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1978

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DIELECTRIC RELAXATION BEHAVIOR OF SOME ETHYLENE-METHACRYLIC ACID COPOLYMERS AND THEIR METHYL ESTERS

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SYNOPSIS

Ethylene-methacrylic acid copolymers containing two different concentrations of the acid groups have been studied by dielectric relaxation and infrared techniques. The infrared measurements, used to determine the number of acid dimers present at a given temperature, indicate a sufficient number of free COOH dipoles present to account for the magnitude of the observed β' dielectric relaxation (frequency plane) in both copolymer systems. Dielectric measurements on the methyl ester derivatives of the above copolymers yield dispersions of unusual width, which precluded attempts to estimate the number of ester dipoles participating in the relaxation. A possible explanation for this behavior is advanced.

INTRODUCTION

In recent years, there has been increased interest in understanding the bulk properties of ethylene polymers containing carboxylic acid side groups in terms of their molecular constitution. In particular, several studies have attempted to establish quantitatively the nature of the carboxylic acid monomer-dimer equilibrium in ethylene-acrylic acid and ethylene-methacrylic acid copolymers by means of infrared and dielectric relaxation [1, 2]. Reference [1] utilizes a frequency-plane study of the dielectric relaxation behavior, which is preferable to the isochronal method of reference [2]. On the other hand, reference [2] utilizes an improved infrared method for estimating the number of free carboxylic acid groups, as compared with reference [1]. These limitations in each separate study prevent an unambiguous correlation of the number of dipoles participating in a given dielectric relaxation with a reliable infrared determination of the concentration of free carboxylic acid groups.

This study attempts to incorporate the aforementioned improvements in technique and thereby establish the extent of the participation of the free acid groups in the dielectric β' relaxation for two ethylene-methacrylic acid copolymers differing in acid concentration. The methyl esters of these copolymers were prepared in order to provide a system, uncomplicated by the effect of hy-

drogen bonding, where an *a priori* known number of dipoles could be compared directly with the magnitude of the dielectric dispersion.

The present results support the previous conclusion [2] that the COOH groups alone are sufficient to account for the magnitude of the dielectric β' dispersion.

EXPERIMENTAL

The ethylene-methacrylic acid copolymers containing 2.1 mole % methacrylic acid, designated A, and 6.1 mole % methacrylic acid, designated B, were obtained from the DuPont Company. It is assumed that the acid groups are distributed randomly along the backbone [2]. Films suitable for the infrared and dielectric studies were prepared by compression molding at 160°C under a force of 10,000 psi for 10 min. The films were then cooled to room temperature over a period of 15 min before being removed from the press with subsequent storage in a desiccator.

The methyl esters were prepared from the corresponding acids via the following route:



The infrared measurements were performed on a Perkin-Elmer 283 Spectrophotometer. The films were placed between KCl plates, one plate having been implanted with an iron-Constantan thermocouple. The area surrounding the absorbing unit was continuously purged with nitrogen gas; readings were taken from 30° to 90°C at approximately 10°C intervals.

Dielectric measurements were carried out using a General Radio Capacitance Measuring Assembly of the transformer-ratio-arm bridge type (model 1620 A) in conjunction with a three-terminal cell (Balsbaugh type LD-3) having 53 mm diameter electrodes. The cell was equipped with electrical resistance heaters enabling a wide variation of temperature to be achieved above, as well as below, ambient. In most of the experiments, the frequency was varied from 40 Hz through 100 kHz at fixed temperature (constant to within 0.5°C).

RESULTS AND DISCUSSION

The infrared evidence for the existence of a temperature-dependent monomer-dimer equilibrium above the glass transition temperature is well known [1-4]. Two methods, each involving a different band system, have been previously used to characterize the equilibrium. The first, which utilizes the 1700 cm^{-1} band assigned to hydrogen-bonded carbonyl stretching, the 1750 cm^{-1} band assigned to free carbonyl group stretching, and the 3540 cm^{-1} band assigned to free hydroxyl group stretching, has fallen into disrepute because a band at 1735 cm^{-1} , produced by adventitious oxidation products, interferes with the bands previously mentioned [2]. In the second technique, the concentration of the hydrogen-bonded dimer species is measured directly, using the absorption

of the 935 cm^{-1} band assigned to the out-of-plane bending of the hydrogen-bonded hydroxyl group [2]. Because no known interference exists at 935 cm^{-1} , this method was used in the current study.

