Dielectric relaxations in poly(hydroxyethyl acrylate): influence of the absorbed water

J. L. Gómez Ribelles, J. M. Meseguer Dueñas and M. Monleón Pradas
Laboratory of Thermodynamics and Physical Chemistry, Universidad Politécnica de Valencia, PO Box 22012, 46071 Valencia, Spain
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Poly(hydroxyethyl acrylate) presents two relaxation zones, labelled γ and α, when it is completely dry. The temperature of the maximum of the γ relaxation, as well as its apparent activation energy, are somewhat higher than in poly(hydroxyethyl methacrylate), a fact that could be explained by higher intermolecular interactions in the series of polyacrylates than in the series of polymethacrylates. The absorption of even slight traces of water causes a new relaxation to appear, the intensity of which increases with the content of water, while at the same time the intensity of the γ relaxation decreases. This fact suggests the formation of an association of the water molecules with the side groups of the polymer. The characterization of the α relaxation is difficult because of the high d.c. conductivity component of the permittivity. Its temperature suggests the presence of hydrogen bonds which render the main chains rigid.

(Keywords: poly(hydroxyethyl acrylate); dielectric relaxation; water sorption)

INTRODUCTION

Poly(hydroxyethyl acrylate) is a highly hydrophilic polymer. It differs from poly(hydroxyethyl methacrylate) in not having the methyl group in the main chain. The dielectric secondary relaxations of this last polymer have been thoroughly studied, and its relaxation spectrum serves as a reference for the study of that of poly(hydroxyethyl acrylate).

EXPERIMENTAL

The samples were obtained by radical block polymerization at 60°C of monomer (Merck), which had previously been distilled at low pressure in order to remove the inhibitor. Azobisisobutyronitrile (0.05% by weight) was employed as initiator of the polymerization. No crosslinking agent was used. After polymerization the sample was held in a vacuum at 70°C until constant weight. The same sample was employed for all the tests. Addition of water was achieved by leaving the sample in ambient conditions until it reached the weight gain corresponding to the desired water content. The sample was then isolated until the time of the measurements. A small portion of the dry sample was subjected to a thermogravimetric analysis with a Du Pont Thermogravimetric Analyzer 951 in nitrogen atmosphere. No loss of weight due to volatile substances (monomer or trace water) was detected at temperatures below 250°C, when degradation of the polymer starts.

The measurements were performed on a General Radio capacitor bridge keeping the measuring cell in a dry atmosphere, for frequencies ranging from 60 to 100 kHz.

RESULTS AND DISCUSSION

The dielectric relaxation spectrum of the dry polymer shows only two relaxation zones: a secondary one, in the temperature range between -150 and 0°C, and the α relaxation zone, associated with the glass transition, between 35 and 58°C, for frequencies ranging from 60 Hz to 100 kHz. By analogy with the spectrum of the poly(hydroxyethyl methacrylate) (PHEMA) the secondary relaxation is attributed to local movements in the lateral group CH_2–CH_2–OH, and will be labelled γ hereafter, following the literature concerning PHEMA[1-5].

γ relaxation in the dry polymer

Figure 1 displays the values of the imaginary part of the complex dielectric permittivity ε'' as a function of the frequency for temperatures ranging from -140 to -9°C. The maxima corresponding to the γ relaxation are somewhat shifted towards lower frequencies when compared with those of PHEMA[1,5,6] or, what amounts to the same, the maxima of the curves of ε'' as a function of temperature are shifted towards higher temperatures. Also, the apparent activation energy found for the PHEA, 13.5 kcal mol^{-1}, is somewhat greater than that measured for PHEMA (between 9 and 10 kcal mol^{-1} (refs. 1 and 6); ref. 5 gives values of 15 to 16 kcal mol^{-1}, but these are calculated following a different method).

Something similar happens with the γ relaxation of poly(propyl acrylate)[7] (PPA) and poly(butyl acrylate)[8] (PBA), whose apparent activation energy is 7 kcal mol^{-1}, when compared with that of poly(propyl methacrylate) (PPMA) and poly(butyl methacrylate) (PBMA), which have the lower value of 5.5 kcal mol^{-1} (refs. 9 and 10).

