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Infrared Studies of Ionic Aggregation of Ethylene- and Butadiene-Based Ionomers

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ABSTRACT: An infrared spectroscopic investigation of the Na$^+$, K$^+$, Rb$^+$, and Cs$^+$ salts of ethylene– and butadiene–methacrylic acid copolymers has been carried out. The absorption due to the asymmetric stretching mode of the carboxylate ion contains two components: one at 1550 cm^{-1} and another at 1565 cm^{-1}. The ratio of peak intensities of these bands depends upon ion concentration, the nature of the cation, and temperature. It is concluded that the ion pairs in these copolymers are likely to exist in at least two types of ionic aggregates of different structures. Infrared dichroism studies established that the dichroic ratios of the 1550- and 1565-cm^{-1} bands depend on ion concentration in copolymers. The model systems, anhydrous salts of fatty acid, were also studied. A combination low-angle x-ray scattering and infrared data leads to a probable model of the ordered structure existing within ionic clusters.

During the past decade considerable attention has been paid to the investigation of physical properties of ion-containing polymers.[1–3] However, several major questions concerning the state of ion aggregation still remain open. Among many experimental techniques employed, infrared spectroscopy,[4,5] x-ray diffraction,[7–9,18] electron microscopy,[7,10] dynamic mechanical,[7,9,11] dielectric,[7,16] and nuclear magnetic resonance relaxation[16] tests should be cited. In spite of these efforts we still do not know whether the ions are dispersed on a molecular level as ion pairs or perhaps quartets, or more extensive clusters. One should add that structural features of ionic clusters are unknown.

In this paper an attempt is made to obtain additional evidence for ion clustering in ethylene- and butadiene-based ionomers using the ir technique. We studied the infrared bonds due to the stretching mode of carboxylate (COO$^-$) ions.

It is well known that the frequencies or infrared absorption bands are sensitive to the surrounding groups and therefore frequencies of absorption bonds assigned to the (COO$^-$) stretching mode can be employed for observation of the states of ionic aggregation. However, no conclusions can be drawn from the quoted studies of these ionomers[4,5] since only a broad featureless band due to the (COO$^-$) stretching vibration is observed. This picture can be explained by the presence of water and nonionized carboxylic groups which is known[18] to influence the degree of ion aggregation. Therefore it is necessary to investigate anhydrous and completely neutralized copolymers in order to observe the clusters with ordered structure.

Experimental Section

The starting material was a partially ionized copolymer of ethylene and methacrylic acid (trade mark "Surlyn"). The methacrylic acid content of the copolymers was 4.1 mol %. The starting material was refluxed in tetrahydrofuran with dilute hydrochloric acid in order to bring the copolymer in the nonionized state. This copolymer was further dissolved in hot xylene and films were cast from the solution. In order to obtain the Na$^+$, K$^+$, Rb$^+$, and Cs$^+$ salts of copolymers, ethoxides of sodium and potassium and hydroxides of rubidium and cesium were used for neutralization. The films were placed in a 95:5 mixture of xylene and ethanol with sodium or potassium ethoxides or with rubidium or cesium hydroxides at 20 °C for 20 min. After this treatment the ionized copolymers were washed with ethanol and dried in vacuo at 100 °C. The starting butadiene–methacrylic acid copolymers ("carboxylate rubber") contain 1.1, 2.4, and 4.9 mol % of methacrylic acid. These copolymers were dissolved in benzene and from this solution films were cast on a CaF$_2$ plate. In order to produce the ionized form these films were introduced in a 95:5 mixture of hexane and benzene with ethoxides of sodium or potassium or hydroxides of rubidium or cesium at 20 °C for 20 min. The subsequent procedures, such as washing and drying, were the same as those employed for the ethylene–methacrylic acid copolymers.

Infrared analysis indicated that the samples were 100% neutralized. The swelling agents used during neutralization favor the ion aggregation. Infrared spectra of the films were obtained on the UR-20; Perkin Elmer M 180, and FIS-3 Hitachi spectrophotometers. Temperature-dependent infrared studies were made using a special temperature cell. Temperature was measured using a calibrated copper–constantan thermocouple.

