Investigations of the structures of styrene–zinc acrylate ionomers

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X-ray and infrared (i.r.) spectroscopic investigations for styrene–zinc acrylate copolymers have been performed. Wide angle X-ray scattering (WAXS) curves exhibit a broad maximum at low angles, which indicates that ionic segments form multiplets. Using the standard theory for a two-phase system, mean sizes of multiplets have been calculated from small angle X-ray scattering (SAXS) data. It has been found that they are independent of ion content in copolymers, and the phase boundary between ionic aggregates and organic matrix is sharp. Infrared spectra of these copolymers exhibit an additional band in the asymmetric carboxylate stretching region. This band can be attributed to multiplets. A good agreement between X-ray and i.r. data indicates that the i.r. method is useful for investigation of ionomers.

(Keywords: microstructure; ionomer; wide angle X-ray scattering (WAXS); small angle X-ray scattering (SAXS); infrared spectroscopy)

INTRODUCTION

The structure of ionomers has been the subject of extensive studies for many years. The considerable attention is a result of the unusual physical properties arising from the presence of a small amount of ionic groups in hydrocarbon chains. The presence of ionic groups causes sweeping changes in viscoelastic, mechanical and optical properties of these materials[1–4]. Changes also occur in X-ray diffraction patterns. A maximum, conditioned by the content of ionic groups and the degree of neutralization, occurs in the range of low angles of small angle and wide angle X-ray scattering (SAXS and WAXS) patterns. Changes in ionomer properties have been attributed to the aggregation of ions. The multiplet-cluster model introduced by Eisenberg[5,6] is the most popular model of supermolecular constitution of ionomers. Ionic units of polymer form arranged aggregates of the order of 0.5–1.0 nm called multiplets. The multiplets do not contain hydrocarbon monomeric units but are surrounded by them. Under certain conditions the multiplets join into larger domains (clusters) 5–10 nm in diameter, containing hydrocarbon units, apart from ions.

Ionomers examined hitherto have been obtained in two stages. A component containing groups capable of ionization has been introduced to a non-ionic skeleton and the groups have been subjected to total or partial ionization. In the present paper we are concerned with the series of ionomers obtained in a one-stage process as a result of direct copolymerization of styrene and zinc acrylate. The copolymers have a completely random distribution of monomeric units[7]. The purpose of this paper is to examine the effect of the content of zinc ions, water and temperature on the aggregation of ions.

Recently, several papers concerning studies on ionomers neutralized with zinc ions have been published[8–11]. With different samples of zinc salt of sulphonated polystyrene, a maximum was found in SAXS patterns. The maximum corresponds to the Bragg distance in the range 2.5–4.0 nm. It has been attributed to the existence of small aggregates arranged similarly to molecules in a liquid. In references 9 and 10 the arrangement within individual aggregates was estimated. The extended X-ray absorption fine-structure (EXAFS) method was employed. It was found that most probably atoms are arranged in this way, that four oxygen atoms of sulpho groups are the nearest neighbours of zinc ions. A similar tetrahedral arrangement has been found for polystyrene carboxylated and neutralized with zinc ions[9] as well as for ionomers perfluorinated and neutralized with zinc and rubidium ions[11].

EXPERIMENTAL

The conditions of the synthesis of the styrene–zinc acrylate copolymers investigated have been described in reference 7. The characteristics of samples obtained with yield $<6\%$ are given in *Table 1*. Run numbers and average lengths of sequences, presented in *Table 1*, have been calculated using equations derived for a completely random distribution of monomeric units[15], taking into account the given copolymer compositions. The values calculated on the basis of initial composition of comonomer mixtures are identical. The microstructure of copolymers is completely random since values of R, $\langle \mathrm{St} \rangle$ and $\langle \mathrm{A_2Zn} \rangle$ calculated by these two methods are in

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Table 1 Copolymer compositions, glass transition temperature, T_g, run number, R, and lengths of sequences, $\langle St \rangle$, $\langle A_2Zn \rangle$

	Copolymer composition								
Sample	St (mol%)	A_2Zn (mol%)	T_g (°C)	R^a	R^b	$\langle St \rangle^a$	$\langle St \rangle^b$	$\langle A_2Zn \rangle^a$	$\langle A_2Zn \rangle^b$
A	96.33	3.67	109	7.07	7.05	27.25	27.33	1.04	1.04
B	94.49	5.51	115	10.41	10.40	18.15	18.17	1.06	1.06
C	92.98	7.02	122	13.05	13.30	14.25	13.97	1.08	1.08
D	90.17	9.83	141	17.73	17.76	10.17	10.15	1.11	1.11
E	82.41	17.59	147	28.99	29.03	5.69	5.68	1.21	1.21
F	80.52	19.48	150	31.37	31.42	5.13	5.13	1.24	1.24

[a] Calculated on the basis of copolymer composition

[b] Calculated on the basis of initial co-monomer mixture composition

agreement and the product of reactivity ratios is close to unity ($r_1 = 1.1$ and $r_2 = 0.9$).

