Molecular motions in poly(vinyl acetate) and in poly(vinyl acetate)/*p*-nitroaniline mixtures

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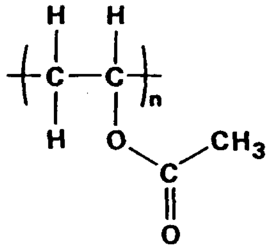
In the present paper we examine the dielectric properties of solid solutions of *p*-nitroaniline in a poly(vinyl acetate) matrix in the frequency range from 16 to 10^5 Hz and the results are compared with those for pure poly(vinyl acetate). It is shown that the presence of the solute increases the activation energy of the α relaxation process of the polymer and broadens the distribution of relaxation times for this process. It is suggested that these observations can be interpreted in terms of the formation of hydrogen bonds between the solute and the side groups of the polymer.

(Keywords: poly(vinyl acetate); *p*-nitroaniline; dielectric relaxation; polymer composite)

INTRODUCTION

Poly(vinyl acetate) (PVAc) is an amorphous polymer whose glass transition is near room temperature. Many studies have been published concerning the relaxation behaviour of PVAc and this polymer is often used as a standard for experimental measurements and to test the current theories of dielectric relaxation. From a chemical point of view it has a main chain formed by carbon–carbon single bonds at which are connected polar acetate side groups:



Two relaxation mechanisms have been identified in this polymer: the main dispersion, the so-called α process, which is associated with the glass transition and is attributed to the Brownian motion of the segments of the main chain; and a lower temperature mechanism, the β process, which is attributed to the motion of the acetate side groups. The α relaxation of PVAc has been studied in great detail since 1941[1]. It has been shown that the dielectric loss (ε'') curves shift to higher frequencies as the temperature increases, but their shapes were reported to remain unchanged in early works, showing the validity of the time–temperature superposition principle. More recently, however, a change in the shape of the dielectric loss peak was observed[2] in studies over a wide temperature range. This change is such that the peaks become broader as the temperature decreases. The well-resolved loss peaks showed an asymmetry, being broader on the high frequency side. This asymmetry, which is also observed for other polymers, was considered to arise from the intrachain interactions, an intrinsic characteristic of the long-chain nature of polymeric molecules. The dielectric strength $\varepsilon_0 - \varepsilon_\infty$ of the α process was found to increase with decreasing temperature, as found for many amorphous polymers above the glass transition temperature (T_g).

The $\log_{10} f_{\max}$ (frequency of maximum loss) *versus* $1/T$ plot is well described by an equation of the Williams–Landel–Ferry (WLF) type. The WLF behaviour of the α process in PVAc near the glass transition temperature was nevertheless contested by Kovacs *et al.*[3] from an investigation on dynamic shear properties. These authors suggested that the lower temperature limit of the validity of this equation was $T_g + 10$°C, and that below this temperature the superposition principle was no longer valid. More recently, the experimental difficulties in measuring the relaxation in the ultra-low frequency region have been overcome and Nozaki and Mashimo[4] were able to confirm, by dielectric measurements, the conclusions of Kovacs *et al.* The dielectric relaxation of PVAc has been interpreted in the context of a model which suggests a coupling between the relaxation of the 'primitive' segmental process and its complex surroundings[2]. In a recent paper, however, Schlosser and Schonhals[5] were not able to confirm the results of Nozaki and Mashimo, finding that the WLF equation is obeyed (in equilibrium) at all temperatures.

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The exact nature of the α relaxation in PVAc is still under discussion[6]. In the present paper we present the results of an investigation of the dielectric behaviour of solid solutions of PVAc with *p*-nitroaniline (pNA). One of the motivations of this investigation was the fact that organic dye–polymer composites have received considerable attention from many researchers[7], and have been considered as candidates for new electro-optic materials[8,9]. On the other hand, we wanted to analyse the influence of a polar solute molecule such as pNA on the relaxation behaviour of the polymer matrix. The effect of adding low-molecular-weight solutes to amorphous matrices is a well-known phenomenon called plastification; it lowers T_g and the α relaxation temperature. At a given temperature the effect of the plasticizer is to shift the loss factor/frequency curves to higher frequencies and this is ascribed to an enhancement of the chain mobility arising from the increase in free volume (or decrease in the interchain interactions). The solute pNA molecule is very polar and can be oriented in static electric fields and has terminal electron donor and acceptor groups. In particular, the NH_2 group is able to act as a proton donor in hydrogen bonds which can be formed with the acetate side groups of the PVAc chains. This could induce modifications in the relaxation behaviour of the polymeric chains.

