$tg^{\pm}t\text{–}tg^{\mp}t\text{–}tg^{\mp}t\text{–})_2$, which yields a large oxygen-lined hole. Oxygen atoms connected by 12 covalent bonds are separated by 7.1 Å. Infrared spectroscopy demonstrates that 24-crown-8 adopts this conformation in the crystalline state.[20]

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Vibrational Spectra of Polymers. 2.[1] Variable-Temperature Raman Spectroscopy as a Probe for Ion Clustering in Ionomers

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ABSTRACT: The Raman spectra of a series of ethyl acrylate–sodium acrylate copolymers with sodium acrylate contents varying from zero to 100 mol % have been measured in the 425–100-cm^{-1} region at room temperature, 150, 200, and 250 °C. The bands observed at 246 and 175 cm^{-1} have been attributed to ion multiplets and clusters, respectively. At all four temperatures investigated, the intensities of the multiplet and cluster bands increase steadily with increasing sodium acrylate content up to ca. 10 and 35 mol %, respectively, and thereafter remain essentially composition invariant. With increasing temperature, the multiplet band intensity increases while the cluster band intensity decreases throughout the complete composition range studied. A similar variable-temperature Raman study was also carried out for a series of styrene–sodium methacrylate ionomers, in which the band intensities showed practically no variation with temperature. The results of both studies indicate that the variation with temperature of the ion contents in multiplets and clusters is strongly dependent on the proximity to the glass-transition temperature. Furthermore, it is seen that the total amount of ions in clusters or multiplets depends on the dielectric constant of the polymer, a high dielectric constant favoring multiplets at the expense of clusters.

Recent studies on ion-containing polymers, such as the copolymers of ethylene, butadiene, or styrene with acrylic acid salts, have shown that the state of aggregation of the ions has considerable influence on the mechanical and rheological properties of these materials.[2-7] Most investigations have been focused on ionomers having ionic component concentrations below 10–15 mol %. In this composition range, the ionic sites of the polymer chains and the metal ions form ion pairs due to the low dielectric constant of the major component present (e.g., ethylene, butadiene, styrene, etc.). These ion pairs are thought to associate further into multiplets of a few ion pairs and into larger entities called clusters.[8] The latter are surrounded by the matrix which consists of the polymer chains and the multiplets.

Multiplet and cluster formation in ethyl acrylate–sodium acrylate copolymers was initially deduced from an accelerated rise of the glass-transition temperature (T_g) with increasing ion concentration.[9] This occurred at approximately the same sodium acrylate concentration at which time–temperature superposition in viscoelastic measurements failed (12–16 mol %),[10] since the latter phenomenon is also associated with clustering. Thus, it was concluded that the clusters dominate the rheological behavior above ca. 12 mol % of ions, whereas the multiplets are of primary importance below this concentration. No information, however, was available from these studies as to the relative numbers of ion pairs in multiplets or clusters at a given ion content.

Vibrational spectroscopy has rarely contributed to the elucidation of supermolecular structure.[3] Infrared results have been claimed to show ionic aggregation in ethylene- and butadiene-based copolymers of methacrylic acid salts.[11-14] Also, Rouse et al.[14] have attributed specific bands in the far-infrared spectra of styrene–metal methacrylate ionomers to multiplets and clusters. Recently, we have found a quantitative linear correlation between the intensities of the low-energy Raman bands associated with the multiplets and the clusters in the same ionomers and the multiplet and cluster concentrations obtained from

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Table I
Raman Spectra (cm^{-1}) of Ethyl Acrylate-Sodium Acrylate Copolymers and Their Homopolymers at Room Temperature[a]

sodium polyacrylate	poly(ethyl acrylate)[16]	ethyl acrylate-sodium acrylate copolymer (±2 cm^{-1})[d]	proposed assignment
	2978	2977	ν (C-H)[17]
2950[b]		2945 sh	
	2931	2928	
1560 w[b]			ν_{asym} (COO$^-$)[17]
1455[b]	1454	1457	δ (CH$_2$)[17]
1415[b]		1417	ν_{sym} (COO$^-$)[17]
1350[b]		1349	wag (CH$_2$)[17] or twist (CH$_2$)[17]
1325[b]		1327 sh	
	1298	1297	
1220 w[b]			
1175[b]		1178	
1110[b]	1115	1117	ν (C-C) of (C-CH$_2$)[17]
1050 w[b]			rock (CH$_2$)[17]
905[b]		903	ν (C-C) of (C-COO$^-$)[17]
	876	880	ν (C-C) of (C-COOEt) and of the polymer backbone[17]
	860	859	
246[c]		246[e]	multiplet mode
175[c]		175[e]	cluster mode

[a] The spectra recorded at 150-250 °C did not differ significantly except for the intensities of the bands labeled *e* in this table. [b] In aqueous solution.[17] [c] Measured as a powdery precipitate. [d] The values quoted refer to the copolymer containing 49.6 mol % sodium acrylate, except for those bands labeled *e*. [e] These values are the average values obtained from all the spectra recorded.

dielectric measurements.[1] However, these data were limited to an ion content range below 11 mol %.