WAXS investigations were carried out with a Rigaku-Denki SG-9 Geigerflex diffractometer. CuK_α radiation was used (40 kV, 30 mA). The monochromatic beam was obtained by nickel filtration and using a high pulse analyser. A scintillation counter was used as the detector. Investigations at different temperatures were performed in a 2421 Rigaku-Denki camera for the sample which has the highest ionomer peak intensity. The effect of water on the intensity of the analysed maximum was examined for the same sample. The sample was immersed in distilled water at room temperature. From time to time the sample was taken out of water and kept in air for 15 min and then inserted in water again. The number of water molecules per zinc ion was calculated as a result of subtraction of wet and dry sample masses. To secure a constant moisture content during the measurements, the samples were placed in a holder with the mylar foil. The scattering from the mylar foil has been neglected.

SAXS investigations were performed using a Rigaku-Denki camera with slit collimation. The investigations were made in the range of angles 0.09–5.41°, with a step of 0.02°. The experimental curves were corrected for sample absorption and de-smeared from collimation distortions by means of the procedure of Vonk[16]. The weight functions for the slit system used were calculated according to Hendricks[17]. Infrared spectroscopic investigations were conducted on a 4220 Beckman spectrophotometer. The ratio of ionomer to KBr in a tablet was equal to 1:100.

RESULTS AND DISCUSSION

The WAXS patterns obtained for the copolymers investigated are shown in *Figure 1*. The copolymers of low ion content (Curves A and B) have X-ray patterns similar to the pattern for pure polystyrene. The broad haloes at $2\theta = 18.5$ and 9.5° are connected with the short-range order which is characteristic of this polymer. The first maximum is connected with intermolecular interference effects, the second corresponds to intramolecular effects caused by the arrangement of benzene rings within one chain[22]. These maxima decrease with increasing zinc acrylate content in copolymers. For the mole fraction of 7.02% (curve C) a new maximum appears at $2\theta = 5.5°$. The intensity of the maximum increases with increasing concentration of zinc ions in the copolymer and its angular position varies too. With 19.48 mol% A_2Zn the maximum has the highest intensity and its angular position is $2\theta = 4.6°$. This maximum is characteristic of ionomers and is usually taken as evidence for ionic aggregation.

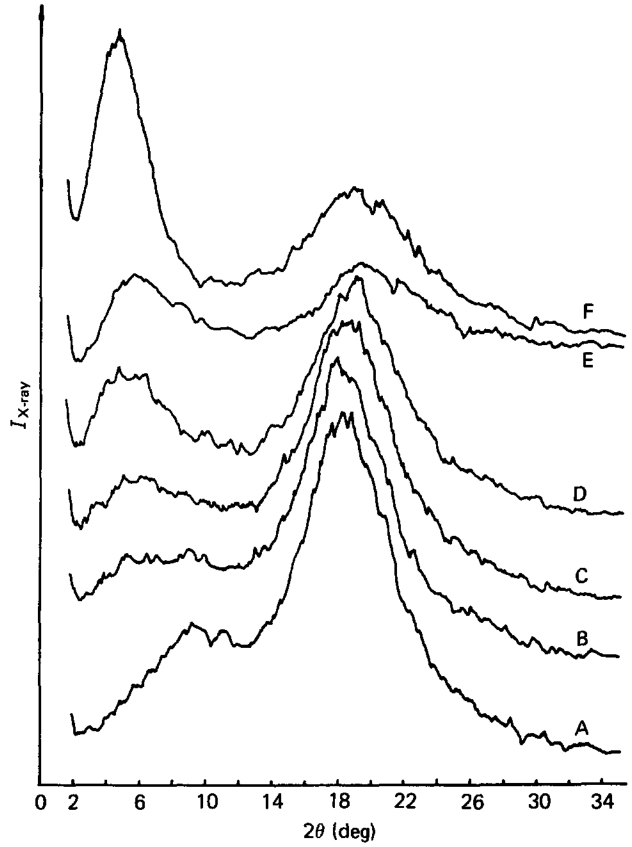

Figure 1 Effect of zinc acrylate concentration on ionomer reflexes for styrene–zinc acrylate copolymers. Zinc acrylate concentration (mol%): A, 3.67; B, 5.51; C, 7.02; D, 9.83; E, 17.59; F, 19.48