Results and Discussion

The infrared spectra of the three samples investigation are shown in Figure 1. It is obvious that both the 1740- and 1700-cm^{-1} –C=O stretching vibrations are absent. Instead of them two new peaks appear: one at 1530–1580 cm^{-1} interpreted as a (COO$^-$) asymmetric vibration and another at 1400–1420 cm^{-1} corresponding to a (COO$^-$) symmetric stretching vibration (Figure 3). It is seen from Figure 1 that the absorption due to the asymmetric stretching mode of the carboxylate (COO$^-$) ion consists of at least two compo-

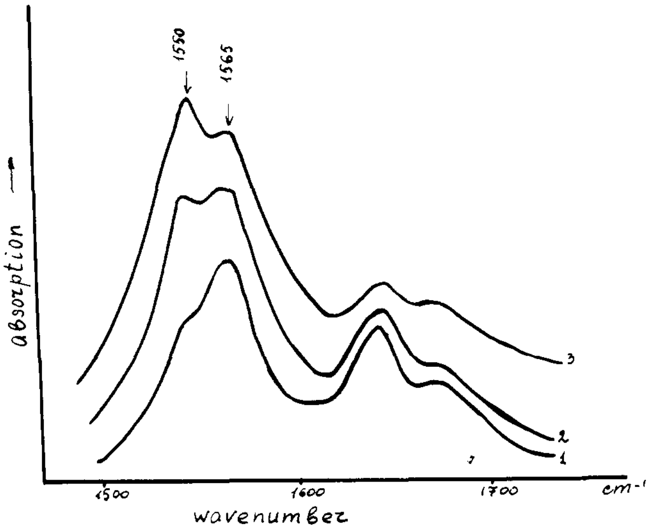

Figure 1. Infrared absorption spectra of the K$^+$ salts of butadiene–methacrylic acid copolymers in the region of the (COO$^-$) asymmetric stretching mode: (1) 1.1 mol % acid, (2) 2.4 mol % acid, (3) 4.9 mol % acid.

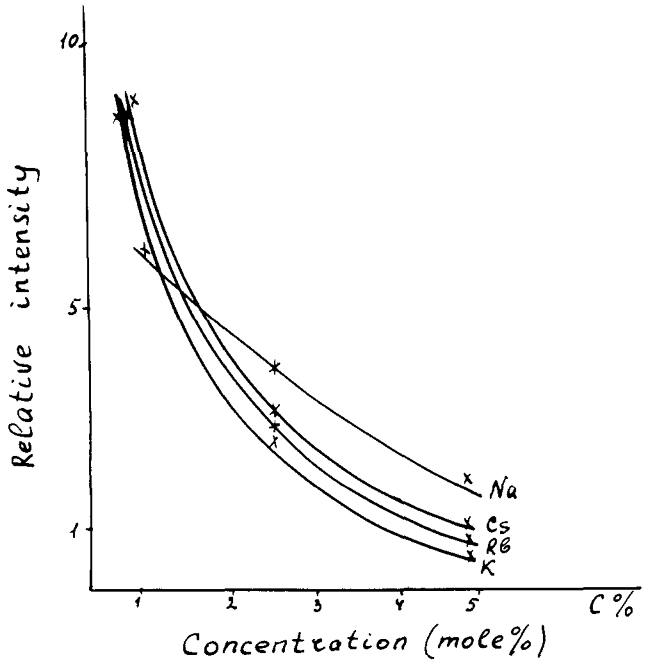

Figure 2. Ratio of the peak intensities of the 1565- and 1550-cm^{-1} bands vs. ion concentration for the salts of the butadiene–methacrylic acid copolymers.

nents: at 1550 cm$^-$ and at 1565 cm^{-1}. The relative intensities of these bands depend on the ion concentration in such a way that with increasing ion concentration the corresponding ratio decreases. This is illustrated in Figure 2. When the ion concentration is high enough to observe the absorption due to the symmetric stretching mode of the carboxylate ion, we observe two new bands at 1410 and 1370 cm^{-1} which are shown in Figure 3 for the K salt.

The results of the temperature-dependent infrared studies on the salts of these copolymers are shown in Figure 4. It is of interest that the increase in temperature affects the bands at 1550 and 1565 cm^{-1} in a different manner. The peak intensity of the 1565-cm^{-1} band is independent of temperature while the 1550-cm^{-1} band increases with temperature. Besides, it should be pointed out that the latter band has a constant integrated intensity. The effect of the counterion nature on the peak intensities of the 1550- and 1565-cm^{-1} bands was also investigated. In Figure 5 the ratios of the corresponding peak intensities are plotted against the metal ion size for the ionized ethylene–methacrylic acid copolymers. Figure 6 shows the peak intensity of the 1565-cm^{-1} band plotted as a function of the ion concentration for the ionized butadiene–methacrylic acid copolymers. A detailed study of these salts' spectra indicates

