Dielectric Relaxations in Poly(methyl Acrylate), Poly(ethyl Acrylate), and Poly(butyl Acrylate)

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Synopsis

A comparative study is undertaken of the dielectric relaxation spectra of poly(methyl acrylate), poly(ethyl acrylate), and poly(butyl acrylate), taking into consideration the spectra of the corresponding polymers in the series of the polymethacrylates. The three polymers, PMA, PEA, and PBA, present an α relaxation zone clearly separated from the secondary relaxations. Its shape is not altered with temperature, and it is possible to construct a master curve. With increasing length of the side chain, its distribution of relaxation times broadens and the temperature of the maximum of the relaxation decreases. A β relaxation with decreasing intensity as the length of the side chain increases is clearly perceptible in PMA and PEA, but almost not perceptible at all in PBA. In PEA this relaxation appears split into two peaks. Computer simulation of restricted motions of the side chain discard an origin similar to that of the γ relaxation in PPA or PBA for the lowest temperature component of the relaxation, and suggests the conjunction of two rotation mechanisms in this relaxation for the polyacrylates. For the experimental temperatures of our tests a γ relaxation shows up only in PBA. Its apparent activation energy, higher than in related polymers of the polymethacrylate series, suggests that the tighter packing of monomeric units in polyacrylates leads to a significant increase in the intermolecular contribution to the potential energy barrier responsible for the relaxation.

INTRODUCTION

The mechanical and dielectrical spectra of the polymers of the series of the polymethacrylates have been extensively studied. By comparing the spectra of the different members of the series the influence of the various elements in the polymeric chain on the relaxations has been determined.[1-8] There still remain points which need further reflection, such as the role in the secondary relaxations of the motion of the main chain and of the intermolecular interactions.

By contrast, the polymers in the series of the polyacrylates have been comparatively less studied.[2,9-12] In poly(methyl acrylate) (PMA) the α relaxation, related to the glass transition of the polymer, is clearly separated from the secondary relaxations and it has been possible to study the applicability of the time–temperature superposition principle in dielectrical measurements.[12] The β relaxation of this polymer has also been studied by several authors with mechanical as well as dielectrical measurements. It has been questioned whether its molecular origin was the same as in poly(methyl methacrylate), with its position shifted to lower temperature because of a lower potential

barrier to be overcome, or if its origin was of a different nature.[3,4,13] The relaxation spectra of other polymers in the series have been less studied.

In the present work we attempt a comparative study of the dielectric relaxation spectra of poly(methyl acrylate) (PMA), poly(ethyl acrylate) (PEA), and poly(butyl acrylate) (PBA), relating them to those of their analogues in the series of the polymethacrylates [poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), and poly(butyl methacrylate) (PBMA)].

EXPERIMENTAL

The samples were obtained by radical block polymerization of the corresponding monomers of Merck at 56°C during 14 h with 0.05% in weight of azobisisobutyronitrile as initiator. Polymerization was completed at 90°C during 6 h, and the samples were dried in vacuum until their weight remained constant.

The mean molecular weight was determined by GPC at 25°C with a flux of 1 mL/min of tetrahydrofurane and columns of μ-styragel of 10^5 and 10^6 Å. The values obtained were 1.90×10^6 for PMA, 6.02×10^6 for PEA, and 6.76×10^6 for PBA, all of them showing a high polydispersity because of the polymerization method employed. GPC also showed the absence of residual monomer in the dried samples.

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

RESULTS AND DISCUSSION

Figure 1 displays the relaxation spectra at 200 Hz and 1 kHz of the three polymers studied. In all of them the α relaxation is sufficiently separated from the secondary relaxations. PMA and PEA show a β relaxation at about $-80°C$, which is almost indistinguishable as a shoulder in PBA, whereas this last polymer shows a γ relaxation not present in the other two. Nevertheless, the β relaxation of PEA appears to be split in two peaks, as will be discussed later. The results and their discussion we present separately for the three relaxation zones α, β, and γ.

