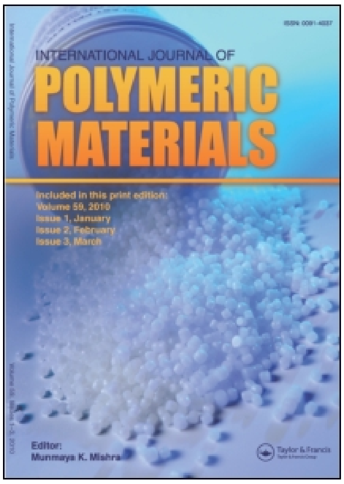

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Electric and Dielectric Properties of Some Fluorescent Dye/PMMA Solar Concentrators

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The effect of dye concentrations of perylene, RH-6G and K_1 *doped in polymethylmethacrylate (PMMA) as matrix material, on the electrical properties of some fluorescent solar concentrator (FSC) have been investigated. The samples were prepared by dissolving grains of both PMMA and dyes in chloroform, which were then left at room temperature to evaporate the solvent. The samples were characterized by differential scanning calorimeter (DSC). The results of both dc conductivity* (σ_{dc}) *and ac conductivity* (σ_{ac}) *showed that the total conductivity* $\sigma_{tot}(w)$ *is higher than* σ_{dc} *and the activation energy of* σ_{tot} *is lower than that of* (σ_{dc}) *due to the increase of the applied field frequency, which enhances the carrier jumping and subsequently the conductivity value. The dielectric properties (dielectric constant* (ε')*, dielectric loss* (ε'')*, and dielectric tangent* ($\tan\delta$) *have been studied. They show that* ε' *increases by increasing the concentration of the dyes doped in PMMA. All the dielectric constants, the dielectric loss and loss tangent temperature dependence, show a peak value affected by the dye concentration as well the frequency changes. The temperature dependence of the exponent S shows that at low temperature the conduction obeys a quantum mechanical tunnel model, while at high temperature the conduction obeys the correlated barrier-hopping model.*

Keywords: dielectric loss tangent, dielectric permittivity, polymer/conductivity

INTRODUCTION

Organic dyes play an important role in the development of many optical systems. Among these systems, luminescent solar concentrators (LSCs) are of special interest [1] since they reduce considerably the cost of solar energy production [2–4]. Therefore such dyes have been widely employed in various industrial and many domestic applications. They

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can be used also as substrates for the fluorescent species of organic laser dyes in luminescent solar concentration [2]. Various substrate materials have been studied, including polymethylmethacrylate (PMMA) as fluorescent solar concentrators (FSCs) basic matrix. This material is known usually as "Plexiglas" or organic glass, where it is a transparent amorphous polymer with considerably high strength [5].

The physical properties of PMMA have led to its extensive use in outdoor electrical applications [6–9]. According to the published literature, it was found that its optical properties have been extensively studied [5,10] while its electrical properties still need much more research.

Dc electrical conductivity is a macroscopic quantity, which represents an average property of carriers as they move from site to site. A carrier (e.g., an electron) may either hop over or tunnel through the barrier. The relative importance of these two mechanisms depends on the shape of barrier and availability of thermal energy [6]. Also, the investigation of dielectric properties is one of the most convenient and sensitive methods of studying polymer electronic band structure [7]. The basis of dielectrics are volume resistivity, electric strength, permittivity or dielectric constant and dielectric loss. The choice of dielectric for each particular purpose is determined by the temperature and electric field frequency dependence of these quantities.

This study aims to investigate the changes in the electric and dielectric properties, such as dc and ac electrical conductivity, activation energy and dielectric constant, of three dyes doped in PMMA which are used in fluorescent solar concentrator applications in comparison to the factory coded K_1 prepared by BASF.

EXPERIMENTAL

Polymethylmethacrylate, perylene, Rh-6G (rhodamin-6G) and K_1, having molecular weights of 996, 252.32 and $497\,g \cdot mol^{-1}$, respectively, were used in this study. Perylene, Rh-6G and PMMA were obtained from Aldrich and K_1 from BASF, Germany (K_1 is a factory code for the dye developed specifically for solar concentrators). The samples were prepared by a casting method in which grains of both PMMA and dyes were dissolved in chloroform [5]. The homogeneous mixture was poured in a glass container and left at room temperature for the solvent to evaporate. After curing, the sheet was removed and then cut as desired.