Figure 2 shows SAXS curves for samples which exhibit distinct maxima in the WAXS patterns. None of the SAXS curves contains any interference maximum. The absence of the SAXS maximum can be interpreted as being due to an absence of large ionic domains (clusters). An alternative interpretation can also be presented, namely that the characteristic sizes of ionic clusters are so large that the scattering maximum is situated too close to the primary beam and cannot be detected. If, however, such an interpretation is true we must recognize the ionomer peak on the WAXS curves as a second-order maximum. But in such a case the angular position of the first-order maximum should be at ~2°. It is evident from *Figure 2* that none of the SAXS curves exhibits any

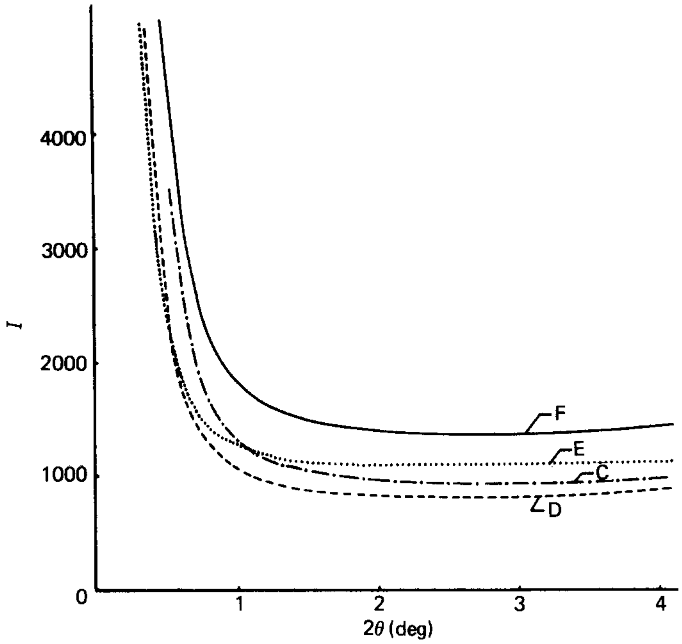

Figure 2 SAXS patterns for copolymers with different zinc acrylate contents before cutting off the background. Zinc acrylate concentration (mol%): C, 7.02; D, 9.83; E, 17.59; F, 19.48

maximum at this angular range. So we conclude that our X-ray data testify more to the presence of small ionic aggregates than to large clusters.

Such an interpretation is confirmed by infrared spectroscopic investigations which will be discussed further. More precise analysis of X-ray results has to be based on an assumed model of the structure. The existing models of ionomer structure differ in that some of them attribute the origin of the ionomer peak to either an interference between small aggregates or to the internal structure of independent ionic particles. The most penetrating analysis of the models has been presented by Yarusso and Cooper[8], who have calculated theoretical SAXS patterns for each model and have compared them with experimental curves for various ionomers. This analysis has led to the conclusion that no model gives total agreement between these curves. Yarusso and Cooper[8] have proposed a new model which gives satisfactory results but does not solve all doubts. Moreover, the number of parameters involved in the model calculations contributes to the many ambiguities arising. To avoid such ambiguities, standard scattering theory for a two-phase system can be used to analyse the SAXS profiles[23]. Then Bragg's law can be applied to the value of 2θ at the maximum intensity. This corresponds to a distance d between the small ionic domains. The broad maximum, however, makes this calculation rather difficult.

So we assume that the ionomer is a two-phase system with an arbitrary electron density difference between the phases. We also assume a constant electron density within the phases and sharp phase boundaries. Porod has derived the asymptotic form of the scattered intensity:

$$\frac{\lim_{s\to\infty}(s^4 I)}{\int_0^\infty s^2 I(s)\,\mathrm{d}s} = \frac{K}{Q} = \frac{S/V}{2\pi^2\phi(1-\phi)} \qquad (1)$$

where S/V is the specific surface of the phase boundary, K is the Porod constant, Q is the scattering invariant, ϕ is the volume fraction of one of the phases, and s is a scattering vector ($s = 2\sin\theta/\lambda$, where λ is the wavelength of the X-ray). Equation (1) provides a direct measurement of the surface to volume ratio of the scattering entities. Knowing ϕ and assuming a spherical shape of the ionic domains permits an approximate calculation of the radius of the ionic domains R.