In order to extend our vibrational approach to other systems and to complement our stress-relaxation and glass-transition results for ethyl acrylate-sodium acrylate copolymers,[9,10] we have investigated the Raman spectra of a series of ethyl acrylate based ionomers containing from zero to 100 mol % of the ionic component, sodium acrylate. Moreover, since clusters had been predicted to break down to multiplets with increasing temperature above the glass-transition temperature,[8] we have also investigated the Raman spectra of these particular ionomers up to 250 °C. Furthermore, to supplement our previous study,[1] Raman data have also been obtained for the styrene copolymers at elevated temperatures.

Experimental Section

The copolymers of ethyl acrylate with acrylic acid and sodium acrylate were the same as those prepared for a previous study,[9] as were the styrene-sodium methacrylate copolymers.[1] The samples were dried at 80 °C under vacuum for 24 h prior to recording their Raman spectra. One ethyl acrylate-sodium acrylate copolymer (containing 62.0 mol % of the salt) was also kept under vacuum at 150 °C for 6 h; its Raman spectrum was identical with that of the sample which was dried at 80 °C.

The Raman spectra were recorded on a Jarrell-Ash Model 25-300 spectrometer using the 488.0-nm line of an argon-ion laser (Coherent Radiation Ltd., Model 52K) for excitation. The ethyl acrylate-sodium acrylate and styrene-sodium methacrylate copolymers were measured as powdery precipitates in standard Pyrex capillary tubes. The non-ionized ethyl acrylate-acrylic acid copolymer and the salts of low T_g were measured as rubbers using a front-reflection technique.[15] All the polymers fluoresced strongly. While survey spectra could be obtained using a laser power of ~180 mW at the samples, the greatest signal-to-noise ratios for the intensity measurements were obtained using a laser power of 90 mW at the samples. The positions of the observed bands were calibrated against the emission lines of a standard neon lamp and are considered to be accurate to at least ±2 cm^{-1}.

At elevated temperatures, the spectra were recorded using an evacuated, variable-temperature cell designed by Dr. K. R. Plowman. It consists of a heated metal block with a groove for the capillary containing the sample. A glass vacuum shroud covers the metal block and permits evacuation in order to prevent sample oxidation. The temperature of the metal block near the sample was measured with a standard iron-constantan thermocouple.

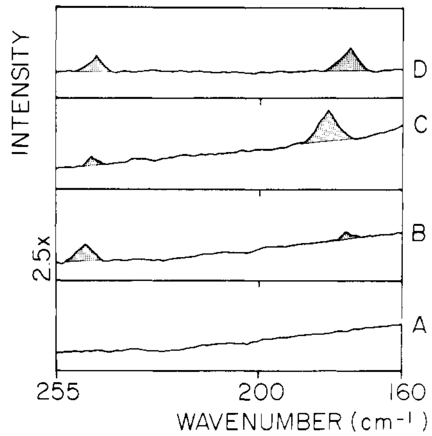

Figure 1. Typical Raman spectra in the 255-160-cm^{-1} region of an ethyl acrylate-acrylic acid copolymer containing 49.6 mol % acrylic acid (A), two ethyl acrylate-sodium acrylate copolymers containing 6.7 (B) and 49.6 (C) mol % of sodium acrylate at room temperature, and of the latter at 250 °C (D). (Note that the more intense band shifts about 6 cm^{-1} to lower energy in going from room temperature to 250 °C, i.e., spectrum C to spectrum D.)