The samples were prepared in the form of discs of thickness 0.05–0.08 cm and area $0.8–1.3\,cm^2$ for the electrical conductivity measurements. The two parallel surfaces of each disc were coated with silver paste to achieve good contact. The samples were heated in a non-inductive furnace and the dc electrical conductivity data were collected using a Poland multi-meter type U722A. The temperature was controlled using T-type thermocouple, and the measuring accuracy was ±1°C. The ac electrical properties were measured using a programmable automatic multi-frequency LCR meter (4275, Hewlett Packard, with frequency range from 10 kHz to 10 MHz).

Differential scanning calorimetry (DSC) measurements were carried out at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Measurements of dc electrical conductivity σ_{dc} as a function of temperature for the pure PMMA and dye/PMMA samples have been carried out and then calculated from the basic equation [11],

$$\sigma_{dc} = \left(\frac{t}{aV}\right)I$$

where I is the current flowing through the sample, t is the sample thickness, a is the cross-sectional area and V is the potential difference across the sample. The obtained results of σ_{dc} temperature dependence are presented in Figure 1. It can be seen that σ_{dc} values increased gradually up to a peak value (σ_p) at a certain temperature (T_p), which lies approximately in the same range of the glass transition temperature. It is supposed that σ_{dc} is thermally activated and obeys an Arrhenius relation [11,12].

$$\sigma_{dc} = \sigma_0 \exp(-\Delta E_{dc}/kT),$$

where σ_0 is a temperature independent parameter, ΔE_{dc} is the activation energy of conduction, k is Boltzmann's constant and T is the absolute temperature.

The dependence of the electrical conductivity on the dye concentration, due to confined solvent molecules which act as carrier acceptors in the polymer matrix, has also been studied and the obtained results are plotted in Figure 2. It is also noticed that the electrical conductivity is thermally activated up to a peak value σ_p at certain temperature T_p, which lies also in the same range of the glass transition temperature. This activated part can be interpreted by analyzing the acid-base properties of the polymer (PMMA) and the solvent. PMMA is described as a basic polymer or an electron donor, according to the Lewis concept [13]. The presence of ester functional groups with the carbonyl oxygen atom being a basic site is the reason why PMMA

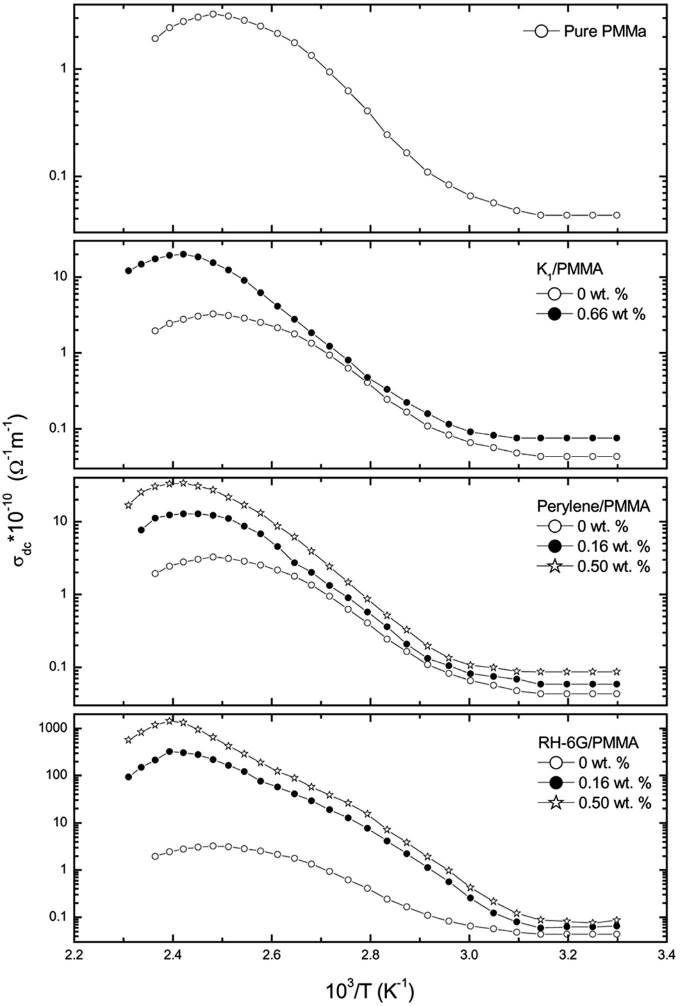

FIGURE 1 Temperature dependence of dc electrical conductivity.

exhibits electron-donor ability. So, the conduction process may occur by electron jumping (hopping) and/or tunneling between donor atoms and empty sites located in the energy band gap. The basic polymer (PMMA) is able to undergo strong acid-base interactions with acidic sites, which are the hydrogens of the C−H bonds. So, the confined chloroform molecules surrounding the main chain of the polymer will lead to an increase in the density of localized states which enhances the probability of electron jumping.