If the potential barrier which causes the relaxation were due only to intramolecular interactions, without any influence of the environment, it would be difficult to account for these differences. Nevertheless, studies of molecular dynamics[11,12] have shown that the intramolecular interactions can account for only about 50% of the value of the apparent activation energy of the β relaxation in poly(methyl methacrylate) (PMMA) when this last is assumed to originate in the rotation of the

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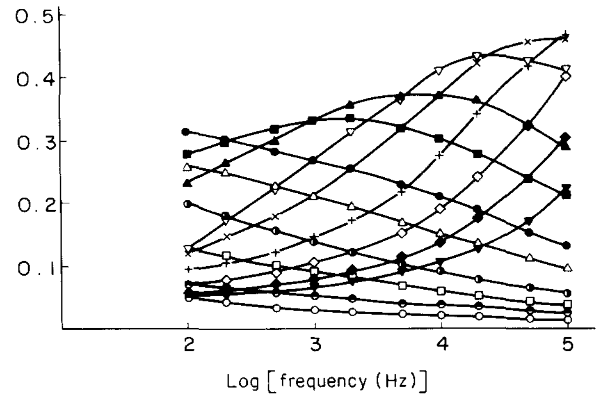

Figure 1 Curves of ε'' as a function of frequency for dry PHEA in the temperature range of the γ relaxation. ○, −140.1°C; ◓, −129.3°C; □, −118.8°C; ◑, −108.7°C; △, −98.7°C; ●, −88.6°C; ■, −78.9°C; ▲, −68.9°C; ▽, −58.8°C; ×, −49.0°C; +, −38.9°C; ◇, −28.6°C; ◆, −18.8°C; ▼, −8.7°C

carboxymethyl group around the bond with the main chain, so that environmental effects, modelled by fixing angles and distances between carbons in the main chain, could be responsible for the remainder. In poly(methyl acrylate) (PMA) intramolecular potential barriers explain only 20% of the value of the apparent activation energy of the β relaxation found by mechanical or dielectrical means: Heijboer[11] has calculated a value of 2.1 kcal mol^{-1} whereas we have found a value between 12 and 14 kcal mol^{-1} with both mechanical and dielectrical measurements. This means that, in PMA, intermolecular interactions are more important, possibly due to the tighter packing of molecular chains. Thus, PMMA with a density of 1.23 g cm^{-3} (ref. 13) has 7.4×10^{21} monomeric units cm^{-3}, whereas PMA, with a density of 1.22 g cm^{-3} (ref. 14), has 8.5×10^{21} monomeric units cm^{-3}.

The increment in the activation energy of the γ peak of the polyacrylates with respect to the polymethacrylates can originate also in an increased intermolecular interaction due to the decreased mean distance between chains: the PHEA employed in this work had a density of 1.32 g cm^{-3} determined by means of a picnometer, which corresponds to a value of 6.3×10^{21} monomeric units cm^{-3}, whereas in PHEMA with a density of 1.25 g cm^{-3} (ref. 1) there are 5.7×10^{21} monomeric units cm^{-3}.

The shape of the relaxation has been adjusted to the model of Fuoss and Kirkwood[15],

$$\frac{\varepsilon''}{\varepsilon''_{\max}} = \operatorname{sech} m \ln \frac{\omega}{\omega_{\max}} \qquad (1)$$

Table 1 gives the values of the form parameter m as a function of the temperature.

Influence of the absorbed water on the secondary relaxations

Similarly to what happens to the mechanical γ relaxation in PHEMA, the addition of water produces a new relaxation, labelled β_{sw}, at higher temperatures than the γ relaxation. The position, intensity and apparent activation energy of the β_{sw} relaxation depend strongly upon the water concentration in the polymer.

