967 (1968)].
91. A. Eisenberg, Macromolecules, 3, 147 (1970).
92. S. Bonotto and E. Bonner, Macromolecules, 1, 510 (1968).
93. E. P. Otocka and T. K. Kwei, Macromolecules, 1, 401 (1968).
94. E. P. Otocka and F. R. Eirich, J. Polymer Sci., A-2, 6, 921 (1968).
95. B. Vollmert and W. Schoene, Angew. macromol. Chem., 19, 157 (1971).
96. M. W. Williams, Amer. Chem. Soc., Polymer Prepr., 14, 896 (1973).
97. S. R. Rafikov, Yu. B. Manakov, I. A. Ionova, G. P. Gladyshev, A. A. Andrusenko, O. A. Ponomarev, A. I. Vorob'eva, A. A. Berg, L. F. Antonova, E. I. Ablyakimov, M. F. Sisin, and A. A. Smorodin, Vysokomol. Soed., 15A, 1974 (1973).
98. O. A. Ponomarev and I. A. Ionova, Vysokomol. Soed., 16A, 1023 (1974).
99. A. Eisenberg and M. Navratil, Macromolecules, 6, 604 (1973).
100. M. Navratil and A. Eisenberg, Macromolecules, 7, 84 (1974).
101. L. S. Bolotnikova, A. G. Zak. I. S. Lishanskii, Yu. N. Panov, and S. Ya. Frenkel', Vysokomol. Soed., 17B, 98 (1975).
102. Yu. N. Boyarchuk, E. D. Andreeva, L. V. Konovalov, and V. N. Nikitin, Zhur. Prikl. Spektrosk., 23, 101 (1975).
103. E. D. Andreeva, V. N. Nikitin, and Yu. M. Boyarchuk, Vysokomol. Soed., 17B, 773 (1975).
104. A. Eisenberg, H. Matsura, and T. Yokoyama, J. Polymer Sci., A-2, 9, 2131 (1971).
105. C. Braud and E. Selegny, Europ. Polymer J., 9, 749 (1973).
106. D. A. Seanor and M. L. Hair, Amer. Chem. Soc., Polymer Prepr., 14, 908 (1973).
107. S. M. Kochergin and V. P. Barabanov, Vysokomol. Soed., 4, 135 (1962).
108. V. P. Barabanov and B. L. Bogdanov, Trudy Kazan. Khim.-Tekhnol. Inst., No. 34, 115 (1965).
109. V. P. Barabanov and A. L. Kurmaeva, Trudy Kazan. Khim.-Tekhnol. Inst., No. 34, 231 (1965).
110. V. P. Barabanov and A. I. Kurmaeva, Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol., 9, 645 (1966).
111. V. P. Barabanov and B. L. Bogdanov, Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol., 8, 829 (1965).
112. V. P. Barabanov and A. I. Kurmaeva, Trudy Kazan. Khim.-Tekhnol. Inst., No. 36, 301 (1967).
113. V. P. Barabanov and N. I. Kurmaeva, Elektrokhimiya, 3, 734 (1967).
114. V. P. Barabanov and B. L. Bogdanov, Trudy Kazan. Khim.-Tekhnol. Inst., No. 34, 220 (1965).
115. S. R. Rafikov, Yu. V. Revizskii, Yu. B. Monakov, and V. P. Budtov, Vysokomol. Soed., 17A, 2029 (1975).
116. B. L. Bogdanov and V. P. Barabanov, Trudy Kazan. Khim.-Tekhnol. Inst., No. 36, 309 (1967).
117. J. S. Tan and S. P. Gasper, Macromolecules, 6, 741 (1973).
118. R. J. Rauscher, L. J. Garfield, and R. W. Connelly, J. Polymer Sci., Polymer Symp., 45, 165 (1974).
119. I. Smid, Uspekhi Khim., 42, 799 (1973) [Russ. Chem. Rev., No. 5 (1973)].
120. N. F. Proshlyakova, P. I. Zubov, and V. A. Kargin, Kolloid. Zhur., 20, 202 (1958).
121. W. Schoene and B. Vollmert, Angew. macromol. Chem., 13, 23 (1970).

122. R. Varogui and E. Pefferkorn, J. Phys. Chem., 79, 169 (1975).
123. Yu. V. Revizskii, Yu. B. Monakov, V. P. Budtov, and S. R. Rafikov, Vysokomol. Soed., 16A, 398 (1974).
124. N. G. Marina, Yu. B. Monakov, S. R. Rafikov, V. P. Budtov, and Z. A. Sankina, Dokl. Akad. Nauk SSSR, 226, 589 (1976).
125. N. G. Marina, Candidate's Thesis, Institute of Chemistry of the Bashkir Branch of the USSR Academy of Sciences, Ufa, 1976.