Because the polymer films were too thin to be measured accurately for thickness, the following procedure was adopted. The extinction coefficient from reference [2] was used, along with the assumption that at 10°C all the acid is present in the dimer form. This assumption is justified on the basis that at or below the glass transition temperature of the amorphous phase, the dimer is the dominant species [4]. The dimer concentration is known from the molecular constitution of the copolymer.

$$C_D^0 = \rho/M \quad (1)$$

where ρ is the bulk polymer density, M is the molecular weight of the copolymer repeat unit, and C_D^0 is the concentration of dimer at 10°C . The thickness can be determined from the absorbance; this thickness is then used to obtain the dimer concentration C_D^T at elevated temperatures. The monomer concentration C_M^T is obtained from

$$C_M^T = 2(C_D^0 - C_D^T), K_d = (C_M^T)^2/C_D^T \quad (2)$$

Table I lists the values of K_d , the dissociation constant, and monomer concentration as a function of temperature for copolymers A and B.

Dielectric relaxation measurements, performed isochronally on both A and B, display two dominant relaxations similar to those shown in Figure 3 of ref. [2]. The low temperature relaxation, designated γ , was not studied here; the high temperature relaxation β' was characterized at various fixed temperatures in the frequency plane.

Impurities aside, the monomer is the only species which can give rise to a di-

TABLE I
Comparison of the COOH Concentrations Calculated from the Infrared Technique (C_M^T) with those Obtained from Dielectric Measurements (N) for Copolymers A and B

Sample	Temperature ($^\circ\text{C}$)	C_M^T (moles/ $\text{cm}^3 \times 10^4$)	N (moles/ $\text{cm}^3 \times 10^4$)	K_D (moles/ $\text{cm}^3 \times 10^4$)
A	25	0.47		0.071
	31	0.66		0.141
	40	0.95		0.31
	52	1.31		0.61
	62	1.67	0.24	1.10
	71	1.96		1.61
B	21	0.84		0.082
	33	1.86		0.43
	42	2.63	1.25	0.90
	52	3.50		1.68
	63	4.41		2.86
	72	5.18		4.17

electric dispersion; the dimer has a zero net dipole moment. Figure 1 displays a plot of ϵ'' , the dielectric loss factor, versus log frequency at three different temperatures for A. A single broad dispersion is observed whose structure changes with temperature; this is most likely a result of the crystallinity present which gives rise to an additional relaxation, α [2]. Figure 2 displays the ϵ'' behavior for B; here, the β' spectrum is uncomplicated by a contribution from an α peak. It displays the usual temperature shift of the frequency where ϵ'' attains its maximum value f_{\max} ; i.e., f_{\max} increases with increasing temperature.

If both the relaxed, ϵ_0 , and unrelaxed, ϵ_∞ , dielectric constants are known, it