Figure 2 shows clearly how the height of the β_{sw} relaxation increases with the molar fraction of water in the sample, and how at the same time the height of the γ relaxation diminishes. The intensity of each of the two relaxations γ and β_{sw} cannot be determined separately with enough precision, but the intensity of both relaxations jointly can, with the help of Cole–Cole arcs. *Figure 3* shows some examples of these diagrams. As seen on this figure, the value of ε_∞ is reasonably constant at 2.9, independently of temperature and water content. For temperatures where ε_∞ cannot be determined accurately enough the extrapolated value of 2.9 has been employed in the calculation of $\Delta\varepsilon$. *Figure 4* shows $\Delta\varepsilon_{\beta_{sw}+\gamma}$ as a function of the molar fraction of water in the sample.

The fact that the γ relaxation decreases while the height of the β_{sw} relaxation increases suggests, following the interpretation of Janáček *et al.*[2–4] for the mechanical measurements on PHEMA, that there is a form of association of the water molecules with the polar groups of the side chains, in such a way that the internal motions in the group resulting from this association are further hindered, producing a different relaxation. There is no linear relationship between the joint intensity of both relaxations and the molar fraction of water. Probably not all the water molecules present associate with the lateral groups.

In *Figure 2* it is observed that for water concentrations higher than 13% the curve of ε'' versus T starts to increase rapidly at temperatures above −40°C. This can be attributed to a significant increase of the conductivity due to the presence of free ions. The contribution of the d.c. conductivity to the permittivity can provoke a faster increase in the intensity of the relaxation for water concentrations higher than 21% than the increase it would have if the relaxation had a purely dipolar nature.

The curve in *Figure 4* for water concentration less than 21% is very similar to that found for the height of the

Table 1 Values of the form parameter m of equation (1) as a function of temperature

T (°C)	m
−78.9	0.26
−68.9	0.28
−58.8	0.30

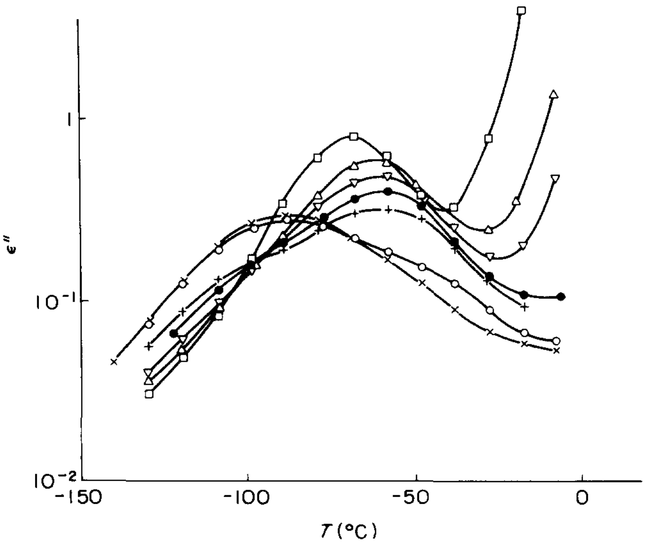

Figure 2 Values of ε'' as a function of temperature at 100 Hz for the γ and β_{sw} relaxation of dry PHEA (×) and with water molar fraction of 0.02 (○), 0.07 (+), 0.13 (●), 0.21 (▽), 0.28 (△), 0.44 (□)

