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STRUCTURE AND PROPERTIES OF ETHYLENE-METHACRYLIC ACID COPOLYMERS AND THEIR SODIUM SALTS: DIELECTRIC AND PROTON MAGNETIC RELAXATION STUDIES*

By B. E. READ, E. A. CARTER, T. M. CONNOR and W. J. MacKNIGHT†

Dielectric and proton magnetic relaxation data have been obtained for an ethylene-methacrylic acid copolymer (containing about 4 mole% methacrylic acid units) and its 53% ionised sodium salt. The degrees of crystallinity and percentage ionisation of the samples investigated were estimated by infra-red methods.

The dielectric results were obtained principally in the frequency range 100 Hz to 10 kHz and at temperatures ranging from 80° to -120°. A few results are also reported at frequencies down to 0.1 Hz and up to 100 MHz. For the acid copolymer, two dielectric loss regions are observed and these are correlated with the reported mechanical β' - and γ_a -processes respectively. The partly ionised copolymer exhibits three dielectric relaxation regions which correlate with the mechanical α -, β - and γ_a -relaxations respectively. In addition, a dielectric peak appears at about -40° in the presence of absorbed water, a result similar to that found in the polyamides.

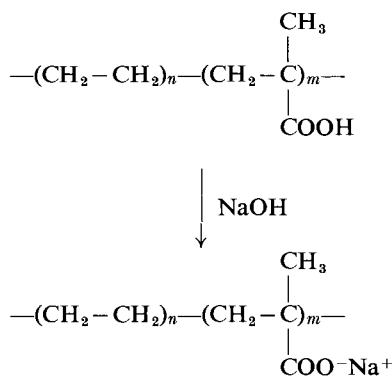
The proton magnetic relaxation results were obtained by pulse methods which yielded the spin-lattice relaxation times T_1 (at 30 MHz) and $T_{1\rho}$ (at kilohertz frequencies) as a function of temperature from -180° to 100°. Two components were generally observed for $T_{1\rho}$. For the acid copolymer the β' - and γ -processes have been observed from these results, as well as a lower-temperature (δ) process which has not been detected by the mechanical or dielectric methods. For the sodium salt the γ - and δ -processes are also found, in addition to a high-temperature process in the region of the merged α - and β -processes.

The present data are consistent with previous assignments for the β' -, α -, β - and γ -processes. The 'water' relaxation appears to involve some rotation of water molecules, or of ionic segments to which water molecules are attached, in the proposed ionic domains. The δ -process is ascribed to the rotations of methyl groups present in the methacrylic acid units.

Introduction

A variety of experimental techniques have been employed to investigate the structure and properties of ethylene-methacrylic (or acrylic) acid copolymers and their ionic salts. These methods include infra-red spectroscopy,¹⁻⁴ differential scanning calorimetry (d.s.c.),^{3,5} X-ray diffraction,^{1,6-8} electron microscopy,^{1,7,9} dynamic mechanical^{1,3,5,7,8,10,11} and dielectric¹⁰ relaxation. Measurements of tensile strength and melt flow viscosity have also been reported.^{4,12}

The present work is principally concerned with an ethylene-methacrylic acid copolymer, containing about 4 mole% methacrylic acid units, and its partly ionised sodium salts. Structurally, these may be represented as follows:



with n equal to 24 on average for m equal to unity.

Since the copolymers are usually prepared by a high-pressure free-radical process, the distribution of acid (or

ionic) groups within the copolymer would be expected to be random. Furthermore, the presence of some short hydrocarbon branches and carbonyl groups (due to oxidation) might be expected on the polyethylene sequences. In the case of acrylic acid copolymers, each of these groupings has been detected by infra-red analysis.³ Infra-red measurements have also been used^{2,4} to determine the percentage of acid groups which are converted to the salt (percentage ionisation). Temperature-dependent and polarised infra-red studies have shown that the -COOH groups are mostly hydrogen bonded together in the form of interchain dimers.^{2,3} A monomer-dimer equilibrium has been proposed between the acid groups which is quantitatively comparable to that for low molecular weight carboxylic acids in non-polar solvents.²

X-ray^{1,6,7} and d.s.c.^{3,5} studies have shown that at low acid contents (less than about 8 mole%) both the original acid copolymers and their ionised salts are partly crystalline. However, the degrees of crystallinity are low relative to those for low-density polyethylene and decrease with increasing acid content. Evidence^{2,3} suggests that the crystalline phase consists only of polyethylene sequences, the acid and ionic groups being too large to be accommodated in the polyethylene crystal lattice. The degree of crystallinity decreases with increasing ionisation for unannealed samples, but becomes independent of ionisation after annealing.^{1,5-7} The relatively large effect of annealing on the ionic copolymers has been ascribed to their high internal viscosity,⁷ and is consistent with a relatively high degree of supercooling observed by d.s.c. measurements.⁵

Electron microscopy studies^{1,7,9} have shown that the original acid copolymers (at low acid contents) exhibit a lamellar spherulitic morphology, typical of polyethylene.

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However, after ionisation the spherulitic structure is destroyed, the lamellae can hardly be distinguished, and a fine-grained structure is observed. On the basis of these experiments, it has been proposed that in the ionic copolymers the ions segregate into separate domains having sizes ranging from about 100–500 Å. The ionisation also produces a marked change in the X-ray diffraction patterns,^{6,7} notably the appearance of a low-angle diffraction peak at about 4°, corresponding to a spacing of about 20 Å. This peak is little affected by the nature of the cation, persists to temperatures of at least 300°, and is virtually eliminated by saturating the polymer with water. It has been ascribed to a separate ionic phase within which clusters of carboxyl groups are arranged in a periodic fashion to give a repeat distance of about 20 Å. The disappearance of the peak when the polymer is saturated with water has been attributed to the effective dissolution of the ionic domains.