Results

The bands observed in the Raman spectra of the homopolymers and the ethyl acrylate-sodium acrylate copolymers are listed in Table I, together with the proposed vibrational assignments. The spectra of the homopolymers have been reported previously, but only above 300 cm^{-1}.[16,17] For comparative purposes, these results are also included in Table I. Above 300 cm^{-1}, the Raman data for the copolymers correlated well with those for the homopolymers. However, below 300 cm^{-1}, some differences are apparent in the 255-160-cm^{-1} region. Typical spectra in this region are shown in Figure 1. At ambient temperature (spectra A-C), the intensity of the band at 175 cm^{-1} clearly increases with increasing mole percent of the ionic comonomer, whereas the band at 246 cm^{-1} shows little change. At constant ion concentration (spectra C and D), the intensity of the 175-cm^{-1} band

Table II
Intensities of the Raman Bands Associated with Ion Multiplets and Clusters in Ethyl Acrylate–Sodium Acrylate Copolymers[a]

	$10^4 I_m$(246 cm^{-1})			$10^4 I_c$(175 cm^{-1})			$10^4(I_m + I_c)$		
c_s, mol %	RT	150 °C	250 °C	RT	150 °C	250 °C	RT	150 °C	250 °C
6.7	3.1	3.2	3.5	0.9	0.9	1.0	4.0	4.1	4.5
9.4[c]	2.8	3.4	4.2	3.5	3.1	2.7	6.3	6.5	6.9
18.1	2.5	4.8	7.9	9.5	8.1	5.8	12.0	12.9	13.7
24.7[d]	2.7	4.1	8.5	14.3	12.8	9.8	17.0	16.9	18.3
34.2	3.5	3.9	7.8	19.7	18.8	15.9	23.2	22.7	23.7
42.3	3.4	3.8	8.6	20.2	21.2	16.7	23.6	25.0	25.3
49.6[e]	3.3	3.9	9.0	22.0	20.7	16.6	25.3	24.6	25.6
62.0	3.9	3.8	8.5	21.6	21.0	16.9	25.5	24.8	25.4
87.0	3.5	4.1	9.2	21.9	20.1	17.1	25.4	24.2	26.3
100.0[b]	3.7	3.6	9.0	21.8	20.6	16.4	25.5	24.2	25.4

[a] I_m and I_c are relative to the intensity of the reference peak at 1297 cm^{-1} which was corrected for the variable ethyl acrylate content. [b] I_m and I_c are relative to the same reference peak as at all other concentrations. They were determined using the 903-cm^{-1} band of poly(sodium acrylate) (eq 2 and 3). [c] At 200 °C, $10^4 I_m$(246 cm^{-1}) = 3.7, $10^4 I_c$(175 cm^{-1}) = 2.7, and $10^4(I_m + I_c)$ = 6.4. [d] At 200 °C, $10^4 I_m$(246 cm^{-1}) = 5.7, $10^4 I_c$(175 cm^{-1}) = 11.7, and $10^4(I_m + I_c)$ = 17.4. [e] At 200 °C, $10^4 I_m$(246 cm^{-1}) = 5.8, $10^4 I_c$(175 cm^{-1}) = 19.3, and $10^4(I_m + I_c)$ = 25.1.

decreases while that of the 246-cm^{-1} band increases with rising temperature.

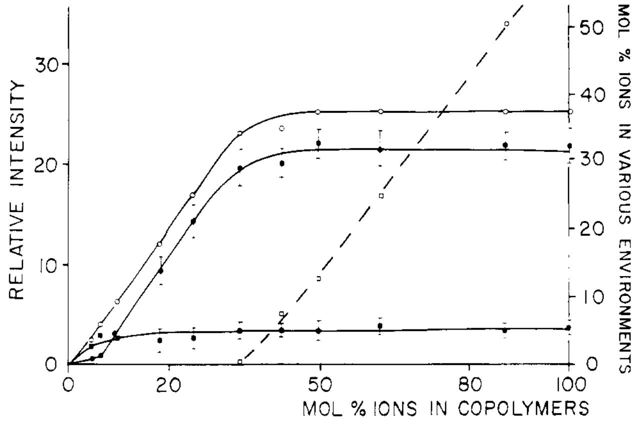

Figure 2. Relative intensities of the bands at 246 cm^{-1} (I_m) and 175 cm^{-1} (I_c) vs. c_s (mol % sodium acrylate) for the entire series of ethyl acrylate–sodium acrylate copolymers investigated where I_m = ■, I_c = ●, and $I_m + I_c$ = ○. Calculated intensity corresponding to the nonobserved ionic species = □. The correlation coefficient for the linear portion of the $I_m + I_c$ plot is 0.992.