126. S. E. Bresler, A. M Pirkov, S. Ya. Frenkel', A. A. Laius, and S. I. Klenin, Vysokomol. Soed., 4, 250 (1962).
127. H. Inagaki, Macromolek. Chem., 86, 289 (1965).
128. G. E. Molau, J. Polymer Sci., A-3, 4235 (1965).
129. G. E. Molau and W. M. Wittbrodt, Macromolecules, 1, 260 (1968).
130. M. Cirolamo and I. R. Urwin, Europ. Polymer J., 7, 693 (1971).
131. I. Sakurada, Y. Sakaguchi, K. Fukami, and K. Takashima, Kobunshi Kagaku (Chem. High Polymer), 20, 81 (1963).
132. N. G. Marina, Yu. B. Monakov, S. R. Rafikov, V. P. Budtov, N. V. Duvakina, O. A. Ponomarev, Yu. I. Lysikov, and E. S. Filatova, Vysokomol. Soed., 18A, 542 (1976).
133. A. M. Golub, Uspekhi Khim., 45, 961 (1976) [Russ. Chem. Rev., No. 6 (1976)].
134. V. P. Barabanov and B. L. Bogdanov, Vysokomol. Soed., 9A, 744 (1967).
135. M. Rinaudo and M. Milas, Macromolecules, 6, 879 (1973).
136. O. Iwaki, K. Hikichi, and M. Kaneko, Polymer J., 4, 623 (1973).
137. N. Ise, Adv. Polymer Sci., 7, 536 (1971).
138. A. Katchalsky, Pure Appl. Chem., 26, 327 (1971).
139. G. S. Manning, Annalen Rev. Phys. Chem., Vol. 23, Palo Alto, Calif., 1972, p.117.
140. D. J. R. Laurence, Physical Methods in Macromolecular Chemistry, New York, Vol. 2, 1972, p.91.
141. R. J. Eldridge, Proc. Roy. Austral. Chem. Inst., 40, 143 (1973).
142. M. Nagasawa, "Polyelectrolytes", Dordrecht–Boston, 1974, p.57.
143. U. P. Strauss, "Polyelectrolytes", Dordrecht–Boston, 1974, p.79.
144. H. P. Gregor, "Polyelectrolytes", Dordrecht–Boston, 1974, p.87.
145. N. G. Marina and Yu. B. Monakov, Symposium, "Khimiya i Fiziko-Khimiya Vysokomolekulyarnykh Soedinenii" (The Chemistry and Physical Chemistry of Macromolecular Compounds), Ufa, 1976, p.116.
146. F. E. Harris and S. A. Rice, J. Phys. Chem., 58, 725 (1954).
147. S. A. Rice and F. E. Harris, J. Phys. Chem., 58, 733 (1954).
148. H. P. Gregor, L. B. Luttinger, and E. M. Loebl, J. Amer. Chem. Soc., 76, 5879 (1954).
149. H. P. Gregor and M. Frederick, J. Polymer Sci., 23, 451 (1957).
150. S. J. Gill and G. V. Ferry, J. Phys. Chem., 66, 995 (1962).
151. S. J. Gill and G. V. Ferry, J. Phys. Chem., 66, 999 (1962).
152. L. A. Noll and S. J. Gill, J. Phys. Chem., 67, 498 (1963).
153. U. P. Strauss and Y. P. Leung, J. Amer. Chem. Soc., 87, 1476 (1965).
154. H. P. Gregor, L. B. Luttinger, and E. M. Loebl, J. Phys. Chem., 59, 34 (1965).
155. R. J. Eldridge and F. E. Treloar, J. Phys. Chem., 74, 1446 (1970).
156. C. Tondre and R. Zana, J. Phys. Chem., 75, 3367 (1971).
157. C. Tondre and R. Zana, J. Phys. Chem., 76, 3451 (1972).
158. A. F. Nikolaev, V. M. Bondarenko, and V. G. Rupyshev, Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol., 16, 1732 (1973).
159. A. K. Makhkamov, S. A. Zainutdinov, and K. S. Akhmedov, Dokl. Akad. Nauk Uzbek SSSR, No. 8, 48 (1972).
160. A. M. Frost, I. A. Kolosentseva, and V. V. Razumovskii, Zhur. Prikl. Khim., 46, 1246 (1973).
161. N. F. Proshlyakova, P. I. Zubov, and V. A. Kargin, Kolloid. Zhur., 20, 199 (1958).
162. J. Eliassaf and A. Silberberg, Polymer, 3, 555 (1962).
163. A. Silberberg and P. F. Mijnlieff, J. Polymer Sci., A-2, 8, 1089 (1970).

Institute of Chemistry of the Bashkir Branch of the USSR Academy of Sciences, Ufa