The dynamic mechanical results are consistent with the structural features outlined above. At a frequency of 1 Hz, the methacrylic acid copolymers containing 4 mole% acid units exhibit a $\tan \delta$ peak at 25° which has been labelled β' .⁵ The temperature of this peak decreases with decreasing acid content and can be extrapolated to about –20° at zero acid content, corresponding to the well-known β -peak for branched polyethylene. The β' -peak has been attributed to main chain motions in the amorphous phase related to the glass transition of the acid copolymer, and may involve the breaking and reforming of the hydrogen bonded acid groups.^{3,5,10} When the acid groups are ionised, the β' -peak is depressed and replaced by two peaks, labelled α and β .⁵ The β -peak is located at about –10°, close to the temperature of the β -peak for branched polyethylene. It increases in height (but remains at the same temperature) with increasing percentage ionisation, and is observed both for monovalent and bivalent cations.^{5,8} The α -peak is located at temperatures above that of the β' -peak and shifts to higher temperatures with increasing ionisation. These results are consistent with the proposed structure consisting of ionic domains embedded in a hydrocarbon matrix. Thus the β -peak has been ascribed to the motions of branched chain segments in the amorphous hydrocarbon phase¹⁰ (a process identical to that in low-density polyethylene) with some possible contribution or restriction from the ionic groups.⁸ The α -peak has been assigned to the ionic region.¹⁰ Both the acid copolymers and the partly ionised salts exhibit a mechanical loss peak in the temperature region of –140°. By the application of various heat treatments, this relaxation has been clearly resolved into two components which have been labelled γ_a and γ_c .^{8,11} The high temperature component (γ_a) decreases in magnitude with increasing crystallinity and is attributed to local main chain motions in the amorphous phase. The low temperature component (γ_c) increases in magnitude with increasing crystallinity and is thus ascribed to a motion of lattice defects within the crystal phase. The few dielectric results so far reported¹⁰ are consistent with the above interpretations.

The structural picture which has emerged from the above studies is as follows. In the acid copolymers there is a crystalline phase consisting of polyethylene chain folded lamellae arranged into spherulitic structures. The lamellae are interconnected by an amorphous phase comprising hydrocarbon chains and carboxylic acid groups hydrogen bonded together. The ionised copolymers have a three-phase structure comprising polyethylene crystals and ionic domains interconnected by an amorphous hydrocarbon matrix. For the partly ionised copolymers it does not yet seem clear whether the unionised carboxylic acid groups reside predominantly in the hydrocarbon phase or have a tendency to be located in the ionic domains.

The object of the present paper is to describe some recent

studies, employing both dielectric and proton magnetic relaxation methods, on the methacrylic acid copolymer containing 4 mole% acid units and a partly ionised (53%) sodium salt. The effect of absorbed moisture on the dielectric behaviour of the sodium salt will also be described. These results will be correlated with the dynamic mechanical data and discussed in the light of the structure outlined above.

Experimental

Materials

Details of the synthesis of the acid copolymer and the partly ionised sodium salts have been given in previous publications.^{2,5}

For the dielectric measurements, samples were compression moulded into circular discs measuring about 5 cm in diameter and 0.07 cm in thickness. The moulding was effected at 175°, and the subsequent cooling to room temperature required about 3 hours. The samples so far investigated have been unannealed. Prior to the dielectric measurements, the samples were dried by pumping under vacuum to a constant weight. In order to study the effect of absorbed water on the dielectric behaviour of the partly ionised copolymer, the moulded specimen was conditioned in a vacuum desiccator over water (100% relative humidity) for various time periods (up to one week). After surface drying, the sample was weighed to determine the weight percentage water uptake.

Infra-red characterisation

The percentage ionisation of the partly ionised sodium salt was estimated from the integrated absorbance of the infra-red peak at 1700 cm^{–1} as described previously.² The infra-red measurements were made on a Grubb Parsons type GS 2A grating instrument and yielded a value of 53% ionisation for the sample employed in the present studies.

Infra-red measurements were also made to determine the degrees of crystallinity of the samples used in the dielectric study. For the acid copolymer the degree of crystallinity was estimated from the extinction coefficients, ϵ_{1894} and ϵ_{2016} , of the bands at 1894 cm^{–1} and 2016 cm^{–1} respectively. The extinction coefficients are here defined as the peak absorbance per cm sample thickness, where the absorbance is given by $\log_{10}(I_0/I)$, I and I_0 being the transmitted intensities at the maximum and at the baseline of the peak. The baselines and sample thicknesses employed for these determinations are indicated in Fig. 1(a). The volume fraction of crystallinity (X_c) is given by:¹³

$$X_c = \epsilon_{1894} / 6.4 \quad \dots (1)$$

$$\text{and } X_c = (\epsilon_{2016} - 2.1) / 6.0 \quad \dots (2)$$

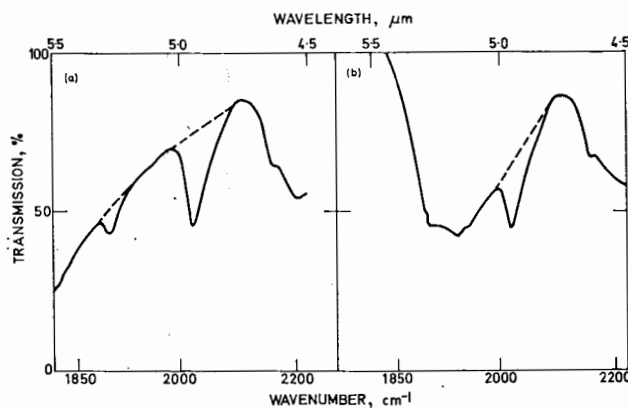


Fig. 1. Infra-red spectra of (a) the acid copolymer and (b) the 53% ionised sodium salt, illustrating the bands at 1894 cm^{–1} and 2016 cm^{–1}, used for crystallinity determinations

Baselines are shown by dashed lines. Sample thicknesses: (a) 0.064 cm; (b) 0.066 cm

For the acid copolymer, close agreement was found between the X_c values estimated from Equations (1) and (2) respectively, and an average value of $X_c = 0.178$ was obtained. For the partly ionised copolymer, the 1894 cm^{-1} peak was submerged beneath a broad peak centred at about 1940 cm^{-1} . The band at 2016 cm^{-1} was resolved, however, and ϵ_{2016} was determined using the baseline indicated in Fig. 1(b). From Equation (2), a value of $X_c = 0.122$ was obtained. The degrees of crystallinity determined by these infra-red methods compare fairly closely with those previously determined from d.s.c. measurements.⁵

Dielectric measurements

Most of the dielectric measurements have been made at frequencies ranging from 50 Hz to 10 kHz, using a three-terminal cell in conjunction with a General Radio transformer ratio-arm bridge.¹⁴ To ensure a good contact between the sample surface and electrodes, metal foil was attached to the specimen with the aid of a thin film of silicone grease. For temperature variation in the range $+80^\circ$ to -120° , the sealed dielectric cell was immersed in liquid baths thermostated to $\pm 0.1^\circ$. To obtain reproducible data (particularly with the partly ionised sodium salt in the temperature range 10° to -20°), it was found necessary to ensure that a dry atmosphere surrounded the specimen. This was achieved by placing drying agent in the dielectric cell and sealing the lead entrance with a polythene bag.