If the electron density does not change stepwise between separated phases but changes continuously in a certain transition region with a finite thickness SAXS method allows the determination of the thickness of such a transition layer. Assuming that the electron density varies sigmoidally in the transition region,

$$I(s) = \frac{K}{s^4}\exp(-4\pi^2\sigma^2 s^2) \qquad (2)$$

The parameter σ can be determined from the slope of the plot of $\ln[s^4 I(s)]$ *versus* s^2 for high values of s. The thickness of the phase boundary, E, can be estimated as $E = 2(3\sigma)^{1/2}$.

Before any analysis of equations (1) and (2), a correction for the continuous background can be made. For this purpose we used a procedure proposed by Vonk[23].

Results obtained for styrene–zinc acrylate copolymers, summarized in *Table 2*, lead to the following observations:

1. Ionic domains are small ($R \approx 4$ Å) and their dimensions do not vary significantly within experimental error, estimated at ±12%. It seems that R is independent of the content of ionic groups in the copolymer.
2. The phase boundary between the ionic domain and the polystyrene is sharp. The values of E are effectively zero within experimental error.
3. The average distance d between domains is constant within experimental error.
4. The increase of ionic-group content causes an increase of the SAXS invariant Q, which can be associated with an increasing of the volume fraction of the domains.

These results are in agreement with conclusions obtained for model ionomers by Russell and co-workers[18]. They stated that the radius of the ionic domains and the thickness of the phase boundary are independent of the average molecular weight of a polymer chain among ionic groups. Molecular weight $\bar{M}_n$ influences the volume fraction of the domains, which decreases as $\bar{M}_n$ increases. From *Table 1* we can conclude that the increase of the content of ionic groups in the copolymers studied is followed by a decrease of the average molecular weight of a polymer chain between these groups. So the increase of the content of ionic groups induces an increase in the ionic microdomains but does not change their dimensions. The

Table 2 SAXS data for styrene–zinc acrylate ionomers of different ion contents

Sample	A_2Zn (mol%)	Q $(\mathrm{mol\,cm^{-3}})^2$	d (Å)	R (Å)	E (Å)
C	7.02	$0.109\cdot10^{-3}$	17.3	3.7	1.5
D	9.83	$0.147\cdot10^{-3}$	17.7	3.8	1.1
E	17.59	$0.211\cdot10^{-2}$	15.8	3.7	1.3
F	19.48	$0.534\cdot10^{-2}$	19.8	4.0	0.9

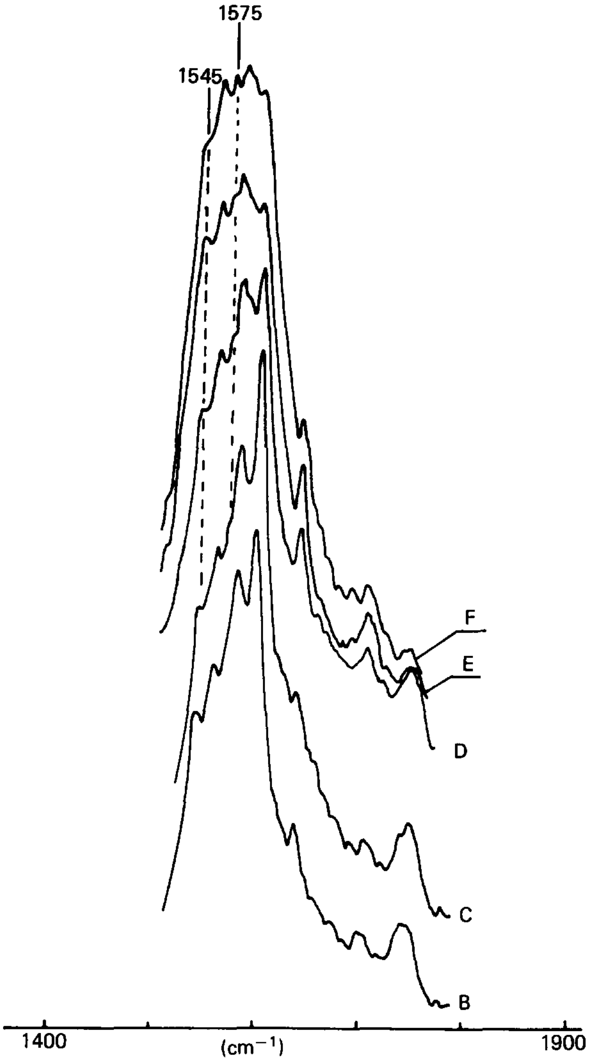

Figure 3 I.r. spectra in the range 1400–1900 cm^{-1} for copolymers with different zinc acrylate contents (mol%) as follows: B, 5.51; C, 7.02; D, 9.83; E, 17.59; F, 19.48

increase of the intensity of the ionomer maximum which is visible in *Figure 1* should be associated with it.

