Infrared Spectroscopic Approaches to Polymer Transitions. II. The Transition of Hydrogen Bonding in Styrene— Methacrylic Acid (St—MAA) Copolymers

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ABSTRACT: Recently, infrared spectrophotometry has been applied as a useful tool for the investigation of polymer transitions. The solid-state transition in styrene— methacrylic acid copolymer was studied by infrared method in the range of 23—170°C. From the temperature dependence of the peak absorbances of 1700- and 1745 cm^{-1} bands, transition at 120°C was detected, and its mechanism was presumed to be associated with the association-dissociation process of intermolecular force between chains, namely with the breakdown of intermolecular hydrogen bonding. These results are in good agreement with Andrews' definition for polymer transitions (or T_g). Thus the transition at 120°C was interpreted by the normal thermodynamic equilibrium consideration.

KEY WORDS   IR Spectrophotometry / Solid-State / Transition / T_g / Acid Copolymer / Ionomer / Intermolecular / Hydrogen Bonding / Andrews' Definition /

Recently, several authors have demonstrated that infrared absorption spectrophotometry may be used to detect thermal transitions (or T_g) in solid-state polymers.[1-8] In our previous paper,[9] it was proved that the infrared method was useful for detection of multiple transitions in polyacrylonitrile. However, the transition mechanism could not be interpreted by the infrared results.

In general, the solid-state transitions (or T_g) in amorphous polymers have been interpreted in terms of "molecular motion." Andrews and his coworkers,[10-13] however, have recently proposed a quite different interpretation on the nature of the transitions (or T_g), namely, that solid-state transitions represent merely the loosening of various types of intermolecular cohesive (secondary) bonding in the solid-state.

In the present study, the temperature dependence of the infrared spectrum of St—MAA copolymer was examined, and the transition point at 120°C was detected. This temperature agreed well with the T_g determined by DTA, DSC and dynamic mechanical measurements, and it is interesting to note that the behavior

of the infrared spectrum in tne transition region satisfactorily supports the Andrews' definition. Thus, the transition (or T_g) of this acid copolymer is discussed in terms of the breakdown of intermolecular hydrogen bonding and interpreted by the ordinary thermodynamic equilibrium consideration. These results may also be useful for understanding the behavior of the cation in ionomer of this acid copolymer.[14]

EXPERIMENTAL

Polymer

The material used in this study was a copolymer of styrene and methacrylic acid, the composition and properties of which are given in Table I.

Table I. Composition and properties of St—MAA copolymer

Polymer	St/MAA, wt%	n_{sp}[a]	Melt index
St—MAA Copolymer	85/15	0.405	8.3 (200°C)

[a] $c = 0.50$ g/100 ml of DMF, at 25°C.

Preparation of Samples

Films for infrared measurements were cast from 10-% acetone solutions onto CaF_2 plates. After the acetone was evaporated under vacuum at room temperature, the samples were dried at 100°C for 3 hr to remove residual solvent.

Infrared Measurements

The film sample, which was about 10 μ in thickness, was placed between two CaF_2 plates.

Figure 1. The infrared heated cell and the thermal programming controller system.

The temperature was raised and cooled at a rate of 2°C/min. The temperature of the sample was controlled within ±0.5°C with an AGNE HPC-1500 Programming Controller and measured by a thermocouple attached to the CaF_2 window. The heated cell and the progamming controller system used in this work is shown in Figure 1. The temperature was varied in the range of 23—170°C and the spectra were measured on a JASCO Model 402G infrared spectrophotometer. The band intensities were determined by the "base line" method. The base lines are indicated in Figure 2.
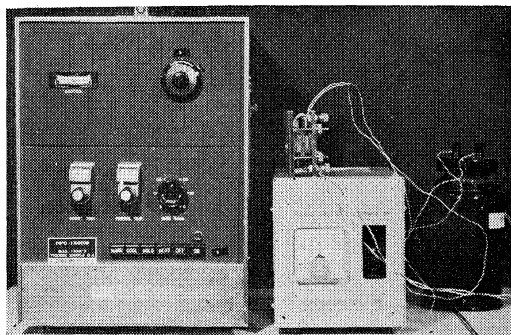
RESULTS AND DISCUSSION

