(2) Th. Förster in "Modern Quantum Chemistry", Part III, O. Sinanoglu, Ed., Academic Press, New York, 1965, p 93, and references therein.

(3) D. Wong, K. Vorcek, M. Merkelo, and Govindjee, *Z. Natur-forsch., C*, **33**, 863 (1978); J. A. Ferreira and G. Porter, *J. Chem. Soc., Faraday Trans. 2*, **73**, 340 (1977).

(4) Th. Förster and K. Kasper, *Z. Phys. Chem. (Wiesbaden)*, **1**, 275 (1954).

(5) J. B. Birks, "Photophysics of Aromatic Molecules", Wiley-Interscience, New York, 1970, Chapter 7.

(6) B. Stevens, *Adv. Photochem.*, **8**, 161 (1971).

(7) E. Loewenthal, Y. Tomkiewicz, and A. Weinreb, *Spectrochim. Acta, Part A*, **25**, 1501 (1969).

(8) R. J. McDonald and B. K. Selinger, *Aust. J. Chem.*, **24**, 249 (1971).

(9) P. Avis and G. Porter, *J. Chem. Soc., Faraday Trans. 2*, **70**, 1057 (1974).

(10) See, for example, R. G. Bennett and R. E. Kellogg, *Photochem. Photobiol.*, **7**, 571 (1968), and references therein.

(11) N. Mataga, M. Obashi, and T. Okada, *Chem. Phys. Lett.*, **1**, 133 (1967).

(12) W. Klöpffer, *J. Chem. Phys.*, **50**, 1689 (1969).

Infrared Studies of Hydrogen Bonding in Ethylene–Methacrylic Acid Copolymers and Ionomers

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ABSTRACT: The temperature dependencies of hydrogen-bond formation between carboxylic acid groups in two ethylene–methacrylic acid copolymers and a partially neutralized sodium salt have been investigated by infrared spectroscopy. The concentrations of hydrogen-bonded acid groups were determined by using absorbances at 1700 and 1750 cm^{-1} assigned to the dimer and monomer carbonyl stretching vibrations, respectively. Thermodynamic parameters were calculated by using carbonyl peak absorbances as well as integrated absorbances, both methods giving a heat of dissociation of 12 kcal mol^{-1}. Thus each hydrogen bond has a strength of about 6 kcal mol^{-1}. It is shown that the concentration of hydrogen-bonded dimers cannot be unambiguously determined by using only the 935-cm^{-1} absorbance assigned to the out-of-plane OH bend in a dimer. The carboxylic acid groups in the partially neutralized salt also establish a temperature-dependent equilibrium between bonded and nonbonded species with a heat of dissociation of 20 kcal mol^{-1}. The carboxyl asymmetric stretch of the salt consists of two overlapping peaks at 1565 and 1580 cm^{-1}. The relative absorbances of these bands are reversibly temperature dependent, suggesting that the salt groups exist in at least two kinds of environments.

Polar moieties attached as pendent groups along a polymer chain or directly incorporated into the backbone are known to interact with each other, thereby affecting the polymer's physical properties. For polymers containing carboxylic acids, amides, alcohols, amines, etc., the possibility of hydrogen bonding exists. Structural integrity, crystalline habits, and the location of the glass transition temperature can be influenced by the presence of hydrogen bonding.

Early investigations into the possibilities of realizing thermally reversible polymer gels were focused on carboxylic acid containing rubbers[1,2] and styrene–methacrylic acid copolymers.[3] It was found that incorporation of acid comonomer generally increases modulus and viscosity but does not produce a mechanically stable network. Efforts were then directed at elucidating the behavior of the carboxylic acid monomer–dimer equilibrium, principally by using infrared techniques. Longworth and Morawetz[3] used the absorbances at 1750 and 1700 cm^{-1}, respectively, to determine the temperature dependence of the relative concentrations of free and hydrogen-bonded carbonyl for styrene–methacrylic acid copolymers. Dimerization constants were calculated at 110 °C to be 0.36 and 0.12 mol/L for a 4.6 and 10.6 mol % acid copolymer, and the heat of dimerization was found to be 8–10 kcal/mol. They also reported that when the copolymers were cooled below T_g, a fraction of free carbonyl was "frozen in" and that this amount was independent of cooling rate. Fitzgerald and Nielsen[4] also investigated the temperature dependence of infrared spectra for styrene–methacrylic acid copolymers. Using the ratio of the absorbances at 1750 and 1700 cm^{-1}, they reported the energy difference between nonbonded

and bonded forms as 3.61 kcal/mol.

