Dielectric relaxation in poly(n-alkyl methacrylate)s and their mixtures with *p*-nitroaniline

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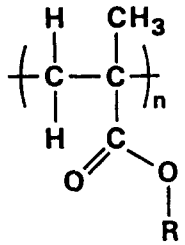
In the work described in this paper the dielectric properties of solid solutions of *p*-nitroaniline in poly(methyl methacrylate), poly(ethyl methacrylate) and poly(n-butyl methacrylate) were measured in the frequency range from 20 to 10^6 Hz and the results obtained were compared with those of the pure polymers. It is shown that the presence of the solute has a strong influence on the relaxation process of poly(methyl methacrylate), and this is ascribed to the formation of hydrogen bonds between the amino group of the solute and the side groups of the polymer. In poly(ethyl methacrylate) this effect is less pronounced and it is absent in the case of poly(n-butyl methacrylate), suggesting that the increasing size of the n-alkyl group prevents hydrogen bond formation between the solute and the polymer.

(Keywords: poly(n-alkyl methacrylate)s; dielectric relaxation; *p*-nitroaniline)

INTRODUCTION

The poly(n-alkyl methacrylate)s (PnAMAs) are polymers of general formula



The relaxational behaviour of these polymers has received much attention and the studies published before 1967 have been reviewed[1]. It has been observed that at 1 atm and high temperatures the two relaxation processes α and β merge into a complex $\alpha\beta$ process as a consequence of the coupling of the side-group motions of the repeat unit with the global motions of this unit attached to the chain backbone. With decreasing temperature or increasing pressure it is possible to resolve this $\alpha\beta$ process into two well-defined and separated processes, α and β. The molecular origin of the α process is considered to be the micro-Brownian motions of the main-chain backbone. The β process, on the other hand, is considered to arise from the partial rotation of the side-chain carboxy groups and is dominated by interchain interactions. The β relaxation in PnAMAs has been extensively studied by Hideshima *et al.*[2–4], and it has been found that the shape of the corresponding peak, as well as its activation energy, is independent of the size of the n-alkyl side group, suggesting a general molecular mechanism for this relaxation process in all these polymers. Contrastingly, the intensity of this process decreases with increasing length of the n-alkyl group, and it is observed that this decrease is proportional to the dipolar density (the number of monomeric units per unit volume). The fact that the location of this process is independent of the pressure suggests that the process is intramolecular in nature[5]. The β process in PnAMAs is broader than the α process, and this is ascribed to the fact that the local barriers to the rotation of the side groups are different along the chain as a consequence of the irregularity of the vitreous state[6]. In fact, for a simple barrier the peak would be narrow (narrow distribution of relaxation times), but for a complex barrier the peak should narrow with increasing temperature, which is not observed. An alternative explanation is that the correlation of a polymeric segment with its environment is stronger below the T_g than above that temperature[7]. On the other hand, an increase in the size of the n-alkyl side group does not change the shape or frequency of the β process, but makes the α process more Debye-like since the α relaxation becomes more independent of the environment (of the intermolecular forces) as the side-group size increases.

In recent years considerable attention has been focused on polymer composites consisting of organic polar

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molecules as guests in a polymeric host matrix[8,9], since these composites constitute a family of new, potentially electro-optical materials[9,10]. Different studies have been published on this subject, including an analysis of the diffusion processes of the solute molecules in the polymer host[11], a study of the non-linear optical properties of polymer host/guest systems[12], and a study of the influence of the solute on the relaxational behaviour of the polymeric matrix[13].

In the present work the dielectric relaxation of solid solutions of *p*-nitroaniline in some PnAMA polymers (R = methyl, ethyl and n-butyl) has been studied and the dielectric behaviour of such mixtures has been compared with that of the pure polymers. Since the aim of our work was to see how the presence of a polar solute affects the relaxational behaviour of the polymeric matrix, we carried out experimental work on pure polymers as well as on the mixtures. The samples were prepared in a similar way, thus allowing an easy comparison between the results obtained for the mixtures and the pure polymers.

The *p*-nitroaniline (*p*NA) molecule was chosen as the guest solute because of its molecular structure. On the one hand, it has an electron-donating amino group and an electron-accepting nitro group connected to the aromatic ring in a *para* arrangement and as a consequence it has a high dipole moment. On the other hand, the hydrogen atoms of the amino group are acidic and can thus interact by hydrogen bonding with the proton-accepting sites of the ester moiety of the polymer.

EXPERIMENTAL

Poly(methyl methacrylate) (PMMA) was a low molecular weight material from Aldrich (catalogue no. 18,223-0) with $T_g = 114°C$. Poly(ethyl methacrylate) (PEMA) was from Aldrich (catalogue no. 18,335-0) with $M_w = 340\,000$ and $T_g = 66°C$. Poly(n-butyl methacrylate) (PnBMA) was from Aldrich (catalogue no. 18,153-6) with $M_w = 320\,000$ and $T_g = 27°C$. *p*-Nitroaniline was also from Aldrich (catalogue no. 18,531-0), had a purity of 99 + % and was used without further purification.

The films of the mixtures were prepared by dissolving the polymer and the solute in a common solvent (dichloromethane) and then evaporating the solvent. The films were then heated for several days in a vacuum oven at 50°C in order to eliminate most of the remaining solvent. A blank sample (polymer without *p*NA) was prepared in the same way for each polymer. This preparation method ensured a nearly constant sample thickness so that the geometric capacitance of the cell C_0 was nearly the same for all the results presented in *Tables 1* and *2*.

The dielectric measurements were performed on a Hewlett–Packard 4284A precision LCR meter (frequency range from 20 to 10^6 Hz) for PMMA and PEMA and on a General Radio 1620-A capacitance-measuring assembly (frequency range from 50 to 10^5 Hz) for PnBMA. The sample films were placed between the electrodes of a three-terminal, parallel plate capacitor described elsewhere[14]. The experimental results on permittivity and dielectric loss are expressed respectively as $\varepsilon' C_0$ and $\varepsilon'' C_0$ (units pF), where C_0 is the geometric capacitance of the cell. We were concerned with the variations in dielectric strength and frequency of the loss peaks with sample composition and temperature. We were able to obtain this information from $\varepsilon' C_0$ and $\varepsilon'' C_0$, and our data were entirely sufficient to show how the relaxation behaviour varied from sample to sample.

