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A TSD current dielectric investigation of the effects of xanthene and perylene dye incorporation in PMMA

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SUMMARY: The potentials of developing tunable lasers with the use of photostable dyes, incorporated at solid-state hosts of high optical quality, have attracted considerable scientific interest. A critical factor determining the optical response of the dye is related to the extend to which its intrinsic physical and chemical properties are maintained in the environment provided. The thermally stimulated depolarization (TSD) current technique has been employed in order to investigate possible interactions between the typical thermoplastic carrier PMMA and dispersed xanthene and perylene derivatives. The dielectric β-relaxation of PMMA, related to the (re)orientation of the polar ester carbonyl side groups, exhibits a broad distribution in the relaxation times that remains unaffected by the presence of the dye molecules. The result is supportive of the model considering the chromophores being encapsulated in the polymer without strong (chemical) bonding, in agreement with the observed laser behavior. Further aspects of the dielectric response are discussed in terms of the specific sample preparation procedures and structural relaxation phenomena occurring in PMMA.

1. Introduction

A critical factor determining the optical response of the dyes is related to the extend to which their intrinsic physical and chemical properties are maintained. Among the properties of a good laser dye are strong absorption, high quantum yield of fluorescence, a region of strong luminescence far out of the absorption band and photochemical stability under intense excitation [1]. The incorporation of dye molecules in liquid media adversely affects many thermodynamic, spectroscopic and kinetic properties of the dye. Several efforts to develop components based on solid state matrices with embedded dyes are concentrated in pure polymers [2-4], oxide glasses [5], polymer-inorganic glass composites [2], and organically modified silicate matrices (*ormosils*) [6]. The thermoplastic polymethyl methacrylate (PMMA) in considered as one of the most efficient dye matrices with excellent thermal, photochemical and dimensional stability. As such it has been widely used for laser and nonlinear optical materials [3,7]. In the present case, the thermally stimulated depolarization (TSD) current dielectric technique has been employed in order to investigate possible

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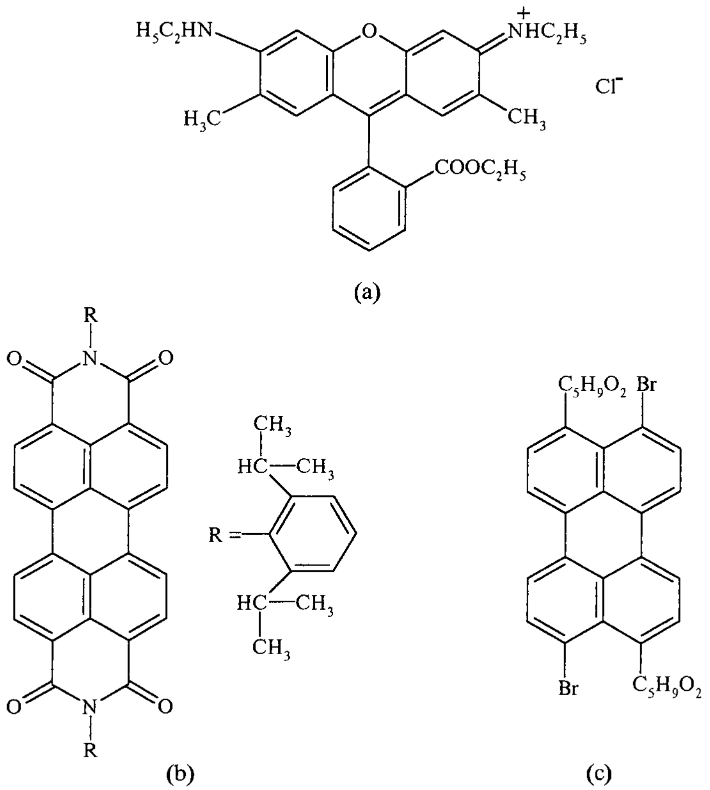
interactions between the macromolecular structure and the chromophores. It is to be expected that any interaction should principally reflect the rotational mobility of the polar pendant groups of PMMA (e.g. by chemical bonding and steric hindrances), and the corresponding dielectric *β*-relaxation. In the present paper we report a detailed study of the energy spectrum for the dipole disorientations associated with the above local transition.