EXPERIMENTAL

Poly(vinyl acetate) was of medium molecular weight from Aldrich ($M_w = 68\,000$ obtained by viscometry[10]). Its glass transition temperature, obtained by thermally stimulated currents, was 28.5°C. *p*-Nitroaniline was from Aldrich (purity >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 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 (PVAc without pNA) was prepared in the same way. This preparation method ensured a constant sample thickness so that the geometric capacitance C_0 of the cell was the same for all the results presented in *Tables 1* and *2*.

Dielectric measurements were performed in a General Radio 1689 Digibridge (frequency range 16 to 10^5 Hz). The sample films were placed between the electrodes of a three-terminal, parallel plate capacitor described elsewhere[11]. 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 variations in dielectric strength and frequency location of the loss peaks with sample composition and temperature. We were able to obtain this information from $\varepsilon' C_0$ and $\varepsilon'' C_0$.

Table 1 Parameters of the α relaxation of PVAc

T (°C)	f_{max} (kHz)	τ_0 (s)	$\varepsilon''_{max} C_0$ (pF)	$(\varepsilon_0 - \varepsilon_\infty) C_0$ (pF)	β
45	0.0343	4.64×10^{-3}	14.90	54.9	0.56
50	0.1658	9.60×10^{-4}	14.69	50.2	0.58
55	0.6036	2.64×10^{-4}	14.33	47.9	0.59
60	2.0484	7.77×10^{-5}	13.87	46.2	0.60
65	5.8080	2.74×10^{-5}	13.68	45.0	0.61
70	15.8742	1.00×10^{-5}	13.39	43.0	0.61

Table 2 Parameters of the α relaxation of the different PVAc/pNA solid solutions

pNA (wt%)	T (°C)	f_{max} (kHz)	τ_0 (s)	$\varepsilon''_{max} C_0$ (pF)	$(\varepsilon_0 - \varepsilon_\infty) C_0$ (pF)	β
3	45	0.0648	2.45×10^{-3}	18.02	65.6	0.53
	50	0.2862	5.56×10^{-4}	17.44	63.8	0.54
	55	1.0000	1.59×10^{-4}	16.96	59.8	0.54
	60	3.2465	4.90×10^{-5}	16.38	58.3	0.54
	65	9.4493	1.68×10^{-5}	16.08	56.3	0.54
	70	23.4797	6.78×10^{-6}	15.77	55.2	0.54
6	45	0.0643	2.48×10^{-3}	24.70	94.6	0.52
	50	0.2954	5.39×10^{-4}	23.86	86.9	0.53
	55	1.0925	1.46×10^{-4}	23.30	84.8	0.53
	60	3.6225	4.39×10^{-5}	22.61	82.1	0.54
	65	10.5108	1.51×10^{-5}	22.10	80.0	0.54
	70	26.4349	6.02×10^{-6}	21.60	75.9	0.55
12	45	0.1240	1.28×10^{-3}	40.75	156.3	0.48
	50	0.5486	2.90×10^{-4}	38.91	149.4	0.50
	55	1.9923	7.99×10^{-5}	37.62	141.7	0.51
	60	6.4536	2.47×10^{-5}	36.66	139.0	0.52
	65	18.4876	8.61×10^{-6}	35.47	131.5	0.53
17.5	40	0.0818	1.95×10^{-3}	46.54	210.1	0.42
	45	0.4383	3.63×10^{-4}	45.21	204.1	0.42
	50	1.8304	8.70×10^{-5}	43.93	192.9	0.43
	55	6.3096	2.52×10^{-5}	42.81	182.7	0.45
	60	19.0514	8.35×10^{-6}	41.48	171.9	0.46