THE DIELECTRIC RELAXATION IN PURE POLY(n-ALKYL METHACRYLATE)S

It is known that the bigger the alkyl group, the shorter the relaxation time associated with the α relaxation in poly(n-alkyl methacrylate)s at a given temperature. This is a consequence of the enhanced mobility of the chains allowed by the so-called internal plastification phenomenon. The relaxation times presented in *Table 1* confirm this behaviour. This table summarizes the results we obtained for the three polymers studied, which will be discussed in the following paragraphs.

Figures 1 to *3* show the dielectric relaxation spectra we obtained respectively for PMMA, PEMA and PnBMA at different temperatures. From *Figure 1* we observe that the shape of the peak for PMMA changes with the temperature. We can clearly distinguish two different temperature regions: at lower temperatures (60–110°C) the peaks are broad and have a low amplitude, whereas at higher temperatures (110–140°C) they are narrow with a higher amplitude. The same behaviour is observed for PEMA (*Figure 2*), but in this case the low temperature region is narrower (50–90°C) and the high temperature region is wider (90–140°C). For PnBMA (*Figure 3*) this behaviour is no longer observed. For this polymer the shape of the peak does not change significantly with the temperature and the observed behaviour seems to correspond to the high temperature behaviour of the other polymers.

Good fits of the experimental data were obtained using the KWW function[15], and the numerical tables of

Table 1 Parameters of the dielectric relaxation of PMMA, PEMA and PnBMA

Polymer	T (°C)	f_{max} (kHz)	τ_0 [a] (s)	$\varepsilon''_{max} C_0$ (pF)	$(\varepsilon_0 - \varepsilon_\infty) C_0$ (pF)	β
PMMA	60	0.260	6.12×10^{-4}	11.42	80.6	0.27
	70	0.600	2.65×10^{-4}	11.82	84.4	0.28
	80	1.350	1.18×10^{-4}	12.59	86.0	0.31
	90	3.000	5.31×10^{-5}	13.43	90.1	0.31
	100	6.000	2.65×10^{-5}	14.32	92.0	0.32
	110	14.000	1.14×10^{-5}	15.58	92.5	0.33
	120	30.000	5.31×10^{-6}	16.94	95.0	0.35
	130	70.000	2.27×10^{-6}	18.66	101.0	0.36
	140	150.000	1.06×10^{-6}	20.79	110.0	0.36
PEMA	50	0.110	1.45×10^{-3}	7.93	[b]	[b]
	60	0.275	5.79×10^{-4}	9.44	75.0	[b]
	70	0.550	2.89×10^{-4}	10.94	81.1	0.32
	80	1.250	1.27×10^{-4}	12.76	92.6	0.32
	90	3.000	5.31×10^{-5}	14.66	93.0	0.33
	100	9.000	1.77×10^{-5}	16.19	88.5	0.37
	110	27.000	5.89×10^{-6}	17.47	84.0	0.41
	120	57.000	2.79×10^{-6}	18.30	81.0	0.44
	130	140.000	1.15×10^{-6}	18.91	79.0	0.46
	140	370.000	4.30×10^{-7}	19.62	76.5	0.46
PnBMA	55	0.600	2.65×10^{-4}	25.47	[b]	[b]
	60	1.250	1.27×10^{-4}	26.10	[b]	0.40
	65	2.250	7.07×10^{-5}	26.80	119.0	0.43
	70	4.250	3.74×10^{-5}	27.21	114.0	0.46
	75	8.000	1.99×10^{-5}	27.45	115.0	0.48
	80	15.000	1.06×10^{-5}	27.70	113.0	0.51
	85	28.000	5.68×10^{-6}	27.70	112.0	[b]
	90	45.000	3.54×10^{-6}	27.70	111.5	[b]

[a] Relaxation time defined as $\tau_0 = 1/2\pi f_{max}$
[b] The data were not sufficient to calculate the parameter

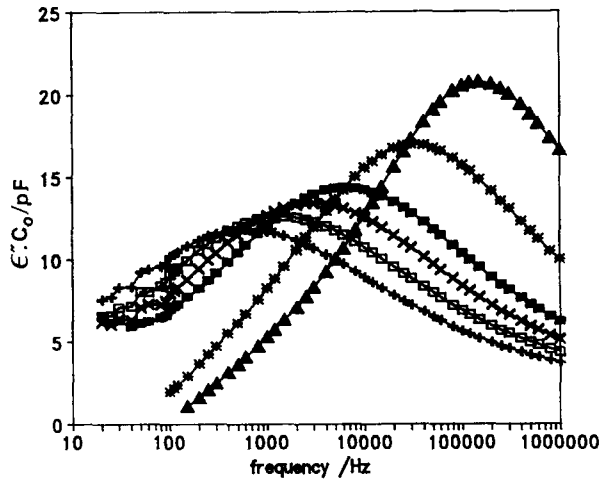

Figure 1 Dielectric relaxation spectra for PMMA at 70, 80, 90, 100, 120 and 140°C (from left to right)