The γ Relaxation in PBA

Figure 2 displays the curves of ϵ'' as a function of temperature in the region of the γ relaxation for PBA. For the sake of clarity not all the curves for each measuring frequency are represented. Figure 3 shows the positions of the maxima of all the curves in an Arrhenius diagram, along with those of the curves of ϵ'' as a function of frequency. For PBA the latter appear slightly shifted towards higher frequencies (or lower temperatures) when compared with the former, a fact already found in other polymers.[14] The apparent activation energy for PBA, as calculated with one or another kind of maxima, is of 7 kcal/mol, which agrees with the value found by Mikhailov[10] for PPA. This value of the activation energy is for both polymers higher than the activation energy of the relaxation in PBMA and PPMA: 5.5 kcal/mol.[15,16]
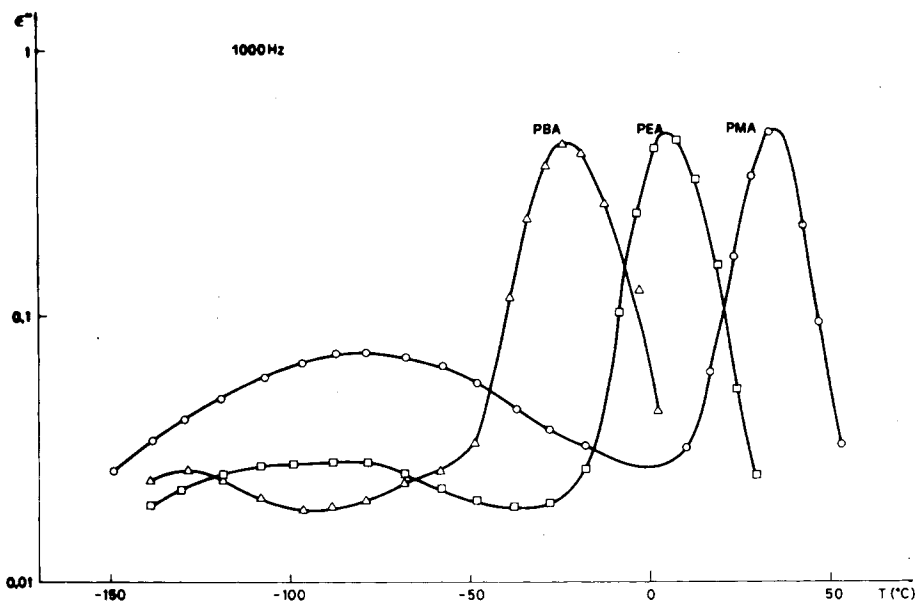
(a)
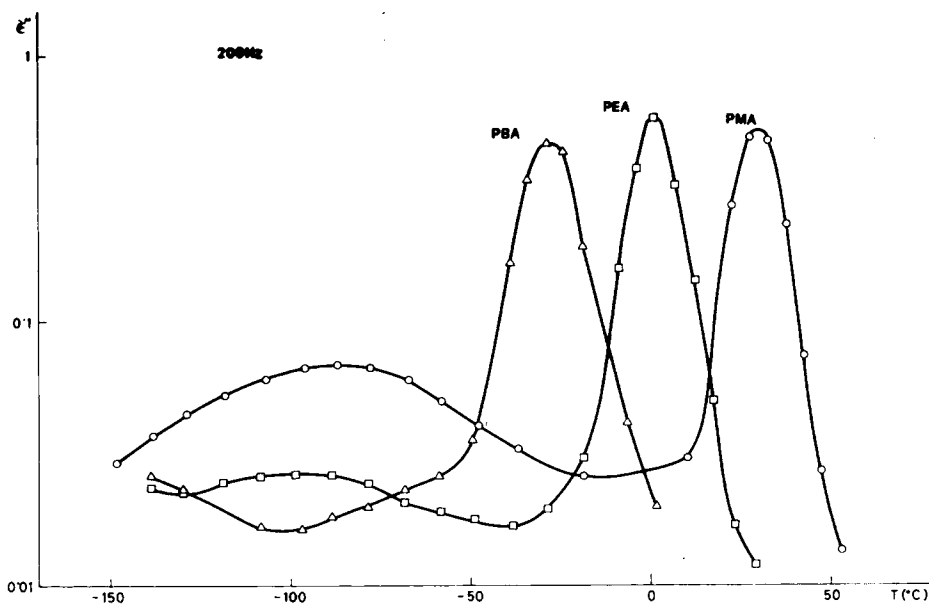
(b)

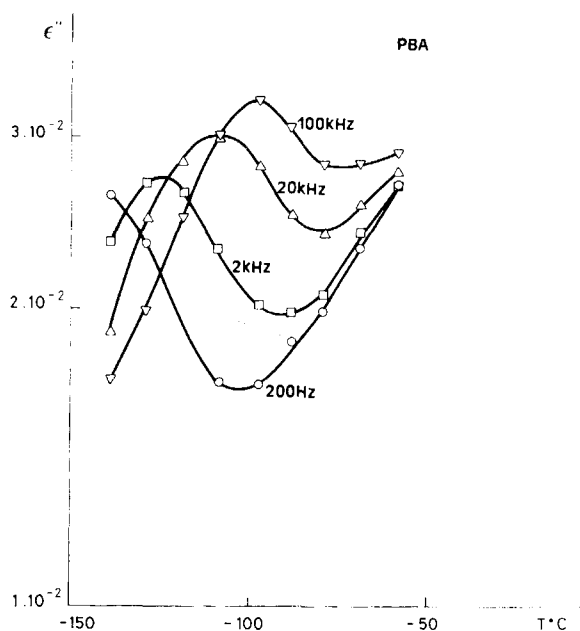Fig. 1.   Relaxation spectra of PMA (○), PEA (□), and PBA (△) at 200 Hz (a) and 1000 Hz (b).