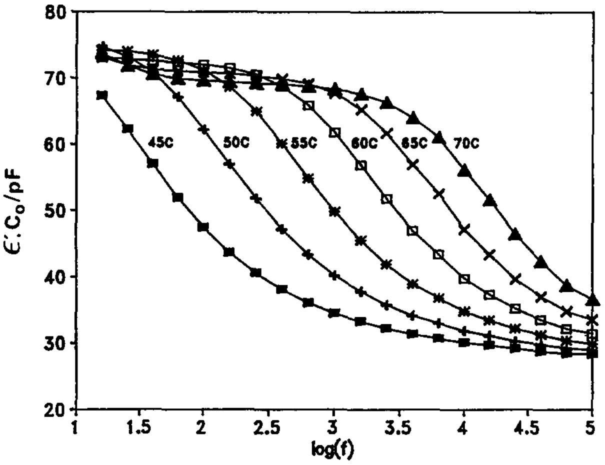

Figure 1 Dispersion curves for PVAc between 45 and 70°C

RESULTS AND DISCUSSION

The α relaxation in poly(vinyl acetate)

The dispersion curves for the blank sample (PVAc without pNA) are presented in *Figure 1* between 45 and 70°C. The corresponding absorption curves are shown in *Figure 2*.

These results are shown in order to characterize this particular sample of PVAc since properties will vary with molecular weight, its distribution and the presence of any residual monomer (acting as plasticizer); they confirm those previously reported in the literature. When the temperature increases the frequency of maximum loss f_{max} increases, with the consequent decrease in the relaxation time τ_0. This is as a consequence of the higher mobility of the polymer chains at higher temperatures. On the other hand, the height of the loss peak decreases slightly

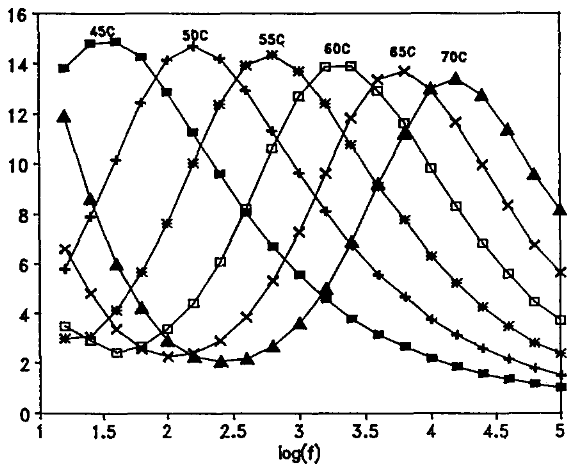

Figure 2 Absorption curves for PVAc between 45 and 70°C

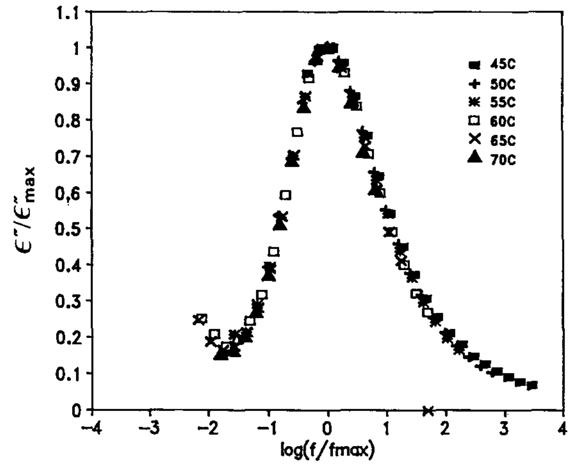

Figure 3 Normalized loss peaks for PVAc at different temperatures

with increasing temperature. If this is not accompanied by a change of the peak shape it means that the area under the peak (the total amount of relaxed dipole) decreases with increasing temperature. *Figure 3* shows the normalized loss peaks ($\varepsilon''/\varepsilon''_{max}$ *versus* $\log_{10}(f/f_{max})$) for PVAc at different temperatures and it is apparent from this figure that there is no change in the shape of the peak in the studied temperature range.

The same conclusion may be reached from the calculation of the β parameter of the Kohlrausch–Williams–Watts (KWW) response function for the dielectric polarization. The β parameter of this empirical function describes the distribution of the relaxation times or, otherwise stated, the shape of the frequency dependence of the complex permittivity. Its value will be unity for a Debye process (half-height width $\Delta \log_{10} f = 1.14$) and values between 1 and 0 are given by $\beta = 1.14/\Delta \log_{10} f$ for complex relaxation processes[12].