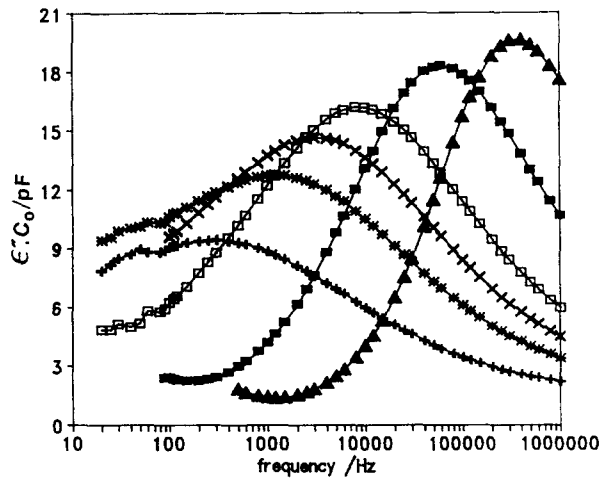

Figure 2 Dielectric relaxation spectra for PEMA at 60, 80, 90, 100, 120 and 140°C (from left to right)

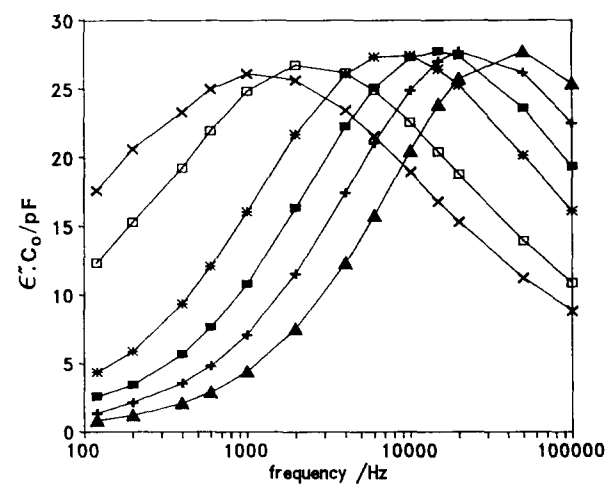

Figure 3 Dielectric relaxation spectra for PnBMA at 60, 65, 75, 80, 85 and 90 °C (from left to right)

Koizumi and Kita[16] were used in order to obtain the corresponding parameters. *Figure 4* shows the variation in the peak amplitude with temperature for the three polymers studied. For PMMA the amplitude of the peak increases with increasing temperature, and this increase becomes larger as the temperature rises. For PEMA also the amplitude increases with temperature but this increase is smaller at higher temperatures. If we consider that the relaxation process in PMMA is a β process at low temperatures and an $\alpha\beta$ process at higher temperatures, we could say that in PEMA the $\alpha\beta$ process is present at lower temperatures when compared with PMMA. On the other hand, in PnBMA the peak amplitude shows its limiting value at much lower temperatures. These results suggest that the effect of internal plastification caused by the alkyl group is somewhat similar to the effect of increasing the temperature, causing a narrowing of the peaks and an enhancement of the α character of the relaxation process.

The dielectric strength $\varepsilon_0-\varepsilon_\infty$ in PMMA (see *Table 1*) increases with increasing temperature, and two temperature regions can be distinguished: below 110°C a smaller slope, and above 110°C a larger slope. In PEMA, on the other hand, $\varepsilon_0-\varepsilon_\infty$ increases with temperature until 90°C and slightly decreases at higher temperatures. It should be noted that a slight decrease of the dielectric strength with temperature is often considered as characteristic of an α relaxation. In this context, our results suggest that the relaxation process in PEMA is mainly an α process above 90°C. For PnBMA the dielectric strength decreases slightly with temperature over the range studied, suggesting an α character for the relaxation process in this polymer at these temperatures.

It is also interesting to observe the behaviour of the quantity $(\varepsilon_0-\varepsilon_\infty)T$, since it is proportional to the square of the relaxed dipole moment. In PMMA this quantity increases with temperature and two regions are observed, the slope of the increase below 110°C being smaller than that above this temperature (see *Figure 5*). In PEMA this quantity increases with temperature until 90°C and then remains constant above this temperature. In PnBMA there is no significant change in $(\varepsilon_0-\varepsilon_\infty)T$ with temperature over the range studied. The conclusion we may draw from these results is that with increasing size of the alkyl group the observed relaxation process becomes a cooperative mixture of the α and β processes. In PnBMA, over the temperature range studied, the relaxation process is essentially an $\alpha\beta$ process.

The analysis of the observed activation energies strengthens the above interpretation. For PMMA two different regions are observed (*Figure 6*). Below 110°C

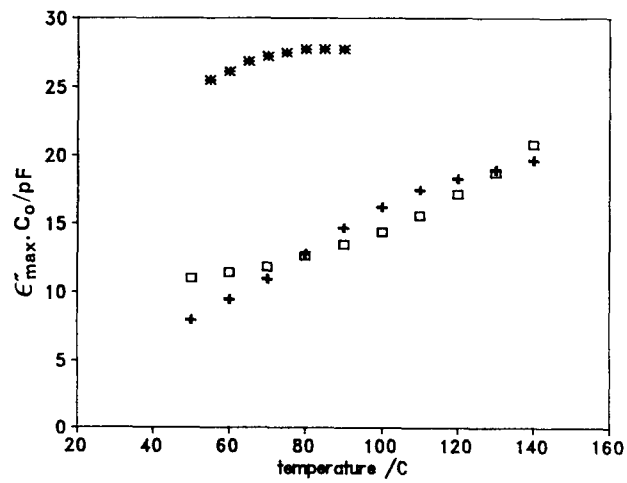

Figure 4 Variation in $\varepsilon''_{max}C_0$ with temperature for PMMA (□), PEMA (+) and PnBMA (*)

