Dielectric Properties of Azo Dye–Poly(methyl methacrylate) Mixtures

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ABSTRACT: The dielectric properties of 4-[ethyl(2-hydroxyethyl)amino]-4′-nitroazobenzene–poly(methyl methacrylate) mixtures have been investigated in the temperature range from −20 to 150 °C and the frequency range from 0.1 to 100 kHz. It is found that the observed permittivities can be interpreted satisfactorily in terms of heterogeneous mixture models on the basis of a simple interfacial polarization mechanism. The empirical equation of Havriliak and Negami can be fitted to the α relaxation data of the mixtures and the results are in agreement with inferences from normalized loss factor curves. Dielectric and DSC data reveal that the azo dye has a plasticizing effect on PMMA. The relaxation results also show that 20% dye is a critical concentration above which the β relaxation disappears and the relaxation behavior of the composites becomes independent of the dye content.

Introduction

Organic dye–polymer composites have received considerable attention as a family of new potential electrooptic materials.[1] Organic dyes, in general, possess conjugated molecular structures with terminating electron donors and acceptors and large dipole moments. Consequently, they can be oriented in a high static electric field. If the oriented state can be frozen in a glassy polymer matrix, the dye–polymer system can exhibit unique electrooptical properties. In 1979, Havinga and Van Pelt[2] investigated the electrochromism of dye–polymer mixtures in which a small amount of the desired dye ($\sim 10^{-4}$ mol/kg) was dissolved in poly(methyl methacrylate) (PMMA) and then oriented in a high static field above the glass transition temperature of the polymer. Orientation of the dye was preserved by maintaining the electric field while cooling rapidly below T_g. More recently, Singer et al.[3] have studied the nonlinear optical properties of 4-[ethyl(2-hydroxyethyl)amino]-4′-nitroazobenzene (an azo dye which will be referred to as DR-1)–poly(methyl methacrylate) mixtures in which the dye was oriented and fixed in a manner similar to that described above. These mixtures have a number of advantages as nonlinear optical materials including high optical quality and processibility. The second harmonic coefficient of DR-1–PMMA mixtures was found to be about 6 times that of potassium dihydrogen phosphate and the composite has an electrooptic coefficient twice that of gallium arsenide. However, the effect of the dye, either in its oriented or unoriented state, on the dielectric properties has not been established. In this paper, we investigate the dielectric behavior of unoriented DR-1–PMMA mixtures containing 0–30 wt % DR-1, which covers both homogeneous and heterogeneous systems.

Experimental Section

The 4-[ethyl(2-hydroxyethyl)amino]-4′-nitroazobenzene (Figure 1) used in this work was purified from the commercial material (Aldrich Chemical Co.) by extraction and recrystallization. The melting point of the purified DR-1 was approximately 162 °C which compares well with the literature values of 161–165 °C.[4-7] PMMA was obtained from Fisher Scientific Co. (atactic, $\bar{M}_\eta$ = 94 000 g/mol) and was used as received. Tetrahydrofuran (THF) was distilled over potassium metal prior to use.

DR-1–PMMA mixtures containing different concentrations of DR-1 were prepared as follows. Varying amounts of DR-1 and PMMA powders were dissolved in THF to produce approximately 5% solutions. The solutions were filtered through filter membranes (0.2-μm pore size) and then cast into Teflon-coated aluminum pans. The majority of solvent was allowed to evaporate at room temperature. Further drying of the films was conducted in vacuum at room temperature, 80 and 115 °C for 24 h each. The dried films were then hot pressed at 180 °C and approximately 20 kg/cm^2 pressure for 20 min and then cooled rapidly to room temperature. The resulting film thicknesses varied between 0.1 and 0.2 mm. The T_g of the DR-1–PMMA mixtures was measured by using a Perkin-Elmer 7 series differential scanning calorimeter.

Measurements of dielectric constant and loss were made with a Hewlett-Packard Model 4274A multifrequency LCR meter. This is an impedance-type analyzer which can be operated at 11 discrete frequencies of the applied potential ranging from 0.1 to 100 kHz. The dielectric constant is calculated by treatment the sample as a parallel-plate capacitor and from a knowledge of the area-to-thickness ratio of the specimen. The phase angle is measured directly, and its complement δ gives the loss tangent, tan δ. The loss factor ϵ'' can be calculated from the relation $\epsilon'' = \epsilon' \tan \delta$. Immediately before measurement, samples were heated to 150 °C and the dielectric data were collected from higher to lower (−20 °C) temperatures. Prior to dielectric measurement, gold electrodes were applied to the films by vacuum evaporation. The electrode diameter was approximately 6.8 mm.