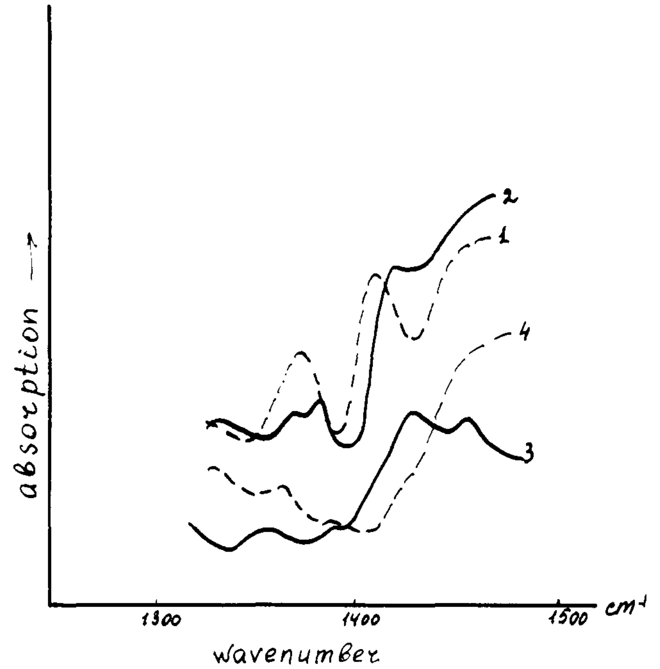

Figure 3. Infrared absorption spectra of the (COO^{-1}) symmetric stretching mode region of: (1) K$^+$ salt of butadiene–methacrylic acid copolymers (4.9 mol % acid), (2) Na$^+$ salt of this copolymer, (3) sodium caprylate, (4) the nonionized copolymer.

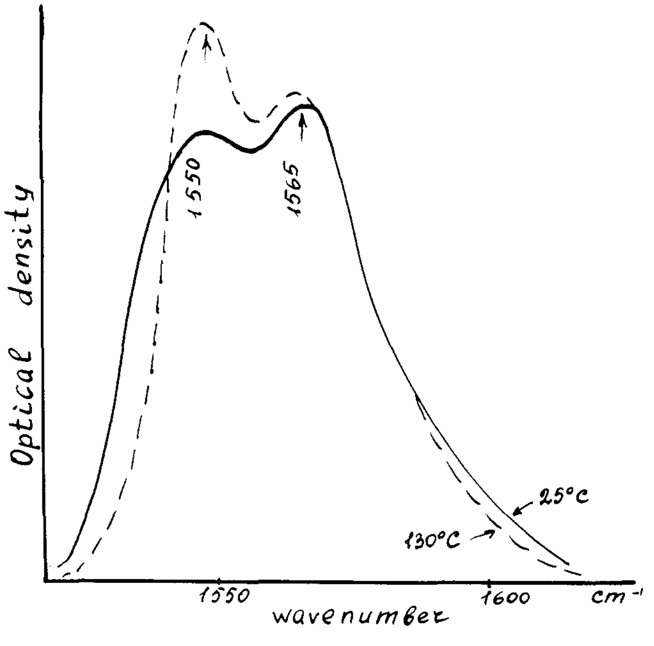

Figure 4. Temperature dependence of the infrared spectra of the K$^+$ salt of butadiene–methacrylic acid copolymer (4.9 mol % acid) in the (COO$^-$) asymmetric stretching mode at 25 and 130 °C.

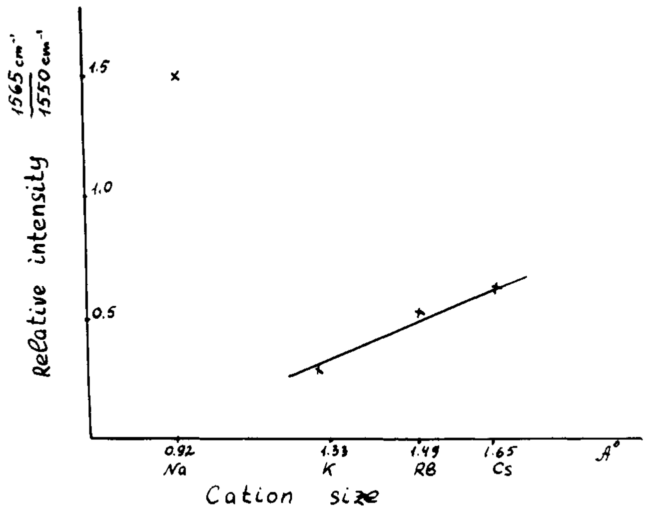

Figure 5. Change in relative intensities of the 1565- and 1550-cm^{-1} bands with ion size for salts of ethylene–methacrylic acid copolymer (4.1 mol % acid) at 130 °C.