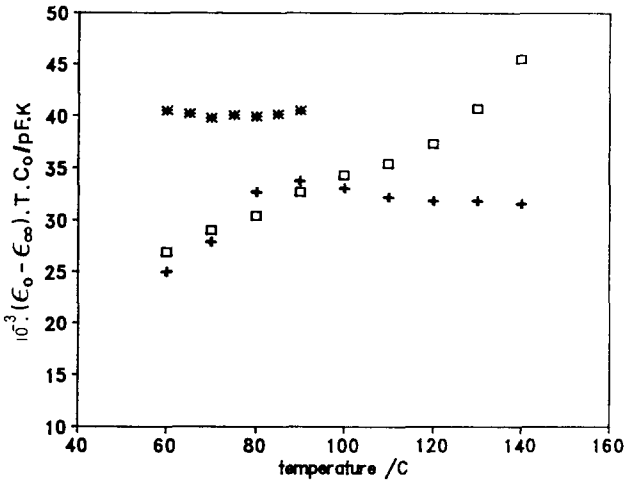

Figure 5 Variation in $(\varepsilon_0-\varepsilon_\infty)T$ with temperature for PMMA (□), PEMA (+) and PnBMA (*)

a 20.2 kcal mol^{-1} (1 cal = 4.2 J) activation energy is obtained, whereas at higher temperatures a value of 26.0 kcal mol^{-1} is obtained. For PEMA the activation energy corresponding to the low temperature region (50–90°C) is 18.9 kcal mol^{-1}*, whereas in the high temperature region (>90°C) we obtained 30.0 kcal mol^{-1}. For PnBMA the activation energy over the temperature range studied is 29.4 kcal mol^{-1}, which is similar to the observed values for the high temperature ranges of the other polymers. The present results suggest, confirming previous work reported in the literature, that in PMMA we have essentially a β relaxation at low temperatures which becomes an $\alpha\beta$ process with increasing temperature. In this $\alpha\beta$ process the side groups cooperate with the backbone motions in micro-Brownian motion to relax all the available $\langle\mu^2\rangle$, and it has some properties which are similar to a pure α process. An increase in the size of the n-alkyl side groups in PnAMAs decreases the intensity of the β process in proportion to the dipolar density (number of monomeric units per unit volume)^2. On the other hand, the internal plastification phenomenon accelerates the α process so that in PnBMA the isolated β process is no longer observed.

THE DIELECTRIC RELAXATION IN POLY(n-ALKYL METHACRYLATE)/*p*-NITROANILINE MIXTURES

Figures 7 to *9* show the dielectric relaxation spectra as a function of temperature for some of the studied mixtures of PMMA, PEMA and PnBMA, respectively, with *p*-nitroaniline. These results, as well as others obtained for other mixtures of different concentrations, are summarized in *Table 2*. In the following we will discuss the significance of the comparison between *Figures 7* to *9* and *Figures 1* to *3* (or between *Table 2* and *Table 1*).

The first comment to make regarding *Figure 7* is the contrast with *Figure 1* for the pure polymer. What appears as a β process at low temperatures in *Figure 1* has disappeared and the magnitude of the overall loss process has increased by a factor of about 4. It is evident that the solute is moving cooperatively with its polymer environment, the overall process carrying with it the relaxation strength (mean square dipole moment times solute concentration) of the solute. The fact that the curves at higher temperatures have a shape which is similar to the curve shape of an α process means that the solute and polymer relax together, which might be surprising but is consistent with our previous work on the dielectric α relaxation in solute/solvent systems composed of small molecules[17–20]. Comparing the f_{max} values shown in *Table 2* for the mixtures with those shown in *Table 1* for the pure polymers, we conclude that for PMMA the addition of the solute shifts the peaks

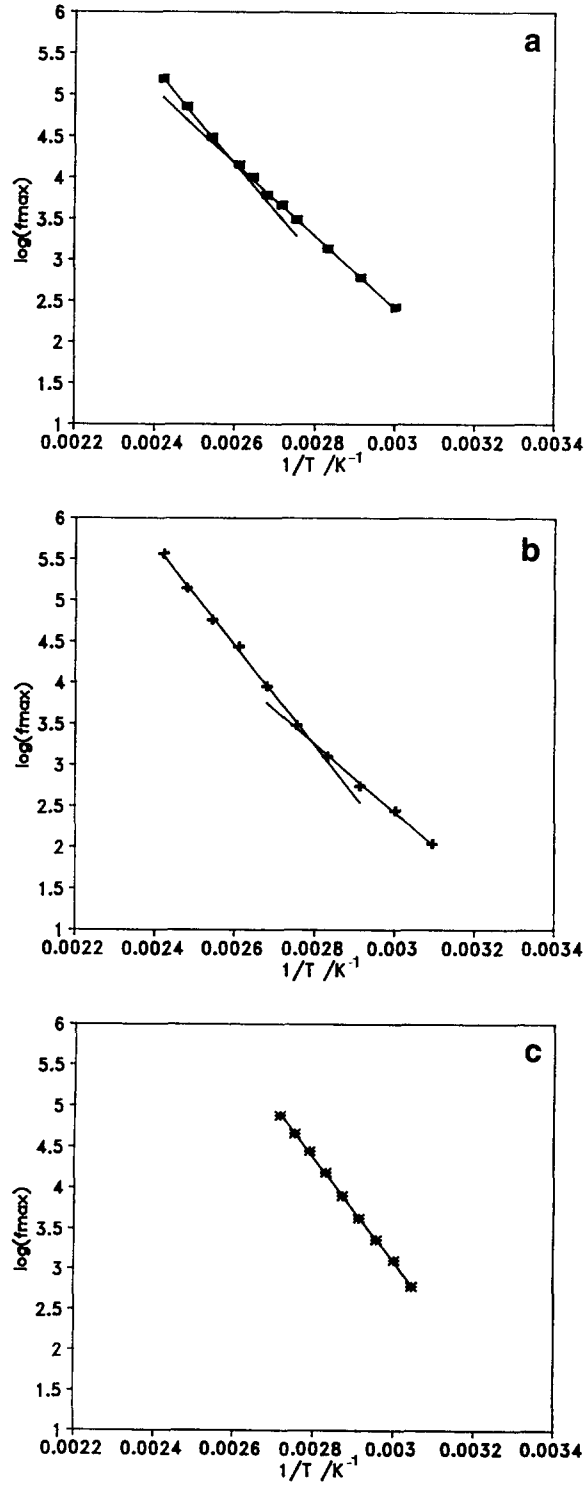

Figure 6 Arrhenius plots for (a) PMMA, (b) PEMA and (c) PnBMA

* It should be noted that the activation energy obtained by Hideshima *et al.* for the separated β process is 19 kcal mol^{-1}, and this value is independent of the size of the n-alkyl side group[2,4]