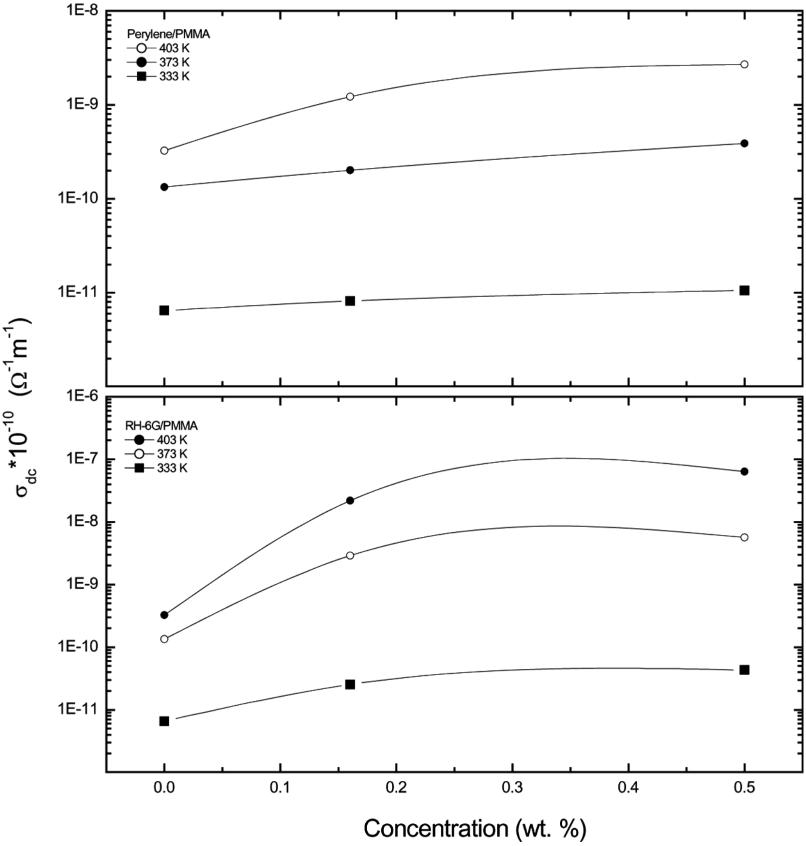

FIGURE 2 Concentration dependence of dc electrical conductivity.

The linearity of $\ln \sigma_{dc}$ against $10^3/T$ indicates that $\sigma_{dc}(T)$ exhibits activated behavior in accordance with the Arrhenius relation [11]. The values of σ_p, T_p, ΔE_{dc} and σ_0 were obtained and are listed in Table 1. The attenuated part in the conduction process above T_p could be explained by the fact that the conduction process is opposed by the large deformations characteristic of the viscoelastic state permitted by segmental motion [14]. In other words, beyond T_g the electron phonon coupling becomes more pronounced no reduces the charge carrier mobility.

Figure 2 shows the perylene/PMMA and Rh-6G/PMMA concentration dependence of dc conductivity. The effect of dye concentration on the dc conductivity was found to obey the following empirical relation [15]:

$$\sigma_{dc} = \sigma^* \exp(\pm c/c_0)$$

TABLE 1 Values of Temperature Peak T_p, Conductivity Peak σ_p, Activation Energy ΔE_{dc}, and Temperature Independent Parameter σ_0 for Dyes/PMMA.