In 1968 MacKnight and co-workers[5] published results of infrared studies on an ethylene–methacrylic acid copolymer containing 4.1 mol % acid comonomer. They investigated the temperature dependence of the relative intensities at 3540 and 1700 cm^{-1} assigned to the free hydroxyl stretch and the hydrogen-bonded carbonyl stretch, respectively. The extinction coefficient for the 3540-cm^{-1} band was determined indirectly by using the 1750-cm^{-1} band at the highest temperature and assuming the ratio of extinction coefficients (ϵ_{1750}:ϵ_{3540}) to be constant with temperature. The dimerization was found to be essentially complete at room temperature and the heat of dissociation of the dimers was reported to be 11.6 kcal/mol, in excellent agreement with literature values for low molecular weight carboxylic acids. Subsequently, Otocka and Kwei[6] criticized the use of the 1700- and 1750-cm^{-1} carboxyl absorbances to determine thermodynamic parameters. Owing to the high-pressure polymerization process utilized in preparing the ethylene–carboxylic acid copolymers, carbonyl groups are present as oxidation products. A curve analyzer revealed an additional peak at 1735 cm^{-1} in the IR spectra which can interfere with the analysis if the 1700- and 1750-cm^{-1} bands are used.

Otocka and Kwei selected the 935-cm^{-1} absorption to follow the temperature dependence of hydrogen bonding. This band is assigned to the out-of-plane OH bend in the dimer and is observed to decrease in intensity with increasing temperature in ethylene–acrylic acid copolymers. They assumed 100% dimerization at room temperature and found the ΔH for dimer formation to be –11.5 kcal/mol. The method using the 935-cm^{-1} band determines the

association constant, K_a, which, of course, should be the reciprocal of the dissociation constant, K_d, that is determined in the method described above. However, in a study comparing the dissociation and association constants of acrylic and methacrylic acid copolymers,[7] the reciprocal relationship did not hold. The K_d's were found to be 2–4 orders of magnitude smaller than the reciprocal of the K_a's, meaning that the concentration of free carboxyl groups will differ by 1 order of magnitude or more, depending on whether K_d or K_a is used. Although no conclusive evidence was available for choosing the proper method, calculations based on the 935-cm^{-1} band were chosen because of the possibility of interfering absorbances at 1735 cm^{-1}.

More recently, Ogura and co-workers have published results of detailed IR studies on styrene–methacrylic acid copolymers.[8,9] They reported a break in the absorbance vs. temperature plots for the 1700- and 1745-cm^{-1} carboxyl bands and for the 3440-cm^{-1} free-OH band. These breaks occur at temperatures corresponding to the copolymer T_g. The dissociation constants were calculated by using the 1700- and 1745-cm^{-1} absorbances, and the heat of dissociation, ΔH, is given as 7.32 kcal/mol for a copolymer containing 15 wt % methacrylic acid.

The infrared spectra of ionomers have also been of interest. Ogura et al.[9] have investigated the hydrogen-bonding behavior of partially neutralized styrene–methacrylic acid copolymers. Again employing the 1700- and 1745-cm^{-1} bands, they found an increase in the heat of dissociation, ΔH, with increasing neutralization from 8.1 kcal/mol for the acid copolymer to 14.5 kcal/mol for a 74% neutralized sodium salt. The authors suggested that this increase is related to a strengthening of residual intermolecular hydrogen bonding by the introduction of ions.

Infrared spectroscopy has also been used to investigate the surrounding environment of chemical groups in ethylene ionomers. Cation environments have been studied by far-infrared spectroscopy.[10,11] Li$^+$, Na$^+$, K$^+$, and Cs$^+$ salts of ethylene–methacrylic acid copolymers were investigated at ambient and low temperatures. A model consisting of cations present in the vicinity of both carboxylate sites and hydrocarbon regions was suggested. Investigating the asymmetric stretching mode of the carboxylate ion in ethylene- and butadiene-based methacrylic acid ionomers, Andreeva and co-workers[12] concluded that ion pairs exist in at least two types of ionic aggregates. The asymmetric stretch was observed to have two components: one at 1550 cm^{-1}, assigned to groups in ionic multiplets, and one at 1565 cm^{-1}, assigned to the same vibration in ionic clusters. The relative amounts of each component were found to depend upon concentration, ion size, and temperature. For K$^+$ salts, the peak absorbance of the 1550-cm^{-1} band increased while the peak absorbance at 1565 cm^{-1} remained constant with temperature up to 130 °C. They also noted that the total integrated absorbance is constant for the 1550-cm^{-1} absorbance.

The present work was undertaken in order to determine the proper method for determining thermodynamic parameters of hydrogen bonding in ethylene–methacrylic acid copolymers and the reasons for discrepancies between values of K_d and K_a as determined by different methods. In addition, it was hoped that the IR technique could give additional information about ionic structure in the partially neutralized polymers.

Experimental Section

Two ethylene–methacrylic acid copolymers were obtained from du Pont through the courtesy of R. Longworth. A 3.5 mol % copolymer was received as the zinc salt and was converted to the free acid, denoted S3.5A, by refluxing in tetrahydrofuran with

sulfuric acid. Details are given in ref 13. The 6.1 mol % copolymer, denoted S6.1A, was received in the acid form. Partial neutralization of S6.1A was accomplished in dilute (1% solids) xylene solution by the addition of freshly prepared sodium methoxide. This procedure has been previously described.[5] Determination of the degree of neutralization was accomplished by using the integrated absorbance at 1700 cm^{-1}. The ionomer investigated was 45% ionized and is denoted S6.1NA(45).