2. Choice of materials

From the commercially available dyestuffs we have selected rhodamine 6G/Cl$^-$ (Rh6G) and two of the perylene derivatives (PO, PG; Fig. 1). The widely used ionic chromophore of Rh6G has an absorption peak in the range 515 to 535 nm and an emission peak between 560-620 nm [1,8]. Several lasing properties of many perylene derivatives, incorporated in PMMA matrices, have been studied by Seybold and Wagenblast [3].



(a)

(b)

(c)

Fig. 1: Structures of the, a) rhodamine 6G/Cl$^-$, b) perylene orange (PO), and c) perylene green (PG) dyestuffs.

3. Sample preparation

Perylene derivatives are uncharged compounds with relatively low-laying melting points, relatively high vapor pressures and good solubility in non-polar solvents. Their incorporation in PMMA has been performed by dissolving the dye in the liquid monomer (methyl methacrylate, MMA) following polymerization at 40 ^{0}C for 3 days, initiated by 0.125 % by mass of benzoyl peroxide dissolved into the MMA. The estimated dye concentrations are 3×10^{-5} M for PG and 8×10^{-5} M for PO. Bulk PMMA samples were prepared similarly. The highly ionic xanthene dye Rh6G demonstrates good solubility in highly polar solvents like alcohols but only slight solubility in less polar solvents like MMA. Thus, dye impregnation was performed by mixing 8 % 10^{-5} M dye solution in ethanol with 92 % MMA and polymerizing as above (final concentration ~ 8×10^{-5} M).

4. Experimental procedure

TSD is a sensitive *d.c.* technique used to investigate the electrically active relaxation phenomena in dielectrics. The experiment involves the polarization of the sample at some sufficiently high polarization temperature T_p by applying an electric field E_p for time t_p. When the temperature of the sample is lowered to T_0 with the electric field applied and then shortened at this temperature, the non-equilibrium state of the dipole system is "*frozen in*". During the successive heating at a constant rate h, the recovery of the system is monitored by measuring the depolarization current $I(T)$. In accordance with a specific structure, microstructure, morphology and chemical composition of the testing material (e.g. polymeric systems [9-10], minerals [11-12], alkali halide laser crystals [13], liquid electrolytes), current peaks may be assigned to dipole orientation, space charge and interfacial polarization phenomena. Deviations of the theoretical TSD current peaks are frequently attributed to a distribution of relaxation times $\tau(T)$. For a continuous distribution in the activation energies (E) due to dipole-dipole interactions, the current density signal $J(T)$ can be written as

$$J(T) = \frac{P_0}{\tau_0}\int_0^{\infty} g_p(E)\,exp\left[-\frac{E}{k_\beta T} - \frac{1}{h\tau_0}\int_{T_0}^{T} exp\left(-\frac{E}{k_\beta T'}\right)dT'\right]dE\,, \qquad (1)$$

where P_0 is the saturation polarization, τ_0 is the pre-exponential factor of the Arrhenius equation for the temperature dependant relaxation time

$$\tau(T) = \tau_0\, exp(E / k_\beta T), \qquad (2)$$

and $g_P(E)$ is the effective distribution function. A number of refined experimental procedures are usually applicable for the separation of overlapping signals, the identification of their origin and the determination of characteristic single or distributed relaxation parameters. TSD performed in steps enables one to establish whether a dipole distribution arises from a distribution in E or τ_0. The so-called partial heating method [14], is based on the fact that the natural logarithm of the current at the initial slope of the discharge signal, is proportional to the apparent activation energy. In that method, the heating is interrupted at increasingly higher temperatures (cut-off temperature, T_c). After each interruption the sample is cooled and reheated for another TSD run. The activation energy values are determined, with good accuracy, from plots of $ln\ I(T)$ against $1/T$, where the slope of the straight line obtained equals $-E/k_\beta$.