Some preliminary measurements on the acid copolymer have also been made at frequencies between 10^{-1} and 10^3 Hz using a low-frequency Scheiber bridge,¹⁴ and at frequencies between 10^5 and 10^8 Hz using the Hartshorn-Ward resonance method¹⁴ and also a Wayne Kerr B.201 transformer ratio-arm bridge.

Proton magnetic relaxation measurements

Two types of magnetic relaxation measurement have been made, using pulse techniques. The spin-lattice relaxation time, T_1 , has been determined as a function of temperature using conventional pulse methods,^{15,16} i.e. π , $\pi/2$ pulse sequence. These measurements in the laboratory frame were made at a frequency of 30 MHz. Basically, the rate of change of magnetisation along the direction of the static field H_0 (7050 gauss) is observed. Also, the relaxation time in the 'rotating frame', $T_{1\rho}$, has been measured^{17,18,19} as a function of temperature. This technique and the appropriate apparatus have been discussed in a previous paper,²⁰ where the physical significance of the time constants T_1 and $T_{1\rho}$ is considered. Also the relation of T_1 and $T_{1\rho}$ to microscopic quantities characterising molecular motions, e.g. molecular correlation times, τ and activation energies, ΔE , is discussed as are the non-exponential decays of magnetisation which are frequently found when $T_{1\rho}$ measurements are made on polymers. The rotating frame method measures the rate of change of magnetisation along the direction of a small resonant rotating r.f. (radiofrequency) field H_1 , where H_1 can be varied from 3 to 30 gauss approximately. These fields correspond to measuring frequencies (for protons) in the range 13–130 kHz.

The copolymers used were similar to those employed in the dielectric measurements, i.e. they were unannealed. For the T_1 measurements, samples of suitable size were sealed off *in vacuo* in glass tubes, having been pumped after melting to remove oxygen and moisture. The 100% acid copolymer used for the $T_{1\rho}$ measurements was made from the same disc sample used in the dielectric work. In order to obtain a greater filling factor, the $T_{1\rho}$ samples were not enclosed in glass tubes but were made to fit the r.f. coil directly. This was necessary since the $T_{1\rho}$ decays were found to be non-exponential and as large a signal as possible was needed to allow their accurate

decomposition into two components. Care was needed in the case of the 53% ionised sample to exclude moisture which had been shown to have a large influence on the dielectric relaxation properties. It was possible to carry out measurements in a stream of dry nitrogen in the cryostat²¹ used with this apparatus.

Results

Dielectric

The variation of the dielectric loss tangent with frequency f (Hz) for the acid copolymer at 20° is shown in Fig. 2. The broad loss peak centred at a frequency of about $10^{1.8}$ Hz is labelled β' since it is correlated with the high temperature mechanical peak as seen below. At much higher frequencies the onset is observed of the γ -peak, which seems to approach a maximum in the vicinity of 10^8 Hz.

Fig. 3 shows plots of $\tan \delta$ against temperature for the acid copolymer at frequencies of 10^2 , 10^3 and 10^4 Hz. Both the high temperature (β') and low temperature (γ) peaks are again observed. The corresponding variation of ϵ' with temperature for the acid copolymer at two frequencies (10^2 and 10^4 Hz) is included in Fig. 4. The rather abrupt change in ϵ' in the vicinity of -95° may partly be due to the γ -relaxation but may also reflect some experimental artifact connected with the surface film of silicone grease.

Plots of $\log f$ against $1/T$, where T is the temperature of maximum $\tan \delta$ ($^\circ\text{K}$), are included in Fig. 5. This diagram also includes points derived from reported mechanical results

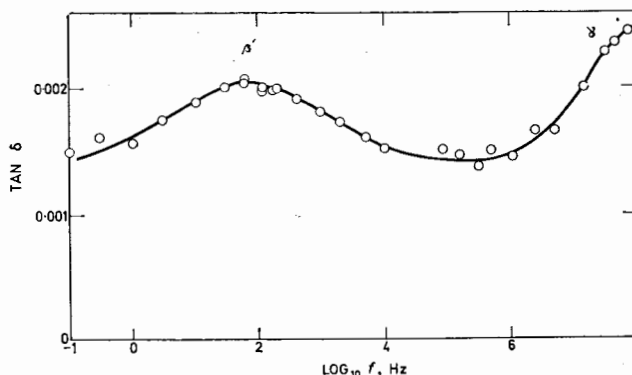


Fig. 2. Frequency dependence of the dielectric loss tangent for the acid copolymer at 20°C

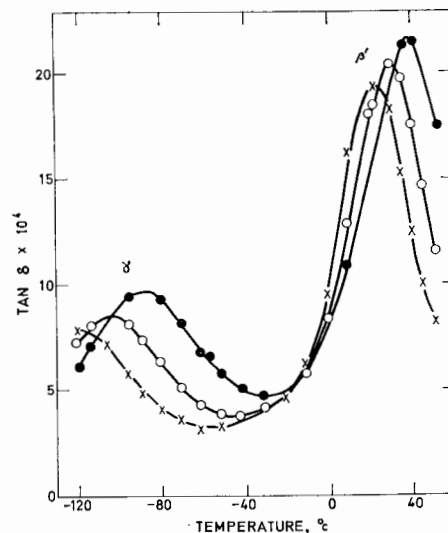


Fig. 3. Plots of the dielectric loss tangent against temperature for the acid copolymer at various frequencies

× 100 Hz; ○ 1 kHz; ● 10 kHz

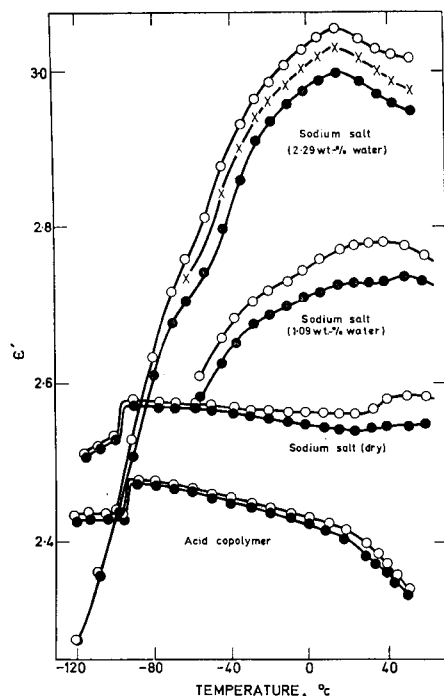


Fig. 4. ϵ' plotted against temperature for the acid copolymer, the dry partly ionized sodium salt and the sodium salts containing 1.09 and 2.29 wt.-% water
Frequencies: $\circ$ 100 Hz; $\times$ 1 kHz; $\bullet$ 10 kHz

