

## CATION MOTION IN IONIC COPOLYMERS

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Far infrared bands for the motion of  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{Cs}^+$  in the field of side groups and paraffinic elements of ethylene-methacrylate ionic copolymers, and a preliminary evaluation of the force field for the vibrations of those ions are reported.

## 1. INTRODUCTION

Understanding the nature and magnitude of the specific molecular interactions in polymers and polyelectrolytes is essential to developing a microscopic theory for their physical and chemical properties [1 - 3]. A system in which the local forces exerted between polymer units can be evaluated, and whose physical properties depend strongly on the nature of a simple and systematically variable constituent is the series of ionomers of ethylene and methacrylic acid.

The physical properties of these ionic copolymers, which result from replacing the carboxylic hydrogen in the acid copolymer with a simple cation such as  $\text{Na}^+$ , depend strongly upon the identity of the cation and the nature of the ion-multipole forces within the copolymer [4, 5]. These properties are, in turn, significantly different from those of the acid form of the copolymer, in which hydrogen bonding plays a dominant role.

Vibrational bands due to motion of cations in the potential field of counterions have been observed in the far-infrared spectra of ionic solutions in solvents of low dielectric constant [6 - 8]. In this letter we report the existence of far-infrared bands due to  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{Cs}^+$  motion in the local potential fields of the carboxylate side groups and the ethylenic chains in ionic copolymers, and a preliminary evaluation of the forces exerted on these ions.

## 2. EXPERIMENTAL

Far-infrared spectra of annealed films of

ethylene-methacrylic acid copolymer (7.6% carboxylic acid by weight) and of its ionomers in which 95% of the acid hydrogens were replaced with  $\text{Li}^+$ ,  $\text{Na}^+$  or  $\text{Cs}^+$  were measured with a Beckman IR-11 spectrophotometer and are shown in fig. 1. These experimental copolymers were prepared and kindly furnished by Dr. R. Longworth of the DuPont Company Experimental Station.

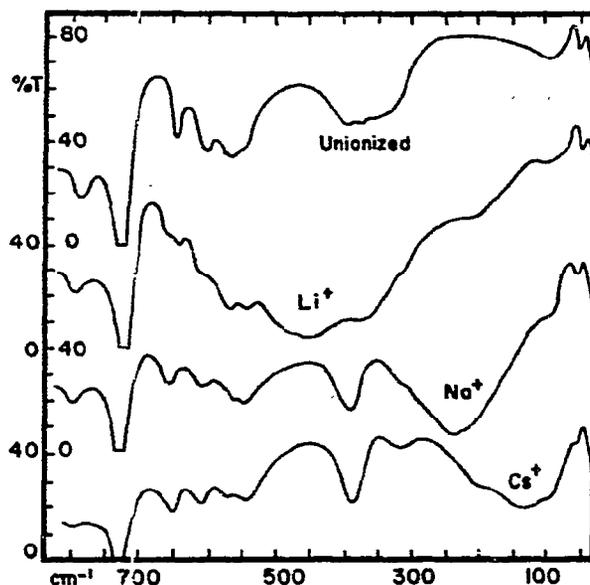


Fig. 1. Far infrared spectra of an ethylene-methacrylic acid copolymer and its alkali metal ionomers with  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{Cs}^+$ . Spectra measured on films of 0.12-0.2 mm thickness.

### 3. RESULTS

There are several features of the ionomer spectra that are strikingly different from those in the spectrum of the acid form of the copolymer. In the spectrum of each of the ionomers a broad well-defined band is observed that shifts markedly upon changing the cation and that is not present in the acidic copolymer. These bands are centered at  $450 \pm 5 \text{ cm}^{-1}$  for the  $\text{Li}^+$ ,  $230 \pm 5 \text{ cm}^{-1}$  for the  $\text{Na}^+$  and  $135 \pm 10 \text{ cm}^{-1}$  for the  $\text{Cs}^+$  ionomers. The frequency variation of these bands is roughly accounted for by the change in mass of the cation. These principal new bands are assigned to cation motion in the copolymer.