Dye concentration wt.%		T_p (K)	$\sigma_p(\Omega^{-1}m^{-1})$	ΔE_{dc} (eV)	$\ln\sigma_0(\Omega^{-1}m^{-1})$
Pure PMMA		408.0	$2.8*10^{-10}$	0.95	7.04
K_1/PMMA		419.4	$1.9*10^{-9}$	0.93	6.61
RH-6G/PMMA	0.16	418.0	$3.5*10^{-8}$	0.94	9.65
	0.50	423.0	$1.3*10^{-7}$	0.93	9.80
Perylene/PMMA	0.16	413.0	$1.2*10^{-9}$	0.92	5.77
	0.50	420.0	$3.0*10^{-9}$	0.89	5.44

where σ^* is a concentration-independent parameter that equals σ_{dc} at $c = 0$ and c_0 is a characteristic concentration for dye doped in PMMA matrix. The positive or negative sign of the exponent in the empirical equation depends on the preparation method. The observed increase in the dc conductivity by increasing the concentration of the dye may be due to the confined solvent molecules which act as carrier acceptors in the polymer matrix.

The temperature dependence of the total conductivity (σ_{tot}) has been measured in the temperature range 303–453 K and the frequency range 10–1000 kHz, for PMMA and dye/PMMA and they are presented in Figure 3. It is observed that $\sigma_{tot}(\omega)$ is thermally activated up to a certain value σ_p and then attenuated with the increase in temperature which was found to be in agreement with the behavior observed for σ_{dc} measurements. The activated part in σ_{tot} against $10^3/T$ relation could be discussed according to the Arrhenius relation, too. The values of the activation energy ΔE_{ac} were calculated for different frequencies and are represented in Table 2. It is observed that the values of $\sigma_{tot}(\omega)$ are higher than σ_{dc}, and the activation energy for $\sigma_{tot}(\omega)$ is lower than that of σ_{dc}. This is due to the increase of the applied field frequency, which enhances the carrier jumping and subsequently the conductivity value. This leads to shift the peak to higher temperature. At the low frequency range, the conductivity is mainly dc, but at higher frequencies the conductivity obeys the universal power relation $\sigma(\omega) = A\omega^s$, where A is a frequency-independent parameter and s is an exponential power. Thus the total conductivity could be given by [16,17]

$$\sigma_{tot} = \sigma_{dc} + \sigma_{ac} = \sigma_{dc} + A\omega^s$$

The values of the exponent s were calculated at different temperatures for the investigated samples using the least square fitting, and are shown

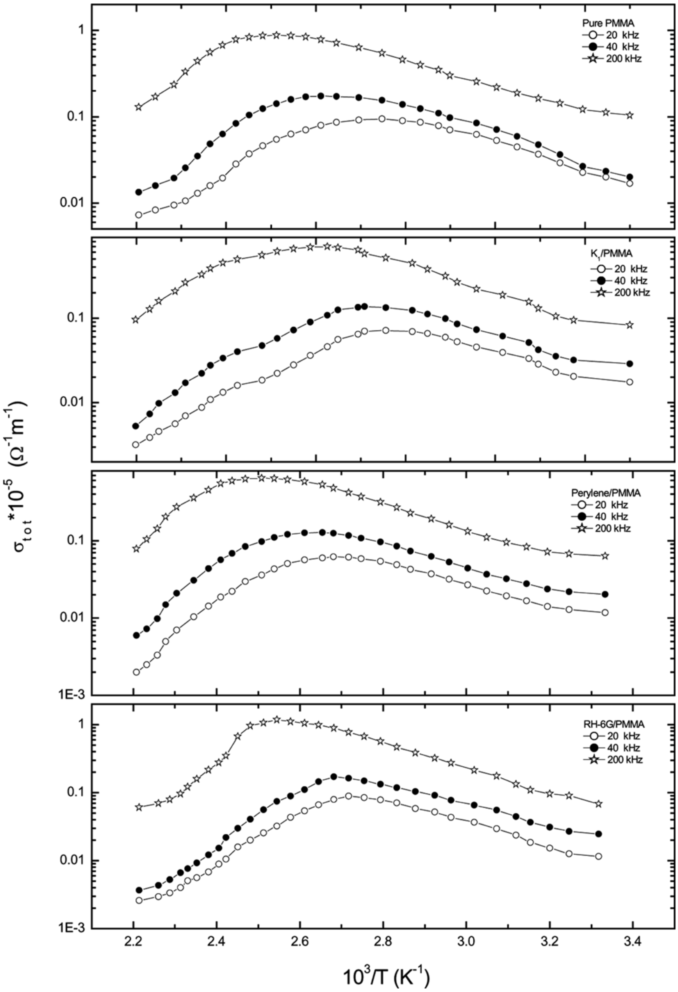

FIGURE 3 Temperature dependence of σ_{tot}, for samples at different frequencies.

in Figure 4. This figure illustrates that the temperature dependence of the exponent *s* shows a peak at a certain temperature value that depends on the dye concentration. It is noticed that the peak temperature T_p is significantly correlated to T_g of the samples (as mentioned later).