The calculated β values are presented in *Table 1* together with other parameters for the α relaxation process of PVAc. The fact that β does not change significantly with temperature in the range 45–70°C indicates that the shapes of the loss curves are identical.

Since the shape of the loss curve remains unchanged and the loss maxima decrease with increasing temperature we must conclude that the dielectric strength $\varepsilon_0 - \varepsilon_\infty$ of the α process decreases with increasing temperature. The most direct method of obtaining the dielectric strength $\varepsilon_0 - \varepsilon_\infty$, where ε_0 is the static permittivity and ε_∞ is the permittivity for induced polarization, is from the plot of ε'' *versus* ε', the so-called Cole–Cole plot. *Figure 4* shows such a plot obtained from our data for PVAc at 55°C. The values of $(\varepsilon_0 - \varepsilon_\infty)C_0$ which we obtained differ from the $\varepsilon_0 - \varepsilon_\infty$ values reported by Yamafuji and Ishida[13] by a factor of 7.9. We can thus conclude that 7.9 pF is the value of the geometric capacitance C_0 of our measuring cell.

A similar value was obtained by measuring the electrode diameter and the thickness of the sample after the experiments. It is clear from *Figure 1* and *Table 1* that our values of the dielectric strength decrease significantly with increasing temperature and a similar behaviour is reported in ref. 5. The fact that the dielectric strength decreases does not mean that the relaxed dipole moment decreases. Since the dielectric strength is proportional to $\mu^2/3kT$, it is the product of that quantity with the absolute temperature which is found to be constant (μ is constant). If we calculate the dipole moment from the Onsager equation

$$\mu^2 = \frac{9kTM_w}{4\pi N_A \rho}\,\frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty + 2)^2}$$

where M_w is the molecular weight of the monomer, N_A is the Avogadro constant and ρ is the mass density, we in fact obtain a value of 2.09 D independent of the temperature (the dipole moment of the vinyl acetate monomer measured in solution in an apolar solvent is 1.79 D).

The WLF equation is obeyed by our data and *Figure 5* shows how well our experimental points are correlated with this equation. The activation energy obtained from this plot is 54.2 kcal mol^{-1} (1 cal = 4.2 J) at 55°C, which is of the same order as the values reported in the literature[14].

*The α relaxation in poly(vinyl acetate)/*p*-nitroaniline solid solutions*

p-Nitroaniline is a strongly polar substance ($\mu = 6.22$ D[15]), possessing in its molecule an amino group which is very active in hydrogen bond formation. In the present section we report our results on the α relaxation process in mixtures of this solute with PVAc in different concentrations (3, 6, 12 and 17.5 wt%).

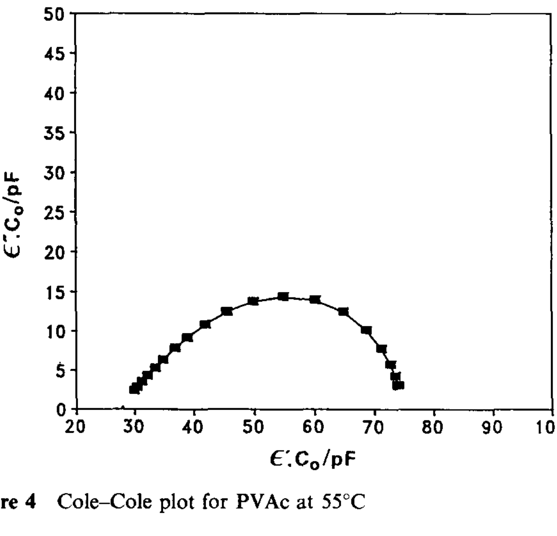

Figure 4 Cole–Cole plot for PVAc at 55°C

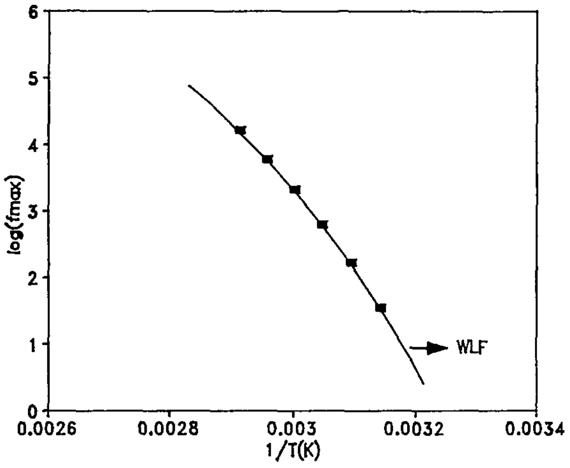

Figure 5 Arrhenius plot for PVAc and correlation with the Williams–Landel–Ferry equation