Thin films of the acid copolymers were cast onto sodium chloride salt plates from 1% xylene solutions at 70 °C. Excess solvent was evaporated and the films were finally dried at 90–100 °C in vacuo. Film thickness was determined by two methods. The first used the total integrated absorbance of the 1700-cm^{-1} band and the second employed the peak absorbance of the 935-cm^{-1} band, for which a calibration curve was constructed for ambient temperature by using thick compression-molded films. Agreement between the two methods was excellent for film thickness of the order of 10^{-3} cm. Thin films of the ionomers were compression molded at 180 °C and 20000-psi pressure. The solution-cast or compression-molded films were sandwiched between two rectangular sodium chloride windows and fitted into a homemade heating cell. Infrared measurements were conducted with a Perkin-Elmer Model 283 spectrophotometer. Temperature was monitored with a calibrated copper–constantan thermocouple inserted into a hole drilled in one of the NaCl windows. Temperature was continuously monitored by a digital readout. Dry nitrogen was used to purge the heating cell. A cooling coil immersed in liquid nitrogen allowed the purge gas to be precooled for subambient measurements. The temperatures could be controlled to within ±1 °C. Spectra were recorded by using both ordinate and abscissa expansion, with instrument settings selected for quantitative measurements.

Results and Discussion

For quantitative infrared measurements the usual procedure is to use Beer's law (eq 1). In eq 1, A is the peak

$$A = \epsilon bc \qquad (1)$$

absorbance of the vibrating species in question, ϵ is the molar extinction coefficient, b is the path length, and c is the molar concentration. Known concentrations are used to calculate the extinction coefficient ϵ; then an unknown concentration can be determined by measuring A and b. However, the band half-width and therefore the peak absorbance may vary as a function of temperature. Absorption bands will sometimes narrow and grow as the temperature is lowered. This problem can be circumvented by using the total integrated absorbance. This is essentially the area under the curve of absorbance vs. wavenumber. In general, this integrated absorbance is constant with temperature, assuming ϵ, b, and c do not vary with temperature.

For determining the thermodynamic parameters of hydrogen bonding in ethylene–carboxylic acid copolymers, Otocka[6] has advocated following the temperature dependence of the 935-cm^{-1} absorbance. This band has been assigned to the out-of-plane OH bending motion of the hydrogen-bonded dimer.[14] The peak intensity of this band decreases with temperature, as would be the case if the concentration of hydrogen-bonded OH groups decreased. Figure 1 shows the results for the 935-cm^{-1} band in the case of S3.5A. It can be seen that both the peak absorbance and the integrated absorbance increase monotonically with decreasing temperature. The effect is significant, being greater than a 50% change over a small temperature range. Also of interest is the fact that this large increase occurs below the glass transition temperature of the polymer (T_g = 25 °C[13]). The analysis by Otocka has assumed that the absorbance at room temperature represents 100% dimerization and the subsequent decrease in peak absorbance with increasing temperature is due to a concentration change of hydrogen-bonded OH groups. Clearly from
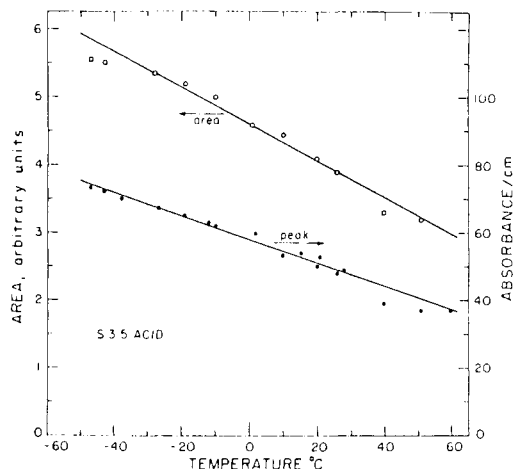
Figure 1. Temperature dependence of the 935-cm^{-1} peak absorbances (●) and peak areas (O) for S3.5A.

the plots in Figure 1 the changes in peak absorbance and integrated absorbance cannot be entirely the result of changes in dimer concentration, and, therefore, this assumption is not valid.

In general, as noted above, the integrated absorption coefficient is assumed to be independent of temperature. However, for hydrogen-bonding systems, Davies and Sutherland, as early as 1938, observed a variation of ϵ with both concentration and temperature for several carboxylic acids in solution.[15] For associated alcohols it has also been observed that the integrated intensity of the 3540-cm^{-1} OH stretch increases with decreasing temperature in a linear fashion.[16,17] For alcohols capable of intermolecular hydrogen bonding only, the increase in integrated intensity can be the order of 60% from 300 to 200 K.[18] A valid explanation for this behavior has not been agreed upon in the literature. However, it may be due to a decrease in the distance between hydrogen-bonding species as the temperature is lowered.[18] Zerbi and co-workers have recently reported on the infrared spectra of acetic acid in the solid state.[19] Their study indicates that the out-of-plane OH deformation mode is an unusually broad, weak band whose position, width, and area are strongly phase, temperature, and solvent dependent. They observed a 25% increase in integrated area occurring for an 80 °C decrease in temperature. They concluded that the behavior of this band can be accounted for by a distribution of various bent geometries of the O–H⋯O group. This distribution then changes with temperature, resulting in changes in the force constant for the vibration.