At $T < T_p$, *s* increases with the temperature, which is consistent with the charge carriers transport according to the quantum mechanical

TABLE 2 The Calculated Values of AC Activation Energy (ΔE_{ac})

Dye concentration wt.%		10 KHz	20 KHz	40 KHz	100 KHz	200 KHz	400 KHz	1 MHz
Pure PMMA		0.620	0.560	0.530	0.420	0.310	0.330	–
K_1/PMMA		0.570	0.550	0.530	0.340	0.325	0.345	0.72
RH-6G/PMMA	0.16	0.450	0.360	0.320	0.270	0.250	0.460	0.74
	0.50	0.344	0.300	0.280	0.270	0.260	0.320	0.59
Perylene/PMMA	0.16	0.413	0.380	0.360	0.359	0.347	0.330	0.78
	0.50	0.270	0.267	0.264	0.250	0.220	0.256	0.61

(Column headers above: Frequency)

tunneling model [18]. But at $T > T_p$, the values of s decrease with temperature which may be due to conduction mechanism based on the predominance of the correlated barrier-hopping model [19].

The temperature dependence of dielectric permittivity (ε'), dielectric loss (ε'') and dielectric loss tangent ($\tan\delta$) have been studied for pure and doped samples at different frequencies. The dielectric constant ε' was calculated from the equation [14]:

$$\varepsilon' = \frac{c}{\varepsilon_0} \times \frac{t}{a}$$

where c is the samples capacitance, ε_0 is the free space permittivity, t is the thickness and a is the cross-section area of the sample. Also, the dielectric loss ε'' was calculated using the relation [9]:

$$\varepsilon'' = \varepsilon' \tan\delta$$

where $\delta = (90 - \phi)$, ϕ is the phase angle, and $\tan\delta$ is the dielectric loss tangent.

The dielectric properties $\varepsilon', \varepsilon''$ and $\tan\delta$ have been studied in the temperature range 300–553 K and frequency range 10–1000 kHz. Figure 5 shows that the trend of the dielectric constant $\varepsilon'(T)$ for pure PMMA and dye/PMMA is typical for a polar dielectric [14], with increasing temperature the orientation of the acrylate group increases, and thereby increases the permittivity ε', up to a maximum value and then drops at a certain temperature. These drops can be attributed to the intensified thermal oscillations of the polymer molecules which lowers the order of their orientations. Increasing the frequency of the applied field acts to lower ε' value and shifts its