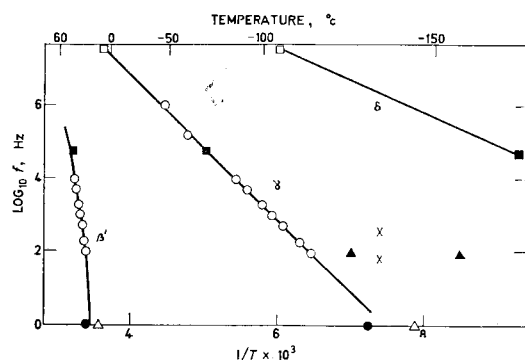


Fig. 5. Plots of $\log_{10} f$ against $1/T$ for the acid copolymer
 f is the measuring frequency (Hz) and T the temperature of maximum loss from mechanical and dielectric data or the temperature of minimum T_1 or $T_{1\rho}$ from n.m.r. data.
 $\circ$ $\tan \delta$ dielectric; $\bullet$ $\tan \delta$ mechanical; $\triangle$ G'' mechanical; $\blacktriangle$ E'' mechanical; $\square$ T_1 n.m.r.; $\blacksquare$ $T_{1\rho}$ n.m.r.
Also included are two n.m.r. points ($\times$) derived from the Slichter-Ailion theory

and the present magnetic relaxation data (see below). For the β' -relaxation, the dielectric frequency-temperature plot is only slightly curved over the limited frequency range so far covered and yields an activation energy (ΔE) of 56 kcal/mole. The frequency-temperature plot for the γ -relaxation is accurately linear over a wide frequency range and gives an activation energy of 8.9 kcal/mole.

The magnitude of each dielectric relaxation region may be represented by the respective values of $\epsilon_R - \epsilon_U$, where ϵ_R and ϵ_U are the relaxed (low frequency) and unrelaxed (high frequency) values of ϵ' . Values of $\epsilon_R - \epsilon_U$ were estimated from the areas ($\int_0^\infty \epsilon'' d(1/T)$) beneath plots of ϵ'' vs. reciprocal absolute temperature according to the equation:²²

$$(\epsilon_R - \epsilon_U)_{T_{\max}} = \frac{2\Delta E}{\pi R} \int_0^\infty \epsilon'' d(1/T) \quad \dots (3)$$

where $(\epsilon_R - \epsilon_U)_{T_{\max}}$ is the value of $\epsilon_R - \epsilon_U$ at the temperature corresponding to the loss maximum, and R is the gas constant. The values of $\epsilon_R - \epsilon_U$, estimated according to Equation (3), using the ΔE values quoted above, are shown in Fig. 6 and Table I.

From the $\epsilon_R - \epsilon_U$ values, ϵ_R and ϵ_U can then be estimated, assuming that $\epsilon' = (\epsilon_R + \epsilon_U)/2$ at the temperature of maximum ϵ'' . This assumption would seem reasonable for a symmetrical dispersion. Values of ϵ_R and ϵ_U calculated in this way are included in Table I.

From the estimated values of $\epsilon_R - \epsilon_U$, ϵ_R and ϵ_U values of $N\mu^2$ have been calculated, where N is the number of dipolar groups/cm³ and μ the dipole moment of each group. These calculations, in which it is assumed that the dipoles are sufficiently well spaced along the polymer chains

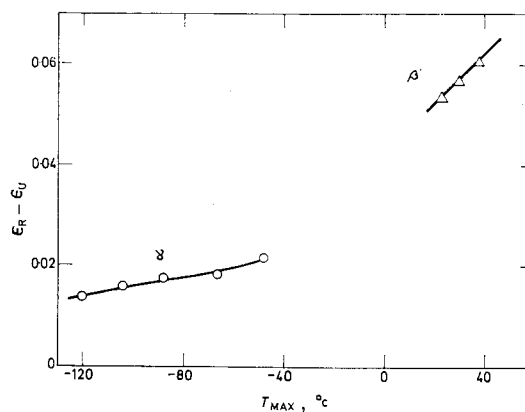


Fig. 6. Calculated values of $\epsilon_R - \epsilon_U$ from Equation (3) plotted against temperature for the β' - (Δ) and γ - ($\circ$) relaxations of the acid copolymer

TABLE I

Calculated values of $\epsilon_R - \epsilon_U$, ϵ_R , ϵ_U and $N\mu^2$ for the β' - and γ -relaxation regions of the acid copolymer

Relaxation region	Frequency, Hz	Temperature of $\epsilon''_{\max}$, °C	ϵ' at the temperature of $\epsilon''_{\max}$	$\epsilon_R - \epsilon_U$	ϵ_R	ϵ_U	$N\mu^2 \times 10^{16}$, ergs
β'	10^2	23	2.409	0.0535	2.436	2.382	2.426
β'	10^3	30	2.388	0.0569	2.417	2.360	2.673
β'	10^4	38	2.364	0.0610	2.394	2.333	2.968
γ	10^2	-120	2.478	0.0140	2.485	2.471	0.317
γ	10^3	-104	2.477	0.0158	2.484	2.469	0.395
γ	10^4	-88	2.472	0.0174	2.480	2.463	0.479
γ	10^5	-66	2.497	0.0180	2.506	2.488	0.548
γ	10^6	-48	2.528	0.0211	2.539	2.518	0.688

The absolute value of ϵ' could be determined to within $\pm 2\%$, but the variation in ϵ' with both frequency and temperature could be measured to within ± 0.001 .

for their orientation correlations to be negligible, involved the Onsager relation:¹⁴

$$N\mu^2 = \frac{3kT}{4\pi} \left(\frac{2\epsilon_R + \epsilon_U}{3\epsilon_R} \right) \left(\frac{3}{\epsilon_U + 2} \right)^2 (\epsilon_R - \epsilon_U) \dots (4)$$

in which k is Boltzmann's constant. The values of $N\mu^2$ for the acid copolymer calculated from Equation (4) are listed in Table I.