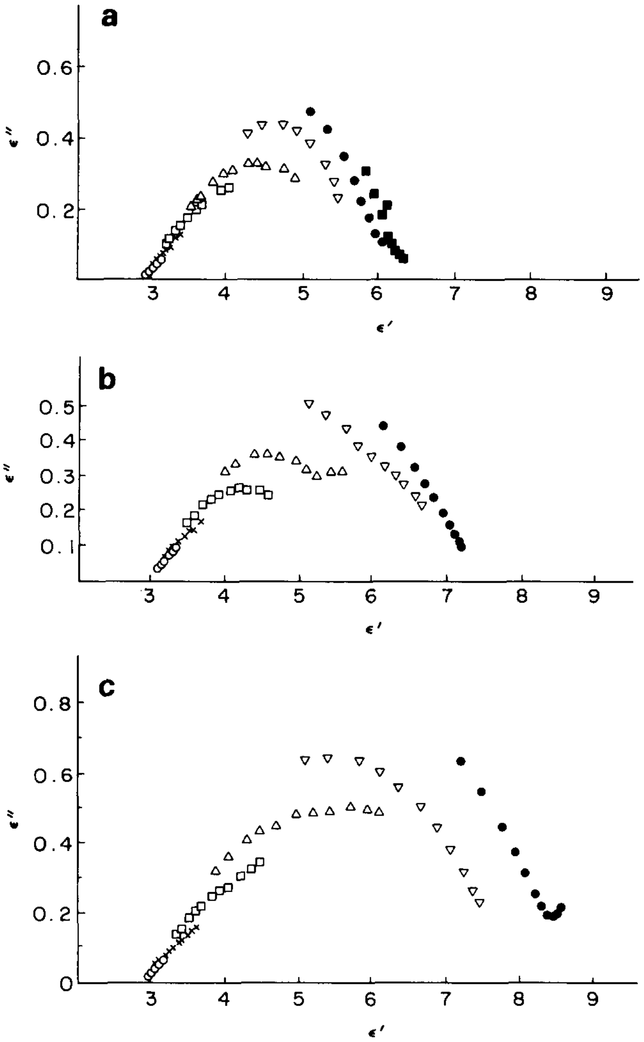

Figure 3 (a) Cole–Cole arcs for dry PHEA at −140.1°C (○), −118.8°C (×), −98.7 (□), −78.9 (△), −58.8 (▽), −38.9 (●), −18.8 (■). (b) Cole–Cole arcs for PHEA with molar fraction of water of 0.07 at −118.6°C (○), −98.0°C (×), −78.7°C (□), −59.0°C (△), −38.6°C (▽), −17.7°C (●). (c) Cole–Cole arcs for PHEA with molar fraction of water of 0.21 at −119.5°C (○), −99.0°C (×), −79.5°C (□), −59.1°C (△), −39.8°C (▽), −18.5°C (●)

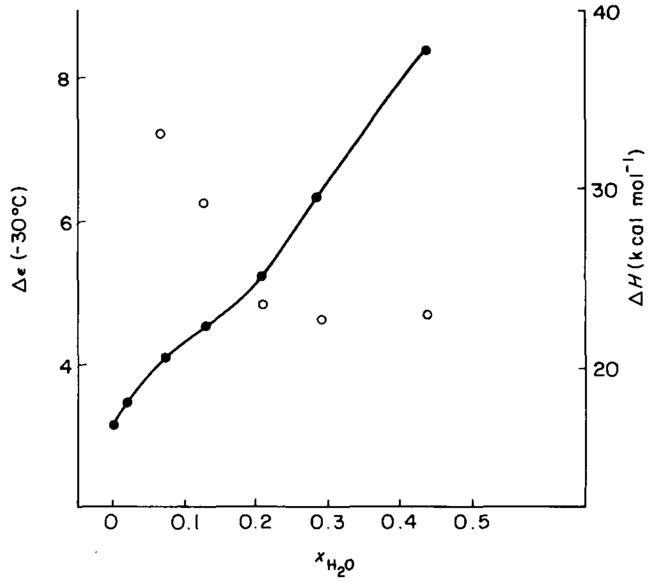

Figure 4 Intensity of the γ and β_{sw} relaxation zones at −30°C (●) and apparent activation energy (○) as a function of the molar fraction of water in the sample