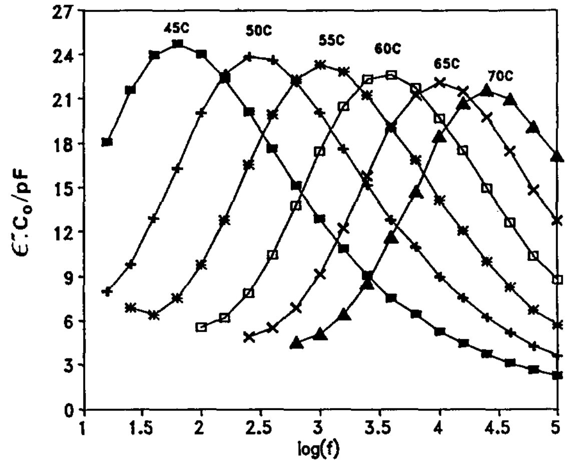

Figure 6 Loss peaks for the 6 wt% PVAc/pNA mixture

The first observation we can formulate from our results is that the addition of pNA has the expected plasticizing effect on the PVAc, inducing a shift of the α loss peaks to higher frequencies. We have also observed this effect through thermally stimulated currents: the depolarization temperature decreases with increasing pNA concentration.

Figure 6 shows the loss peaks obtained for the 6 wt% mixture. The behaviour is similar for the other mixtures.

As was the case for pure PVAc, the height of the peak decreases (as well as the dielectric strength) with increasing temperature, but the nature of the α relaxation process seems to remain unchanged. This is suggested by the normalized loss curves shown in *Figure 7* for the same mixture (the behaviour is the same for the other mixtures) and confirmed by the β values of the KWW function presented in *Table 2*.

For a given mixture the β value does not show any significant variation with temperature, meaning that the distribution of the relaxation times is the same at the different temperatures. The WLF equation is also obeyed in the present case and this is observed for all the studied mixtures (*Figure 8* shows the WLF correlation with the experimental data for the 6 wt% mixture).

The Arrhenius activation energies have been calculated for the 3, 6, 12 and 17.5 wt% mixtures and the values are presented in *Table 3*. The temperatures at which the activation energies were calculated are those at which the peaks for the different mixtures have the same location ($\log_{10} f_{\max} = 3.0$)*. The observed increase of the activation energy with increasing solute concentration will be discussed later.

The most obvious conclusion we can draw from the results in *Table 2* is that the height of the loss peak and the dielectric strength of the α relaxation process increase significantly with increasing solute concentration. *Figure 9*, which shows the absorption

