first term in each of eq 12, 19, 24, and 29). The second is independent of L or n except for factors such as $1 - e^{-L/a}$, $1 - \alpha^n$, or $\mathbf{E} - \mathbf{S}^x$, which may be neglected in all but short chains. This common mathematical structure leads to the similarity of the two models. Therefore, eq 12–14 provide excellent approximations to RIS chains within the Daniels approximation. Once C_∞ and D are determined, by eq 30 and 31 for example, they will provide simple expressions for $\langle R^2 \rangle$ for all but short chains.

Yamakawa and co-workers[14-25] have developed the so-called helical wormlike model, and they have been successful in demonstrating agreement between their model and with both polymer molecules in solution[18,24,25] and RIS chains.[14,16,19,23] Agreement with RIS chains was seen both beyond the Daniels approximation and with $D < 0$. Although we have not studied the problem, it is probable that the additional adjustable parameters available in the helical wormlike chain model account for its improved ability to match RIS behavior.

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Low-Frequency Raman Spectroscopic Study of Ionomers

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Introduction

Ionomers are defined as polymers with nonpolar backbones containing up to 10 mol % salt group substituents, either present as pendant groups or directly incorporated into the main chain. It has been well established that the mechanical properties of these polymers, such as modulus, tensile strength, and melt elasticity, are significantly affected by the presence of these salt group substituents.[1,2] It is generally accepted that ionomers are phase separated and that the driving force for this phase separation is electrostatic in nature. Information obtained by electron microscopy, small-angle X-ray measurements, and infrared spectroscopy has led to the proposal of several morphological models.[3-6] However, each model differs considerably in its description of the nature and size of the phase-separated ionic domains. Therefore, additional characterization methods are still needed.

Table I
Mole Percent of Carboxylic Group and Degree of Ionization of Ethylene–Methacrylic Acid Copolymer and Its Salts

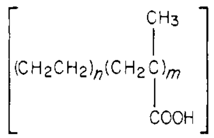
acid or salt	mol % carboxylic group	degree of ionization, %
acid	2.3	
Na	4.0	50.7
K	6.1	69.9
acid	6.1	

Recently, a number of low-frequency vibrational spectroscopic analyses showing spectroscopic features sensitive to the concentration and chemical nature of salt groups present have been carried out.[7-10] In contrast to pure modes, such as CH_2 and C=O stretching modes, vibrational bands in the low-frequency region are delocalized in nature; i.e., they involve a number of atoms. The positions and shapes of such bands are conformationally dependent and may also be quite sensitive to both the specificity and magnitude of intermolecular interactions. However, because of their complex nature, band assignments in this region are often unclear.

Ethylene–methacrylic acid copolymer and its salts have been studied in the past.[1,2,11] The structure of this polymer involves a number of phases. They are (1) the lamellar structure involving crystalline polyethylene, (2) the amorphous phase of polyethylene, and (3) the ionic domains. We have carried out a Raman spectroscopic study of this ionomer. Our preliminary results are reported here.

Experimental Section

Ethylene–methacrylic acid copolymer (1) and salts were supplied by du Pont. The neutralization of the copolymer containing 6.1 mol % methacrylic acid was accomplished in dilute xylene solution by the addition of freshly prepared potassium methoxide. Copolymer compositions are collected in Table I. These samples were dried under vacuum for several days and then used for Raman spectroscopy.



$$\left[(CH_2CH_2)_n(CH_2\overset{\displaystyle CH_3}{\underset{\displaystyle COOH}{C}})_m\right]$$

1

The degree of neutralization of the ethylene–methacrylic acid ionomers used was estimated from the ratio of the intensity of the C=O stretching vibration associated with the carboxyl group (1700 cm^{-1}) to that of the asymmetric vibration of the carboxylate ion (1560 cm^{-1}). The values (Table I) obtained for our samples are in the same range found previously.[11,12]

Raman spectra were obtained with a computer-controlled Jobin-Yvon HG.2S laser Raman spectrometer, which offers the advantage of having extremely high discrimination against Rayleigh scattering, yielding high signal-to-noise ratios in the low-frequency region. However, the Raman spectra were usually difficult to obtain because of the high fluorescence background

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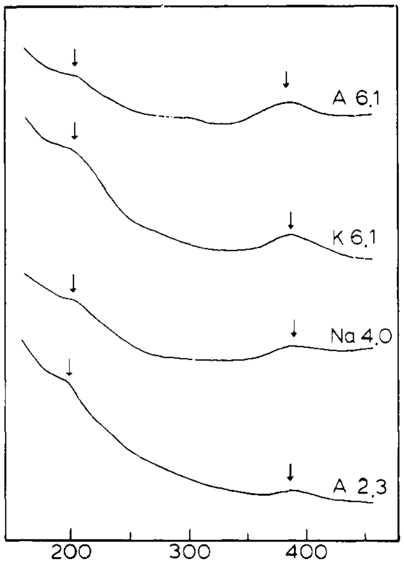

Figure 1. Raman spectra of ethylene–methacrylic acid copolymer and its salts in the 150–450-cm^{-1} region: A6.1, ethylene–methacrylic acid copolymer (6.1 mol % methacrylic acid); K6.1, potassium salt of ethylene–methacrylic acid copolymer (6.1 mol % potassium methacrylate); Na4.0, sodium salt of ethylene–methacrylic acid copolymer (4.0 mol % sodium methacrylate); A2.3, ethylene–methacrylic acid copolymer (2.3 mol % methacrylic acid).

in the ionomers. The low-frequency Raman spectra obtained for the ethylene–methacrylic acid copolymers and salts are shown in Figure 1.