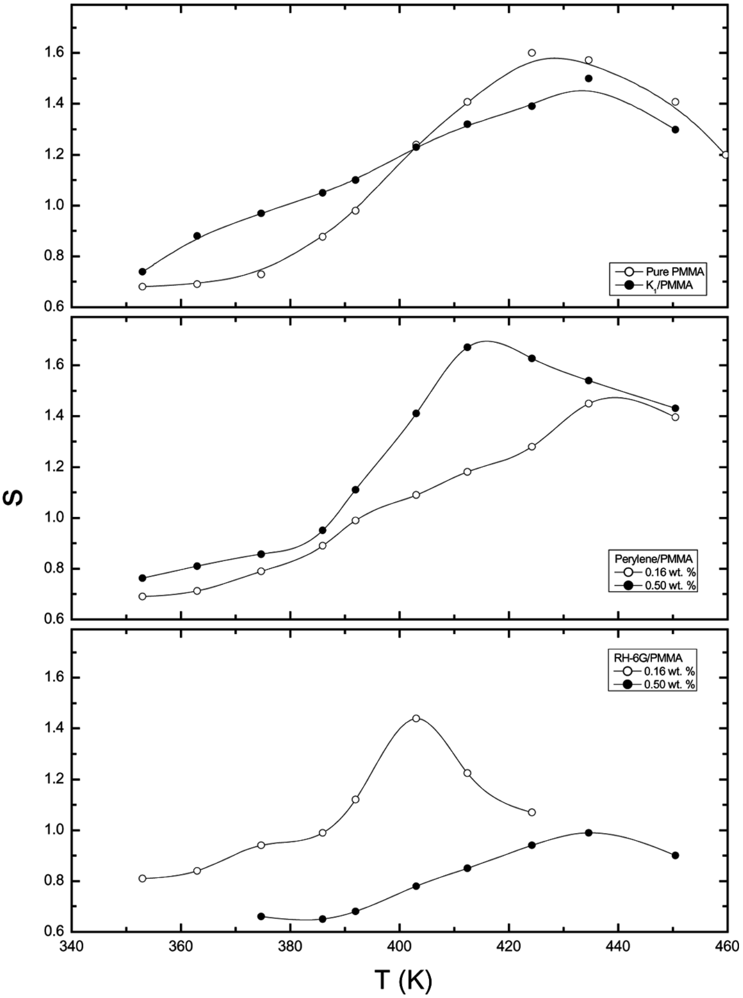

FIGURE 4 Temperature dependance of the exponents.

maximum to higher temperatures. The decrease in ε' with frequency can be attributed to the lag of dipole oscillations behind those of the field at high frequencies, and the higher mobility of the acrylate group in the presence of solvent molecules.

Figure 6 shows the temperature dependence of the dielectric loss ε'' at different frequencies for pure PMMA and all investigated samples. A single peak in ε'' curve can be observed. Its position depends on

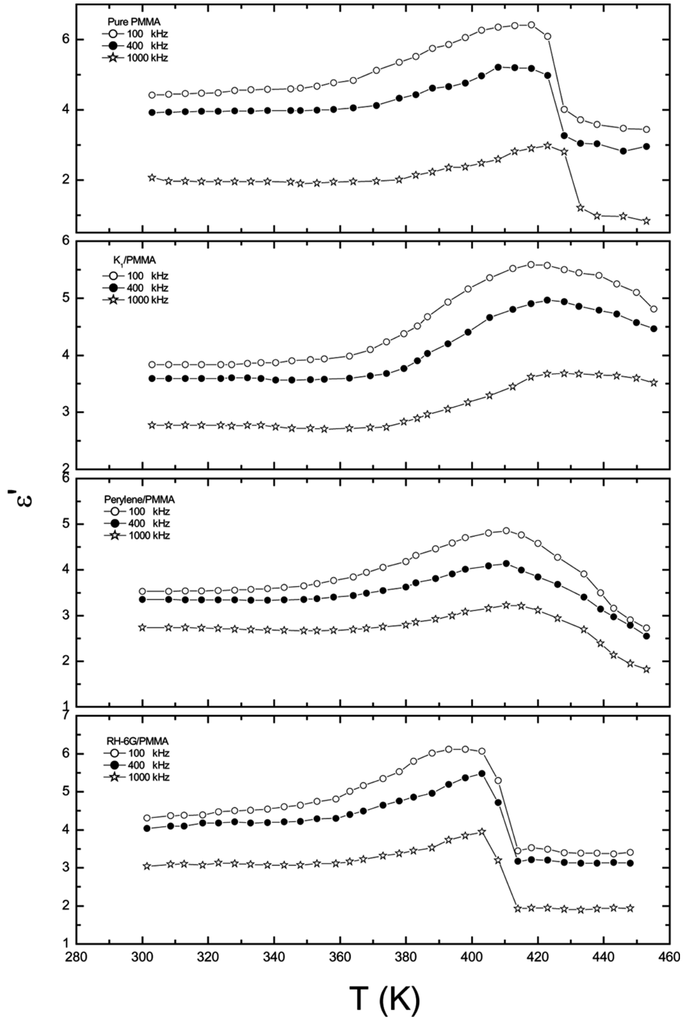

FIGURE 5 Temperature dependence of dielectric permittivity ε' at different frequencies.

the frequency of the applied field, and with increasing frequency the position of the peak shifts towards higher temperatures.

It is observed from Figure 7 that each tan δ curve shows a maximum position that depends on the frequency of the applied field. The maximum values of tan δ are shifted to higher temperature by increasing the applied frequency. The observed attenuation above the