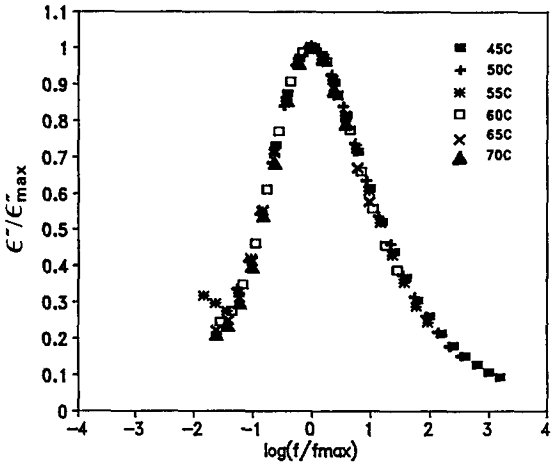

Figure 7 Normalized loss curves for the 6 wt% PVAc/pNA mixture

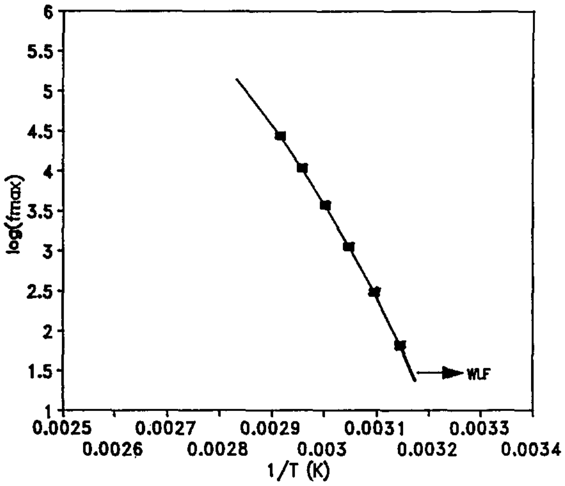

Figure 8 Arrhenius plot for the 6 wt% PVAc/pNA mixture and correlation with the Williams–Landel–Ferry equation

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*As correctly pointed out by a referee, it is better to compare slopes at constant T_0/T, where T_0 is the critical temperature in the WLF equation

$$\log_{10} f_{\max} = A - \frac{B}{T - T_0}$$

This should be equivalent to comparing the B parameters of this equation for the different mixtures since, from its differentiation with respect to $1/T$, we have

$$\frac{\mathrm{d}\log_{10} f_{\max}}{\mathrm{d}(1/T)} = -B\left(1 - \frac{T_0}{T}\right)^{-2}$$

Nevertheless, the fact that the temperature range of our experiments is narrow does not enable us to obtain accurate values for the parameters of the WLF equation

Table 3 Activation energies of the α relaxation for the different PVAc/pNA solid solutions

pNA (wt%)	T (°C)	E_a (kcal mol^{-1})
3	54.8	51.8
6	54.6	54.0
12	52.4	54.8
17.5	47.8	56.9

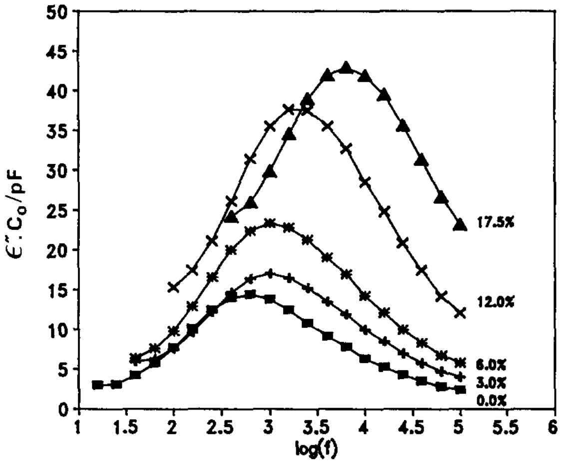

Figure 9 Absorption peaks for the different mixtures at 55°C

peaks for the different mixtures at 55°C, illustrates this behaviour.

The same is shown in a different way in *Figure 10* where the dielectric strength $\varepsilon_0 - \varepsilon_\infty$ and the maximum loss $\varepsilon''_{\max}$ are plotted as functions of the concentration of the mixture (at 55°C).

These results suggest that the solute molecule is engaged in the relaxation process of the polymeric matrix, thus strongly increasing the polarization of the α process. We were not able to detect any independent relaxation mechanism of the solute in these mixtures in the available range of frequencies and temperatures. We carried out experiments at lower temperatures (down to −20°C) to look at higher frequency processes and we also carried out transient current experiments to give access to the low frequency range but no independent solute relaxation mechanism was observed in either case.

Another observation which could be significant is the broadening of the loss peak for the mixture of higher concentration, which is revealed by the smaller β value obtained for this mixture (*Table 2*). The solution of 17.5 wt% pNA corresponds to a relationship of more than one solute molecule to 10 monomers. If the solute is able to form hydrogen bond complexes with the polymer chain, we can say that, at this concentration, the monomers of the chain are hydrogen bonded to the solute in a significant fraction. Unfortunately, the solubility limit of pNA in PVAc did not enable us to prepare more concentrated, homogeneous and transparent mixtures. This hydrogen bonding could cause the observed broadening of the absorption peak as a result of an increase in the number of individual relaxation modes involved in the α relaxation process. The hydrogen bonding between the solute and the polymer chains could be, on the other hand, at the origin of the increase in the activation energy of the relaxation process with increasing solute concentration. This increase would be a consequence of the need for hydrogen bond disruption to enable the chains to move or, alternatively, of the increase in the free volume needed for chain movements in case the solute moves together with the polymer chains.