Results and Discussion

Even though the infrared spectra obtained for the ethylene–methacrylic acid copolymers contain a number of bands peculiar to the copolymers, the corresponding Raman spectra are quite similar to the ones obtained for polyethylene. The vibrational spectrum of polyethylene is understood in great detail[13] and can be useful in our analysis. In our Raman spectra, only one weak band, at 760 cm^{-1}, can be unambiguously assigned to the methacrylic acid segment. This band is the strongest Raman band in poly(methacrylic acid).[14] In addition, three bands, at 390, 210, and approximately 40 cm^{-1}, can be found in the low-frequency region for the various copolymers studied. The two bands at 390 and 210 cm^{-1} were found for all the copolymers studied, whether in the acid or salt form. Their positions are independent of whether the cation is sodium or potassium. We have found that the relative intensity of the 390-cm^{-1} band increases with molar concentration of the carboxylic group. These intensity measurements were normalized to the localized CH_2 twisting vibration at 1295 cm^{-1}. The validity of such a procedure has been established in a previous publication.[15] On the basis of group frequency analysis, this 390-cm^{-1} band has been assigned to the bending deformation of the O–C–O group in styrene–methacrylic acid ionomers.[10] However, it should be pointed out that the deformational vibrations of the COOH groups for formic acid, acetic acid, and adipic acid crystals exist approximately in the 550–650-cm^{-1} region, well above the 390 cm^{-1} observed.[16-18] Thus the origin of this band is uncertain and needs to be clarified.

Since the 210-cm^{-1} band is observed in both the copolymer and salts, it also cannot be assigned to a vibration associated with ion aggregates in ethylene–methacrylic acid ionomers. The bands characteristic of such a superstructure should obviously appear only for the salt forms. The normalized intensity of the 210-cm^{-1} band also increases with molar concentration of the carboxylic acid groups and the degree of ionization. Two possible types of assignment can be made for this band in ethylene–methacrylic acid ionomers. First, this band may be assigned as a conformational defect band. The density of states for the ν_9 branch of polyethylene would be expected to have its greatest intensity near this position.[13] This band has been observed in the Raman spectra of liquid alkanes, varying from 270 cm^{-1} in C_9H_{20} to 204 cm^{-1} in molten polyethylene.[19] An infrared band has also been observed in this region.[20,21] With increasing carboxylate concentration, we would expect a lowering of crystallinity, giving rise to a more intense 210-cm^{-1} band, as observed.

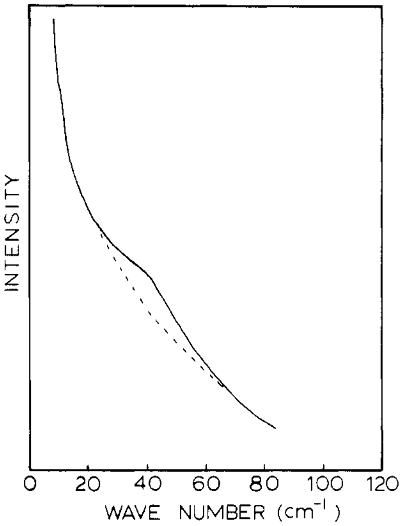

Figure 2. Typical Raman spectrum of ethylene–methacrylic acid copolymer (6.1 mol % methacrylic acid) in the low-wavenumber region 10–90 cm^{-1}: (—) spectrum obtained; (- - -) smoothed base line assumed.

The second possibility is to assign it to the carboxylate ion. If this band is assignable to superstructures such as "clusters" or "multiplets", one would expect its frequency to be sensitive to the ionic radius and valency of the counterions. In fact, the frequency of this band did not vary with the various ions introduced, i.e., Na^+, K^+, and Zn^{2+}. In ethylene–methacrylic acid copolymers and salts, our results suggest that this band arises from defects of ethylene segments.