Figure 2 shows a typical series of infrared spectra observed for the St—MAA copolymer at a range of temperature both in heating and cooling. Samples were reheated twice up to 170°C and yet gave reproducible spectra at each temperature with no significant signs of a hysteresis effect. In addition, neither significant temperature-dependent changes in peak positions nor new peaks were observed and thus oxida-
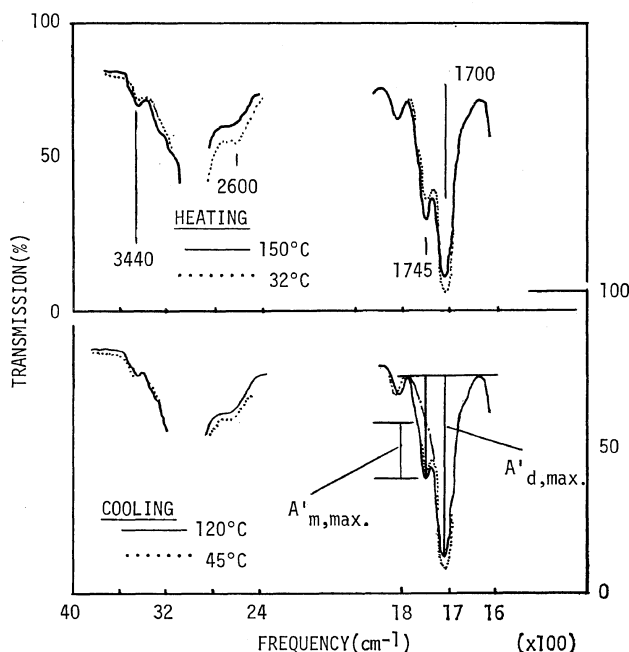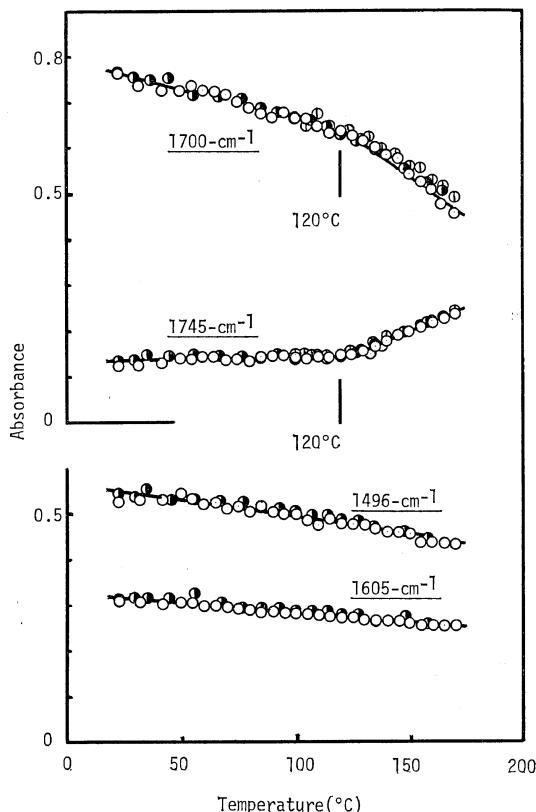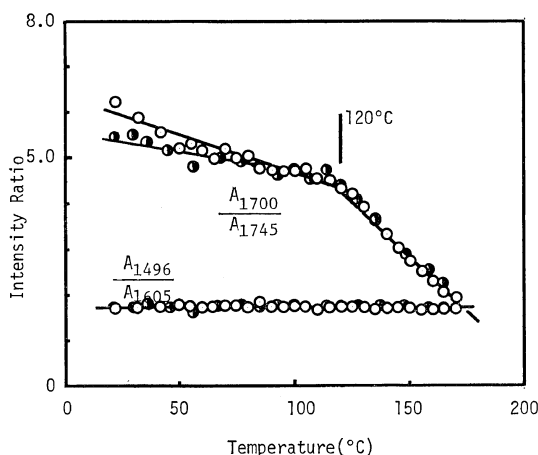