Fig. 7 shows the variation of $\tan \delta$ with temperature for the dry partly ionised sodium salt. Three loss regions are observed and these are labelled α , β and γ . In these temperature plots, the β -region is observed only as a shoulder to the intense α -peak. However, definite maxima are observed for the β -relaxation in plots of $\tan \delta$ against frequency at temperatures between -5° and 40° . These frequency maxima have been used in constructing the frequency-temperature diagram for the β -relaxation in Fig. 8. The frequency-

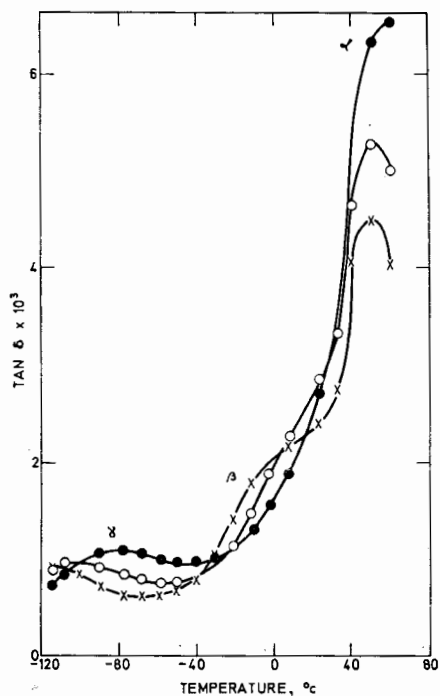


Fig. 7. Plots of the dielectric loss tangent against temperature for the dry 53% ionised copolymer at various frequencies
× 100 Hz; ○ 1 kHz; ● 10 kHz

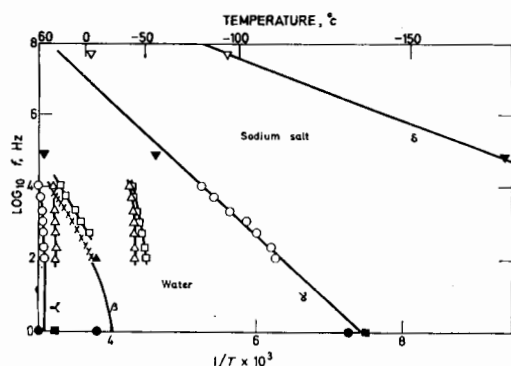


Fig. 8. Plots of $\log_{10} f$ against $1/T$ for the 53% ionised sodium salt
○, × $\tan \delta$ dielectric; ● $\tan \delta$ mechanical;^{1,5} ■ G'' mechanical;^{5,10} ▲ E'' mechanical;⁸ ▽ T_1 n.m.r.; ▼ $T_{1\rho}$ n.m.r.; △ ($\tan \delta$ dielectric (1.09 wt. % water); □ $\tan \delta$ dielectric (2.29 wt. % water). Except where stated the points refer to measurements on the dry sample. The symbol × corresponds to the frequency of maximum $\tan \delta$ in constant temperature experiments. All other points denote the temperatures of maximum loss or minimum T_1 or $T_{1\rho}$ in constant frequency experiments.

temperature plots for the α - and γ -regions in Fig. 8 correspond to temperatures of maximum $\tan \delta$ from Fig. 7. For the α -relaxation the frequency-temperature plot is curved, corresponding to an apparent activation energy which increases with decreasing temperature. The frequency-temperature diagram for the β -relaxation is also slightly curved. For the γ -relaxation the frequency-temperature plot is again linear, the derived activation energy being 8.3 kcal/mole.

Plots of $\tan \delta$ against temperature are shown in Fig. 9 for the partly ionised copolymer containing 1.09 wt. % water. In addition to the α -, β - and γ -regions, an additional peak is observed due to water at about -40° , which is labelled the 'water peak'. Fig. 10 shows that this peak is enhanced when the water content is increased to 2.29 wt. %. The water absorption also causes a marked increase in ϵ' values, in the temperature region of the water relaxation (Fig. 4). At lower temperatures, however, ϵ' appears to decrease with water absorption, but it is not yet certain whether this effect is due to the polymer, or due to some experimental artifact such as the silicone grease, as mentioned above. The frequency-temperature plots for the two water-containing samples are included in Fig. 8. This diagram (and Figs 9 and 10) shows that the α -relaxation is moved to lower temperatures (plasticised) and its apparent activation energy has been decreased by the water absorption. The magnitude of the α -peak, however, seems unchanged. Fig. 10 also illustrates that the water peak is only slightly shifted to lower temperatures with increased water content. The frequency-temperature plots for the water relaxation are slightly curved and give high apparent activation energies (ΔE_a). Values of ΔE_a are quoted in Table II. Table II also lists values of $\epsilon_R - \epsilon_U$, ϵ_R , ϵ_U and $N\mu^2$ for the water relaxation, estimated with the aid of Equations (3) and (4).

Magnetic relaxation

The T_1 and $T_{1\rho}$ data for the dry acid copolymer are shown in Fig. 11 as a function of temperature. The $T_{1\rho}$ measurements were made at two different values of the r.f. field H_1 ,

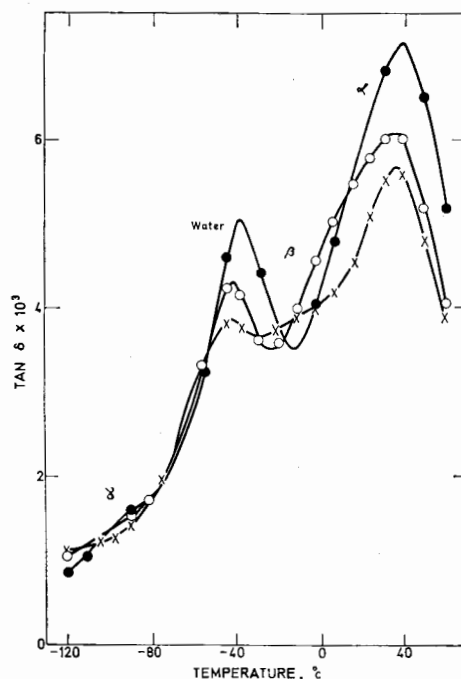


Fig. 9. Plots of the dielectric loss tangent against temperature for the partly ionised sodium salt containing 1.09 wt. % water
Frequencies: × 100 Hz; ○ 1 kHz; ● 10 kHz

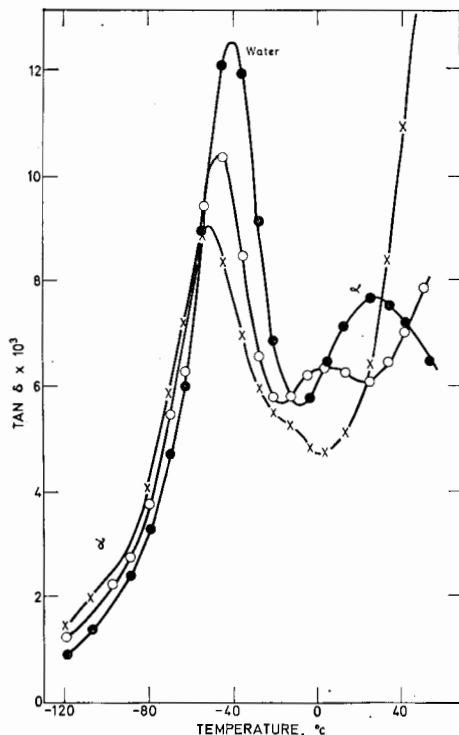


Fig. 10. Plots for the dielectric loss tangent against temperature for the 53% ionised sodium salt containing 2.29 wt.% water
Frequencies: $\times$ 100 Hz; $\circ$ 1 kHz; $\bullet$ 10 kHz