Fig. 2. Plot of ϵ'' as a function of temperature for the relaxation zone of PBA. For the sake of clarity only some of the experimental curves have been drawn: (○) 200 Hz; (□) 2 kHz; (△) 20 kHz; (▽) 100 kHz.

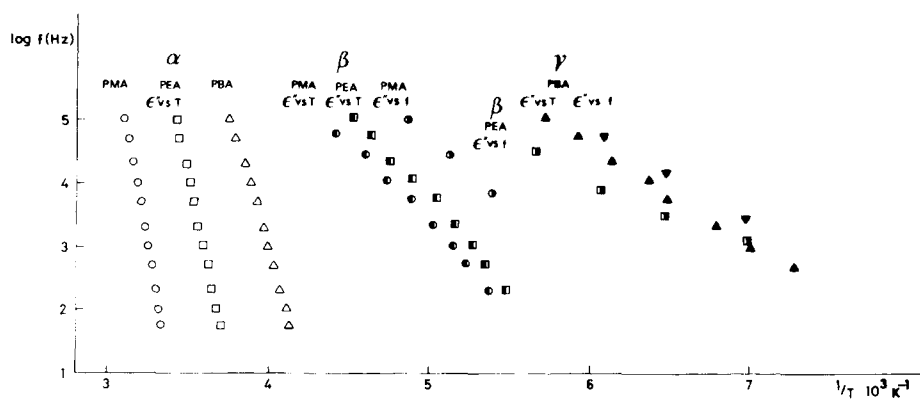Fig. 3. Position of the maxima characterizing the relaxations studied: Maxima of the curves of ϵ'' vs. T for the α relaxation in PMA (○), PEA (□), and PBA (△); maxima of the curves of ϵ'' vs. T for the β relaxation in PMA (◐) and PEA (◨); maxima of the curves of ϵ'' vs. frequency for the β relaxation in PMA (◑) and PEA (◪); maxima of the curves of ϵ'' vs. T (▲) and of ϵ'' vs. frequency (▼) for the γ relaxation in PBA.

The same phenomenon has been found for the activation energy of the γ relaxation of PHEA, with a value of 13.5 kcal/mol,[17] against the values reported for PHEMA, ranging from 8 to 10 kcal/mol.[14, 18]

It is difficult to explain the above-mentioned differences if the relaxation is understood as being caused by internal motions of the lateral group overcoming potential barriers of only intramolecular origin.

In fact, Shimizu et al.[15] concluded with the help of studies of molecular mechanics that the apparent activation energy for this relaxation should have a value around 4.8 kcal/mol. This value is acceptable for PPMA and PBMA but too low for PPA and PBA, although the determination should be valid in principle for polyacrylates as well as for polymethacrylates. This leads us to consider the presence of intermolecular components in the potential barrier. The potential energy of intermolecular interaction is related to the degree of packing of the molecular chains. The free volume can be taken as a measure of this packing. The free volume in T_g increases with the value of the glass transition temperature.[19-21] Thus it is less in the acrylates than in the corresponding polymers of the series of the methacrylates: the former have T_g's 80–100°C below the latter. This fact favors a greater intermolecular interaction in PBA than in PBMA. Nevertheless, the free volume does not remain constant with temperature in the glassy state,[20,21] so that the relationship between the values of the free volumes at T_g is not directly conclusive for the values of the free volume at the temperatures where the γ relaxation takes place in both polymers.

The studies of molecular dynamics of Ferguson and Cowie[8] and Heijboer[7] on the β relaxation of PMMA and PMA also support the hypothesis of a greater intermolecular contribution to the activation energy of secondary relaxations in the polyacrylates than in the polymethacrylates. In the two cited papers it is found that intramolecular barriers can explain only 50% of the value of the apparent activation energy for PMMA as determined from mechanical or dielectrical measurements; the rest must be attributed to intermolecular interactions, which are introduced in the model of the cited works by rigidifying portions of the main chain. By contrast, only 20–30% of the experimental value of the apparent activation energy for the β relaxation of PMA is justified by consideration of intramolecular potentials when the rotation around the $C - COO$ bond is considered as the origin of the β relaxation. One is led thus to conclude that intermolecular interactions be more important in PMA than in PMMA, at least for the β relaxation.