This behavior of the extinction coefficient as a function of temperature can be expressed by eq 2, where α is the

$$\epsilon = \epsilon_0 + \alpha(T - T_0) \qquad (2)$$

temperature coefficient and ϵ_0 is determined at a reference temperature T_0. In the case of the 935-cm^{-1} band, the temperature coefficient α cannot be determined because the concentration of bonded OH groups is also changing as a function of temperature. The out-of-plane OH band for the monomeric species is found near 635 cm^{-1} for formic acid,[19] but this absorption is obscured by other bands in the spectra of the copolymers. When concentrations of hydrogen-bonded and non-hydrogen-bonded species are determined, it is usually assumed that the temperature coefficient of ϵ is about the same for both the monomer and the dimer bands, and, therefore, relative peak heights or areas can be used.[20] Without the use of the monomeric out-of-plane OH band as a reference to cancel the temperature dependence of ϵ, the 935-cm^{-1} absorbance cannot
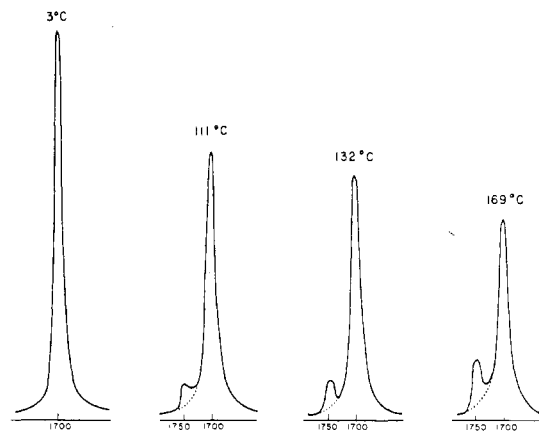

Figure 2. Effect of temperature on the carbonyl region for S3.5A.
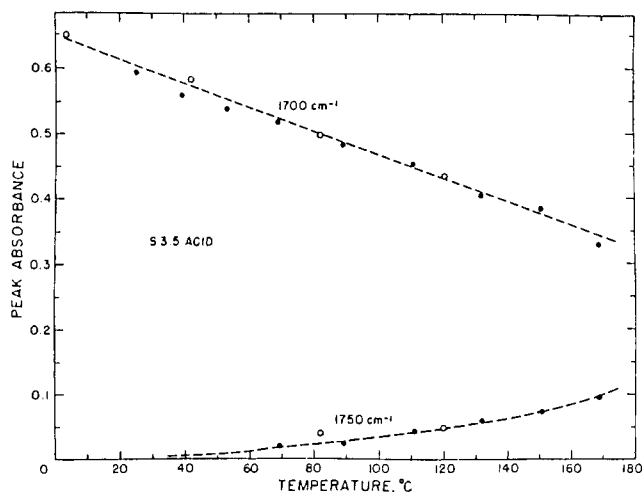

Figure 3. Temperature dependence of the 1700-cm^{-1} (upper curve) and 1750-cm^{-1} (lower curve) peak absorbances for S3.5A: (●) heating cycle; (O) cooling cycle.

be used to determine the concentration of hydrogen-bonding species as a function of temperature.

In the region 1600–1800 cm^{-1} four overlapping bands have been identified in ethylene–acrylic acid copolymers, the most important being the 1700-cm^{-1} hydrogen-bonded carbonyl, the 1750-cm^{-1} free carbonyl, and a band at 1735 cm^{-1}, assigned to carbonyls from oxidation products. The amount of this carbonyl is extremely variable in polyethylenes. However, an analysis of a typical low-density polyethylene (ARCO 161-1) revealed a peak at 1720 cm^{-1}, having an absorbance per centimeter of 0.7 at 25 °C. This value is less than 1% of the 1700-cm^{-1} absorbance for S3.5A at 25 °C and about 10% of the 1750-cm^{-1} absorbance at 100 °C. Although the presence of the 1720–1735-cm^{-1} absorptions at all temperatures biases the K_a calculations, their small magnitudes introduced negligible errors in our case.