corresponding to measuring frequencies of 59 kHz and 20 kHz. Similar data for the dry partly ionised sodium salt are shown in Fig. 12 which shows $T_{1\rho}$ measurements for one value of H_1 only, i.e. 25.5 kHz. In both cases it was found for the T_1 measurements that the decay of magnetisation was exponential and could be described by a single time constant. For the $T_{1\rho}$ measurements the magnetisation decay was non-exponential, and the decay curves were fitted by an expression which is the sum of two exponential decays, as described previously.²⁰ This results in the derivation of three parameters at each temperature, $T_{1\rho}^L$ and $T_{1\rho}^S$, the time constants for the long and short relaxation time components, and the ratio of the magnetisations associated with these components.

Figs 11 and 12 show a number of well-defined features. There are minima in both T_1 curves at $\sim 0^\circ$, whilst the $T_{1\rho}$ curves all show three distinct minima. Also in the T_1 data there are points of inflexion at $\sim -100^\circ$ which indicate the presence of a weak molecular motion superimposed on a stronger process. From the positions of these minima and points of inflexion, molecular correlation times have been derived using the Bloembergen, Purcell & Pound (BPP) theory

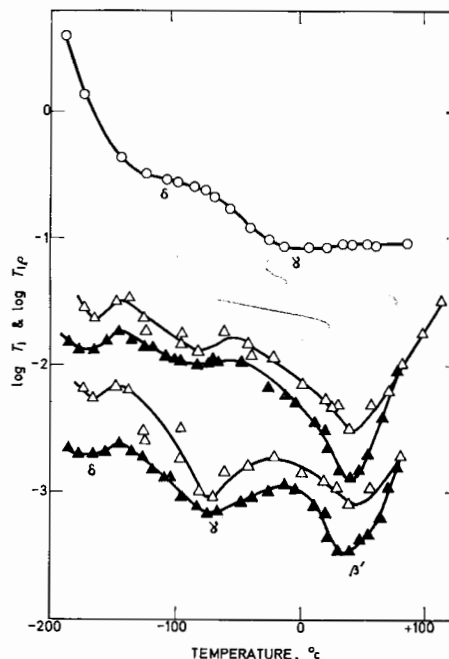


Fig. 11. Temperature dependence of T_1 ($\circ$) and $T_{1\rho}$ (Δ , $\blacktriangle$) for the acid copolymer
Effective measuring frequencies are 30 MHz for T_1 ($\circ$) and 59 kHz (Δ) and 20 kHz ($\blacktriangle$) for $T_{1\rho}$

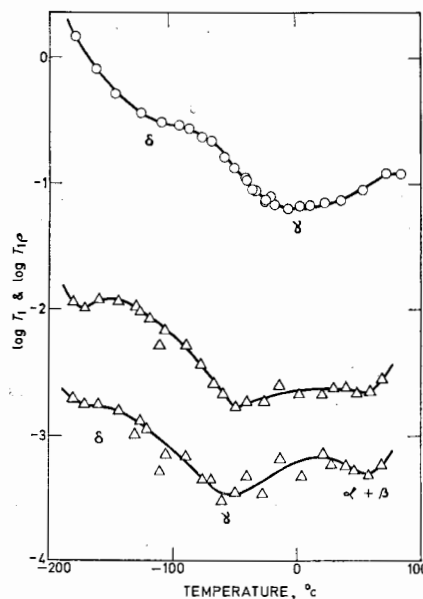


Fig. 12. Temperature dependence of T_1 and $T_{1\rho}$ for the partly ionised sodium salt
Measuring frequencies are 30 MHz for T_1 ($\circ$) and 25.5 kHz for $T_{1\rho}$ (Δ)

TABLE II

Calculated values of ΔE_a , $\epsilon_R - \epsilon_U$, ϵ_R , ϵ_U and $N\mu^2$ for the 'water relaxation' of the partly ionised copolymer

Water, wt. %	Frequency, Hz	Temperature of $\epsilon''_{\max}$	ΔE_a , kcal/mole	ϵ' at the temperature of $\epsilon''_{\max}$	$\epsilon_R - \epsilon_U$	ϵ_R	ϵ_U	$N\mu^2 \times 10^{15}$, ergs
2.29	10^2	-49.9	50.6	2.840	0.5898	3.135	2.545	1.770
2.29	10^3	-45.0	47.3	2.830	0.5861	3.129	2.543	1.800
2.29	10^4	-39.6	42.0	2.829	0.5334	3.096	2.562	1.672
1.09	10^4	-39.4	42.0	2.647	0.1961	2.745	2.549	0.640

in the laboratory and rotating frames as described previously.²⁰ Also some correlation times were derived for the acid copolymer at -138° using the Slichter-Ailion strong collision theory, but this does not seem a reliable procedure in this instance because of the overlap of the various molecular motions. The correlation frequencies are compared in Figs 5 and 8 with the results from dielectric and mechanical measurements.

For the acid copolymer, the process giving rise to the highest temperature $T_{1\rho}$ minimum correlates with the dielectric and mechanical β' -process, whilst the process corresponding to the T_1 minimum at -80° correlates with the γ -process (see Fig. 5). The point of inflexion in the T_1 data at about -100° and the low temperature $T_{1\rho}$ minimum at -165° (Fig. 11) correspond to a process which has not been observed in the dielectric or mechanical data. This latter process is labelled δ in Figs 5 and 11.

For the 53% ionised sample, the highest temperature $T_{1\rho}$ minimum at 53° falls in a region which coincides with the extrapolations of the mechanical and dielectric α - and β -processes (Fig. 5). A correlation is again observed between the n.m.r. data and the dielectric and mechanical γ -process. This correlation is not as good as in the case of the acid copolymer, the $T_{1\rho}$ point lying below and the T_1 point above the extrapolated dielectric plot. The lowest temperature (δ) process giving rise to the $T_{1\rho}$ minimum and T_1 inflexion point correlates with that observed for the acid copolymer. For both polymers an activation energy of about 3.1 kcal/mole is obtained.