The Raman spectra of pure ethyl acrylate and ethyl acrylate–acrylic acid copolymers do not exhibit any bands at 175 or 246 cm^{-1}. This observation, together with the increase in intensity of the 175-cm^{-1} band with increasing ion content, suggests that the two new bands arise from vibrations associated with the ionic species of the copolymer. This proposal is further supported by the intensity increase of the 246-cm^{-1} band and the intensity decrease of the 175-cm^{-1} band at elevated temperatures, because the concentrations of the ion pair aggregates were predicted to vary with temperature.[8]

The clustered ion pairs are considered to oscillate with a larger effective mass in a smaller effective force field than the ion pairs in the multiplets.[11-13] Therefore, clusters may be expected to give rise to vibrational bands at lower energy than those for multiplets. This has been observed in studies on solvated ion pairs.[18] Furthermore, on thermodynamic grounds, it is expected that with increasing temperature, clusters should convert to multiplets.[8] For these reasons, we have assigned the Raman bands at 246 and 175 cm^{-1} to multiplets and clusters of ions, respectively. This is also consistent with their low intensities compared with those of the other polymer bands since vibrations of ion pairs result in relatively small polarizability changes.[19]

The intensities of the 246- and 175-cm^{-1} bands are directly proportional to the ion concentrations present in multiplets and clusters, respectively. The relative intensities of these two bands were measured as a function of the sodium acrylate comonomer concentration at room temperature and at 150, 200, and 250 °C (Table II). The relative intensities were determined as ratios of the areas of the multiplet and cluster bands to the area of a reference peak at 1297 cm^{-1}. [The latter peak has been assigned to a CH$_2$ wag or twist mode of the ethyl acrylate homopolymer.[16] It does not appear in the spectrum of pure poly(sodium acrylate).[17]] The intensity of the reference peak (I_0) was corrected for the variable ethyl acrylate content using

$$I_1 = \frac{I_0}{100 - c_s} \times 100 \tag{1}$$

where c_s is the mole percent of the sodium acrylate comonomer. In the case of pure poly(sodium acrylate), the intensity of the peak at 903 cm^{-1} (I_2) was used for reference purposes. [This 903-cm^{-1} peak has been attributed to the C–C stretching mode of the C–COO$^-$ side group[17] and is absent from the spectrum of pure poly(ethyl acrylate).[16]] The relative intensities of the cluster and multiplet bands with respect to the 1297-cm^{-1} band in pure poly(sodium acrylate) (I_c and I_m, respectively) were calculated from their intensities in the poly(sodium acrylate) spectra (I_3 and I_4) and from the intensities of the 903-cm^{-1} (I_5) and 1297-cm^{-1} (I_1) bands for the copolymer with c_s = 49.6 mol %. It was assumed that the ratio of the relative cluster (or multiplet) band intensities at two different concentrations is invariant with the frequency of the reference band. Hence, the division of I_c by the cluster intensity relative to 1297 cm^{-1} at c_s yields the same result as the division of the cluster intensity relative to 903 cm^{-1} in pure poly(sodium acrylate) (I_3/I_2) by that at c_s. After simplification it yields eq 2. The same assumption results in eq 3 in the case of multiplet intensities.

$$I_c = \frac{100 - c_s}{c_s}\left(\frac{I_3 I_5}{I_0 I_2}\right) \tag{2}$$

$$I_m = \frac{100 - c_s}{c_s}\left(\frac{I_4 I_5}{I_0 I_2}\right) \tag{3}$$

The relative intensities of the multiplet (I_m) and cluster (I_c) bands are plotted against c_s at room temperature in Figure 2. A plot of ($I_m + I_c$) vs. c_s is also shown in this figure; this plot appears to yield a straight line (correlation

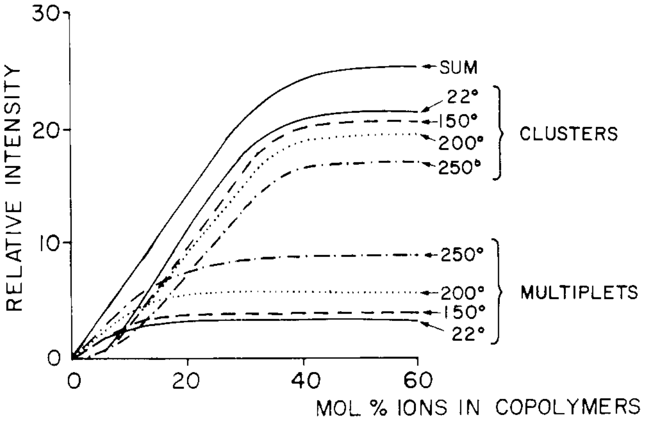

Figure 3. Relative intensities of the bands at 246 cm^{-1} (multiplets) and 175 cm^{-1} (clusters) and of their sum at various temperatures. Since the sum is essentially the same at all the temperatures, only that at 22 °C is shown. The same monotonous trend continues up to 100% ions in the copolymers.