Another interesting observation connected with *Figure 2* concerns the high level of the background, especially for the sample with 19.48% A_2Zn. The intensity in the tail of the scattering curve depends on the level of fluctuations of electron density within the separated phases. The fluctuations arise from thermal density fluctuations and from the presence of isolated ions randomly distributed in the organic matrix or of organic monomers in the ionic phase. The high level of the background for the sample with 19.48% A_2Zn may testify to the fact that there are both microdomains containing a few ionic groups and individual ion pairs dispersed in polystyrene matrix. More direct evidence of the presence of such ion pairs comes from spectroscopic investigations.

The i.r. spectrum of the analysed copolymer has all bands which are characteristic of styrene and zinc acrylate. However, a new band appears at 1575 cm^{-1} and the band at 1545 cm^{-1} disappears with increasing salt concentration. In accordance with observations of Coleman and co-workers[13], additional bands in the range corresponding to asymmetric vibrations of carboxylate groups testify to aggregation of ionic groups into multiplets. *Figure 3* presents fragments of spectra which correspond to asymmetric vibrations of COO^- groups for samples with different A_2Zn contents. The band at 1575 cm^{-1} can be attributed to the formation of multiplets, whereas the band at 1545 cm^{-1} can be attributed to isolated pairs of ions. As can be seen in *Figure 3* the band at 1545 cm^{-1} exists for each sample, which testifies that even for the copolymer with the highest content of ionic groups the large number of isolated ion pairs exists. This fact has great importance as far as the behaviour of the studied copolymers under the influence of water is concerned.

The influence of water upon the behaviour of the ionomer maximum for the copolymer with 19.48% A_2Zn is presented in *Figure 4*. The number of water molecules per zinc ion, *k*, is given for each curve. The considerable water absorptivity is a surprising fact. It must be added, however, that the rate of water absorption was very slow. The highest degree of water saturation has been achieved after immersion of the sample for tens of hours.

It is generally accepted that water can reside preferentially in the ionic domains and is excluded from the organic matrix. This leads to a decrease in the electron density, which in turn causes a decrease in the scattering intensity in the small angle region. Water absorption requires some mechanism which would transport water molecules through the matrix to the ionic domains. Slow absorption suggests that domains are separated from one another. The presence of isolated ion pairs in the matrix, i.e. incomplete aggregation of the ionic groups, considerably facilitates this process. It was shown above

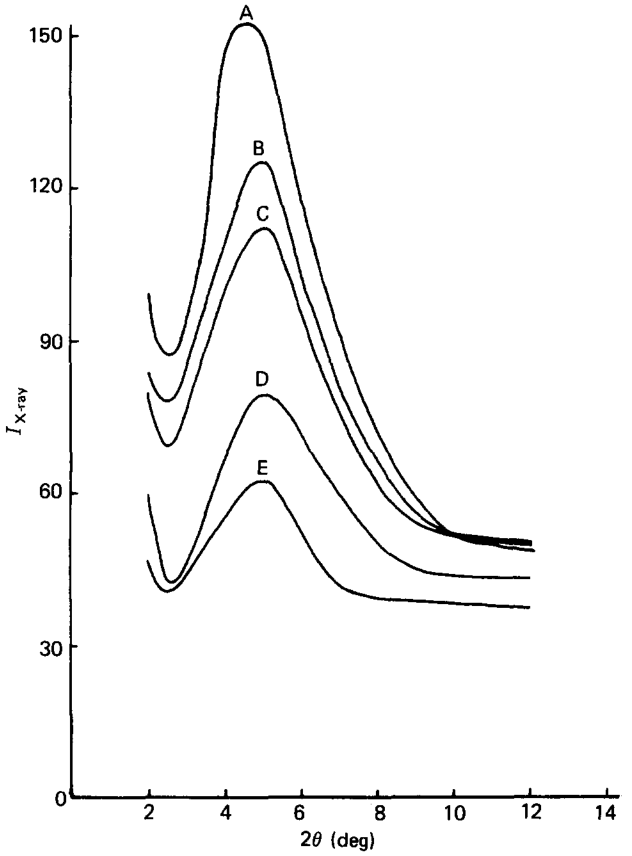

Figure 4 Effect of water absorption, *k*, on ionomer reflex for the copolymer with 19.48% zinc acrylate. $k=[H_2O]/[Zn^{2+}]$: A, dry sample; B, 1.6; C, 3.3; D, 5; E, 6.5