It is not possible to calculate with high precision the intensity of this relaxation; it has a value of about 0.25 at $-118.5°C$ determined through extrapolation in a Cole–Cole diagram.

The β Relaxation Zone

The height of the β relaxation decreases with increasing length of the side chain. The intensity of the relaxation in PEA is half the intensity of the relaxation in PMA, both calculated by extrapolation of the Cole–Cole arcs (ϵ'' vs. ϵ'), whereas in PBA the relaxation is almost not perceptible at 200 Hz and not perceptible at all at 1 kHz.

An interesting point is that in PEA the relaxation splits into two peaks: this is just observable at 1 kHz, while at 200 Hz the lowest temperature peak is shifted to temperatures below the experimental range.

In what follows these peaks will be labelled β_1 and β_2 in order of decreasing temperature. Figure 3 shows the positions of the maxima characteristic of the β relaxation of the ϵ'' vs. T curves along with those of the ϵ'' vs. frequency curves (these are given in Fig. 4). The positions of both types of maxima are
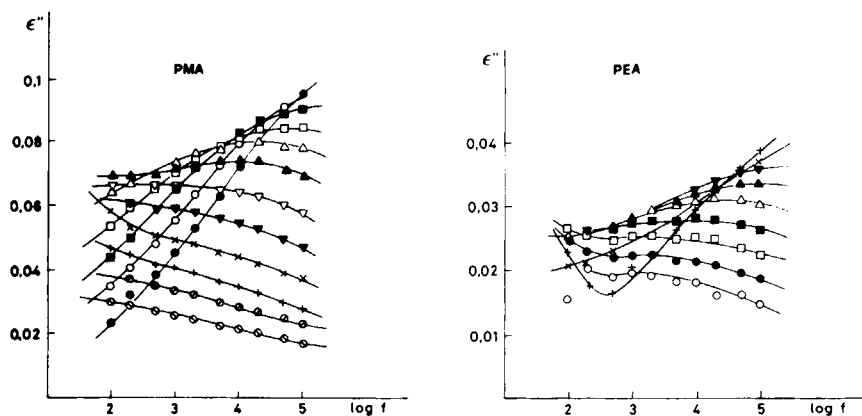
Fig. 4.   (a) Plots of ϵ'' vs. frequency for different temperatures (°C) for the β relaxation zone in PMA: (⊘) -148.6; (⊘) -138.6; (+) -128.8; (×) -118.3; (▼) -107.4; (▽) -96.3; (▲) -87.5; (△) -78.1; (□) -67.5; (■) -58.1; (○) -47.9; (●) -37.4. (b) Plot of ϵ'' vs. frequency in the β relaxation zone of PEA for different temperatures (°C): (○) -139.3; (●) -130.2; (□) -118.8; (■) -108.2; (△) -98.5; (▲) -88.3; (▼) -78.7; (×) -68.5; (+) -48.7.

clearly separated; this means that the β_1 relaxation is more pronounced in the ϵ'' vs. T curves, whereas the β_2 relaxation is more prominent in the ϵ'' vs. frequency plots. A similar fact has been found in other polymers.[22,23] The apparent activation energy of the β_1 relaxation is 12 kcal/mol; no value can be determined with enough accuracy for the β_2 relaxation.

In the β relaxation zone of the PMA it is not possible to distinguish the overlapping of two peaks. Nevertheless, the positions of the maxima of the ϵ'' vs. T and ϵ'' vs. frequency curves in an Arrhenius plot (Fig. 3) are still anomalously separated, thus allowing the determination of the apparent activation energy from both data, which yields a common value of 12 kcal/mol when calculated from the curves of ϵ'' vs. T. The curves of ϵ'' vs. frequency have only three experimental points; they lead to a value of 10 kcal/mol for the apparent activation energy.

The molecular origin of the β relaxation in PMA has been extensively studied.[2,3,12,13] It most probably lies in the rotation of the carboxymethyl group around the bond with the main chain, partially hindered by barriers of intra- as well as intermolecular nature, to which certain localized motions in the main chain should perhaps be added.

The fact that the β relaxation of PEA (and maybe of PMA also) decomposes in two peaks should lead to think about other possible molecular motions active in this temperature range. Another possibility is that the β_2 relaxation in PEA has a similar origin as the γ relaxation in PPA or PBA.