For this type of motion the mass of  $\text{Li}^+$  is expected to be close to the vibrational reduced mass. Thus, if we assign the  $\text{Li}^+$  band center as that due to the vibration of  ${}^7\text{Li}^+$ , the  ${}^6\text{Li}^+$  band  $\omega_6$  is calculated to be at  $486 \text{ cm}^{-1}$  from  $\omega_6 = (7/6)^{1/2} \omega_7$ . A pronounced shoulder is observed on the main  $450 \text{ cm}^{-1}$  band at ca.  $485 \text{ cm}^{-1}$ . Naturally, the  $m^{-1/2}$  frequency dependence is only approximate even if the interaction potential energies are identical for the two cases.

In addition to the dominant spectral features, the bands associated with motions of the carboxylate group and its near neighbors on the polymer backbone are significantly altered by the perturbations of the  $\text{M}^+$  ions and the disappearance of nearly all of the hydrogen bonding present in the acidic copolymer. We may briefly account for the observed spectral changes as follows.

On the basis of the assignment of a  $782 \text{ cm}^{-1}$  band in the sodium salt of polyacrylic acid to an O-C-O bending mode [9], the  $785 \text{ cm}^{-1}$  band of the acid copolymer can be tentatively assigned to this carboxylate vibration which is cation sensitive and shifted by about  $10 \text{ cm}^{-1}$  to higher frequencies in the ionomers. The bands in the  $540$ ,  $380$  and  $310 \text{ cm}^{-1}$  regions probably contain large components of  $\omega(\text{C-C-C})$  and the  $722 \text{ cm}^{-1}$  band is assigned as a methylene rocking-twisting motion of the paraffinic backbone, both as found for  $n$ -paraffins and are expected since the carboxylate groups are separated, on the average, by a  $(\text{CH}_2)_n$  chain of about  $n = 20$  [10]. The  $300 - 420 \text{ cm}^{-1}$  region for the acidic form contains a complex band envelope in which there are at least three bands with at least one of them associated with hydrogen bonding. The disappearance of this hydrogen bonding absorption at about  $360 \text{ cm}^{-1}$  is responsible for the altered band contour. In the spectra of polymeric

esters having a pendant  $-\text{COOR}$  group, a band is observed in the  $500 - 650 \text{ cm}^{-1}$  region that is assigned to a bend of the C-O-R linkage with respect to the C-C=O group and is quite frequency and intensity sensitive to mechanical coupling with the R group. This behavior is similar to that in the  $530 - 570 \text{ cm}^{-1}$  region of the ionomer spectra.

The  $598 \text{ cm}^{-1}$  band of the acid copolymer is shifted to  $605 - 608 \text{ cm}^{-1}$  upon ionomer formation. A similar shift of the  $588 - 595 \text{ cm}^{-1}$  Raman band in polyacrylic acid to  $603 - 610 \text{ cm}^{-1}$  in its sodium salt has been observed [11, 12] for a C-C-C bending motion. The shift in frequency was ascribed to a conformational change, but this may result mainly from a highly localized ion-multipole interaction between the cation and its nearest neighbor  $\text{CH}_2$  group. Indeed, the appearance of the cooperative torsional mode of the paraffinic backbone at  $200 - 210 \text{ cm}^{-1}$  [2], which is not observed for the acidic copolymer, may be due to such an interaction.

### 4. DISCUSSION

The local potential field representing the forces of interaction between the polymer side groups and the cation can be estimated by employing the spectral information presented here and postulating models for the vibrating assembly. In postulating such models we note that the breadth of the cation motion bands indicates that there are several environments for the cations, that they differ somewhat in the forces exerted on them, and that the vibrations of the resulting assemblies are likely to be anharmonic. Two cation environments (models 1 and 2) are expected to consist principally of one and two carboxylates, respectively. This is consistent with the presence of ionic domains in the bulk copolymer. Some of the cation environments are modeled to consist of a pendant carboxylate group and a  $(\text{CH}_2)_n$  segment of an adjacent molecule. This model (model 3) is consistent with the spectral data interpreted in terms of a perturbation of the C-C-C bending modes and skeletal modes. This model is particularly interesting because the resulting interaction may provide a mechanism for the cation dependence of the copolymer viscoelasticity.