coefficient $\bar{r} = 0.992$) up to $c_s = 35$ mol %. This linearity supports our assumption that the relative intensities, I_m and I_c, provide measures of ion pair concentrations in multiplets and clusters. Above the point at which the deviation begins ($c_s^0 \simeq 35$–40 mol %), ($I_m + I_c$) seems invariant with c_s. In turn, a certain amount of the ionic component ($c_s - c_s^0$) fails to correlate with either cluster or multiplet intensities. Of course, this may give rise to some band that is buried beneath the strong fluorescence background or other bands that are not associated with ionic aggregation. This deficit ($c_s - c_s^0$) is also included in Figure 2.

Essentially the same types of plots resulted from the measurements at elevated temperatures, as shown in Figure 3. However, the cluster band intensity diminishes while the multiplet band intensity increases progressively on going from lower to higher temperatures, whereas their sum apparently remains constant. Although the temperature dependence calls for further comment (see Discussion), it also lends credence to our previous assumption that the above two relative intensities are proportional to the ion pair concentrations in multiplets and clusters because the same trend was predicted qualitatively for these two concentrations, respectively.[8] The same type of variable-temperature Raman analysis was performed for the styrene ionomers investigated previously.[1] No changes in intensities of the multiplet and cluster band were observed with increasing temperature up to 250 °C.

Discussion

Insofar as the identification of the two Raman bands with multiplets and clusters, as proposed in our previous paper,[1] is correct, it is clear that in the ethyl acrylate ionomers the cluster concentration decreases and the multiplet concentration increases as temperature rises. This must be a reflection of the fact that elastic forces tend to pull clusters apart because they are held together by relatively weak electrostatic interactions, whereas the interactions within the multiplets are much stronger, and therefore the multiplets are not subject to breakdown due to the increase of elastic forces with temperature. This is generally consistent with the previously developed theory.[8] However, the assumption in the theory that clusters break down at some critical temperature is not supported by our experiments.

A comparison of Figure 2 of this study with Figure 2 of ref 1 clearly reveals that at comparable total ion contents at room temperature the total number of ion pairs in the multiplets is larger in the ethyl acrylate system than in styrene. In the former case, the multiplet saturation limit is reached at ca. 10 mol % of ionic groups, while in styrene this limit is reached at ca. 2%. This suggests that the multiplet solubility limit is definitely a function of the polymers and that it probably increases with increasing dielectric constant of the backbone (ϵ for poly(ethyl acrylate) is ca. 4.0 while that for amorphous polystyrene is ca. 2.5).[20]

Two puzzling features emerge from this study. One is the fact that the sum of the relative intensities of the cluster and multiplet bands remains essentially constant above ca. 35–40 mol % of ions. This suggests that at that approximate total ion content the matrix becomes saturated with the clusters also, just as it became saturated with the multiplets at about 10% of ions at room temperature. In that case, above about 10% ionic concentration, any additional ion pairs go into clusters. Now it also appears that beyond ca. 40%, i.e., the cluster solubility limit, any additional ionic groups go into a still different type of structure which has not been detected by means of Raman spectroscopy. The second puzzling feature concerns the independence of the cluster solubility limit on temperature. As shown in Figure 3, the sum of the clusters and the multiplets accounts for only about 35–40 mol % of the ions, and this number is invariant with temperature. This feature suggests that the thermodynamics of this new structural unit may be very different from that of the clusters or the multiplets. In addition, it should be stressed that the Raman data reflect only the thermodynamics of ion association but do not state anything about the rate with which ionic groups enter or leave the various aggregates. On the other hand, the rheological properties are expected to be affected very strongly by both the thermodynamic and the kinetic aspects.

Finally, it is worth noting that in the styrene ionomers at 250 °C, the relative intensities of the bands associated with the clusters and multiplets are not different from those at room temperature. It should be recalled that the glass-transition temperature of pure polystyrene is about 100 °C, while that of pure poly(ethyl acrylate) is −20 °C. Thus, relative to the glass transition of the non-ionic host polymer, a run in polystyrene at 250 °C is equivalent to one in poly(ethyl acrylate) at about 130 °C. In the latter case, only a very small change in the relative intensities of the cluster and multiplet bands was observed relative to room temperature. Consequently, it seems that the proximity to the glass-transition temperature is of great importance in determining the variation of ion contents in clusters and multiplets.