The study of the energetics of limited motions of the side chain of PEA was performed with the help of the ALLINGER MMP2 molecular mechanics program. Calculations were done by Dr. Ferguson and Professor Cowie of Stirling University, Scotland, with a Digital Equipment Corp. UAX 11/780 and an Acorn Cambridge Coprocessor running at 10 MHz. A model was generated consisting of an ethyl acrylate trimer in isotactic configuration. Thus the effect of two lateral chains on the motion of a side chain was studied, in order to determine whether the rotations around the bonds
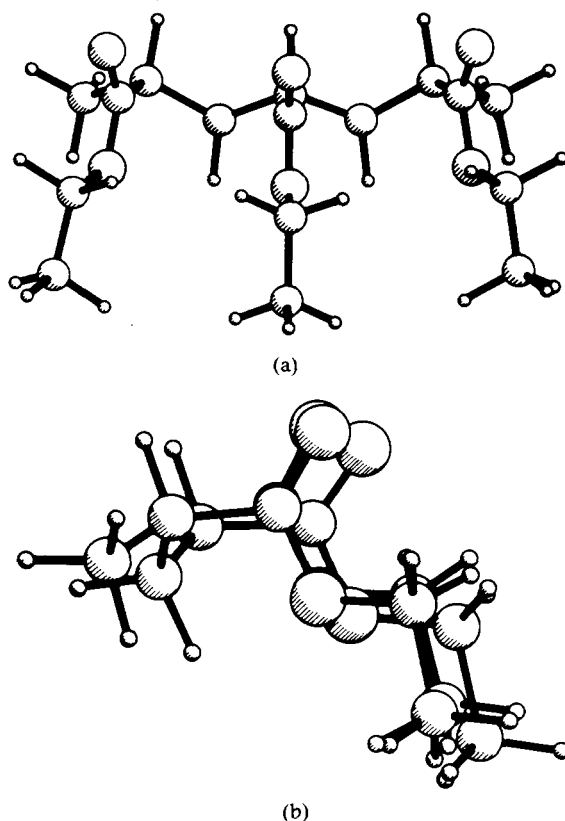
(a)

(b)

Fig. 5.   Projections of the PEA trimer model in isotactic configuration used for the study of the energetics of the local motions of the side chain: (a) transverse view; (b) view in the direction of the main chain.

C13–O14 and O14–C15, which usually are not considered as relevant for the secondary relaxations in the methacrylates, can participate in them. The isotactic configuration was chosen in order to strengthen the possible effect of the side chains in the model. Figure 5 shows two different projections of the geometry of the final minimal energy configuration. The MMP2 program was then used in order to make the selected bonds rotate from 0 to 360° in steps of 10°, and calculate the deformation energy as a function of the angle for the given bond. Moreover, selected atoms were fixed in their space positions and the possible influence of constraints in the glassy state was studied. The methodology is thoroughly described in Ref. 8. Figure 6 shows the labeling scheme for the atoms of the trimer. All the atoms of the main chain were held fixed during the calculations. The results can be summarized as follows:

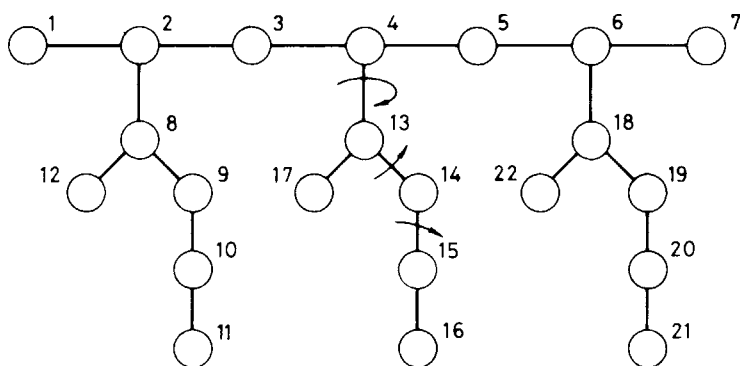|	Rotated bond	Energy required for complete rotation
A	C12–O14	ca. 11 kcal/mol
B	O14–C15	ca. 4 kcal/mol

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Fig. 6. Labeling scheme employed in the model.

The apparent activation energy found for the rotation O14–C15 (what would mean a similar origin as the γ relaxation of PPA and PBA) is too low for the temperatures at which the relaxation appears experimentally. Even if, as mentioned, intermolecular interactions could have a nonnegligible influence, the relaxation produced by this group in PEA should appear at temperatures equal or less than the γ relaxation in PBA.

The rotation C13–O14 possesses a single minimal energy position, in accord with what happens in the polymethacrylates as found by Heijboer and others.[7] Nevertheless, a computer-generated graphic of the configurations adopted by the trimer starting from that position and rotating 10° each step reveals that there exist cooperative motions of the side groups of the monomeric units adjacent to that which is being rotated ending in positions different from the initial ones after the 360° rotation; moreover, the group C=O in the rotated lateral chain oscillates in an interval of 70° about its original position. And at last there is the possible influence of the intermolecular interactions. All these facts suggest that a contribution of this rotation to the dielectric relaxation spectrum of PEA should be considered. Thus it seems plausible that the rotation C4–C13 (traditionally considered the cause of the β relaxation in polyacrylates and polymethacrylates) as well as the rotation C13–O14 take part in the β relaxation of PEA.