The behaviour may be summarized as follows. The dielectric α process in the pure polymer carries with it essentially all of the mean square dipole moment per repeat unit $\langle \mu_r^2 \rangle$ which is available for relaxation since the strength of the secondary processes is rather small for this polymer[1]. Solutions of *p*-nitroaniline in poly(vinyl acetate) give for the dielectric α process: (i) a systematic increase in relaxation strength as solute concentration is increased (*Figure 9* and *Table 2*); (ii) approximately constant peak shape up to about 12 wt% solute concentration, beyond which the loss curve is broadened significantly (as judged by the β values in *Table 2*); and (iii) only a small shift in the frequency location up to about 6 wt% solute concentration, beyond which $f_{\max}$ increases markedly, consistent with enhanced mobility of the chains due to plasticization by the presence of the low-molecular-weight solute at high concentrations.

An important conclusion from these observations is that the guest molecules move cooperatively with the host polymer chains to give one overall α process. This need not have been the case since limited motions of the solute, independent of the motions of the chains, could have been observed, leading to a partial relaxation of the solute molecules at high frequencies. Such behaviour has been observed in some systems. For example, an independent rotational motion of the solute *p*-dimethylamino-*p*′-nitroazobenzene in a polystyrene matrix has been reported[16] on the basis of a thermally stimulated depolarization current study. Our data, however, give no indication of such a process, but resemble closely what we had observed earlier in amorphous glass-forming solutions of different solutes in the essentially non-polar solvent *o*-terphenyl[17-20]. In those cases the solutes (e.g. fluorenone, anthrone, phthalic anhydride), which in normal low-viscosity solvents would have reorientational correlation times in the range 10^{-10} to 10^{-12} s, move with the solvent molecules which in the temperature region just above the glass transition temperature corresponds to much longer correlation times (10^{-6} to 10^3 s). Also, in the small-molecule,

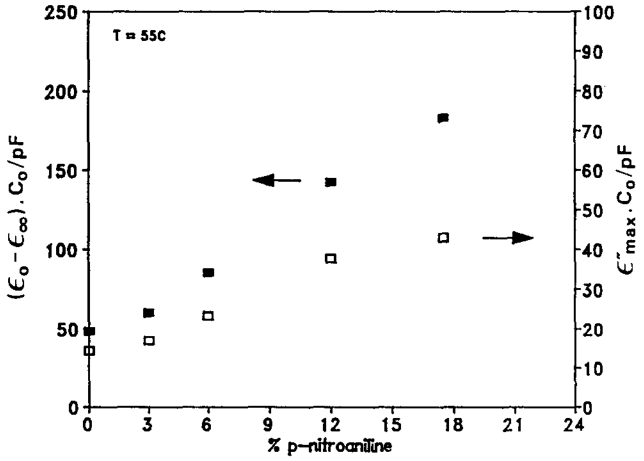

Figure 10 Dielectric strength $\varepsilon_0 - \varepsilon_\infty$ and maximum loss $\varepsilon''_{\max}$ as functions of the concentration of the mixture (at 55°C)

glass-forming liquids the correlation function for dipole reorientation closely follows the KWW function, as is the case for the present solute/polymer system. The comparison is even more obvious since β values for the small-molecule, glass-forming liquids ($\beta \approx 0.55$) are very close to the values found for the present solute/polymer system (*Table 2*). Thus the dipole moment correlation functions $\langle \mu_i(0)\, \mu_i(t) \rangle_{\mathrm{polymer}}$ and $\langle \mu_i(0)\, \mu_i(t) \rangle_{\mathrm{solute}}$ for chain-segmented motions and solute molecule motions respectively are essentially the same in a given solution at a given temperature, and both are expressed fairly accurately by the KWW stretched exponential function $\phi(t) = \exp[-(t/\tau)^{\beta}]$, where $\beta \approx 0.55$ for most compositions. Our results also suggest that poly(vinyl acetate) is a suitable host for solute molecules having non-linear optical properties. Since the solute appears to move only in cooperation with the polymer chain segments, a poled sample held below its glass transition temperature should retain the perturbed orientation of solute molecules on removal of the poling field.

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