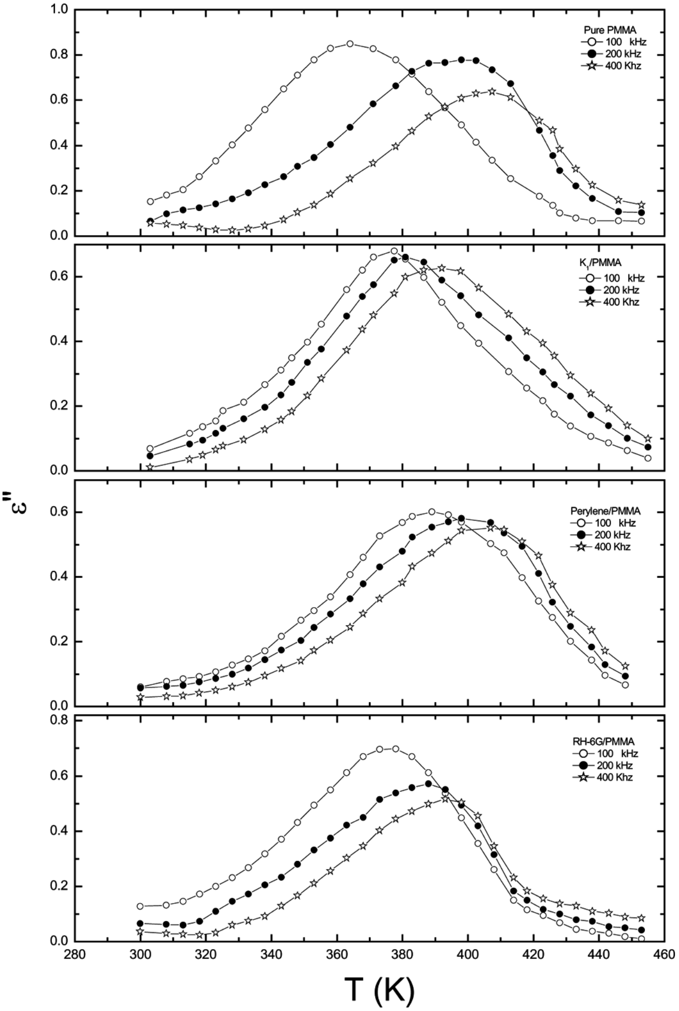

FIGURE 6 Temperature dependence of dielectric loss ε'' at different frequencies.

maximum is due to the phonon dipole interaction which leads to a lowering of the energy transferred to the dielectric medium. This behavior characterizes amorphous polymers [20].

Figure 8 shows the effect of dye concentration on both ε' and ε'' for the investigated samples. It is observed that ε' is higher than ε'' and both values are increasing with increasing dye concentration (for Rh-6G/PMMA and perylene/PMMA samples). Increasing the dielectric

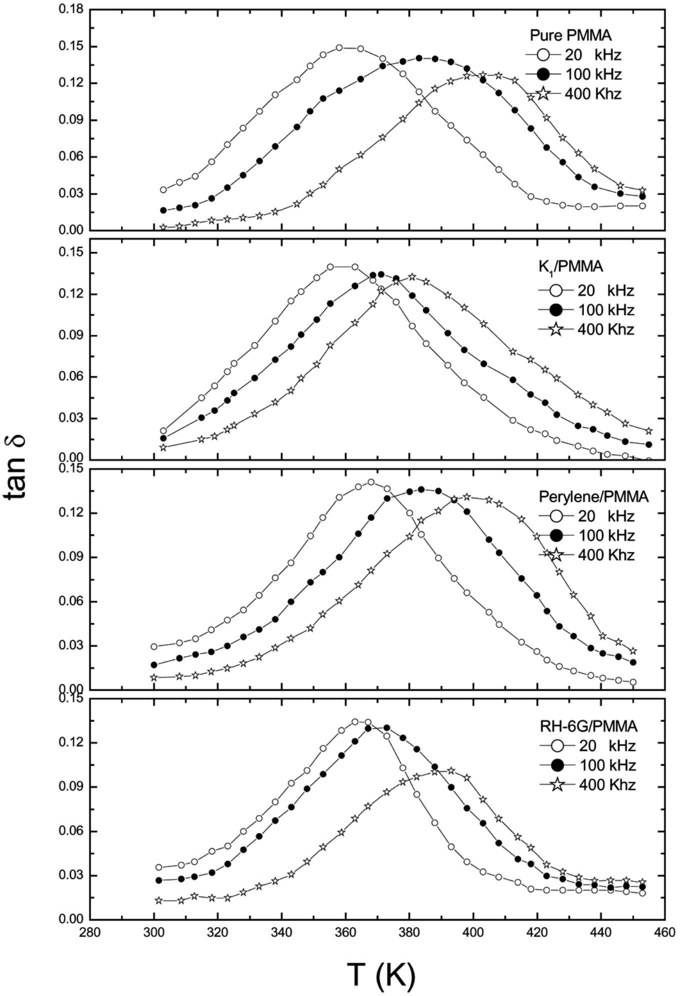

FIGURE 7 Temperature dependence of dielectric loss tangent tan δ at different frequencies.

constant ε' with the dye concentration is in agreement with the conductivity measurements, since the conductivity of a real dielectric is directly related to the dielectric permittivity [21].