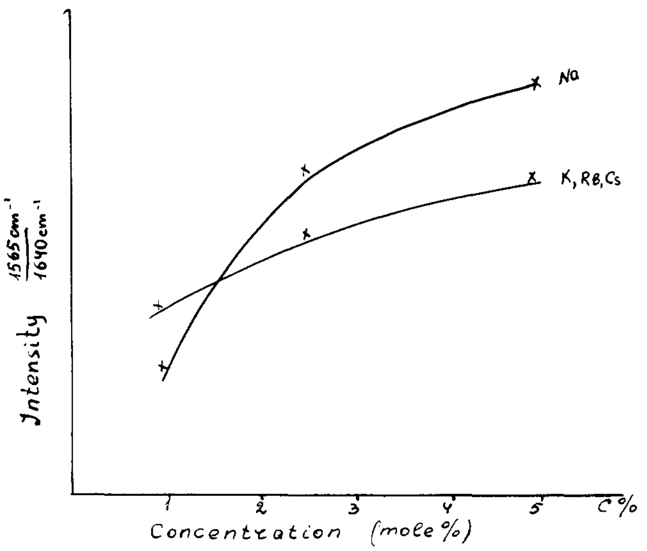

Figure 6. The intensity of the 1565-cm^{-1} band vs. ion concentration for salts of the butadiene–methacrylic acid copolymers.

that the total integrated intensity of the asymmetric COO$^-$ stretching absorption follows Beer's law for all cations. However, the ratio of the intensities of the components of this band (1550 and 1565 cm^{-1}) changes with ion concentration and counterion nature. These changes are considerable as shown in Figures 1, 5, and 6.

From the results obtained one can conclude that the ion pairs in the copolymers under investigation are likely to exist in at least two types of ionic aggregates. Their structures are substantially different. The concept of ionic multiplets and clusters can explain most of the results presented. Considering the peculiarities of the 1550- and 1565-cm^{-1} bands it seems reasonable to assign the 1550-cm^{-1} band to the asymmetric stretching vibration of the carboxylate (COO$^-$) ions of ionic multiplets and to assign the 1565-cm^{-1} band to the same vibration in ionic clusters. The temperature dependence of the 1550-cm^{-1} band shape can be explained by the superposition of different spectra of various ionic multiplets. The absence of temperature dependence of the 1565-cm^{-1} band shape reflects the stability of ionic cluster structures in this temperature range.

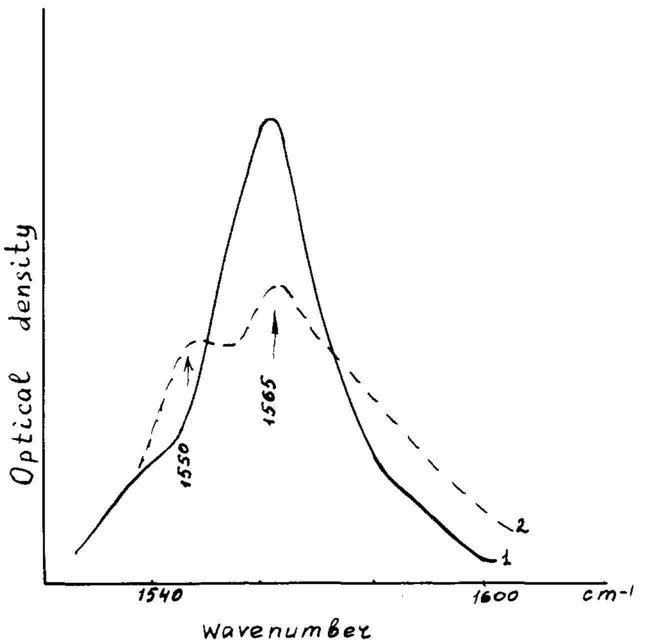

Figure 7. Infrared spectra of crystalline potassium caprylate dissolved in the polyethylene matrix in the region of the (COO$^-$) asymmetric stretching mode: (1) 25 °C, (2) 160 °C.

In order to confirm these assumptions and to obtain additional data on the structure of ionic clusters several model systems (anhydrous salts of fatty acids) have also been studied. These salts contain one polar group in a large hydrocarbon molecule. Its crystalline structure has been described earlier.[19] Metal cation and oxygen atoms form double layers which are separated from each other by hydrocarbon chains. Each cation is surrounded by four oxygen atoms in the same part of the double layer and two more in the opposite part. With increasing the temperature these salts subject to the transition to liquid–crystalline state. As was shown by Luzzati[20,23] the three-dimensional crystalline organization of hydrocarbon chains is destroyed at $T > 100$ °C while crystalline organization of polar groups remains at sufficiently high temperature. With further increasing the temperature the crystalline organization of polar groups is destroyed through several stages and instead of double planar sheets long ribbons of finite width or disks of finite size are observed. Figure 7 shows the infrared spectra of the crystalline potassium caprylate. The absorption due to the asymmetric stretching mode of the (COO$^-$) ions is located at 1565 cm^{-1} and the band due to the symmetric stretching mode of the (COO$^-$) ions occurs at 1410 cm^{-1}. At 150–170 °C these bands are broadened. However, any additional structural features of these bands are not observed. Since this salt is not soluble in aliphatic hydrocarbons, it is impossible to produce ionic multiplets in the form of pairs, triplets, quartets, etc. However, we made an attempt to break partially this ionic double layer using a polyethylene matrix.[21] In this case the appearance of ionic multiplets is probably owing to partial "solution" of the salt in polyethylene at high temperature. At 170 °C the appearance of the band at 1550 cm^{-1} is readily observed. Thus it seems reasonable to attribute the 1550-cm^{-1} band to the carboxylate ion stretching mode in ionic multiplets.