Figure 2. Absorption in the regions 2400—4000 and 1600—1900 cm^{-1} for the St—MAA copolymer at various temperature. Base lines used are indicated.

tion with heating was neglected. Figure 2 shows the following two interesting points. First, with increasing temperature, the band intensity at $1700 \, cm^{-1}$ decreases, and that at $1745 \, cm^{-1}$ increases conversely. The former band has been assigned to the dimerized carbonyl stretching vibration and the latter to the monomeric carbonyl one.[15,16] The band at $3440 \, cm^{-1}$, which also increases in intensity with increasing temperature, is therefore assigned to the free hydroxyl stretching vibration. Second, band intensities at 1496-, 1605-, and $3060 \, cm^{-1}$, which have been assigned to the stretching vibrations of the benzene ring of polystyrene,[17] showed little changes with temperature. In Figures 3 and 4, the results of the temperature-dependent infrared studies on the St—MAA copolymer are

Figure 4. Temperature dependence of the peak absorbances ratios for the A_{1700}/A_{1745} and A_{1496}/A_{1605}.

shown. Figure 3 illustrates the peak absorbances for 1700-, 1745-, 1605-, and $1496 \, cm^{-1}$ bands as a function of temperature. The intensity ratios of the A_{1700}/A_{1745} and A_{1496}/A_{1605} are plotted in Figure 4. From these results, is evident that a clear abrupt change (near 120°C) is observed on the curves of 1700- and $1745 \, cm^{-1}$ bands related to the carbonyl group in methacrylic acid, and that, on the other hand, no abrupt change is observed on the curves of 1496-, 1605-, and $3060 \, cm^{-1}$ bands related to polystyrene. This temperature of 120°C agrees well with the T_g (or transition) detected by DTA,[18] DSC,[19] dynamic mechanical measurements[20,21] and method of the relaxation behavior.[22] Ide *et al.*,[18] and Fitzgerald and Nielson[20] have said that this temperature corresponds to the T_g of this acid copolymer.

It is generally known that solid-state transitions (or T_g) in amorphous polymer occur at temperatures where thermal expansion has produced free volume sufficient to permit motion of segment or rotation of the side group. On the contrary, Andrews and his coworkers[10-13] have recently proposed that solid-state transitions (or T_g) in such polymers as polyacrylonitrile and poly(methyl methacrylate) are attributed to the loosening of various types of intermolecular cohesive (secondary) bonding in the solid states, and that the association-dissociation processes involved are governed by normal thermodynamic
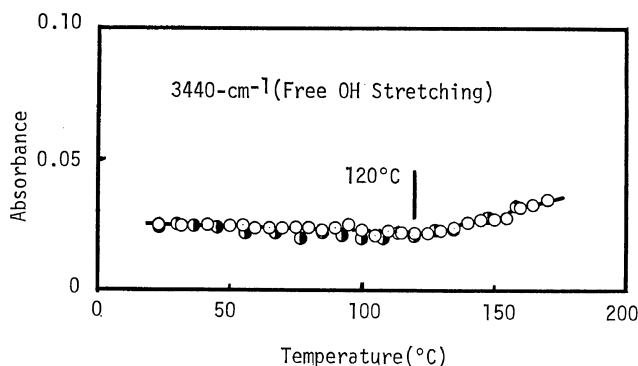

Figure 3. Temperature dependence of the peak absorbances of 1700-, 1745-, 1605-, and $1496 \, cm^{-1}$ bands in the infrared spectrum of St—MAA copolymer: ○, on heating; ◖, on cooling; ◌, on reheating.

Figure 5. Temperature dependence of the peak absorbance of the 3440 cm^{-1} free hydroxyl stretching vibration band.

equilibria.

Stein, *et al.*,[23-25] have proposed that the structure of acid copolymer such as ethylene—methacrylic acid copolymer may be schematically represented by the following formula
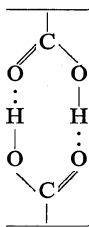
Considering the appearance of the shoulder at at 2600 cm^{-1} (Figure 2) which is attributed to the characteristic stretching vibration of the hydrogen bonded OH group,[23] the St—MAA copolymer may have a similar structure to ethylene—methacrylic acid copolymer.