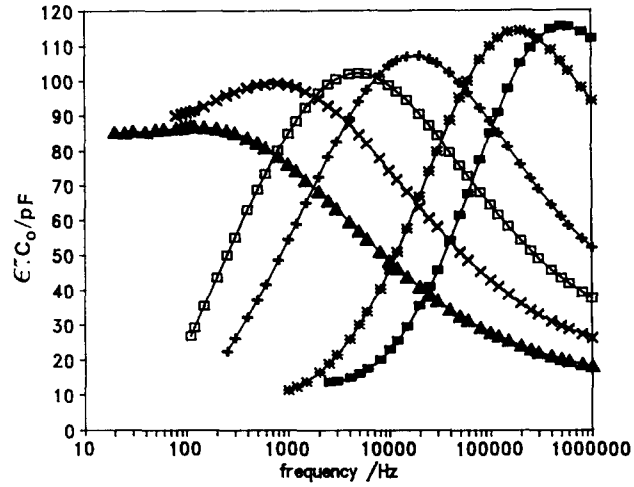

Figure 7 Dielectric relaxation spectra for the mixture PMMA/20% *p*NA at 70, 80, 90, 100, 120 and 130°C (from left to right)

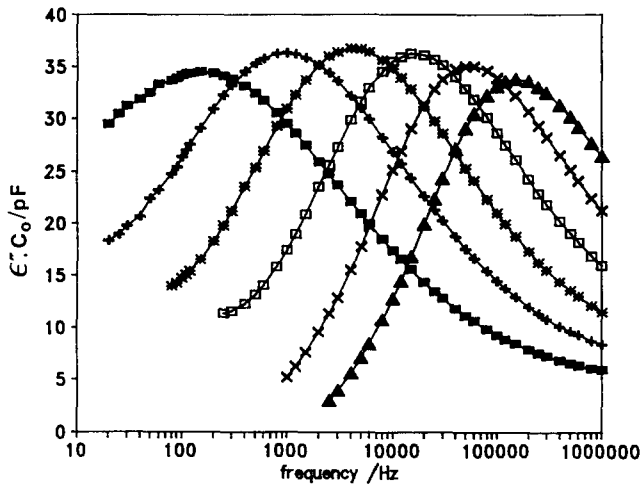

Figure 8 Dielectric relaxation spectra for the mixture PEMA/12.6% *p*NA at 60, 70, 80, 90, 100 and 110°C (from left to right)

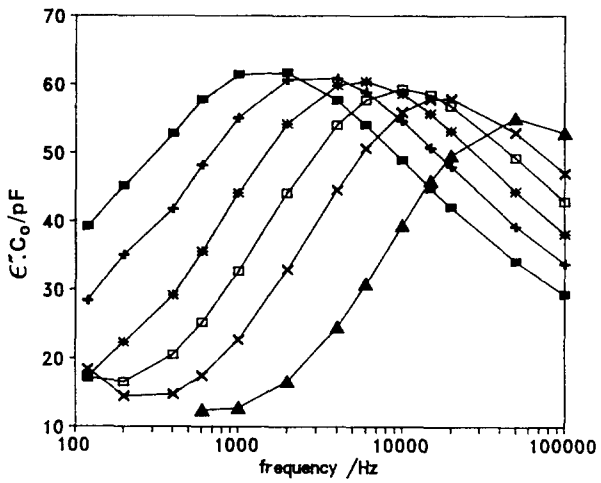

Figure 9 Dielectric relaxation spectra for the mixture PnBMA/10% *p*NA at 50, 55, 60, 65, 70 and 75°C (from left to right)

to lower frequencies (longer relaxation times) at the lower temperatures and that the opposite is observed at higher temperatures, where the peaks are shifted to higher frequencies. The behaviour at higher temperatures corresponds to the normal plastification effect: the solute enhances the chain mobility as a result of the decrease in the interchain interactions and thus decreases the relaxation time of the α process. In contrast, at lower temperatures the observed relaxation is the β relaxation and our results suggest that the presence of the solute hinders this process (the internal rotation of the side groups). The marked broadening of the loss curve at low temperatures suggests that the motions are more complex and possibly correspond to two components. The first is a high frequency component involving the motions of the side groups of the polymer together with the local motions of the solute molecules. These processes do not relax all the mean square dipole moments of these dipolar units, so the remainder are relaxed by a second, low frequency process whose mechanism will resemble that for the α processes of other amorphous polymers such as poly(vinyl acetate). The suggested hindering of the β process by the solute could arise, for example, from the existence of hydrogen-bonding interactions between the side groups and the *p*NA solute. In a study of the dielectric properties of an azo dye/PMMA system[13], in which the solute was 4-[ethyl(2-hydroxyethyl)amino]-4'-nitroazobenzene, it was reported that the peaks were shifted to higher frequencies, at all temperatures, as the solute concentration was increased. This observation is reasonable considering that this solute has a considerably larger molecular volume when compared with *p*-nitroaniline, thus leading to a stronger plastification effect. On the other hand, the hydrogen-bonding capability of *p*NA is probably stronger since it possesses two hydrogen atoms bonded to a nitrogen atom, and these are not so hindered as the hydroxylic hydrogen of the azo dye. For PEMA, the β process in *Figure 2* is not apparent in *Figure 8*. We should remember that PEMA has a complicated pattern of an α process joining a β process with increasing temperature to form the $\alpha\beta$ process, as described in detail elsewhere[6]. The loss curves for the solution (*Figure 8*) appear to correspond to an α or $\alpha\beta$ process at higher temperatures that carries with it the relaxation strength of the polymer and the solute molecules. The marked increase in relaxation magnitude on going from pure polymer to solute/polymer system, which was observed in the PMMA system, is also found in this case. At lower temperatures the broadening may be interpreted in one of two ways: (i) that an $\alpha\beta$ process is changing into resolved α and β processes on decreasing the temperature, with the same interpretation as given above for the PMMA system; or (ii) that an α process is resolving into two components, each of which has an α character, with one (the higher frequency component, possibly) being due to the solute and the other being due to the polymer backbone. The second explanation is unlikely since it does not include side-group motion, which is a β process. The first explanation is almost certainly the case here since it is consistent with the explanation given for the PMMA system and involves the concept of partial and total relaxation of dipolar groups that has been consistently and successfully applied to dielectric relaxations in amorphous dipolar polymers[21]. Comparing the f_{max} values shown in *Table 2* for the mixtures with those shown in *Table 1* for the pure polymers, we conclude that for PEMA the shift of f_{max} to lower frequencies due to the solute is observed only at 60°C. For PnBMA, on the other hand, the addition of the solute shifts f_{max} to higher frequencies at all the temperatures studied. If the shift of f_{max} to lower