DSC thermograms for pure PMMA sample were recorded at a heating rate of 10°C/min. The values of T_g (glass transition temperature) and T_s (solvent evaporation temperature) are listed in Table 3. There appears a correlation between the change in the values of T_s and the

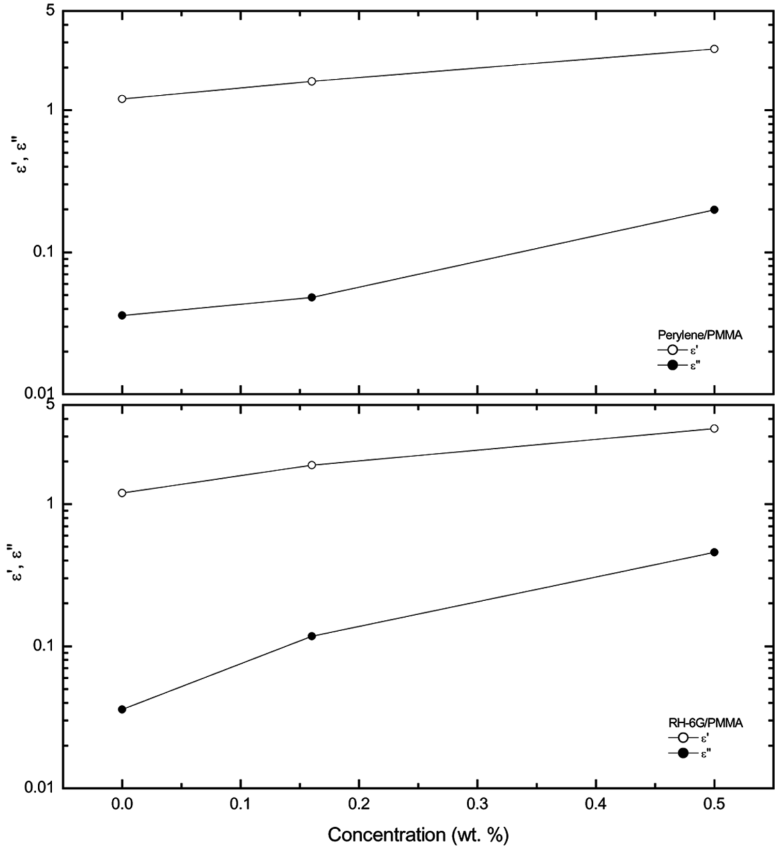

FIGURE 8 Effect of perylene and RH-6G concentration on the dielectric constant ε' and dielectric loss ε'' at temperature 400 K and frequency 1 MHz.

TABLE 3 Values of T_g and T_s for Dyes/PMMA

Dye concentration wt.%		T_g (K)	T_s (K)
Pure PMMA		405.9	425.9
K_1/PMMA		419.8	439.6
RH-6G/PMMA	0.16	414.6	445.9
	0.50	420.0	452.4
Perylene/PMMA	0.16	419.5	439.9
	0.50	420.6	443.7

obtained T_g values. The apparent increase in T_s by increasing dye content may be due to the aggregation of dye molecules, which tends to hinder the total evaporation of the solvent and trap in the black polymer [22]. The variation of T_g with dye concentration can be attributed to a reduction of chain mobility of the polymer matrix by the large size of the rigid dye molecules. This leads to a decrease in free volume and chain flexibility.

CONCLUSION

Electrical properties and DSC investigation showed that the physical properties of polymers are strongly affected by the presence of the dye and the acidicbase character of the solvent. The dc electrical conductivity of the dye/PMMA increases by increasing the dye concentration, due to the confined solvent molecules which act as carrier acceptors in the polymer matrix. The addition of the dye to PMMA causes a variation in both the values and the position of the maximum of the dielectric loss. This variation is due to the large size of rigid dye molecule compared to that of the size of the polymer group, which tends to trap the solvent between chains and subsequently increases the intermolecular interactions. It can be concluded that at low temperature the conduction follows the quantum mechanical tunneling model while at high temperature it follows the barrier-hopping model.

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