Therefore, the transition at 120°C given in Figures 3 and 4 is probably associated with the breakdown of the intermolecular hydrogen bonding, and consequently at this temperature the peak absorbance of the free hydroxyl group band (3440 cm^{-1}) increases with increasing temperature as shown in Figure 5. Time dependence of the peak absorbances of the 1700- and 1745 cm^{-1} bands at various temperatures are illustrated in Figure 6. Both absorbances are approximately constant. From these results, the transition (or T_g) of this acid copolymer is regarded as having a considerable similarity to a melting point, which has been proposed by Andrews.[13]
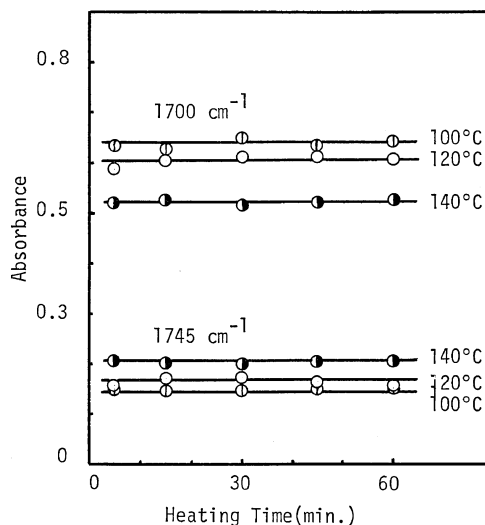

Figure 6. Time-temperature dependence of (A) 1700- and (B) 1745 cm^{-1} bands in the absorbance of infrared spectrum of the St—MAA copolymer.

In the present papar, this association-dissociation process is interpreted by normal thermodynamic equilibria. If the peak absorbances are expressed as absorbances per centimeter, the following relationship can reasonably be assumed to apply, considering the overlapping of 1700- and 1745 cm^{-1} bands

$$A_{m,max} = \varepsilon_{m,1745} \cdot C_m + \varepsilon_{d,1745} \cdot C_d \qquad (1)$$

$$A_{d,max} = \varepsilon_{d,1700} \cdot C_d + \varepsilon_{m,1700} \cdot C_m \qquad (2)$$

where $A_{m,max}$ is the peak absorbance per centimeter of 1745 cm^{-1} band, $\varepsilon_{m,1745}$ and $\varepsilon_{d,1745}$ are

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molar extinction coefficients of the 1745 cm^{-1} band in square centimeters per mole, and C_m and C_d are concentrations in moles per cubic centimeter of the monomeric and dimerized carboxyl group, respectively. $A_{d,max}$ is the peak absorbance per centimeter of 1700 cm^{-1} band, $\varepsilon_{d,1700}$ and $\varepsilon_{m,1700}$ are molar extinction coefficients of the 1700 cm^{-1} band. In eq 1 and 2, it may be possible that the $\varepsilon_{m,1700} C_m$ in eq 2 is negligible and $\varepsilon_{m,1745} C_m$ in eq 1 is obtained from Figure 2. Therefore, we obtain the following eq 1' and 2'

$$A'_{m,max} = \varepsilon_{m,1745} \cdot C_m \qquad (1')$$

$$A'_{d,max} = \varepsilon_{d,1700} \cdot C_d \qquad (2')$$

where $A'_{m,max} = A_{m,max} - \varepsilon_{d,1745} C_d$. The dissociation constant, K, is evaluated from eq 1' and 2'.

$$K = [-COOH]^2/[(-COOH)_2]$$
$$= (\varepsilon_{d,1700}/\varepsilon_{m,1745}{}^2)(A'_{m,max}{}^2/A'_{d,max}) \qquad (3)$$