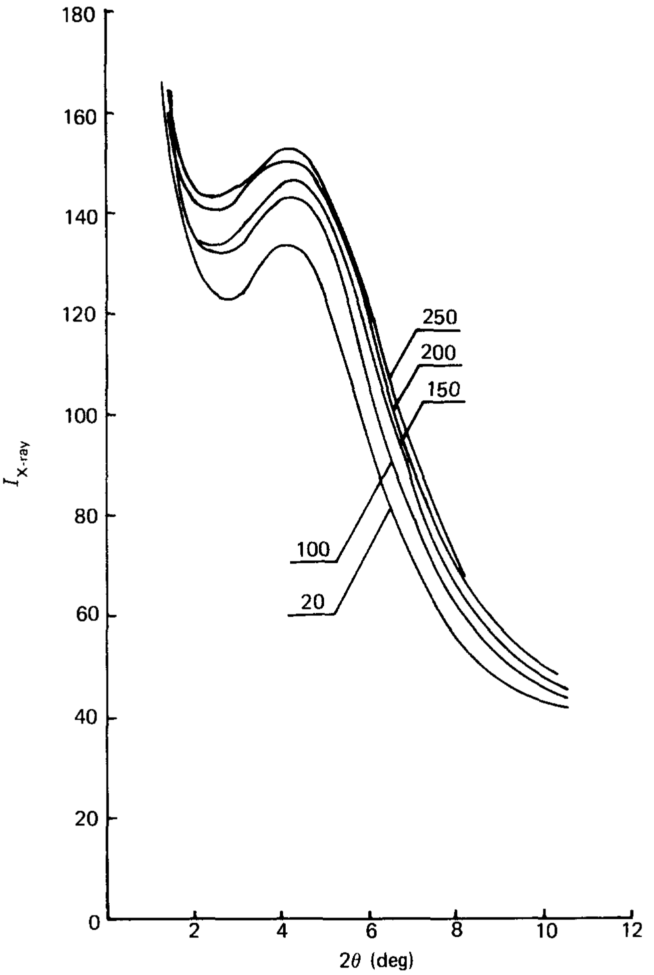

Figure 5 Effect of temperature on ionomer reflex for the copolymer with 19.48% zinc acrylate. Numbers on curves give temperature in °C

that the copolymer with 19.48% A_2Zn has many such ionic groups. It can explain the large amounts of water absorbed by this copolymer. It seems that small distances among ionic domains (a few tenths of nanometres) can also facilitate transport of water.

The good agreement between X-ray and i.r. data allows the following conclusion to be drawn concerning the usefulness of the i.r. method for investigating ionomers. As can be seen in *Figure 3*, the band at 1575 cm^{-1} occurs for the sample with 7.02 mol% A_2Zn. The WAXS pattern of this sample has an ionomer peak distinctly outlined (*Figure 1*, curve C). Comparison of these results demonstrates that new bands in the range of asymmetric vibrations of carboxylate groups can be attributed to changes which take place in the local structure of the copolymer. Coleman and co-workers[14] have questioned the interpretation of i.r. data for ionomers. Our results confirm that i.r. investigations are useful for the examination of the local structure within multiplets.

Figure 5 shows the variation in intensity of the ionomer peak as a function of temperature for the sample with 19.48 mol% A_2Zn. The intensity of this maximum increases with temperature rise, but the position of the ionic maximum does not vary up to a temperature of 250°C. One should consider that the angular position of the maximum is constant in the investigated temperature range within experimental error. Previously, differential scanning calorimetry (d.s.c.) and thermogravimetric studies showed that $T_g = 150°C$ and the decomposition temperature of the multiplets is 327°C for the sample with 19.48% A_2Zn[26]. Above T_g the mobility of the matrix chains increases and the isolated ionic groups that are present in the matrix can aggregate when the ionomer is heated. This mechanism has been defined by Weiss and co-workers in a paper about the kinetics of phase separation in ionomers[20]. It seems to us that the increase in the ionomer peak intensity should be connected with it.

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