The α Relaxation

The study of the α relaxation of these polymers is greatly facilitated by the fact that their secondary relaxations are sufficiently separated. Similarly to what happens with the polymethacrylates, the relaxation appears at lower temperatures the longer the side chain (Figs. 1 and 3), and the same feature is revealed by the glass transition temperature.[2,24]

The shape of the relaxation has been fitted to the phenomenological model of Havriliak and Negami[25]:

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \left[1 + (i\omega\tau_0)^{(1-\alpha)} \right]^{-\beta} \tag{1}$$

where ϵ^* is the complex dielectric permitivity.

TABLE I
Parameters of the Model of Havriliak and Negami for the α Relaxation of PMA, PEA, and PBA and Effective Dipolar Moment at Different Temperatures[a]

T (°C)	ϵ_0	ϵ_∞	α	β	τ_0	μ_{eff} (Debye)
			PMA			
22.7		4.25				
27.7	6.93	4.25				
32.6	6.88	4.25	0.2	0.29	1.5 10	0.790
37.6	6.82	4.25	0.2	0.28	2.7 10	0.788
42.4	6.76	4.25	0.2	0.28	6.1 10	0.785
47.2	6.70	4.25	0.2	0.27	1.7 10	0.782
53.2	6.60					
			PEA			
−8.7	6.71	3.70				
−3.7	6.62	3.69				
2.3	6.52	3.65	0.25	0.34	3.5 10	0.931
7.4	6.43	3.64	0.25	0.32	4.0 10	0.929
12.3	6.35	3.61	0.25	0.31	7.0 10	0.934
17.2	6.26	3.60	0.24	0.30	1.8 10	0.931
22.0	6.15	3.58				
26.9	6.09	3.55				
			PBA			
−34.1	5.88	2.80				
−29.0	5.79	2.80				
−24.0	5.70	2.75	0.32	0.28	2.0 10	1.23
−19.2	5.60	2.75	0.32	0.28	3.5 10	1.22
−12.8	5.48	2.80	0.32	0.29	5.5 10	1.19
−6.50	5.38					
1.50	5.25					

[a]The increase of the value of the parameter α as the length of the side chain increases is characteristic of the broadening of the relaxation.

The parameters found are given in Table I. The parameter α, characteristic of the breadth of the distribution of relaxation times, increases with the length of the side chain; i.e., the relaxation broadens. α and β are almost constant with temperature; the shape of the relaxation is not altered with temperature and it becomes possible to construct a master curve in a $\log(\epsilon''/\epsilon''_{\max})$ vs. $\log$(frequency/freq. max.) plot by means of horizontal as well as vertical shifts, the latter demanded by the dependence of the relaxation intensity on temperature. Figure 7 shows the master curves for the three polymers. In it the broadening of relaxation with the length of the side chain can be noticed.