In general, it is assumed that the absorption coefficient is independent of temperature.[26,27] If it is approximately constant over the experimental temperature range studied, the ratios, $A'_{m,max}{}^2/A'_{d,max}$, are related to the dissociation constant for the dimer—monomer conversion. Therefore, the heat of dissociation, ΔH, can be obtained from the van't Hoff equation

$$d \ln K/dT = \Delta H/RT^2 \qquad (4)$$

A plot of logarithms of the ratios vs., the reciprocal of the absolute temperature is shown in Figure 7. From the slope of the two straight lines obtained, the heat of dissociation, ΔH, was estimated to be 7.32 kcal/mol ($t > 120°C$) and 0.58 kcal/mol ($t < 120°C$), respectively. It is interesting to note that MacKnight, et al.,[23] have reported the value of 11.6 kcal/mol in ethylene—methacrylic acid copolymer in the range of 20—110°C. However, a physicochemical explanation for this difference cannot be presented at this time. Fitzgerald and Nielson[20] reported, from a plot of logarithm of the $A_{m,max}/A_{d,max}$ vs., the reciprocal of the absolute temperature, that the value of energy difference, ΔE, between the non-hydrogen bonded and hydrogen bonded forms of the acid group was 3.61 kcal/mol for the St—MAA copolymer con-
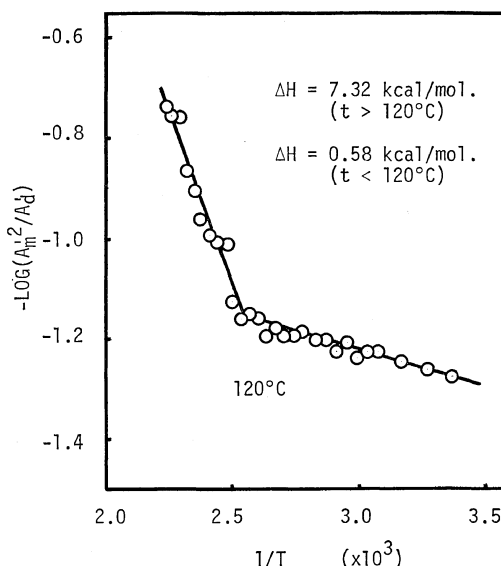

Figure 7. Van't Hoff plot (log K vs. $1/T$) of the dissociation constant for the acid monomer—dimer equilibrium.

taining 7.5-mol% methacrylic acid and 92.5-mol% styrene in the range of 100—180°C. From these results, Fitzgerald and Nielson[20] have proposed that hydrogen bonding plays a very minor part in determining the mechanical and rheological properties of polymeric acids. On the other hand, Longworth and Morawetz[28] have reported, from melt viscosity measurements, that very high viscosities for the St—MAA copolymers when compared with polystyrene can be attributed to hydrogen bonding in this acid copolymer. In their discussion, Fitzgerald and Nielson[20] contradicted the statement that this increase in viscosity can be attributed only to the higher glass transition temperature in the acid copolymer rather than that of polystyrene. This indicates clearly that they do not recognize that the T_g of this acid copolymer greatly depends upon hydrogen bonding. However, the T_g for this type of copolymer is associated with the breakdown of the intermolecular hydrogen bonding, as we have shown in this paper. Therefore, we would propose that hydrogen bonding is very important in determining the physical properties such as the mechanical and rheological properties for this type of polymeric acid contrary to Fitzgerald and Nielson's des-

cription.

CONCLUSION

In conclusion, from the infrared results, the transition of the St—MAA copolymer can be interpreted as follows: the transition (or T_g) at 120°C is associated with the breakdown of intermolecular hydrogen bonding between chains. It is not therefore appropriate to interprete the T_g in this acid copolymer only in terms of "molecular motion." In these polymers, the transitions (or T_g), which are governed by Andrews' definition for polymer transitions, are clearly recognized. From the energetic considerations of hydrogen bonding, the heat of dissociation, ΔH, was estimated to be 7.32 kcal/mol ($t > 120°C$) and 0.58 kcal/mol ($t < 120°C$), respectively. These values are relatively small compared with those of the ordinary stable hydrogen bonding. However hydrogen bonding in this type of polymeric acid is very important in considering of the properties of these polymers, because the T_g of this type of copolymer is governed by intermolecular hydrogen bonding. This infrared result may be very useful for understanding the relation between the physical structure and properties of the ionomer of this acid copolymer.

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