Results and Discussion

1. Dielectric Permittivities. The temperature dependence of the relative dielectric permittivities at 1 kHz of DR-1–PMMA mixtures containing 0–30 wt % DR-1 is presented in Figure 2. It is apparent that the dielectric constant increases with increasing DR-1 concentration and that the location of the α transition (associated with T_g-like motion) shifts to lower temperatures. T_g values obtained from DSC experiments (Figure 3) show that the T_g declines regularly with increasing DR-1 content. Figure 4 illustrates the linear relationship between $1/T_g$ and DR-1 concentration. The results support the idea that DR-1 has a plasticizing effect on PMMA.

The increase in both the relaxed and unrelaxed dielectric permittivities (obtained from Cole–Cole plots, as discussed later, and as estimated from the high- and low-temperature permittivity values in Figure 1) can be attributed to the larger dipole concentration as dye content increases. The dependence of the dielectric relaxation strength, i.e., the difference between the relaxed and unrelaxed permittivities, on DR-1 content is shown in Figure 4. When plotted as a function of dye concentration, the relaxation strength increases rapidly because of the larger dipole moments.

We found that expressions derived for heterogeneous mixtures can be used to describe the variation in dielectric permittivity with DR-1 concentration. Hayakawa and Wada[8] considered a heterogeneous system in which spherical particles with dielectric constant ϵ_2 are dilutely dispersed in a uniform polymer matrix with dielectric

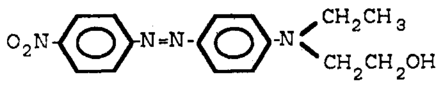

Figure 1. Chemical structural formula of DR-1.

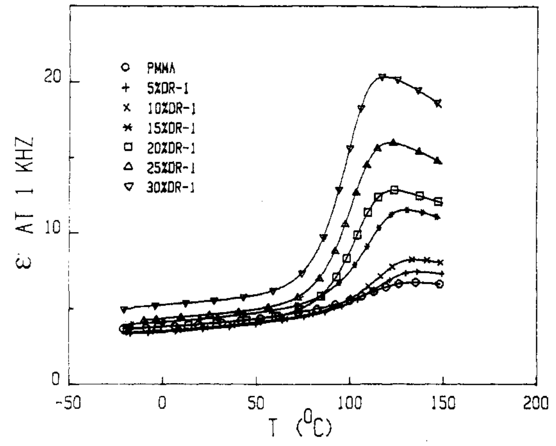

Figure 2. Temperature dependence of dielectric permittivities of DR-1–PMMA mixtures at 1 kHz.

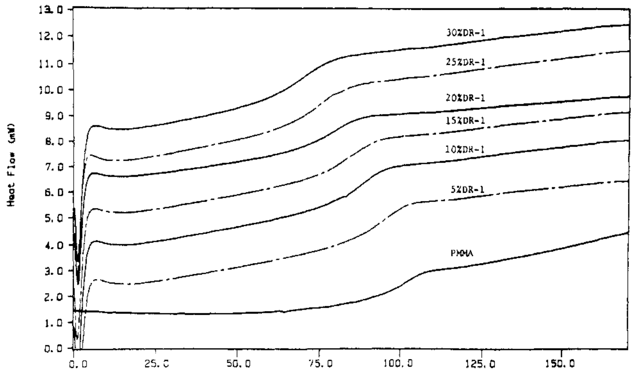

Figure 3. DSC thermograms of DR-1–PMMA mixtures.