It is well known[7,8] that upon neutralization of carboxylic acid groups a new peak is observed at $2\theta = 4°$ in the low-angle x-ray diffraction pattern. This reflection has been attributed to a separate ionic phase within which clusters of

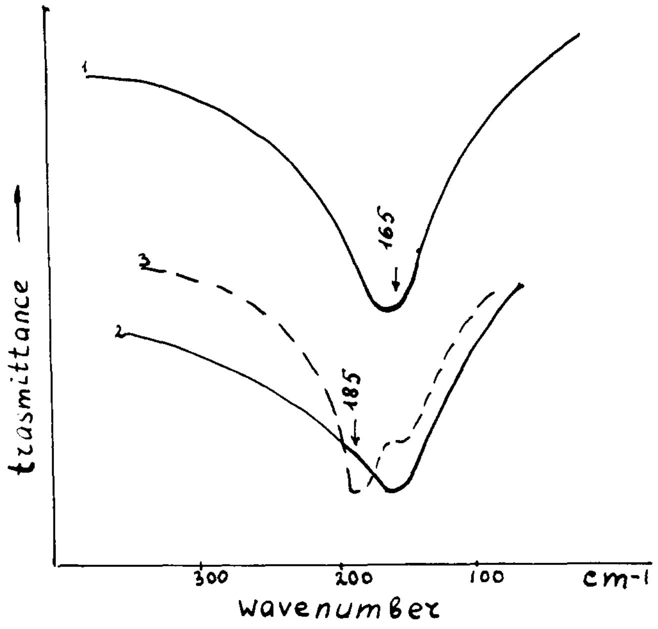

Figure 8. Far-infrared spectra of the crystalline potassium caprylate (1), of the K^+ salt of ethylene–methacrylic acid copolymer (4.1 mol % acid) (2), and of the 90% ionized with potassium ethylene–methacrylic acid copolymer (4.1 % acid) (3) at 25 °C.

carboxylate ions are arranged in some periodic fashion. We carried out a low-angle x-ray investigation of caprylates and ionized copolymers and have also observed a peak corresponding to a 20-Å spacing in all the samples investigated.

Moreover, we compared the far-infrared spectra of caprylates and of the salts of the copolymers in the 400–100-cm^{-1} region at ambient temperature. We observed bands which were assigned to cation motion within an anionic field in the copolymers. The frequencies of these bands depend on the state of ion aggregation stronger than the frequencies of a (COO^-) stretching mode. As is shown in Figure 8 the spectra of potassium caprylate and the K salt of the copolymer are similar but the 165-cm^{-1} band is broader in the salt spectra. This broadening may be associated with a higher concentration of defects in the ionic aggregate structure in ionomers. The 185-cm^{-1} band reported in ref 6 was observed by us only in the spectra of the 90–95% ionized copolymers.[22]

One can assume from the low-angle x-ray and infrared measurements that the same structures are present in caprylates and ionic clusters.

Using the advantages of ir spectroscopy and in connection with the assumptions made about the regular structure of clusters one can attempt to answer the following question. How is the state of ion aggregation affected by the ion concentration and the nature of the counterion? As mentioned above, with increasing ion concentration the relative intensity of the 1550-cm^{-1} band increases. This result indicates that the fraction of ion pairs existing in the form of ionic multiplets increases. This fact is connected with peculiarities of polymeric chain behavior during ion clustering. Since cluster formation depends on the properties of polymer chains, such as elasticity and entanglement spacings, and on steric hindrance in the course of chain packing, a critical ion concentration (C_{cr}) along the chain must exist above which clustering of all ions becomes unfavorable. Then, above C_{cr} with increase in ion concentration the fraction of ion pairs existing as ionic multiplets increases. The value of C_{cr} depends on the size of the ions, the nature of polymer chains, the cluster geometry, and other factors.