The intensity of the relaxation (Fig. 8) decreases with temperature in the three polymers, in accord with the predictions of the theory of Ishida and Yamafuji for the polymethacrylates,[1] and for a given temperature it decreases with increasing length of the side chain. Because of the fact that in these polymers the permanent dipole lies in the lateral chain, the α relaxation in dielectric measurements has a different meaning than in viscoelastic measurements. At temperatures far above the glass transition temperature the application of an electric field forces the permanent dipoles to orientate by means of rotations around the bonds in the main chain and the bond that links the
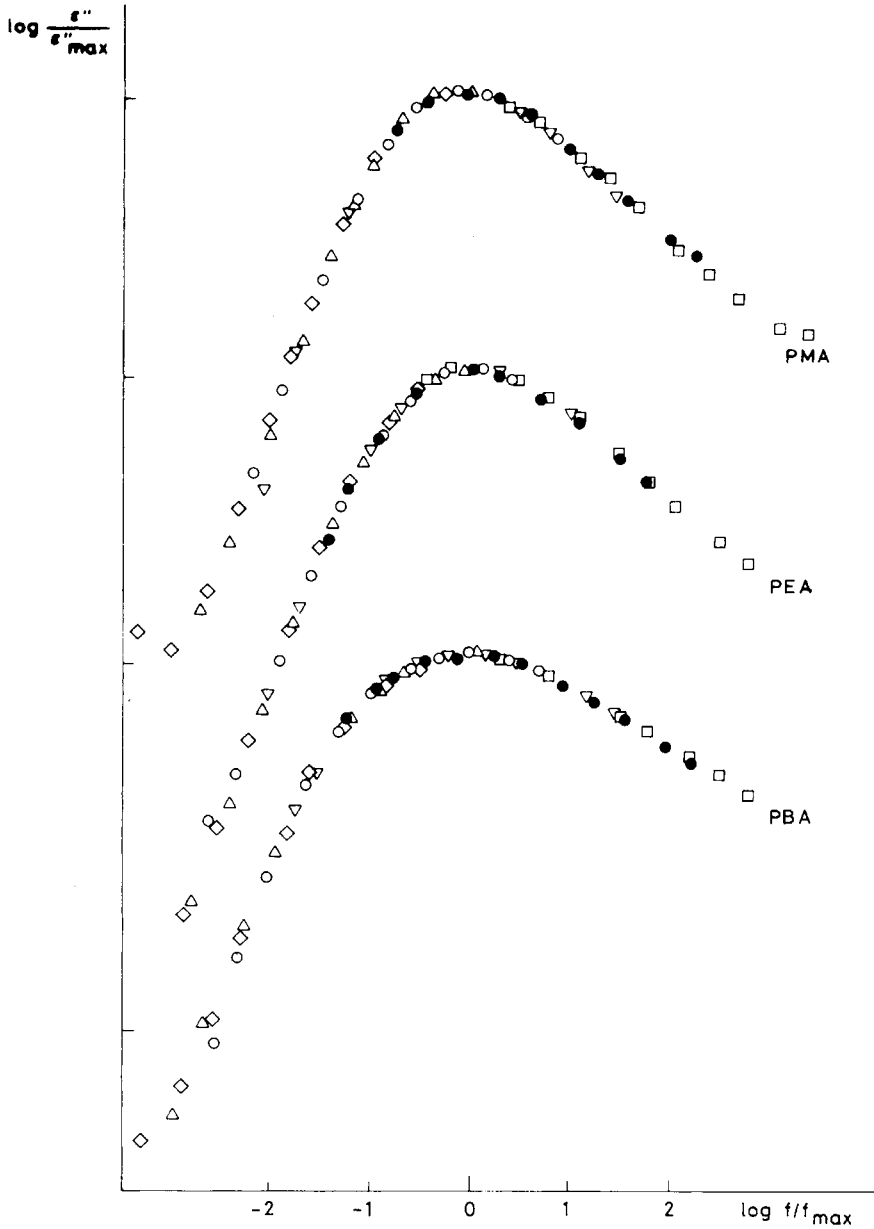
Fig. 7. Master curves for the α relaxation of the three polymers studied. (The curves have been vertically shifted for the sake of clarity.) The following values of temperature are represented (°C): for PMA, 53.2 ($\diamondsuit$), 47.2 ($\triangle$), 42.2 ($\circ$), 37.6 ($\triangledown$), 32.6 ($\bullet$), and 27.7 ($\square$); for PEA, 26.9 ($\diamondsuit$), 22.0 ($\triangle$), 17.2 ($\circ$), 12.3 ($\triangledown$), 7.4 ($\bullet$), and 2.3 ($\square$); for PBA, 1.5 ($\diamondsuit$), -6.5 ($\triangle$), -12.8 ($\circ$), -19.2 ($\triangledown$), -24.0 ($\bullet$), and -29.0 ($\square$).
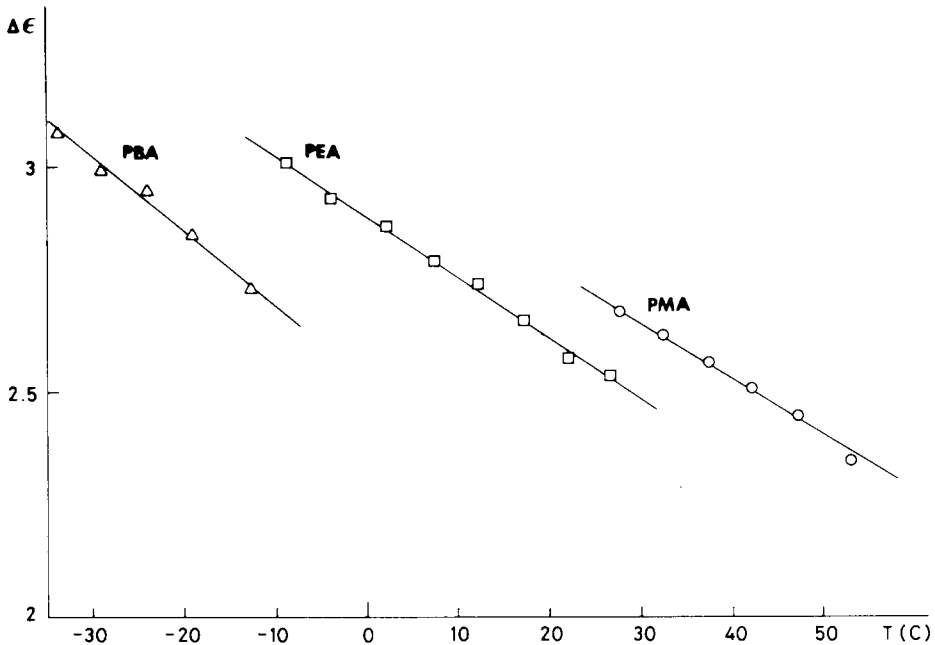
Fig. 8. Intensity of the α relaxation as a function of temperature in PMA ($\bigcirc$), PEA ($\square$), and PBA ($\triangle$).