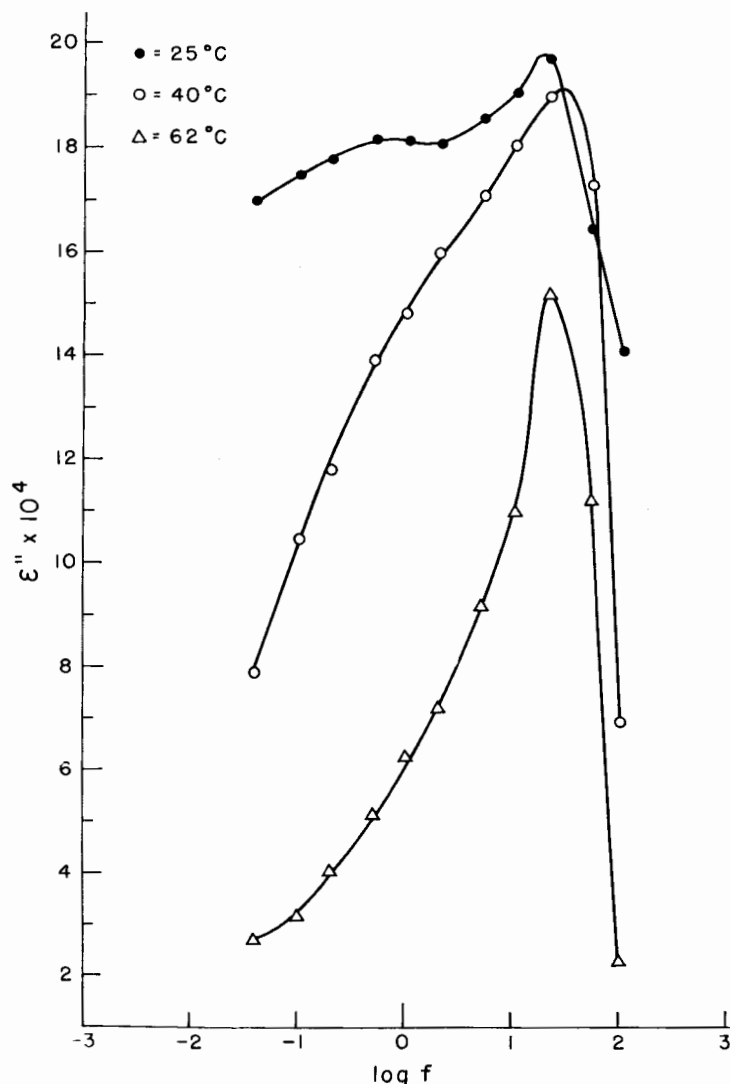


FIG. 1. ϵ'' vs $\log f$ (f in kHz). Behavior is depicted for sample A at 3 different temperatures.

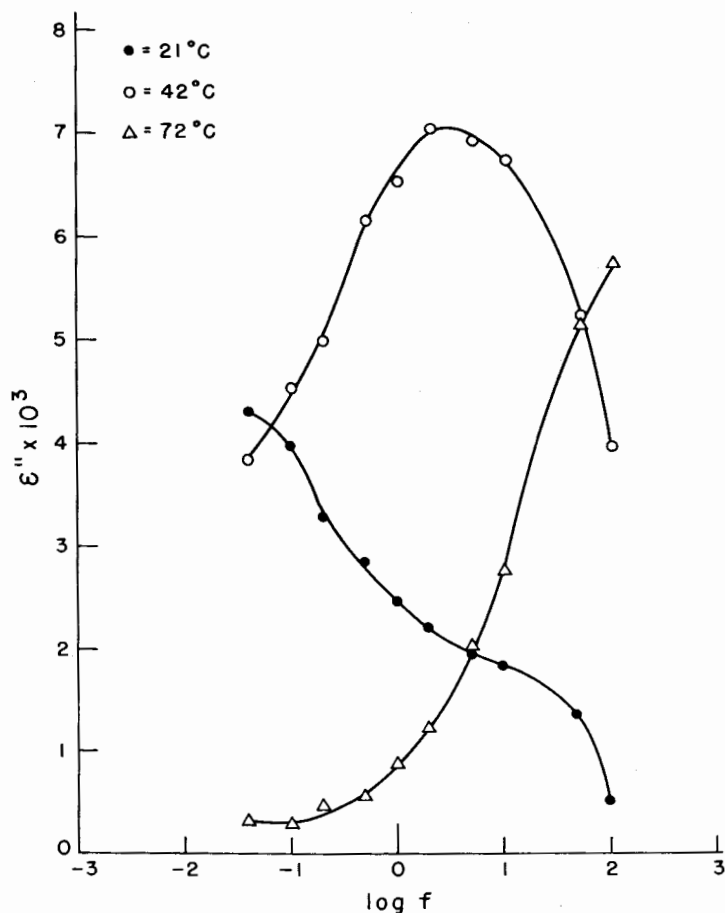


FIG. 2. ϵ'' vs $\log f$. Behavior is depicted for sample B at 3 different temperatures.