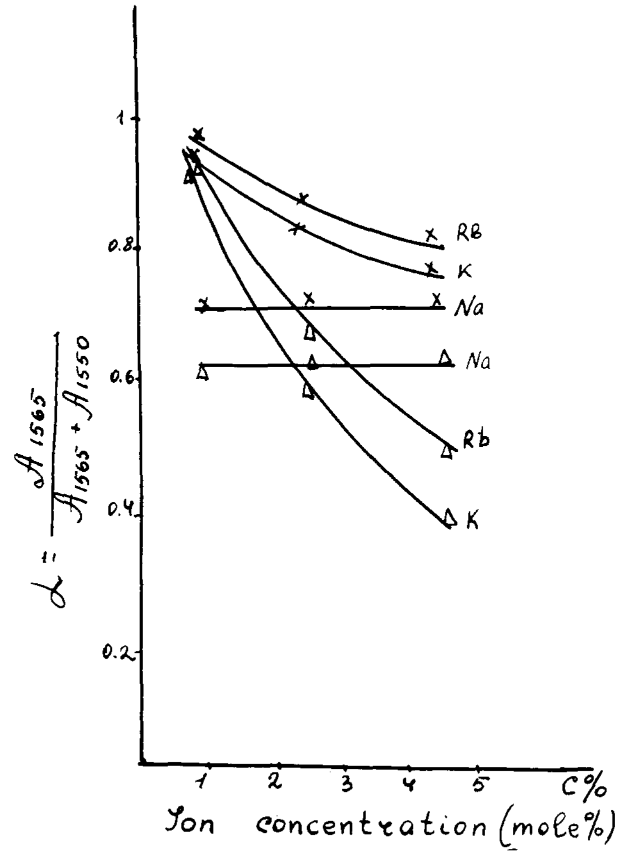

Figure 9. Plots of $\alpha = A_{1565}/(A_{1565} + A_{1550})$ vs. ion concentration for salts of (Δ) butadiene– and (×) styrene–methacrylic acid copolymers.

As a consequence of the fact that the surface of crystalline bimolecular ion layer increases with the ion size it seems reasonable to suggest that the fraction of ion pairs existing in the form of ionic clusters of fairly regular structure increases with increasing sizes of counterions. Actually, as is seen from Figure 5, the fraction of the ion pairs existing in the form of ionic clusters correlates with the counterion size. The pronounced difference between the behavior of the sodium salts and other salts of polymers can easily be seen from the same figure. Although the size of the sodium ion is smaller than that of the other ions, the fraction of ion pairs existing in the form of ionic clusters is larger in this case as compared with other ions. Figure 6 also shows the special features of the Na salts.[24] Preliminary studies of styrene–methacrylic acid systems show that the salts of these copolymers are similar to the above-mentioned Na salts. The results of these studies are presented in Figure 9 which shows the ratio of integrated intensity of the 1565-cm^{-1} band (A_{1565}) to that of the complex band of asymmetric COO^- stretching absorption ($A_{1565} + A_{1550}$) vs. ion concentration for all the samples investigated. As mentioned above, the total integrated intensity of the asymmetric COO^- stretching absorption follows Beer's law. Thus we may use this ratio for the evaluation of the fraction of ion pairs existing in the form of ionic clusters.

All the results obtained may be explained if we assume that ion pairs could form two types of ionic clusters with regular structure. We suggest that for salts of large-size cations (>Na) and in the absence of steric hindrance in the

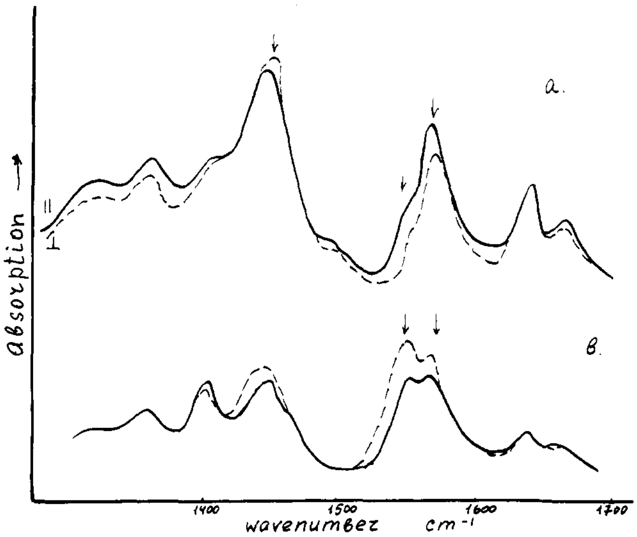

Figure 10. Polarized infrared spectra of the K^+ salt of butadiene–methacrylic acid copolymers (at 600% extension): (a) 1.1 mol % acid, (b) 4.9 mol % acid.