Table 2 Parameters of the dielectric relaxation of PMMA, PEMA and PnBMA mixtures with *p*-nitroaniline

Mixture	T (°C)	f_{max} (kHz)	τ_0 (s)	$\varepsilon''_{max}C_0$ (pF)	$(\varepsilon_0-\varepsilon_\infty)C_0$ (pF)	β
PMMA/10% *p*NA	60	0.035	4.55×10^{-3}	33.99	[a]	[a]
	70	0.160	9.95×10^{-4}	38.61	323.5	[a]
	80	0.400	3.98×10^{-4}	45.63	333.1	0.30
	90	1.400	1.14×10^{-4}	54.37	363.0	0.30
	100	4.500	3.54×10^{-5}	60.50	364.0	0.32
	110	16.000	9.95×10^{-6}	64.57	364.0	0.36
	120	50.000	3.18×10^{-6}	66.63	343.0	0.37
	130	160.000	9.95×10^{-7}	67.26	315.0	0.40
	140	450.000	3.54×10^{-7}	68.15	306.0	0.41
PMMA/20% *p*NA	60	0.030	5.30×10^{-3}	68.82	[a]	[a]
	70	0.115	1.38×10^{-3}	86.88	[a]	[a]
	80	0.700	2.27×10^{-4}	99.11	[a]	0.33
	90	5.000	3.98×10^{-5}	102.09	577.8	0.37
	100	17.000	9.36×10^{-6}	106.96	572.8	0.37
	110	60.000	2.65×10^{-6}	110.15	555.0	0.40
	120	190.000	8.84×10^{-7}	114.06	552.5	0.42
	130	520.000	3.06×10^{-7}	115.27	547.5	0.45
PEMA/12.6% *p*NA	60	0.160	9.95×10^{-4}	34.41	[a]	[a]
	70	0.950	1.68×10^{-4}	36.29	215.9	0.36
	80	4.500	3.54×10^{-5}	36.72	194.5	0.40
	90	16.000	9.95×10^{-6}	36.21	177.6	0.41
	100	54.000	2.95×10^{-6}	35.01	167.0	0.43
	110	155.000	1.03×10^{-6}	33.73	160.0	0.45
	120	420.000	3.79×10^{-7}	32.53	154.0	0.45
PnBMA/5% *p*NA	50	0.800	1.99×10^{-4}	40.75	224.3	[a]
	55	1.500	1.06×10^{-4}	42.00	218.8	0.34
	60	3.000	5.31×10^{-5}	40.97	212.9	0.40
	65	6.000	2.65×10^{-5}	41.25	211.0	0.41
	70	10.000	1.59×10^{-5}	41.05	209.0	0.42
	75	17.500	9.09×10^{-6}	40.75	206.3	0.42
	80	35.000	4.55×10^{-6}	40.00	202.5	[a]
PnBMA/7.5% *p*NA	45	0.630	2.53×10^{-4}	50.50	273.0	[a]
	50	1.260	1.26×10^{-4}	50.50	270.9	0.36
	55	2.570	6.19×10^{-5}	50.00	268.3	0.37
	60	5.000	3.18×10^{-5}	49.40	264.0	0.39
	65	9.500	1.68×10^{-5}	48.75	260.0	0.39
	70	17.500	9.09×10^{-6}	48.00	255.0	0.40
	75	30.000	5.31×10^{-6}	47.00	250.0	[a]
	80	50.000	3.18×10^{-6}	46.00	247.0	[a]
PnBMA/10% *p*NA	45	0.700	2.27×10^{-4}	62.49	[a]	[a]
	50	1.500	1.06×10^{-4}	62.00	345.3	0.37
	55	3.000	5.31×10^{-5}	60.80	333.7	0.37
	60	6.000	2.65×10^{-5}	60.32	320.0	0.40
	65	10.000	1.59×10^{-5}	59.23	315.0	0.41
	70	20.000	7.96×10^{-6}	57.81	305.0	0.41
	75	32.000	4.97×10^{-6}	57.20	301.0	[a]
	80	48.000	3.32×10^{-6}	55.00	295.0	[a]

[a] The data were not sufficient to calculate the parameter

frequencies at the lower temperatures corresponds to a hindering of the internal rotation of the side groups due to hydrogen bonding with the solute, we can conclude from the results on PEMA and PnBMA that the n-alkyl group in poly(n-alkyl methacrylate)s may act as a stereochemical hindrance to these intermolecular interactions. For PnBMA it is the $\alpha\beta$ process that is being observed for both solution and pure polymer[21]. The magnitude of the loss peak (*Figure 9*) has increased markedly, as expected for this mechanism, since the relaxation strengths of solute and polymer are contained in the one $\alpha\beta$ process. In this case the solute moves with the polymer chains as an $\alpha\beta$ process at the temperatures studied, and the complications of the partial relaxation

(β) and total relaxation (α) of different groups appear to be absent.