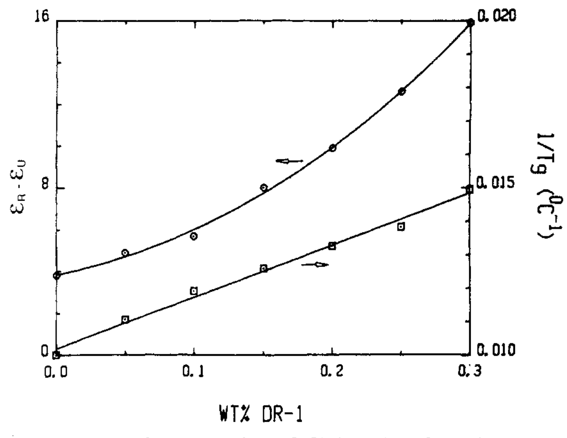

Figure 4. Dependence of T_g and dielectric relaxation strength of DR-1–PMMA mixtures on DR-1 content.

constant ϵ_1. The unrelaxed dielectric constant (ϵ_u) of the heterogeneous system is given by

$$\epsilon_u = \epsilon_1\left[1 + \left(\frac{3(\epsilon_2 - \epsilon_1)}{2\epsilon_1 + \epsilon_2}\right)\phi_2\right] \quad (1)$$

where ϕ_2 is the particle volume fraction. Taking $\epsilon_1 = 3.5$ for PMMA (experimentally observed) and $\epsilon_2 = 10.9$ for DR-1 (estimated from ref 3), the dielectric constants for various concentrations of DR-1–PMMA mixtures were calculated from eq 1 and are listed in Table I. The calculated and observed values are in good agreement.

Table I
Calculated and Observed Dielectric Permittivities for DR-1-PMMA Mixtures

wt % DR-1	ϕ_2	ϵ_U Hayakawa-Wada	ϵ_U measd	ϵ_R Hanai	ϵ_R measd
0	0.00		3.5		7.2
5	0.04	3.7 3.6[a]	3.3	8.2	8.3
10	0.09	3.8 3.7[a]	3.4	9.5	9.1
15	0.13	4.0	4.0	11.0	12.0
20	0.18	4.2	3.9	13.0	13.8
25	0.22	4.4	4.5	15.4	17.1
30	0.27	4.6	5.4	18.6	21.3

[a] From homogeneous system calculation.

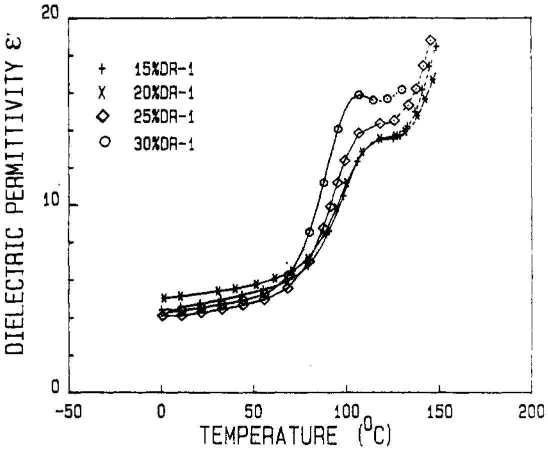

Figure 5. Dielectric permittivity of DR-1–PMMA mixtures at 0.1 kHz.

For the prediction of the dielectric permittivity in the relaxed state, the Hanai equation[9] appears to be suitable for systems where spheroids are dispersed in a homogeneous medium. The Hanai equation for ϵ_R is

$$\epsilon_R\left(\frac{3}{\bar{\sigma} - \sigma_2} - \frac{1}{\bar{\sigma}}\right) = 3\left(\frac{\epsilon_{R_1} - \epsilon_{R_2}}{\sigma_1 - \sigma_2} + \frac{\epsilon_{R_2}}{\bar{\sigma} - \sigma_2}\right) - \frac{\epsilon_{R_1}}{\sigma_1} \quad (2)$$

where ϵ_{R_1}, ϵ_{R_2}, σ_1, and σ_2 represent the relaxed permittivities and conductivities of the medium and inclusions, respectively, and the conductivity of the mixture ($\bar{\sigma}$) is determined by

$$\left(\frac{\bar{\sigma} - \sigma_2}{\sigma_1 - \sigma_2}\right)\left(\frac{\sigma_1}{\bar{\sigma}}\right)^{1/3} = 1 - \phi_2 \quad (3)$$

When the conductivity of the inclusion is much larger than that of the matrix and that of the composite, i.e., $\sigma_2 \gg \sigma_1$ and $\sigma_2 \gg \bar{\sigma}$, eq 2 can be simplified to

$$\epsilon_R = \epsilon_{R_1}/(1 - \phi_2)^3 \quad (4)$$

In this case, ϵ_R becomes independent of σ_2. For DR-1–PMMA systems, assuming that the conductivity of DR-1 is much larger than that of PMMA, eq 4 was used to estimate ϵ_R. We take $\epsilon_{R_1} = 7.2$ for PMMA as observed experimentally. The calculated and observed values are listed in Table I. Considering the assumptions used to arrive at eq 4, the agreement between the calculated and measured values is reasonably good.