Discussion

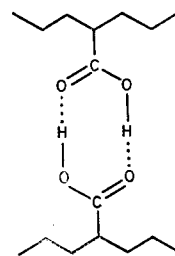
β' -Relaxation

As seen in Fig. 5, the β' -relaxation for the acid copolymer is observed by the mechanical, dielectric and n.m.r. methods. This result suggests that both hydrocarbon (proton containing) segments and dipolar groups are involved in the motional processes. The dielectric process is characterised by a broad loss peak (Fig. 2), a high apparent activation energy (56 kcal/mole) and a slightly curved plot of $\log f$ against $1/T_{\max}$ (Fig. 5). These results indicate long range micro-brownian chain motions associated with the glass transition in the polymer, and thus support the earlier assignments.^{5,8,10} However, the two components observed in $T_{1\rho}$ (Fig. 11) suggest that, in addition to amorphous-phase motions, some motion within the crystal phase may also be involved in the n.m.r. and mechanical processes. The latter result is consistent with the observed splitting of the high temperature mechanical peak after annealing.⁵

In discussing the possible nature of the dipolar species which enable the β' -relaxation to be detected dielectrically, the total number (N_t) of carboxylic acid groups/cm³ is first calculated. This is given by:

$$N_t = N_A \rho / M \quad \dots (5)$$

where N_A is Avogadro's number, ρ is the polymer density and M the molecular weight of the chain segment containing 24 ethylene units and one methacrylic acid unit (i.e. 4 mole% acid units). Taking $\rho = 0.92$ g/cm³ and $M = 758$ gives $N_t = 7.31 \times 10^{20}$ groups/cm³. From dielectric studies on low molecular weight carboxylic acids, the dipole moment of the $-\text{COOH}$ group is reported²³ to be 1.7D. Using this value for μ and the above N_t value, gives $N_t \mu^2 = 2.03 \times 10^{-15}$ ergs, which is much higher than the experimental value of $N_t \mu^2$ in Table I. This result is not surprising since infra-red evidence² shows that the carboxylic acid groups are largely hydrogen bonded together at the temperatures studied. Furthermore, a monomer-dimer equilibrium of the acid groups has been proposed,² where the interchain acid dimers are of the form:



These hydrogen bonded dimers have symmetrical, non-polar, structures which would not be expected to contribute to the dielectric relaxation. However, the small number of dissociated acid groups (monomers) in equilibrium with the dimers are dipolar and could contribute to the dielectric β' -process. This suggestion is consistent with the observed increase in $\epsilon_R - \epsilon_U$ and $N_t \mu^2$ with increasing temperature (Fig. 6 and Table I), since the number of 'free' acid groups similarly increases with temperature. The number (N_f) of free acid groups/cm³ can be estimated as follows. From infra-red results² the dissociation constant K for the acid monomer-dimer equilibrium can be calculated. This may be defined by:

$$K = [\text{COOH}]^2 / [(\text{COOH})_2] \quad \dots (6)$$

where $[\text{COOH}]$ and $[(\text{COOH})_2]$ are the concentrations in groups/cm³ of acid monomers and dimers respectively. It follows that:

$$N_t = 2[(\text{COOH})_2] + [\text{COOH}] \\ = \frac{2}{K} N_f^2 + N_f \quad \dots (7)$$

$$\text{Hence } N_f = \frac{K}{4} \left[-1 \pm \left(1 + \frac{8N_t}{K} \right)^{1/2} \right] \\ \text{or } N_f \sim \left(\frac{KN_t}{2} \right)^{1/2} \quad \dots (8)$$

Table III lists the values of N_f calculated from Equation (8) using values of K (in molecules/cm³) taken from reference 2. Also included in Table III are the values of $N_f \mu^2$ using $\mu = 1.7\text{D}$. The values of $N_f \mu^2$ can only account for about 8–11% of the experimental $N_t \mu^2$ values in Table I. It thus appears that some other dipolar groups must be involved. These could be either longer hydrogen bonded structures, such as carboxylic acid trimers and tetramers, which could be quite highly polar²³ and which may not be discounted from the infra-red evidence, or residual carbonyl groups in the polymer chain due to oxidation. Preliminary estimates suggest that 0.2–0.4 mole% carbonyl groups could account for the observed dielectric relaxation magnitude. Further dielectric studies on the acid copolymers, in which the acid content is varied, should help to resolve this question.

γ -Relaxation

As mentioned earlier, the low temperature mechanical γ -peak has been resolved into two components by annealing, and these have been labelled γ_e (low temperature component) and γ_a (high temperature component). This resolution is

TABLE III
Calculated values of N_f and $N_f \mu^2$ for the acid copolymer

Temperature, °C	$N_f \times 10^{-18}$, groups/cm ³	$N_f \mu^2 \times 10^{17}$, ergs
23	6.73	1.95
30	8.42	2.43
38	10.90	3.14

consistent with the observation of two components in the n.m.r. $T_{1\rho}$ (Fig. 11). Furthermore, the two n.m.r. points in Fig. 5 derived by the Slichter-Ailion method correlate roughly with the two mechanical points at about 100 Hz. This correlation suggests that the minima observed in $T_{1\rho}^S$ and $T_{1\rho}^L$ are associated with the γ_c - and γ_a -components respectively, and shows that each component involves motions of proton-containing (hydrocarbon) segments. The mechanical γ_c -component has been ascribed to motions of defects within the crystal phase and a similar mechanism would seem reasonable for $T_{1\rho}^S$.

However, previous $T_{1\rho}$ measurements²⁰ which have been resolved into two separate components suggest that $T_{1\rho}^L$ should be associated with the crystalline regions and $T_{1\rho}^S$ with the amorphous (or mobile) regions, i.e. in contradiction to the above assignment. This probably applies to polyethylene^{24,25} and polyethylene oxides²⁶ which are both more highly crystalline polymers than those considered here and may therefore exhibit different behaviour. However, in all these cases the assignments of the $T_{1\rho}$ components are only tentative. It might be supposed that this difficulty could be resolved by observing the behaviour of the fractions of magnetisation associated with the two components as a function of temperature, since the fractional mobile region magnetisation, p_m , should increase with temperature.²⁰ It is found that the magnetisation associated with $T_{1\rho}^S$ does do this both for the acid and ionic forms of the copolymer until a temperature of -130° is reached. This is consistent with an assignment to a mobile fraction and is at variance with the above assignment. However, at higher temperatures the behaviour is anomalous, since p_m apparently decreases with increasing temperature until a temperature of $\sim 0^\circ$ is reached after which it increases again. The fractional magnetisation measurements are thus open to question in this and other instances.²⁶ This probably results from the fact that in the present experimental arrangement, the magnetisation is not measured immediately after the r.f. pulse but at some fixed arbitrary time later ($\sim 8 \mu\text{sec}$) due to the blocking of the receiver by the intense r.f. pulse. Steps are being taken to remedy this situation so as to allow more realistic relative magnetisation measurements.