carboxyl group with it. In a sequence of decreasing temperatures, the α relaxation arises when the cooperative motions in the main chain cease to be possible. From this moment on, the dipoles in the glassy state can orient themselves only through the rotations around the bond that links the carboxyl group with the main chain, even when, as stated above with respect to the methacrylates, there could be some contribution of localized motions in the main chain. The α relaxation only partially restricts the contribution of the dipole of the carboxyl group to the dielectric permitivity. By contrast to what happens in the viscoelastic α relaxation, the dielectric α relaxation is thus only indirectly related to the loss of mobility of the main chain, namely through the effect that this loss has on the capability of the dipole to orientate. The carboxyl group loses the remaining mobility at lower temperatures, in the β relaxation. The intensity of this relaxation can be considered as a measure of the residual mobility. So, the intensities of the α and β relaxations are conceptually related, as two faces of a single phenomenon. This notwithstanding, the intensity of a relaxation is not an adequate parameter to compare different relaxations, even less when these take place in different polymers, because it depends on the temperature and the number of dipoles per unit volume, as seen from the equation of Frohlich[26,27]:

$$\epsilon_0 - \epsilon_\infty = \frac{\mu_0^2 g 4\pi N 3\epsilon_0}{3KT(2\epsilon_0 + \epsilon_\infty)}\left(\frac{\epsilon_0 + 2}{3}\right)^2 \tag{2}$$

When applied to polymers in the rubbery state, the factor g takes into

account the reciprocal influence between dipoles of the same chain or of adjacent ones.[28] The effective dipolar moment is defined as $\mu_{\text{eff}} = (g\mu_0)^{1/2}$; comparison of its value with that of μ_0 (permanent dipolar moment of an isolated dipole) can be employed as a measure of the degree of participation of a given kind of permanent dipoles in the relaxation.

The number of monomeric units per cubic centimeter, N, has been calculated from the density of the samples and the molecular weight of the respective units. N had a value of 8.54×10^{21} for PMA, 7.23×10^{21} for PEA, and 5.27×10^{21} for PBA, that is, the sequence PMA : PEA : PBA stands in a relationship $1 : 0.85 : 0.62$, very similar to that found by Tetsutami et al.[5] in the corresponding polymers of the series of the methacrylates. The values of μ_{eff} calculated from eq. (2) are given in Table I. It can be observed that μ_{eff} is practically constant with temperature in the three polymers and increases with the length of the lateral chain, that is, in the sequence PMA : PEA : PBA. At the same time the intensity of the β relaxation decreases, as already noticed. This indicates that in PMA, the polymer with the less bulky side group of the three here considered, the loss of mobility of the main chain in the glass transition affects only partially the orientability of the dipoles of the side chain; these continue to be dielectrically active in the glassy state thanks to the possibility that the carboxyl group has to rotate around the bond with the main chain (μ_{eff} has a value about 0.78 in the α relaxation, whereas its value in solution is $1.37D$).[28] Thus there is an appreciable mobility of the side chains in PMA in the glassy state, which is lost at lower temperatures in the β relaxation.

At the other end, the side groups of PBA retain little mobility in the glassy state: The effective dipole moment in the α relaxation is about 1.2, close to the value found for this polymer in solution,[28] $1.52D$. At the same time, no β relaxation—indicative of a further loss in mobility—is observed in this polymer. It must be noted that a little β relaxation is in fact observed in PBMA,[5,6,16] and it could be the case that also in PBA a small relaxation existed buried between the α and the γ relaxations. PEA represents an intermediate state.

The decreasing mobility of the lateral group in the sequence PMA : PEA : PBA can be adscribed to the fact that the free volume necessary for the motions to take place is increasing in the sequence, whereas the free volume in T_g in the sequence even decreases, as happens with the series of the methacrylates.[20,21]

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