As mentioned, the Hayakawa–Wada and Hanai expressions are derived for heterogeneous mixtures. However, some of the DR-1–PMMA mixtures studied do not appear to be multiphase. At lower dye concentrations (5 and 10 wt % DR-1), the dye apparently dissolves in PMMA to form a homogeneous mixture; at 15% DR-1 and above, the mixtures are heterogeneous. Optical micro-

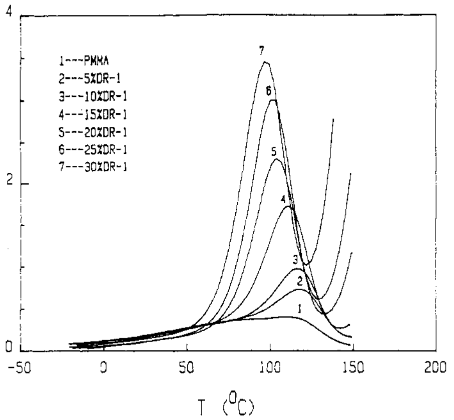

Figure 6. Temperature dependence of the dielectric loss factors of DR-1–PMMA mixtures at 1 kHz.

graphs of films of the mixtures containing 15–30% DR-1 show clearly that a portion of the DR-1 has precipitated and formed aggregates. In addition, we frequently observed an upturn in permittivity at high temperatures and low frequencies in mixtures containing 15–30% DR-1 (for example, see Figure 5), whereas no such effect was seen for the 5 and 10% DR-1–PMMA mixtures. An interfacial polarization phenomenon (Maxwell–Wagner–Sillars effect) is consistent with the behavior of the high DR-1 content mixtures.

Both the optical microscopy observations and the high-temperature/low-frequency dielectric behavior support the idea that at and above 15% DR-1, the mixtures are heterogeneous. This conclusion is in line with indications from ref 3. For completeness, we have estimated ϵ_u for the 5% and 10% DR-1 mixtures from a mixing law of the form frequently applicable to homogeneous mixtures (i.e., $1/\epsilon_u = \phi_2/\epsilon_2 + [(1 - \phi_2)/\epsilon_1]$). The calculated values are very close to those derived from eq 1 and are in good agreement with the measured values.

2. Dielectric Relaxation. The dielectric relaxation behavior of PMMA is well documented.[10,11] Two transitions are observed in the temperature range from 0 to 150 °C. The α transition corresponds to T_g-like motion of the chains while the β relaxation has been assigned to the motion of the $-COOCH_3$ side group. This motion is believed to involve a transition from one equilibrium position to another about the bond linking the group to the main chain.[12,13] For DR-1–PMMA mixtures, the general characteristics of the two types of relaxation still exist. Figure 6 illustrates the temperature dependence of the dielectric loss factors of PMMA and DR-1–PMMA mixtures at 1 kHz. In all cases, a well-defined maximum associated with the α transition is observed. With increasing DR-1 content, the α relaxation shifts to lower temperatures while the area under the loss factor peak increases dramatically.

Examining Figure 6 carefully, one can also see a β transition around 60 °C in mixtures with low DR-1 content. For the sake of clarity, data at 0.1 kHz are plotted in Figure 7. It appears that the β peak diminishes gradually with increasing dye content and disappears above 20% DR-1.

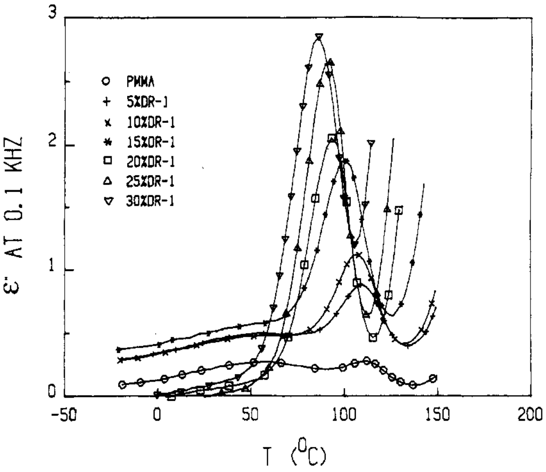

Figure 7. Temperature dependence of dielectric loss factors of DR-1–PMMA mixtures at 0.1 kHz.