Whilst the appearance of two components in the $T_{1\rho}$ data is in general agreement with the observation of two components in the mechanical measurements, the precise form of $T_{1\rho}$ curves calls for comment. It will be observed from Figs 11 and 12 that minima apparently occur in $T_{1\rho}^L$ and $T_{1\rho}^S$ at similar temperatures both for the γ -process and for the other molecular motions. In view of the clear separation of the two mechanical γ -components, this is perhaps surprising, even allowing for the higher frequency of the n.m.r. measurements. The fact that the behaviour of the two $T_{1\rho}$ components is similar may be connected^{20,24} with the possibility of a spin-diffusion mechanism which results in the transfer of magnetisation from one morphological region to another. It is thought that under certain conditions such a transfer may result in the motional behaviour of one phase being reflected in the relaxation behaviour of another and thereby causing one $T_{1\rho}$ component to 'follow' the other.

Fig. 5 indicates that the dielectric γ -process correlates more closely with the mechanical γ_a -component than with the γ_c -component. The γ_a -process has been ascribed to local motions of methylene sequences in the amorphous phase, a mechanism in which neither acid nor salt groups participate.¹¹ This is supported by the observations that both the magnitude (compare Figs 3 and 7) and location (compare Figs 5 and 8) of the dielectric γ -relaxation are unchanged when the carboxylic acid groups are partly ionised. The location and activation energy (8.9 kcal/mole) of the γ -process is also similar to that observed for many polymers containing linear methylene sequences.¹⁴ The dipolar groups which render the

γ -process dielectrically active are not known at present, although they could be carbonyl groups on the methylene chain sequences formed by thermal oxidation.

δ -Relaxation

The lowest temperature (δ) process has been observed only in the n.m.r. results and has an activation energy of about 3.1 kcal/mole. These features suggest that the process may be associated with the rotations of CH_3 groups present in the methacrylic acid units. Although these methyl groups account for only about 3% of the protons present in the copolymers, previous measurements on branched polyethylenes²⁴ and polyethylene oxides with $\text{O}-\text{CH}_3$ end groups²⁷ have shown that CH_3 groups in these small amounts can yield significant minima in T_1 and $T_{1\rho}$. This comes about through a spin-diffusion mechanism similar to that mentioned in the discussion of the γ -process. In this case the process is much more clearly defined, since the magnetisation diffuses along the polymer chain until it reaches the neighbourhood of a CH_3 group which provides a reasonably efficient coupling with the 'lattice', because it is rotating at a frequency comparable to the proton Larmor frequency. The activation energy for this process in these copolymers is slightly lower than the activation energies for the main chain CH_3 group re-orientations in isotactic (3.7 kcal/mole) and syndiotactic (5.4 kcal/mole) polymethyl methacrylate.²⁸ This is not surprising in view of the higher steric hindrance expected for the methacrylate polymer chains.

α - and β -relaxations

For the partly ionised sodium salt, the dielectric loss peak observed at temperatures above room temperature (Fig. 7) consists of the main α -peak and a shoulder on the low temperature side, designated β . The dielectric α - and β -peaks correlate with the corresponding mechanical α - and β -peaks as illustrated by the frequency-temperature diagram in Fig. 5.

On the basis of the three-phase model for the ionised copolymers, consisting of ionic domains and polyethylene crystallites in an amorphous polyethylene matrix, the β -relaxation has been assigned to long-range motions of branched-chain segments in the amorphous polyethylene phase.¹⁰ This process is associated with the glass transition in branched polyethylene. The curvature of the frequency-temperature plot for the β -relaxation (Fig. 8) is further evidence in favour of a glass transition mechanism. The motions could be rendered dielectrically active by acid or extraneous carbonyl groups in the amorphous polyethylene phase.

As mentioned earlier, the mechanical α -process has been attributed to a glass transition in the proposed ionic domains.¹⁰ The relatively high magnitude of the dielectric α -peak, compared with the peak heights observed for the acid copolymer, suggests that ionic groups may, in fact, be involved. The glass transition assignment is also supported by the strong curvature of the frequency-temperature plot in Fig. 8 and the shift of the α -peak to lower temperature (plasticisation) after the absorption of water (see Figs 7, 8, 9 and 10). The marked increase in height of the dielectric α -peak with increasing frequency (or temperature) may partly be due to increased merging of the α - and β -peaks. In addition, it might suggest some local ordering within the ionic phase since a similar effect has been observed by Saito & Nakajima²⁹ in the glass-transition regions of several crystallisable polymers (the so-called dielectric transitions). The latter suggestion is consistent with the observation of the low-angle X-ray peak for the ionised copolymers.⁶

Fig. 8 illustrates that the highest temperature minimum in $T_{1\rho}$ for the sodium salt is located in a region where the

extrapolated dielectric α - and β -plots merge. It is not certain whether this relaxation correlates with the dielectric α -relaxation or the β -relaxation or both. There is some tendency for the n.m.r. point to lie closer to the extrapolated curve for the β region, a result which would support the above assignments of the α - and β -processes. Measurements, on more highly ionised samples, where the α -relaxation would be moved to higher temperatures,⁵ and an extension of the n.m.r. data to lower frequencies, should help to resolve this problem.

Water relaxation

The capacity for water absorption is far greater for the partly ionised sodium salts than for the original acid copolymer.¹² From this result it appears that the absorbed water resides in the ionic regions of the polymer. Wilson *et al.*⁶ have proposed that the water molecules compete with the carboxylates in co-ordinating with the sodium ions in the proposed ionic phase. For the sample containing 2.29 wt. % water in the present work, the water absorption had attained equilibrium saturation. This quantity of water corresponds to two water molecules per sodium ion.

Figs 9 and 10 show that, in addition to the plasticising effect on the α -peak, the presence of water in the sodium salts causes the appearance of a new dielectric peak in the vicinity

of -40° to -50° . The magnitude of the peak is approximately proportional to the water content, but the temperature of the peak is only slightly lowered with increasing water content (see Figs 8, 9 and 10). Fig. 4 shows that the ϵ' values are also increased by the water and that the dispersion magnitude in the region of the water relaxation is roughly proportional to water content. From the calculated values of $N\mu^2$ listed in Table II a dipole moment of about 1.5D has been estimated for the moving group, which compares with a value of 1.8D for the water molecule.³⁰ The above results indicate that water molecules are directly participating in the relaxation process, which might involve the rotation of water molecules within the ionic cage or the motions of ionic carboxylate ions to which water molecules are hydrogen bonded. The present results are similar to those observed for the polyamides, although the apparent activation energy for the water relaxation (42–51 kcal/mole) is appreciably higher than that (13 kcal/mole) found for the polyamide water relaxation.¹⁴

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