The addition of the polar solute to the polymeric matrix increases, as noted before, the amplitude ε''_{max} of the loss peak, as well as its dielectric strength and the quantity $(\varepsilon_0-\varepsilon_\infty)T$ (which is a measure of the square of the relaxed dipole moment), and this can be attributed to an increase in the dipole concentration as the solute content increases. This effect is more pronounced in the case of PMMA, since in this case the solute contributes to the dielectric strength not only via its own polarity but also by markedly changing the nature of the relaxation process (enhancement of its α character).

In *Figure 10* are presented the variations in ε''_{max} with temperature for three polymer/solute mixtures. This figure can be compared with *Figure 4*, which shows the corresponding data for the pure polymers. We observe that in the case of PnBMA the presence of the solute seems not to change markedly the nature of the relaxation process. In fact, in the pure polymer ε''_{max} increases very slightly with temperature, becoming constant after 70°C, and in the mixture it shows a slight monotonous decrease characteristic of an α process. In pure PEMA ε''_{max} increases with temperature (*Figure 4*) but seems to tend to an asymptotic value at higher temperatures. In the mixture, on the other hand, this asymptotic value seems to be already present at low temperatures and ε''_{max} decreases very slightly with increasing temperature. We could say that the presence of the solute in the case of PEMA enhances the α character of the relaxation process, and the same conclusion could be drawn from the PMMA data. In pure PMMA the dielectric strength increases with increasing temperature, whereas in the most concentrated solution (20% *p*NA) it decreases. In pure PEMA the dielectric strength increases with temperature until 90°C and then decreases with increasing temperature. In the mixture, $\varepsilon_0-\varepsilon_\infty$ decreases with increasing temperature over the whole temperature range. The same behaviour was observed for pure PnBMA and its mixtures. These data indicate again that the presence of the solute enhances the α character of the relaxations in PMMA and PEMA. The variation with temperature of the quantity $(\varepsilon_0-\varepsilon_\infty)T$ was previously discussed for the pure polymers (*Figure 5*). In the case of the mixtures, a very slight dependence of this quantity

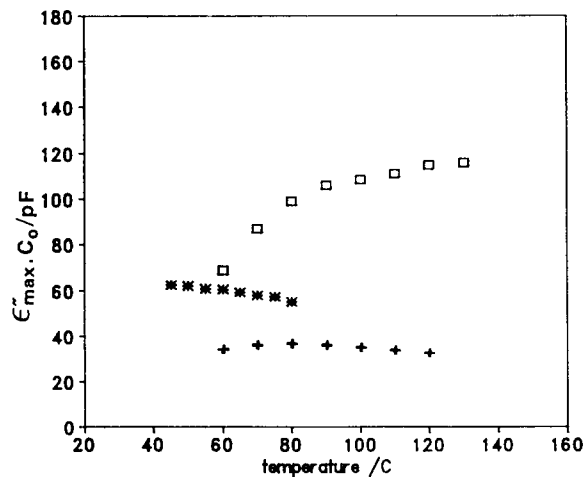

Figure 10 Variation in $\varepsilon''_{max}C_0$ with temperature for the mixtures PMMA/20% *p*NA (□), PEMA/12.6% *p*NA (+) and PnBMA/10% *p*NA (*)

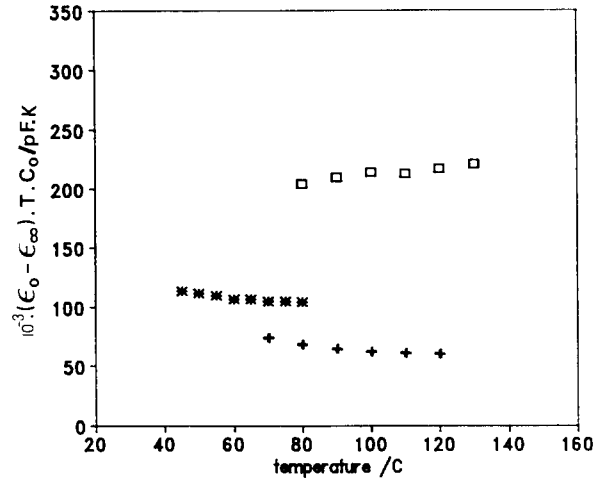

Figure 11 Variation in $(\varepsilon_0-\varepsilon_\infty)T$ with temperature for the mixtures PMMA/20% *p*NA (□), PEMA/12.6% *p*NA (+) and PnBMA/10% *p*NA (*)

on temperature is observed, as shown in *Figure 11*, for the mixtures PMMA/20% *p*NA, PEMA/12.6% *p*NA and PnBMA/10% *p*NA.

If we look now at the distribution of relaxation times (as measured by the β parameter of the KWW distribution function), we observe that the addition of the solute narrows this distribution (higher β values) for PMMA and, to a lesser extent, for PEMA. In these polymers the effect of adding the solute seems similar to the effect of increasing temperature, i.e. there is a change in the nature of the relaxation process and/or a diminishing of the β process. In PnBMA, on the other hand, the addition of the solute does not have this effect; conversely, a very slight tendency of the β parameter to decrease with increasing solute concentration at a given temperature can be detected. The temperature dependence of the KWW β factor does not show any significant modification due to the presence of the solute: in the cases of PMMA and PEMA, β increases with increasing temperature for the pure polymers as well as for the mixtures, and in the case of PnBMA this variation seems to be less pronounced in the mixtures than in the pure polymer.

Finally, looking at the Arrhenius plots of $\log f_m$ *versus* $1/T$ (*Figure 12*), we can see that the two temperature regions that were observed for pure PMMA and PEMA are no longer observed for the respective mixtures. The activation energy for the PMMA/20% *p*NA solution is 39.6 kcal mol^{-1} (higher than the value of 26.0 kcal mol^{-1} for pure PMMA in the high temperature region) and for the PEMA/12.6% *p*NA solution it is 33.9 kcal mol^{-1} (higher than the value of 30.0 kcal mol^{-1} for pure PEMA in the high temperature region). On the contrary, in the case of PnBMA the addition of the solute lowers the activation energy of the relaxation process: 29.4 kcal mol^{-1} for the pure polymer, 26.6 kcal mol^{-1} for the 10% *p*NA solution (for the other mixtures the value is intermediate between these two values).