Figure 2 shows the temperature dependence of the 1700- and 1750-cm^{-1} bands for S3.5A at several temperatures. Similar results were obtained for S6.1A. As the temperature is increased, the emergence of a peak at 1750 cm^{-1} is evident, as is the decrease in the 1700-cm^{-1} peak. Base lines were drawn as shown by the dotted line to calculate the absorbance of the free-acid peak. Figure 3 gives the absorbance of each peak as a function of temperature for S3.5A. Several features should be noted. The 1750-cm^{-1} band is first detected near room temperature and increases in magnitude with increasing temperature. This behavior is the same as for the 3540-cm^{-1} OH absorption.[7] The peak absorbance of the 1700-cm^{-1} band increases linearly with
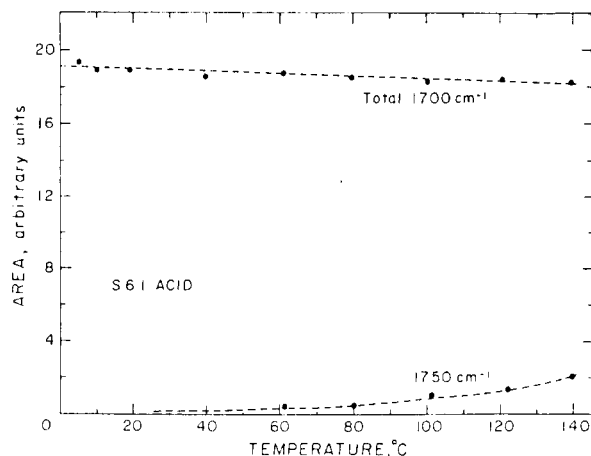
Figure 4. Temperature dependence of the total 1700-cm^{-1} (upper curve) and 1750-cm^{-1} (lower curve) peak areas for S6.1A.

Figure 5. van't Hoff plots for the S3.5A monomer–dimer equilibrium: (O) peak area; (□) peak height.

decreasing temperature, even below the glass transition temperature (25 °C). Finally there is no obvious break in the slope of the 1700-cm^{-1} absorbance as a function of temperature like that observed for the styrene–methacrylic acid copolymers.[8,9] The behavior of the dimer carbonyl peak absorption is then similar to that of the 935-cm^{-1} band in that there is a significantly large increase in peak absorbance at temperatures below which the concentration of hydrogen-bonded carbonyls is assumed to be fixed. Relating this effect back to Beer's law (eq 1) would imply that the extinction coefficient, ϵ, is changing with temperature.

The total integrated absorbance was determined for the carbonyl region in order to decide if the extinction coefficient was actually changing or whether the band shape was being influenced by temperature. Areas under the curves were analyzed by using a planimeter. The dotted base lines shown in Figure 2 were used in obtaining the area under the 1750-cm^{-1} peak as well as the total area under both absorbances. Figure 4 shows the results for the 6.1 mol % acid copolymer. As seen in the figure, there is only a slight change in the total area with temperature of about 5% over a range of 150 °C. The area under the 1750-cm^{-1} peak is resolvable only above room temperature and increases exponentially with increasing temperature.

The shape of the curve of the 1750-cm^{-1} band vs. temperature is expected to be sigmoidal. Because the hydrogen bonding is an equilibrium process, the curve will asymptotically approach zero at low temperatures. If degradation does not occur, the 1750-cm^{-1} curve should also asymptotically approach the curve for the total carbonyl area at high temperatures. Only near 50% dimerization will the integrated absorbance vs. temperature relationship be linear.

The structure of the hydrogen-bonded dimers may be schematically represented as
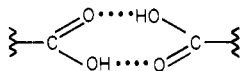
and the chemical equation of the dimerization reaction is

$$-(COOH)_2 \underset{K_a}{\overset{K_d}{\rightleftharpoons}} 2(-COOH) \qquad (3)$$
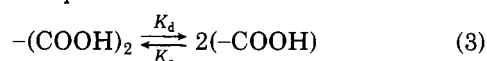
where K_d and K_a are the dissociation and association constants for the reaction. K_d is defined as

$$K_d = [-COOH]^2/[-(COOH)_2] \qquad (4)$$

where [-COOH] is the concentration of monomeric carboxyl groups and [-(COOH)$_2$] is the concentration of dimerized carboxyl groups.

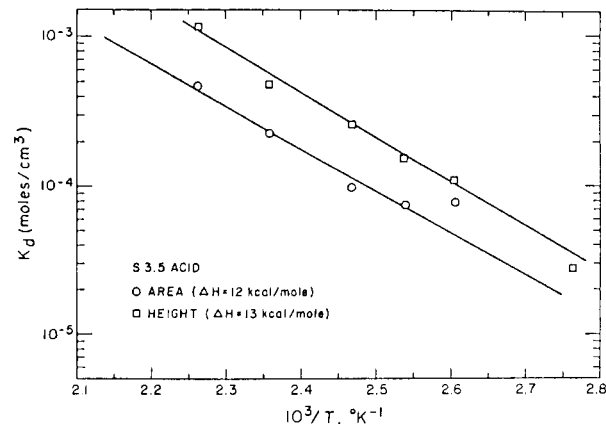K_d was evaluated by two methods for each copolymer. The first method consisted of using the ratio of the 1750- to the 1700-cm^{-1} peak absorbance. This method has been used by several workers with the styrene–methacrylic acid copolymers[3,8,9] and is essentially the method used by MacKnight et al. in previous studies on ethylene–methacrylic acid copolymers.[5] It is established from Figure 2 that the band shape of the 1700-cm^{-1} peak changes with temperature and that the peak absorbance, therefore, is a function of temperature as well as concentration. However, it is assumed that this temperature variation is the same for both the monomer and dimer carbonyl absorbances. The validity of this assumption is borne out by the results obtained in other hydrogen-bonding systems.[3,8,9,20,21] From measurements on pivalic acid in benzene, the extinction coefficients of the free and hydrogen-bonded carbonyl bands are found to be nearly identical.[22] Therefore, the ratio of the two peak absorbances should give the relative fraction of free carboxylic acid groups. Calculation of the total concentration of acid groups then allows the determination of K_d at each temperature. Because the band shape changes with temperature, K_d's were also calculated by using the relative areas of the absorbances due to the monomer and dimer species.