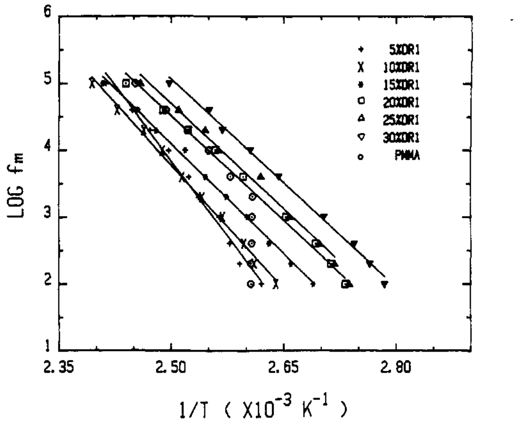

Figure 8. Arrhenius plots for the α transition of DR-1–PMMA mixtures. f_m is the frequency at which the loss factor maximum ϵ''_m occurs.

Table II
Average Activation Energies of α and β Relaxation Processes of DR-1-PMMA Mixtures

wt % DR-1	α relaxtn, kcal/mol	β relaxatn, kcal/mol
0		21
5	69	11
10	58	10
15	50	
20	47	
25	48	
30	47	

Figure 8 shows the Arrhenius plots of the α relaxation process of PMMA and the mixtures. The average activation energies are listed in Table II. According to previous reports,[11] the activation energy associated with the α transition in PMMA is between 100 and 110 kcal/mol and that of the β relaxation is between 19 and 23 kcal/mol. We do not report an activation energy for the α process for pure PMMA due to the severe nonlinearity of the Arrhenius plot. This nonlinearity arises, at least in part, from an overlap of the α and β relaxations. The α/β mergence is also the reason for the unusual location of the PMMA Arrhenius plot in comparison to those of the mixtures. Recall that the T_g decreased in a regular fashion on adding increasing amounts of DR-1. In contrast, examination of Figure 8 shows that, at high frequencies, the PMMA loss peak (a combination of α and β) is located at a *lower* temperature than mixtures containing up to 15% DR-1. This is undoubtedly related to the larger relative intensity of the α process for the mixtures and thus the location of the data points in Figure 8 for the mixtures are dominated by the α-transition. The α and β relaxations for pure PMMA are of comparable magnitude and, at relatively high frequencies, are superimposed, resulting in a lower overall loss peak temperature than would have been observed if the α process was resolvable. In the situation where separate α and β loss peaks were distinguishable (0.1 kHz), behavior comparable to the DSC results were obtained.

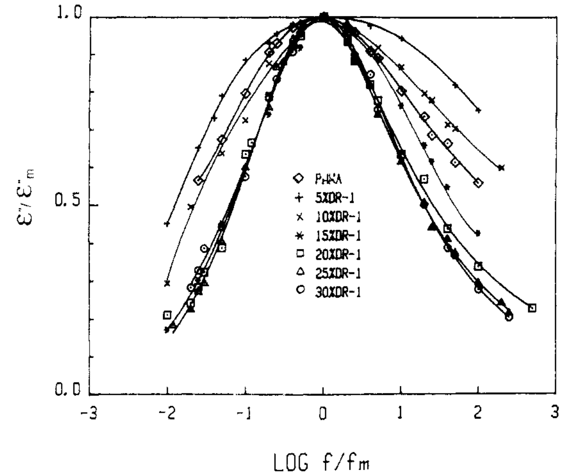

Figure 9. Normalized loss factor curves for DR-1–PMMA mixtures using averaged data.

Our estimate of the β relaxation activation energy for PMMA is nearly the same as that found in the literature but the values listed in Table II are somewhat uncertain because of the paucity of experimental data. For instance, the value of the β relaxation for pure PMMA was obtained from data at only three frequencies due to the inability to distinguish the β from the α process, as discussed above. The activation energy for the α transition for the mixtures can be obtained with some confidence due to the enhancement of the intensity of the α transition from the presence of the dye. The activation energy for the α process decreases as dye content increases up to 20% DR-1, thereafter remaining relatively constant. An interesting question raised here is why the T_g and the position of the α maximum shift regularly to lower temperatures with increasing DR-1 content while the activation energy of the α relaxation remains effectively constant above 20% DR-1.