These results suggest again that in the system PMMA/*p*NA we have hydrogen bonding between the solute and the polymer side groups (as was also observed for poly(vinyl acetate)[22]), which causes a shift to lower frequencies of the β relaxation and an increase in the activation energy of the $\alpha\beta$ process. In PEMA similar behaviour is observed but to a lesser extent. In PnBMA, on the other hand, the presence of the solute decreases

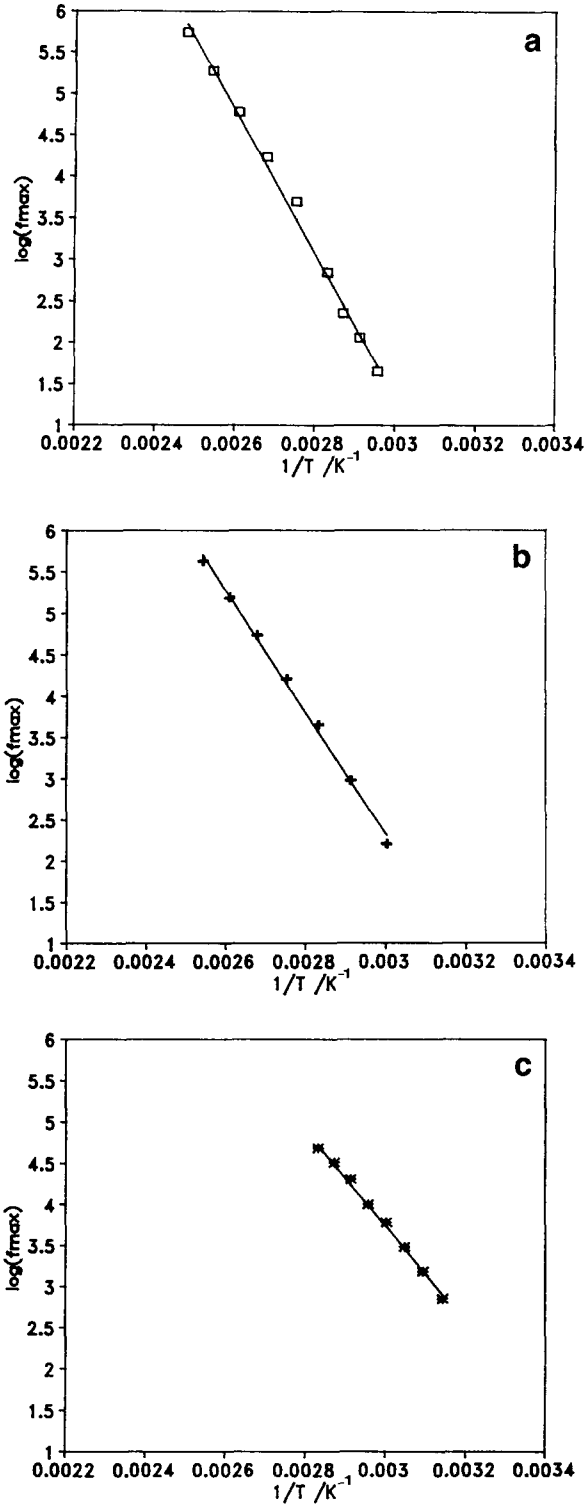

Figure 12 Arrhenius plots for the mixtures (a) PMMA/20% *p*NA, (b) PEMA/12.6% *p*NA and (c) PnBMA/10% *p*NA

the activation energy and shifts the frequency of maximum loss towards higher frequencies, suggesting that the bulky n-butyl group prevents the solute–polymer hydrogen bonding and that the solute essentially causes plastification.

In the study of the azo dye/PMMA system mentioned earlier[13], a decrease in the activation energy of the $\alpha\beta$ process with increasing solute concentration was observed. This observation can be rationalized as follows. The presence of the hydrogen-bonding solute has two opposite effects on the activation energy of the motions of the polymer host: on the one hand, it has the so-called plastification effect, which leads to a reduction in the interchain interactions and consequently to an increase in the rate of the motions of the chain backbone (decrease in the activation energy); on the other hand, the hydrogen bond formation between the solute and the polymer side groups will increase the activation energy of the β process (internal rotations of the ester side groups around the bonds which link them to the main chain) and will also make more difficult the motions of the main chain itself. As pointed out earlier, the azo dye solute in this study had a larger molecular volume and a weaker hydrogen-bonding ability when compared with *p*-nitroaniline. It thus seems reasonable to consider that the effect of the azo dye solute on the motions of PMMA is dominated by its plastification effect. Contrastingly, the *p*-nitroaniline solute in PMMA has a behaviour which is dominated by its hydrogen-bonding ability, but in PnBMA, where the bulky n-butyl group prevents hydrogen bonding with the oxygen atoms of the ester moiety, it has essentially a plastification effect.

CONCLUSIONS

This dielectric study of PnAMA/*p*NA solid solutions has led to the following conclusions.

1. The addition of the polar solute to PMMA hinders the β process (shift to lower frequencies of the low temperature peaks) and enhances the α character of the relaxation process (narrowing of the peak as shown by an increase in the β parameter of the KWW distribution function).
2. The activation energy of the $\alpha\beta$ process in PMMA is increased by the addition of *p*NA.
3. These effects are also observed for PEMA but to a lesser extent, and are absent for PnBMA.
4. It is concluded that there is hydrogen bonding between the *p*NA solute and the ester moiety of the polymer, and that the extent of this hydrogen bonding decreases with increasing size of the n-alkyl side group. Nevertheless, more work needs to be carried out for a better and more general understanding of the effect of the solute on the relaxational behaviour of the polymer host.

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