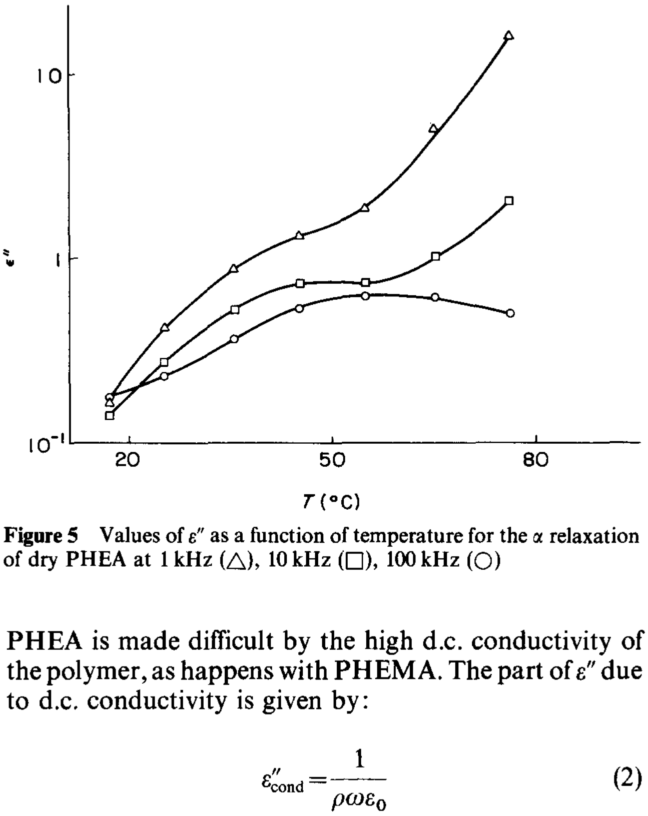

Figure 5 Values of ε'' as a function of temperature for the α relaxation of dry PHEA at 1 kHz (△), 10 kHz (□), 100 kHz (○)

maximum of the modulus G'' in the β_{sw} mechanical relaxation of PHEMA[3]. The apparent activation energy of the β_{sw} relaxation decreases when the water molar fraction increases until $x=0.25$, from then on being almost constant with a value of about 23 kcal mol^{-1}.

By extrapolation, a value of about 37 kcal mol^{-1} could be given as the limit of the apparent activation energy when the water content tends to zero.

The fact that the apparent activation energy of the β_{sw} relaxation is always greater than that of the γ relaxation is indicative of the association of the water molecules with the lateral group of PHEA, forming a new molecular group with internal mobility further impeded. Janáček and Kolarik[3,4] suggested for PHEMA the linking of two lateral groups through water molecules by hydrogen bonds; nevertheless, such a hypothesis cannot be confirmed by our results.

We cannot yet propose a hypothesis that explains the change in slope of the apparent activation energy at a water molar fraction of 0.25.

α relaxation

The characterization of the dielectric α relaxation in PHEA is made difficult by the high d.c. conductivity of the polymer, as happens with PHEMA. The part of ε'' due to d.c. conductivity is given by:

$$\varepsilon''_{\mathrm{cond}} = \frac{1}{\rho\omega\varepsilon_0} \qquad (2)$$

where ρ is the resistivity, which increases exponentially with temperature, ω is the angular frequency of the applied field, and ε_0 is the dielectric permittivity of the vacuum. Thus, $\log \varepsilon''_{\mathrm{cond}}$ increases linearly with temperature at constant frequency. With small traces of water $\varepsilon''_{\mathrm{cond}}$ takes values much higher than the part of ε'' caused by the dipolar relaxation in the temperature range where the α relaxation occurs, so that the latter is not perceptible except in cases where one is very careful in drying the sample. Thus, in the case of PHEMA, some works show the α relaxation but others do not[16,17]. *Figure 5* shows how the relaxation is evident at the highest frequencies, when the conductivity component of ε'' is small (equation 2).

In the series of polyacrylates the temperature of the α relaxation, as well as the temperature of the glass transition, decreases with increasing length of the lateral group, when this is linear. Thus, the maximum of the α peak of PMA is at 39.5°C for 1 kHz whereas it is at – 17°C for the same frequency in PPA[18]. Nevertheless, the α relaxation of PHEA, which has a lateral group of length comparable to that of PPA, appears at higher temperatures than in PMA. This is attributed to the formation of hydrogen bonds between the OH group of the lateral chain and other polar groups of the chain or of neighbouring chains, thus decreasing the flexibility of the main chains.

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