The observed relaxation behavior can be explained in a number of ways. The presence of the dye apparently leads to a reduction in intra- or interchain forces resulting in a lowering of the activation energy for the α process. The reduction in the magnitude of the β relaxation could be associated with the interaction between the hydroxyl group of the dye molecules and the ester moiety of PMMA, strongly suppressing the normal β motion. Alternatively, one can argue that the magnitude of the β transition is simply reduced through dilution and, at higher dye concentrations, cannot be distinguished from the α process since the α transition is increased greatly in magnitude and shifted to lower temperatures. Neither of these two mechanisms, however, suggest a rationale for the observation of a constant activation energy for the α process above 15% DR-1. One can perhaps rationalize the behavior through a mechanism involving a shift of the β relaxation to higher temperatures accompanied by an increase in activation energy (due to the need to overcome dye–ester interactions before the β motion can take place) and a merging of the α and β loss factor peaks. However, this is very speculative and more work needs to be carried out in order to more clearly understand this phenomenon.

Construction of normalized loss factor curves allows us to compare the relaxation time distributions for PMMA and the various mixtures which reflect differences in local environment in the systems.[14] This is done by expressing the values of ϵ'' as fractions of the peak maximum ϵ''_m and plotting ϵ''/ϵ''_m vs. log f/f_m where f_m is the frequency at which the loss factor maximum ϵ''_m occurs. If the shape factors of the curves are insensitive to temperature over a certain temperature range, master curves can be constructed which cover a reasonably wide frequency range. The distribution of relaxation times can be assessed by comparing half-widths and other shape factors graphically. Normalized loss factor curves (plotted using averaged data) for DR-1–PMMA mixtures are presented in Figure 9. For a clearer representation, the curves are scaled vertically and illustrated in Figure 10. All curves are slightly asymmetric and skewed toward the higher frequency side. The curves become narrower and more symmetrical with increasing DR-1 concentration and tend to coincide when the DR-1 content reaches and exceeds 20%. This suggests that the relaxation time distribution declines with increasing DR-1 concentration and becomes constant at about 20% DR-1 content.

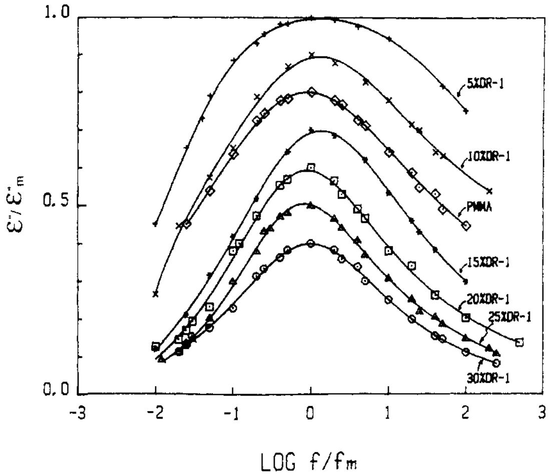

Figure 10. Normalized loss factor curves for DR-1–PMMA mixtures. The curves have been scaled vertically by 0.10, 0.20, 0.30, 0.40, 0.50, and 0.60 scale units.

Table III
Parameters of Havriliak–Negami Equation for DR-1–PMMA Mixtures

wt % DR-1	T, °C	ϵ_U	ϵ_R	a	b
0	125	3.5	7.2	0.48	0.39
5	125	3.3	8.2	0.49	0.39
10	125	3.4	9.1	0.43	0.39
15	125	4.0	12.0	0.26	0.39
20	110	3.9	13.8	0.23	0.39
25	110	4.5	17.1	0.24	0.41
30	110	5.4	21.3	0.25	0.49

The Havriliak–Negami empirical model[15] has been used to describe the relaxation process of a number of polymers. The equation is

$$\frac{\epsilon^*(\omega) - \epsilon_u}{\epsilon_R - \epsilon_u} = [1 + (i\omega\tau_0)^{1-a}]^{-b} \qquad (5)$$

where $\epsilon^*(\omega)$ is the complex dielectric permittivity at the angular frequency ω; τ_0 is the relaxation time, and a and β are empirical parameters, $0 \le a \le 1$ and $0 \le b \le 1$. The parameter a represents the width of relaxation time distribution; the width increases as parameter a increases. The parameter b describes the skewness of the relaxation distribution. Numerical values of ϵ_u, ϵ_R, a, and b can be determined from Cole–Cole arcs. For DR-1–PMMA mixtures, we found that time–temperature superposition can be used at high frequencies thus avoiding problems in drawing Cole–Cole plots because of the lack of high-frequency data. Cole–Cole plots of the mixtures are shown in Figure 11 and the parameters of the Havriliak–Negami equation obtained from these plots are presented in Table III.