From thermodynamics, the dissociation constant can be expressed as

$$K_d = \exp(-\Delta H/RT + \Delta S/R) \qquad (5)$$

where the variables have their usual meaning. Therefore

$$-\ln K_d = \Delta H/RT - \Delta S/R \qquad (6)$$

and a plot of the logarithm of the dissociation constant vs. reciprocal temperature allows the determination of ΔH and ΔS. Figures 5 and 6 are van't Hoff plots from which the heat of dissocation, ΔH, can be extracted from the slope. For S3.5A the data from both peak heights and peak areas give similar lines, with $\Delta H = 13$ kcal/mol from peak heights and $\Delta H = 12$ kcal/mol from peak areas. The values of ΔH for S6.1A are 12 kcal/mol from area measurements and 11 kcal/mol from peak heights. Since these values are for the dissociation of dimers, each hydrogen bond has a bond strength of about 6 kcal/mol, in excellent agreement with literature values for low molecular weight compounds. Values of the change in entropy, ΔS, range from 10 to 16 eu/mol. These numbers are also in agreement with literature values. The thermodynamic parameters are listed in Table I.

The hydrogen-bonding equilibrium was also investigated for the partially neutralized polymer S6.1NA(45), which has 55% of the total carboxylic acid groups available for hydrogen-bond formation. The temperature dependence
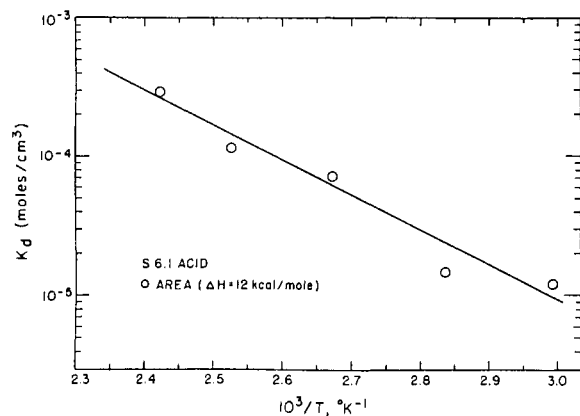
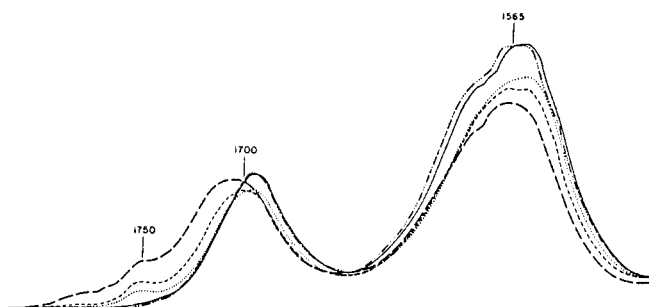**Figure 6.** van't Hoff plot for the S6.1A monomer–dimer equilibrium using peak areas.

Figure 8. van't Hoff plot for the S6.1NA(45) monomer–dimer equilibrium.

Figure 7. Effect of temperature on the carbonyl region for the S6.1NA(45) ionomer film during heating: (—) 28 °C; (–····–) 54 °C; (···) 124 °C; (---) 140 °C; (———) 160 °C.

Table I
Thermodynamic Parameters Obtained
from van't Hoff Plots

polymer		ΔH, kcal/ mol	ΔS, eu/ mol
S3.5A	peak	13	16
	area	12	13
S6.1A	peak	11	10
	area	12	12
S6.1NA(45)	peak	20	35

acrylic acid and suggested the increase to be a result of the introduction of ions.

The entropy change, ΔS, of 35 eu/mol is also found to be much higher than for the acid copolymers. It should be remembered that the values of ΔH and ΔS only reflect differences between the initial and final states and reveal nothing about the barrier between the two states. Many reasons for the different thermodynamic values can be advanced. The process of ionic exchange occurring in the ionomer could affect the dimerization reaction. Also with the introduction of ionic domains, the dielectric constant of the medium is increased, which would affect the equilibrium. An environment of high dielectric constant would favor the monomeric acid species. However, it is not known whether the unneutralized carboxylic acid species are located within the ionic phase or the hydrocarbon phase.