For the ethylene–methacrylic acid copolymer and its salts, we found one additional band at 40 cm^{-1} (Figure 2). The intensity of this band decreases substantially with increasing neutralization. Specimens of the salt containing 4.0% molar concentration methacrylic acid were annealed at 65, 75, 85, and 93 °C for 2 days. The frequency of this band decreased with increasing temperature. This relationship is shown in Figure 3. Recently, there have been a number of studies attempting to elucidate the nature of the longitudinal acoustic mode (LAM) in semicrystalline polymers. The frequency of this vibrational mode is inversely proportional to chain length. Unlike the long periodicity measured by small-angle X-ray diffraction, this vibrational band is sensitive to long-range uniformity of chain conformation. The frequency of this band is usually written

$$\nu = \frac{1}{2cL}\left(\frac{E}{\rho}\right)^{1/2}$$

where ν is the vibrational frequency (in cm^{-1}) of the LAM, L the length of the vibrating chain, E the Young's modulus, ρ the density, and c the speed of light. The crystallinity of a 4.0 mol % ethylene–methacrylic acid copolymer and

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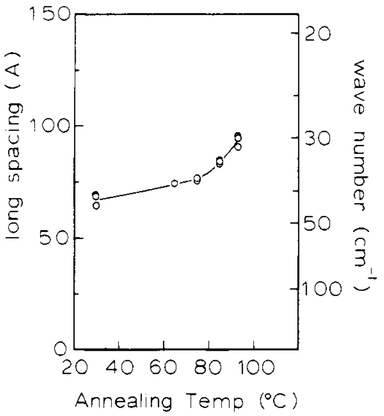

Figure 3. Plot of the band position and the derived long spacing against annealing temperature for the sodium salt of ethylene–methacrylic acid copolymer (4.0 mol % methacrylic acid).

its salts is about 30–40%.[22] The exact value depends on sample preparation. For the as-prepared sample, we would predict, using the E and ρ values applicable to polyethylene, a chain length distribution centered at 70 Å. This value is consistent with the value derived from SAXS measurements.[23] For the annealed samples, the chain lengths calculated from the Raman frequency are also shown in Figure 3. Since the frequency and the intensity of the LAM can be disrupted by conformational and configurational disorder,[23,24] the existence of this mode in a random copolymer is interesting.

In summary, although we have found three bands which are sensitive to the salt group on ion content in ethylene–methacrylic copolymers and their salts, they are characteristic of the lamellar structure associated with the polyethylene component and the conformational defects present. None can be associated unambiguously with structures such as ion "clusters" or "multiplets".

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Light Scattering from Hollow Finite Cylinders[†]

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The advent of laser techniques has stimulated wide interest in employing light scattering to study both structural and dynamical properties of macromolecules in solution.[1] For example, Pecora and Aragon[2] have developed the theory of the light scattering spectrum from hollow spheres and discuss how this system may be employed as a model for dispersions of phospholipid vesicles. In order to obtain useful information on particle structure, it is necessary to have available theoretical expressions for the intramolecular scattering function for a variety of molecular shapes. These theoretical expressions are employed to compare and interpret intensity measurements. Prior interest[3] in the frictional properties of multisubunit microtubule assemblies has led us to note the absence of an explicit theoretical expression for the structure factor of finite-length hollow cylinders, a potentially useful model shape for some rigid molecular aggregates. The purpose of this note is to present an expression for $P(\mathbf{q})$, the dilute-solution structure factor for this case.

For a monodisperse system, the intramolecular interference structure factor is[1,4,5]

$$P(\mathbf{q}) = \frac{1}{N^2}\sum_{j,k}\langle \exp[i\mathbf{q}\cdot(\mathbf{r}_j - \mathbf{r}_k)]\rangle = \frac{1}{v^2}\int \mathrm{d}R\,\mathrm{d}R'\langle \exp[i\mathbf{q}\cdot(\mathbf{R} - \mathbf{R}')]\rangle \qquad (1)$$

where the double sum extends over all N optically isotropic scattering elements of the structure located at positions $\mathbf{r}_i$ and $|\mathbf{q}| = (4\pi/\lambda)\sin(\theta/2)$ is the scattering wave vector, with λ the incident wavelength and θ the scattering angle. In the second equality of eq 1, the sum over scattering elements has been replaced by an integral, with R denoting a position in the hollow cylinder of outer radius b, inner radius a, length L, and volume $v = [\pi L(b^2 - a^2)]$.

The angular brackets denote an isotropic orientational average between the axis of the hollow cylinder and the fixed scattering direction $\mathbf{q}$. The average is evaluated in cylindrical coordinates by decomposing $\mathbf{q}$ into components parallel ($q\cos\theta$) and perpendicular ($q\sin\theta$) to the cylinder axis. The terms involving the perpendicular component are best evaluated by expanding the exponential in a Bessel function, $J_n(x)$, series and then integrating over polar angles. The resulting radial integrals can be accomplished to yield

$$P(q) = \frac{1}{2}\int_0^\pi \mathrm{d}\theta\,\sin\theta\left\{\left[\frac{2}{b^2 - a^2}\right]\left[\frac{\sin[(qL/2)\cos\theta]}{[(qL/2)\cos\theta]}\right]\times \left[\frac{bJ_1(bq\sin\theta) - aJ_1(aq\sin\theta)}{q\sin\theta}\right]\right\}^2 \qquad (2)$$

This is the theoretical expression for the intramolecular structure factor for hollow cylinders. The result is only valid in the Rayleigh–Gans–Debye limit of small refractive index difference between the hollow cylinder and the medium in which it is placed. The result should be compared to the many related results for infinite cylinders that

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