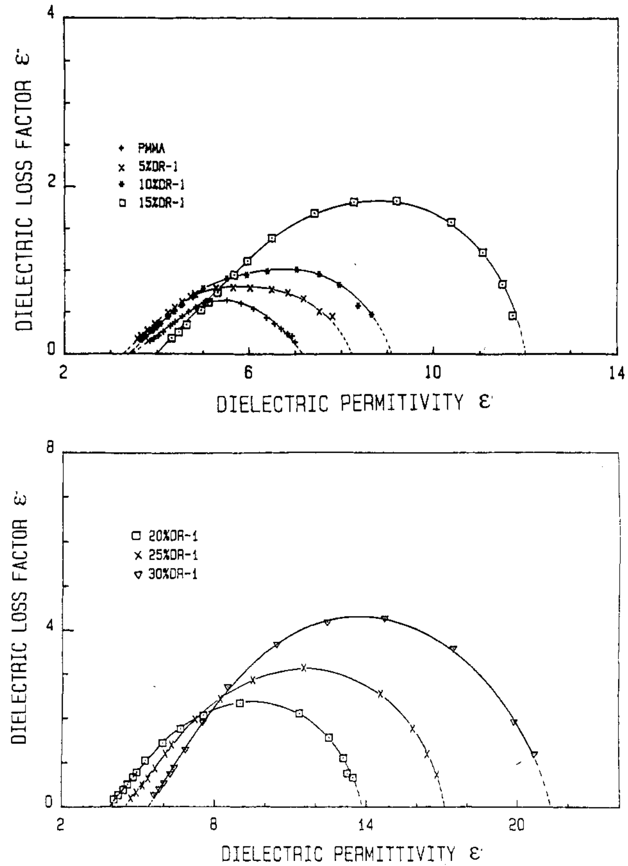

Figure 11. Cole–Cole plots of DR-1–PMMA mixtures.

As shown in Table III, the variation in a is in good agreement with implications from the normalized loss factor curves. With increasing dye concentration a decreases and becomes approximately constant when the DR-1 content reaches 20%. The increase in b indicates that the curves become more symmetric as the DR-1 concentration increases.

The results presented above lead to a common conclusion: 20% DR-1 is the critical concentration where the β relaxation disappears and the activation energy of the α process and the relaxation time distribution become independent of the DR-1 concentration. It is also interesting to note from Figure 9 that the relaxation time distribution of PMMA is narrower than that of the 5% and, possibly, the 10% DR-1 systems. The broader distribution for lower dye concentration mixtures than for pure PMMA can be interpreted as arising from regional fluctuations in dye concentration in the PMMA matrix. In low-concentration plasticizer–polymer or polymer–polymer systems, the minor component can be distributed in such a way as to lead to a gradient of segmental mobility, with varying relaxation times.[16-18] With increasing DR-1 concentration, the dispersion of dye in PMMA apparently becomes more uniform and the relaxation time distributions become narrower until a DR-1 concentration of 20% is reached, whereupon the distribution remains constant with increasing dye content.

Conclusions

A dielectric study of DR-1–PMMA mixtures has led to the following conclusions:

(1) 5 and 10% DR-1–PMMA mixtures appear to be homogeneous; at and above 15% DR-1 content, the mixtures are multiphase.

(2) The observed dielectric permittivity of the DR-1–PMMA mixtures can be interpreted satisfactorily by heterogeneous mixture models based on a simple interfacial polarization mechanism.

(3) The Havriliak–Negami empirical equation can be used to describe the α-relaxation data of the mixtures and the results are in good agreement with inferences drawn from normalized loss factor curves.

(4) DR-1 has a plasticizing effect on the PMMA. 20% DR-1 content is a critical dye concentration above which the β relaxation disappears, the activation energy of the α process remains constant and the relaxation time distribution becomes independent of dye concentration.

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Registry No. DR-1, 2872-52-8; PMMA, 9011-14-7.

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