Reference back to Figure 7 shows that the absorbance assigned to the asymmetric carboxylate stretching motion at 1565 cm⁻¹ is composed of at least two overlapping peaks at room temperature. These are located at about 1560 and 1580 cm⁻¹. This splitting was observed in butadiene–methacrylic acid copolymers previously.[12] It was concluded that the lower frequency absorption, in the present case 1560 cm⁻¹, is due to carboxylate groups located in ionic multiplets and the higher frequency vibration, 1580 cm⁻¹, is assigned to carboxylate groups in ionic clusters. As seen in the figure, the high-frequency shoulder is reduced in size with increasing temperature. Interpreting the behavior of S6.1NA(45) in Figure 7 with the above assignments indicates that the fraction of carboxylate groups located in clusters diminishes with increasing temperature. This conclusion is consistent with theoretical treatments of cluster formation based on elasticity theory.[23] However, the assignment of the two frequencies to carboxylate groups in different environments may be subject to question. For the case of hydrogen bonding, the stretching modes are shifted to lower frequencies by the close interaction with other species. In the above assignments, the vibration due to the more ordered environment (cluster) is at a higher frequency than for the less ordered multiplet. The assignment of the overlapping peaks near 1565 cm⁻¹ must, therefore, remain speculative until further evidence is obtained.

Another notable feature of Figure 7 is that the peak intensity and total integrated absorbance of the 1565-cm⁻¹ band decrease with increasing temperature. This is contrary to the results of both Andreeva and Ogura. Andreeva states that the integrated absorbance is constant while the relative amounts of the two components are changing.[12]

of the infrared spectrum from 1800 to 1500 cm⁻¹ is shown in Figure 7. It can be seen from the figure that, as temperature increases, the absorbance centered at 1700 cm⁻¹ resolves into two peaks—the other being located near 1750 cm⁻¹. As with the acid copolymers, essentially all of the acid carbonyls are hydrogen bonded at room temperature. At the highest temperatures, decomposition occurs, resulting in the formation of anhydride linkages. There is also a wavelength shift of the 1700-cm⁻¹ band with increasing temperature in the 20–140 °C region before anhydride formation occurs. The anhydride formation results in additional absorbances at 1780 and 1725 cm⁻¹ which are characteristic of linear anhydrides. This finding is consistent with the assertion that the carboxylic acid comonomer units are not blocky along the chain. The ratio of peak heights of the 1750- and 1700-cm⁻¹ bands was used in calculating the dissociation constants at each temperature, and a van't Hoff plot was constructed from which ΔH was estimated. This plot is shown in Figure 8; ΔH is calculated to be 20 kcal/mol or about 60% greater than ΔH of the acid. This result agrees qualitatively with the work of Ogura et al.[9] on styrene–methacrylic acid based ionomers. They found a 40% increase in ΔH for a 41% sodium salt of a copolymer containing 20 mol % meth-
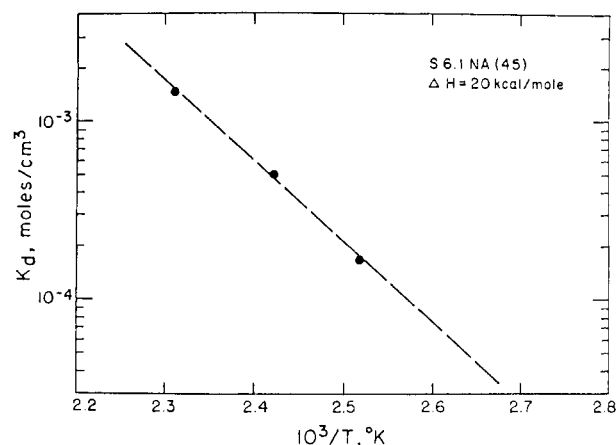
In Ogura's work with styrene–methacrylic acid based ionomers[9] the peak absorbance at 1560 cm^{-1} is shown to be constant from ambient to 200 °C. This phenomenon is not a result of sample loss, as this trend is reversed during the cooling cycle. However, due to anhydride formation, the integrated area is slightly less after the experiment than before. At present there remains no explanation for this behavior.

Conclusions

The absorbances at 1700 and 1750 cm^{-1}, assigned to the dimer and monomer carbonyl stretch, respectively, can be used in an infrared analysis to determine the temperature dependence of hydrogen bonding in ethylene–methacrylic acid copolymers. The presence of carbonyls due to oxidation products introduced during polymerization does not significantly affect the determination of peak absorbances or integrated absorbances in this region. Unambiguous results cannot be obtained by using only the 935-cm^{-1} band to determine thermodynamic parameters. The heat of dissociation for the two polymers investigated was calculated to be 12 kcal/mol of dimer, which is in good agreement with previous values determined for both polymers and low molecular weight carboxylic acids. The dimerization is essentially complete at room temperature.