For each of these models we now compute the net force  $K_i^{\text{net}}$  resisting the vibrational motion of the cation per unit change in the cation-carboxylate separation as follows. We express the vibrational equations of motion [13] ( $T$  is the

kinetic energy):

$$T = \frac{1}{2} \sum_n m_n \dot{\mathbf{e}}_n \cdot \dot{\mathbf{e}}_n = \frac{1}{2} \sum_{i,j} T_{ij} \dot{R}_i \dot{R}_j,$$

where

$$T_{ij} = \sum_n m_n \boldsymbol{\tau}_{ni} \cdot \boldsymbol{\tau}_{nj}$$

and  $\mathbf{e}_n$  is the displacement along the  $n$ th cartesian coordinate,  $R_i$  is the  $i$ th normal coordinate whose form, given by the vectors  $\boldsymbol{\tau}_{ni}$  (assumed eigenvectors), constitutes the model. Then the model geometry, the definition of unit change in the cation-carboxylate separation, and conservation of momentum permit calculation of

$$T_i^{\text{red}} = \sum_n m_n \boldsymbol{\tau}_{ni}^2.$$

The potential energy is

$$V = \frac{1}{2} \sum_{k,l} V_{kl} \Delta r_k \Delta r_l,$$

where  $V_{kl}$  are force constants for internal coordinate changes  $\Delta r$ .

Then

$$K_i^{\text{net}} = \sum_{k,l} V_{kl} \Delta r_{ki} \Delta r_{li},$$

so that for this  $i$ th mode, the vibration modeled, we have

$$K_i^{\text{net}} = 4\pi^2 c^2 \omega_i^2 T_i^{\text{red}}.$$

Thus, from the observed frequency ( $\omega_i$ ) and the form of the vibration (a consequence of the model) which defines  $T_i^{\text{red}}$ , we compute  $K_i^{\text{net}}$  which is the net force resisting the vibrational motion per unit change in the cation-carboxylate separation.

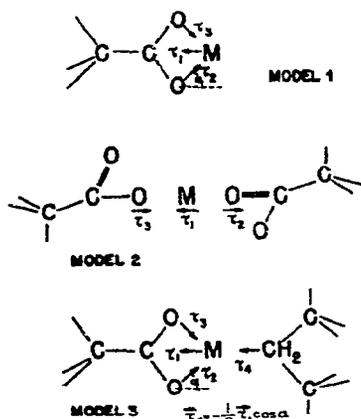


Fig. 2. Vibrational models for cation motion in ethylene-methacrylate ionomers.

Table 1  
Net force  $K_i^{\text{net}}$  (mdynes/Å) resisting vibrational motion of cations, for different cations in different models ( $i$ ).

Ionomer	$\omega$ (cm <sup>-1</sup> )	$K_1^{\text{net}}$	$K_2^{\text{net}}$	$K_3^{\text{net}}$
<sup>7</sup> Li <sup>+</sup>	450 ± 5	0.74	0.69	0.73
Na <sup>+</sup>	230 ± 5	0.47	0.42	0.48
Cs <sup>+</sup>	135 ± 10	0.32	0.28	0.34

The approximate models postulated are shown in fig. 2, and the value of  $K_i^{\text{net}}$  for each cation in each model is given in table 1. The strengths of the interaction fall in the order Li<sup>+</sup> > Na<sup>+</sup> > Cs<sup>+</sup> and are of the order of force constants for gaseous ionic clusters, which may indicate that electrostatic ion-multipole treatments of the interactions will be fruitful.

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