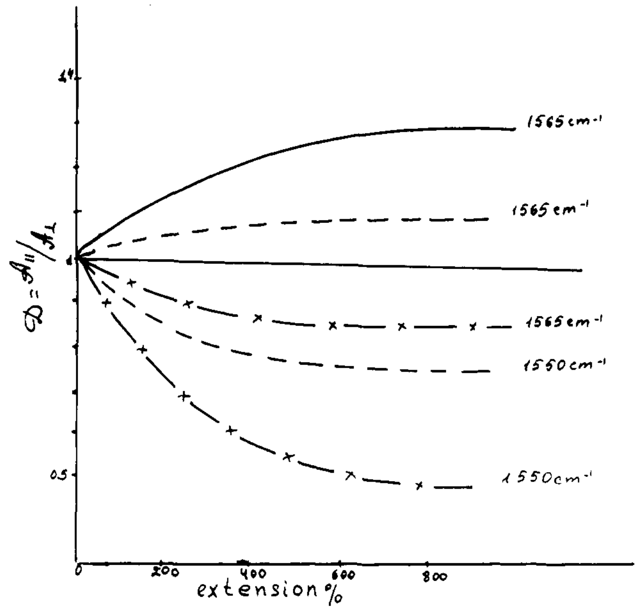

Figure 11. Dichroic ratio vs. percent extension for the bands at 1550 and 1565 cm^{-1} for the K^+ salt of butadiene–methacrylic acid copolymers with 1.1 (—), 2.4 (- - -), and 4.9 (- × -) mol % acid.

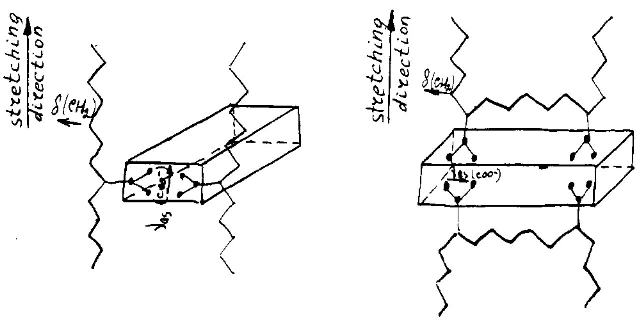

Figure 12. Schematic representation of the packing of polymeric chains around ionic clusters in the salts of butadiene–methacrylic acid copolymers: (a) 1.1 mol % acid, (b) 4.9 mol % acid.

course of polymer packing around the clusters one type of ionic clusters with regular structure is formed which is the most energetically favored. With decreasing size of cation and with increasing steric hindrance in the presence of large side groups in the polymer chain (e.g., styrene) the formation of this ionic cluster is impossible and the other type of ionic clusters with regular structure is formed which is less energetically favored. The data available do not permit us to make conclusions concerning structural peculiarities of both types of ionic clusters. We may only assume that the structure of ionic clusters of the former type is fairly similar to that of the ion layer in crystalline caprylates while the structure of ionic clusters of the latter type (a simpler type, containing a smaller amount of ion pairs) is fairly similar to that of ionic aggregates in liquid crystalline caprylates. Ionic clusters of the first type are formed by the K^+, Rb^+, and Cs^+ salts of the butadiene–methacrylic acid copolymers while the Na salts of these copolymers and all salts of the styrene–methacrylic acid copolymers form the ionic clusters of the second type. It is clear from Figure 9 that the fraction of ion pairs existing in the form of ionic clusters is greater in polymer systems containing simpler ionic clusters. Moreover, it is almost independent of ion concentration. Decrease in the fraction of ion pairs existing in the form of ionic clusters and the appearance of strong concentration dependence for systems containing ionic clusters of the first type may be understood if we bear in mind that increasing complexity of ionic clusters produces increased steric hindrance in the course of chain packing.