The behavior of carboxyl groups in the partially neutralized salt is similar to that of the parent acid copolymer. At room temperature nearly all the free acid groups are paired as hydrogen-bonded dimers. An equilibrium between monomer and dimer is established at elevated temperatures with a heat of dissociation of 20 kcal/mol in the case of S6.1NA(45). The carbonyl asymmetric stretch located near 1565 cm^{-1} in the sodium salt consists of at least two overlapping peaks at room temperature. The shoulder at 1580 cm^{-1} decreases relative to the main peak (1560 cm^{-1}) as temperature is increased. Contrary to results by other workers on similar ionomers, a decrease in peak and integrated absorbance for the total 1565-cm^{-1} peak is observed with increasing temperature. This behavior is reversible with decreasing temperature.

References and Notes

(1) H. P. Brown, U.S. Patent 2 662 874 (1953).
(2) W. Cooper, *J. Polym. Sci.*, **28**, 195 (1958).
(3) R. Longworth and H. Morawetz, *J. Polym. Sci.*, **29**, 307 (1958).
(4) W. E. Fitzgerald and L. E. Nielsen *Proc. R. Soc. London, Ser. A*, **282**, 137 (1964).
(5) W. J. MacKnight, L. W. McKenna, B. E. Read, and R. S. Stein, *J. Phys. Chem.*, **72**, 1122 (1968).
(6) E. P. Otocka and T. K. Kwei, *Macromolecules*, **1**, 244 (1968).
(7) W. J. MacKnight and F. A. Emerson, "Dielectric Properties of Polymers", F. E. Karasz, Ed., Plenum Press, New York, 1971, p 237.
(8) K. Ogura and H. Sobue, *Polym. J.*, **3**, 153 (1972).
(9) K. Ogura, H. Sobue, and S. Nakamura, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 2079 (1973).
(10) A. T. Tsatsas and W. M. Risen, Jr., *Chem. Phys. Lett.*, **7**, 354 (1970).
(11) A. T. Tsatsas, J. W. Reed, and W. M. Risen, Jr., *J. Chem. Phys.*, **55**, 3260 (1971).
(12) E. D. Andreeva, V. N. Nikitin, and Y. M. Boyartchuk, *Macromolecules*, **9**, 238 (1976).
(13) T. R. Earnest, Jr., and W. J. MacKnight, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 143 (1978).
(14) D. Hadzi and N. Sheppard, *Proc. R. Soc. London, Ser. A*, **216**, 247 (1953).
(15) M. M. Davies and G. B. B. M. Sutherland, *J. Chem. Phys.*, **6**, 767 (1938).
(16) J. N. Finch and E. R. Lippincott, *J. Chem. Phys.*, **24**, 908 (1956).
(17) V. Liddel and E. D. Becker, *J. Chem. Phys.*, **25**, 173 (1956).
(18) J. N. Finch and E. R. Lippincott, *J. Phys. Chem.*, **61**, 894 (1957).
(19) P. Teragni, G. Masetti, and G. Zerbi, *Chem. Phys.*, **28**, 55 (1978).
(20) R. C. Milliken and K. S. Pitzer, *J. Chem. Phys.*, **27**, 1305 (1957).
(21) R. Fishman and T. Chen, *Spectrochim. Acta, Part A*, **25a**, 1231 (1969).
(22) L. C.-T. Chang, Ph.D. Thesis, Polytechnic Institute of Brooklyn, Brooklyn, NY, 1955.
(23) A. Eisenberg, *Macromolecules*, **3**, 147 (1970).

High-Resolution NMR Spectra of Hydrogenated Poly(phenylbutadienes). Styrene–Ethylene Alternating Copolymer and Poly(4-phenyl-1-butene)

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ABSTRACT: Alternating styrene–ethylene copolymers are prepared by hydrogenating 1,4-poly(1-phenylbutadiene) and 1,4-poly(2-phenylbutadiene). The stereostructure of the alternating copolymer was not revealed by the ^{1}H NMR spectrum. The ^{13}C NMR spectra, on the other hand, showed fine structure attributed to dyad or triad stereosequence distributions. These spectra indicated that the alternating copolymers obtained from 1,4-poly(1-phenylbutadiene) polymerized in THF and 1,4-poly(2-phenylbutadiene) are atactic and suggested that the sample prepared from 1,4-poly(1-phenylbutadiene) polymerized in benzene is slightly preponderant in syndiotactic sequences. The hydrogenation of 3,4-poly(1-phenylbutadiene) gives the polymer corresponding to poly(4-phenyl-1-butene). The ^{13}C NMR spectrum of the hydrogenated polymer shows that it is not stereoregular, as compared with the spectrum of isotactic poly(4-phenyl-1-butene).

There have been several papers dealing with preparation and characterization of alternating copolymers[1-3] or head-to-head polymers[4,5] by hydrogenation of 1,4-polydienes. It is of interest to prepare polymers which are