is possible to estimate the concentration of participating dipoles N by means of the Onsager equation [2]:

$$N = \frac{9kT}{4\pi u^2} \frac{(2\epsilon_0 + \epsilon_\infty)(\epsilon_0 - \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)^2} \quad (3)$$

where T is the absolute temperature and u is the permanent electric dipole moment of the COOH group, which is taken to be 1.75 D [5]. Ideally, if the frequency range is sufficiently great, ϵ_0 and ϵ_∞ can be obtained directly from the experimental measurements. Since most experiments fall short of this goal, mathematical techniques, such as time-temperature superposition using shift factors to produce Cole-Cole plots, are used to obtain ϵ_0 and ϵ_∞ [6]. Another method employed to obtain $\epsilon_0 - \epsilon_\infty$ is to integrate ϵ'' with respect to $1/T$ over the entire width of an isochronal dispersion [6]. In the present study, at least two factors prohibit the use of the above techniques, the most important being that the concentration of the relaxing species is highly temperature-dependent.

The second problem is related to the fact that the polymer film is under tension between the two electrodes. Over a wide temperature range, it is impossible to be certain that the electrode separation has not changed by several percent as the material softens. If the magnitude of the relaxation ($\epsilon_0 - \epsilon_\infty$) is very small, as in the present case, the change in ϵ' (the real part of the complex dielectric constant) caused by a change in plate separation can cause an error in the determination of $\epsilon_0 - \epsilon_\infty$ of at least 100%.

For these reasons, the following approach was adopted. For A and B alike, a temperature was chosen where the relaxation appeared to be centered as near to 2 kHz, the center of the $\log f$ plane, as possible; the values of ϵ' associated with the extremes of the frequency range, 0.04 and 100 kHz, were taken to be ϵ_0 and ϵ_∞ , respectively. Equation (3) indicates that for systems having very small relaxation magnitudes, N is proportional to $\epsilon_0 - \epsilon_\infty$. Since the $\epsilon_0 - \epsilon_\infty$ value obtained by this method must underestimate the true dispersion magnitude, one obtains a lower bound for the value of N , the number of COOH dipoles per cubic centimeter. Table I compares N with C_M^T for polymers A and B. In both cases, the dielectric estimate N is below the infrared value C_M^T . If the reverse were true, polar impurities or oxidation products would be necessary to account for this. In A, N is nearly an order of magnitude smaller than C_M^T ; this is most likely attributable to the existence of crystallinity which may provide effective "cross-linking" for the amorphous phase, preventing the carboxylic acid dipoles from attaining maximum reorientation.

The results obtained are consistent with the hypothesis that the dielectric β' relaxations in both A and B are caused by carboxylic acid group reorientation.

Dielectric relaxation studies performed in the frequency plane on the methyl ester derivatives of A and B, denoted AE and BE, respectively, demonstrate some unusual behavior. At fixed temperatures ranging from -20 to $+70^\circ\text{C}$, ϵ'' was always observed to increase with increasing frequency; no sign of a relative maximum was observed. Therefore, an isochronal spectrum was taken of AE at 2 kHz; Figure 3 shows a partially resolved peak, extremely broad and centered at -9°C . It is apparent that below -40°C a second dispersion of at least similar magnitude would be observed. A frequency-plane spectrum taken at -9°C is also shown in Figure 3. At first it appears surprising that no relative maximum occurs at 2 kHz; however, some reflection indicates that this behavior can be understood. One must assume that if measurements were performed at sufficiently high frequencies, a relative maximum would be observed, otherwise the relaxation process would not involve dipoles. Previous studies on poly(methyl methacrylate) indicate that the corresponding lower temperature isochronal relaxation is of greater magnitude than the one appearing at the higher temperature [6].

The relaxation depicted in Figure 3 is certainly not characterizable as a single relaxation time process. As a first approximation, one might describe it as a sum of two single relaxation time processes:

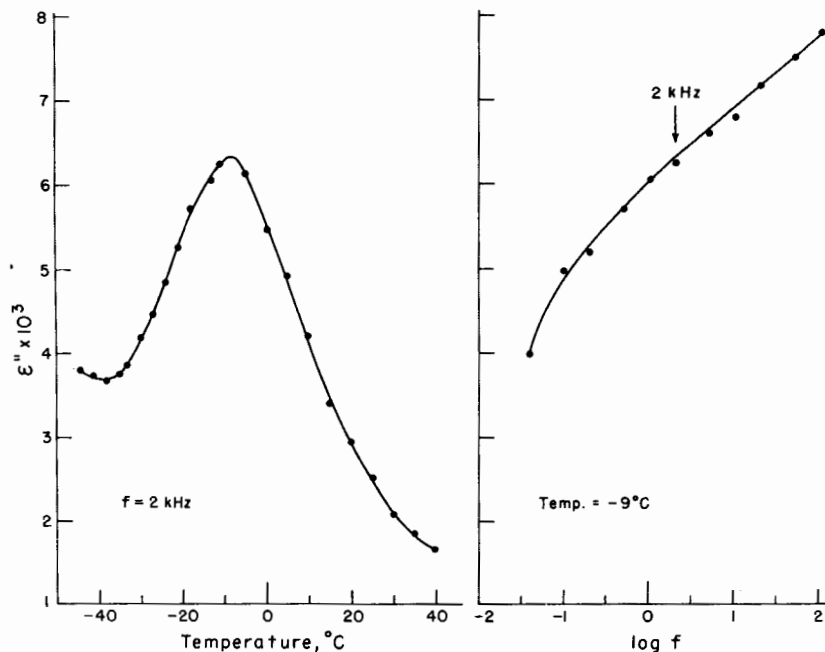


FIG. 3. ϵ'' vs temperature at $f = 2 \text{ kHz}$ (left) and versus $\log f$ at $T = -9^{\circ}\text{C}$ (right) for sample AE.

$$\epsilon'' = \frac{a_1 h_1(w, T)}{1 + h_1^2(w, T)} + \frac{a_2 h_2(w, T)}{1 + h_2^2(w, T)} \quad (4)$$

where $a_i = \epsilon_0^i - \epsilon_{\infty}^i$, $w = 2\pi f$, $h_i(w, T) = \tau_i w \exp(E_i/RT)$, and E_i is the activation energy for process i . The w and T locations of the relative maxima in the frequency plane must satisfy the condition $((\partial \epsilon'')/(\partial w))_{T=T_0} = 0$, which leads to

$$\begin{aligned} g(w_m, T_0) &= \frac{h_1^2(w_m, T_0) - 1}{[1 + h_1^2(w_m, T_0)]^2} \cdot \frac{[1 + h_2^2(w_m, T_0)]^2}{1 - h_2^2(w_m, T_0)} \\ &= \frac{a_2 h_2(w_m, T_0)}{a_1 h_1(w_m, T_0)}; \end{aligned} \quad (5)$$

where $w_m = w_{\max}$. The location of the relative maximum in the temperature plane at fixed frequency w_m is found by solving the equation

$$\left(\frac{\partial \epsilon''}{\partial T} \right)_{w=w_m} = 0$$

for T . One obtains eq. (6);

$$g(w_m, T) = \frac{E_2}{E_1} g(w_m, T_0) \quad (6)$$

It is immediately apparent that $T = T_0$ is not a solution to eq. (6) if $E_2 \neq E_1$.

Therefore, in polymers where the single relaxation time model is no longer applicable, the relative maximum in the frequency plane need not correspond to that in the isochronal experiment; the two must be identical in the single relaxation time model, however.

CONCLUSIONS

The dielectric β' relaxation in the ethylene-methacrylic acid copolymers studied can be attributed solely to the reorientation of the COOH groups in an applied electric field. No adventitious oxidation products need be involved to explain the magnitude of the relaxation, as was needed in reference [1].

The failure to observe a relative maximum for the methyl ester derivatives in the ϵ'' versus frequency plane is most likely caused by the presence of two very broad, partially overlapping dispersions, as are seen in the isochronal experiment. Presumably, if a frequency range beyond 100 kHz had been available, or if the experiments had been conducted at lower temperatures, a relative maximum would have been discernible. Work is currently underway to resolve this difficulty and thereby determine if the known number density of ester dipoles can account for the magnitude of the dielectric relaxation in copolymers AE and BE.

The assistance of Mr. Gregory Riska is gratefully acknowledged. The authors are grateful to the National Science Foundation for partial support of this research under Grant DMR 75-06916. The use of NSF Materials Research Laboratory Facilities is acknowledged.

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