The polarized infrared spectra were used in order to characterize the orientation of the carboxylate ions with respect to the main chain in the stretched sample.[4,5] Figure 10 shows these spectra for the samples investigated. As shown in this figure, the dichroism of the (COO^-) asymmetric stretching mode band is influenced by the ion concentration. In the case of the salts of copolymers containing 4.9 mol % acid these bands show a perpendicular dichrosim as the band assigned to a CH_2 wagging mode of polymer chain.[25] It should be pointed out that the 1550-cm^{-1} band has a higher dichroism than the 1565-cm^{-1} band. This result confirms the assignment of these bands to a (COO^-) stretching mode in different types of ionic aggregates. In the case of the salts of copolymers containing 1.1 mol % acid the (COO^-) stretching mode band shows a relatively weak parallel dichroism. The variation of the dichroic ratio with percent extention is shown in Figure 11. It seems reasonable that with increasing ion concentration in the chain the probability of the incorporation of ion pairs of the given chain in a given ionic cluster also increases. This imposes certain requirements on the chain conformation and on the packing of polymer chains around the clusters. This is a possible reason for the change in the dichroic ratio observed with increasing ion concentration. The assumed mode of packing of the polymer chains around clusters is shown schematically in Figure 12. This consumption concerns systems containing ionic clusters of the first type. Among all systems containing ionic clusters of the second type, only systems with Na salts of the butadiene–methacrylic acid copolymers yielded relatively oriented samples. In these samples the 1565-cm^{-1} band shows a perpendicular dichroism independent of ion concentration.

In conclusion, it should be pointed out that the broad featureless band due to the (COO^-) asymmetric stretching vibration is observed in spectra of samples subjected to the action of water vapors. This is possible owing to the counterion solvation and the breakdown of the regular structure of clusters by water.

Thus the ir spectroscopy permits the observation of the state of aggregation of the ions in ionomers and the investigation of the influence of various factors on the aggregation of the ions. The possibility of observing two types of ion aggregates and the data presented which are in favor of a regular structure of ionic clusters are of great importance and probably may be of use in developing the theory of ionomer structure and properties.

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(25) It should be noted that polarized infrared studies of ethylene–methacrylic acid copolymer (4.1 mol % acid) and of its 78% neutralized sodium salts have been carried out by Stein et al.[4,5] They found that the 1700-, 1560-, and 720-cm^{-1} bands show perpendicular dichroism just as in our case.

Crystallinity and Order in Atactic Poly(acryloyloxybenzoic acid) and Poly(methacryloyloxybenzoic acid)

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ABSTRACT: It has been shown on two examples that α-substituted atactic polymers with sizable side groups can develop crystallinity. These polymers, poly(acryloyloxybenzoic acid) (PABA) and poly(methacryloyloxybenzoic acid) (PMBA), are endowed with hydrogen-bonded benzoic acid moieties. Under favorable circumstances the organization of side groups proceeds beyond the formation of a long range lamellar (smectic) order and crystallization takes place. Hydrogen bonding is shown to play an essential part in the formation of such crystalline structures for both polymers. X-ray data are consistent with a monoclinic unit cell for PABA.

The requirement of stereoregularity as prerequisite to the development of crystallinity in α-substituted polymers with sizable side groups is widely accepted. Atactic polymers of this kind are not considered as crystallizable. Crystallinity had at first been reported in the case of atactic polyacrylonitrile,[1] but it now seems that crystallization develops through long syndiotactic sequences.[2]

Until recently the only well-documented cases of crystallinity in atactic polymers were either those in which the substituant groups on the main chain can isomorphously replace each other, such as for example atactic poly(vinyl fluoride), atactic poly(trifluoroethylene), and possibly atactic poly(vinyl alcohol) or atactic polymers with long linear paraffinic side groups[3,4] in which the paraffinic chain length exceeds ten carbon atoms.[4]

We have shown recently[5] that some polymers with side groups characterized by chemical constitution related to mesomorphic behavior can organize spontaneously to give materials displaying long-range mesomorphic order in the solid state. A number of soluble polymers with flexible backbones and rigid, interacting side groups have been prepared. The long-range order (of the smectic or nematic type) results from the interaction and ordering of side groups.

By pursuing these studies we have discovered that the ordering process in some of these polymers goes beyond a smectic or nematic long-range order and leads to side group crystallization, the extent of which depends on the sample treatment and polymerization rate. The purpose of the present paper is to report on the development of crystallinity in two such polymers: atactic poly(acryloyloxybenzoic acid) (PABA) and atactic poly(methacryloyloxybenzoic acid) (PMBA).

Experimental Section

Monomers. *p*-Methacryloyloxybenzoic acid (MBA) and *p*-acryloyloxybenzoic acid (ABA) were synthesized by condensation of the corresponding acid chlorides with *p*-hydroxybenzoic acid. The procedure was previously described.[6] All monomers were extensively purified by repeated recrystallization from various solvents. MBA and ABA display sharp melting points at 182 °C and 201 °C, respectively.

Polymerization and Characterization of Monomers and Polymers. The bulk melt polymerizations were carried out without initiators due to the high melting points of the monomer. The samples of polymers PABA and PMBA were obtained by heating the corresponding monomers to 212 and 189 °C, respectively, and keeping the temperature constant for 3 h. Solution polymerization was carried out in dimethylforamide (DMF) at 115 °C. The monomer concentration was 30% by weight; the initiator was *tert*-butyl