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Statistical Properties of Alternating Copolymers. 1. Dipole Moments of Poly(thiodiethylene glycol) Chains

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ABSTRACT: Mean-square dipole moments of poly(thiodiethylene glycol), an alternating copolymer of ethylene oxide and ethylene sulfide, were determined from dielectric constant measurements on dilute solutions of the polymer in benzene. Since the configuration-dependent properties of one of the parent homopolymers, poly(ethylene sulfide), are unknown, because of its insolubility in ordinary solvents, the results were preferably compared with those of poly(oxyethylene) chains. It was found that the dipole moments of poly(thiodiethylene glycol) are somewhat larger than those of poly(oxyethylene). The values of the dipole moments were also theoretically calculated using the rotational isomeric state model, in which the required energies of the bonds of the repeat unit, except those of the CH_2—CH_2 bonds, were obtained from previous configurational analysis of poly(oxyethylene) and polyethylene. Agreement between theory and experiment was obtained assuming that the energy from first-order interactions between S and O atoms is larger in gauche than in trans states.

Conformation-dependent properties of polyoxide chains have been intensively investigated in the framework of the rotational isomeric state approximation.[1-7] Rotational energies of the rotational states adopted by the skeletal bonds of the chains were determined through comparisons of calculated and experimental values of at least one configuration-dependent property.[3] The configurational energies thus determined for two or more relatively single chains were successfully used to predict the configuration-dependent properties of other more complicated polyethers such as the linear polyformals [CH_2–O–$(CH_2)_y$–O–], in which poly(oxymethylene) may also be considered the first member of the series.[8,9] The properties of the polyformals vary markedly with the number of methylene groups y in the repeat unit. These polymers may be considered alternating copolymers of methylene oxide and alkylene oxide. However, in the polyformals as well as in other alternating copolymers, a particular configurational property cannot in general be obtained by simply averaging the values of the same property for the parent homopolymers. For example, poly(1,3-dioxepane), an alternating copolymer of methylene oxide and tetramethylene oxide, has possibly the lowest dipole moment ratio of any polymer reported up to date.[9]

It is desirable to extend the analysis to other polymers with sulfur atoms in their structure. The polyoxide chains may be converted schematically to any member of the polysulfide series [$(CH_2)_y$–S–] by simply substituting oxygen atoms for sulfur atoms. The polythioethers, with $y = 1$ and 2, have melting points higher than 200 °C and therefore are insoluble in most solvents. With the increase of the number of CH_2 groups in the repeat unit, the melting points of the polymers decrease abruptly, reaching a minimum value of about 70 °C for poly(trimethylene sulfide), and then increase gradually until they reach that of polyethylene.[10] Because of their relative low melting points, the polymers with $y > 2$ are soluble in ordinary solvents. Their configuration-dependent properties, however, have not been widely investigated. Information on some conformational states of the members of the series may be obtained from the configurational properties of poly(thiodiethylene glycol) (PTDG). This polymer, which may be considered an alternating copolymer of ethylene oxide and ethylene sulfide units, has a relatively low melting point and is readily soluble in a number of common organic solvents. Although the method of preparation of the polymer does not permit us to obtain high molecular weight samples (in fact molecular weight fractions higher than 13 000 were not obtained), dielectric measurements can provide the necessary information to study the chains using the rotational isomeric state model. Actually, the corresponding dielectric property employed to characterize random coil conformations is the dipole moment ratio $\langle \mu^2 \rangle_0 / nm^2$, where n is the number of bonds or group dipoles and m^2 is the average square of their magnitudes. This quantity is one of the most useful of the conformation-dependent properties since it can be determined for chains of any length, either in the bulk or in solution.[11]

The purpose of the present investigation is to determine the dipole moment ratio and its temperature dependence for PTDG chains. Of particular interest will be the molecular interpretation of the results in terms of the rotational isomeric state theory and the comparison of some configurational properties with those of poly(oxyethylene) (POE).

Experimental Section

Preparation of the Samples. Poly(thiodiethylene glycol) was prepared by refluxing thiodiethylene glycol reagent grade with *o*-xylene. The reaction was carried out at nitrogen atmosphere for 72 h, using *p*-toluene sulfonic acid (≈2%) as the catalyst. Water was removed as azeotrope in a Dean-Stark distillation trap. The polymer was precipitated from solution with a mixture of methanol–*n*-hexane. It was washed several times with distilled

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