5. Results and discussion

Sub-glassy relaxations in methacrylic polymers primarily involve the rotational mobility of the polar pendant groups in the polymers (β-relaxations). The mobility is manifested by a local rotation of the groups around their C_1-C_2OOR bond with the backbone chain; certain localized motions in the main chain should possibly be considered. Based on molecular mechanics model calculations of the energetics in an isotactically arranged ethyl acrylate trimer, Gomez Ribelles *et al.* [15] proposed that the internal rotation around the C_2–OR bond, within the lateral group, also produces a significant contribution. For the above kind of rotational motions in PMMA ($R=-CH_3$), the relaxation time τ is the average time between changes in two stable orientations of the ester moiety. As the temperature increases during the TSD heating run, the average time between these changes decreases and dipolar (re)orientation results in a significant depolarization current band. In the case where the disorientation or activation energy is continuously distributed in E, the superposition of the relaxational responses from the slightly different groups of dipoles, each possessing a single pair of relaxation parameters E and τ_0, appearing in eq. (2), results in broad peaks well described by eq. (1).

The dielectric β-relaxation in pure atactic PMMA, with 55% syndiotactic triads, has a TSD current maximum at 232 K (curve A, Fig. 2a). Around 125 K appears a band attributed to the rotational relaxation of polar molecules, usually water. Much lower, around 75 K, the weak band is associated with the rotation of α-CH_3 in PMMA (γ-relaxation). Several observations can be drawn from a careful examination of the spectra presented for pure PMMA and samples containing the chromophores PG (curve B; Fig.2a), PO (curves C_1, C_2; Fig.2a) and Rh6G (curves D_1, D_2; Fig. 2b), The maximum temperature of the secondary relaxation peaks for the PO+PMMA and PG+PMMA blends coincides with that in pure PMMA. However, in Rh6G+PMMA sample the peak maximum is clearly lowered by approximately 10 K. The relative strength of the band appearing in the range 100-150 K is low in bulk PMMA and the samples containing perylene derivatives, when compared to the amplitude of the same band in Rh6G+PMMA.

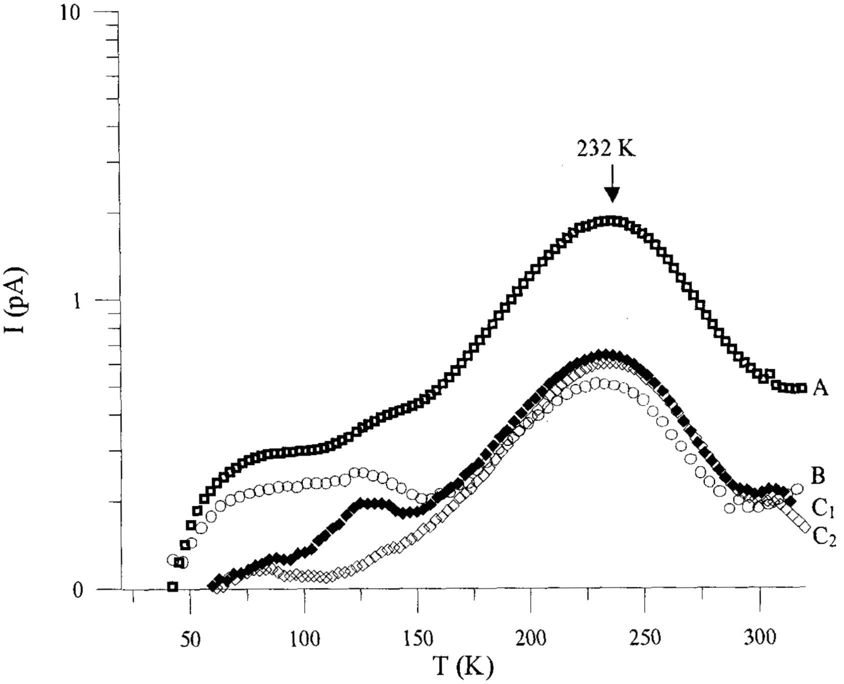


Fig. 2a: TSD current spectra of (A) pure PMMA, (B) PG+PMMA and (C) PO+PMMA samples (C_1 is the initial and C_2 the current spectrum after vacuum treatment). Poling conditions: T_p=320 K, E_p=20 kV/cm, t_p=5 min.

Further studies indicate that upon prolonged evacuation times the corresponding signals virtually disappear (e.g. compare thermogram C_1 with C_2, Fig.2a), in contrast to the behavior encountered in the Rh6G+PMMA blend (compare D_1 and D_2, Fig. 2b). The xanthene blend is the only one to demonstrate strong high temperature (HT) current signals above 275 K. Their intensity gradually falls in the course of consecutive TSD runs, in the range 10-340 K, under vacuum conditions (10^{-4} – 10^{-5} Torr).

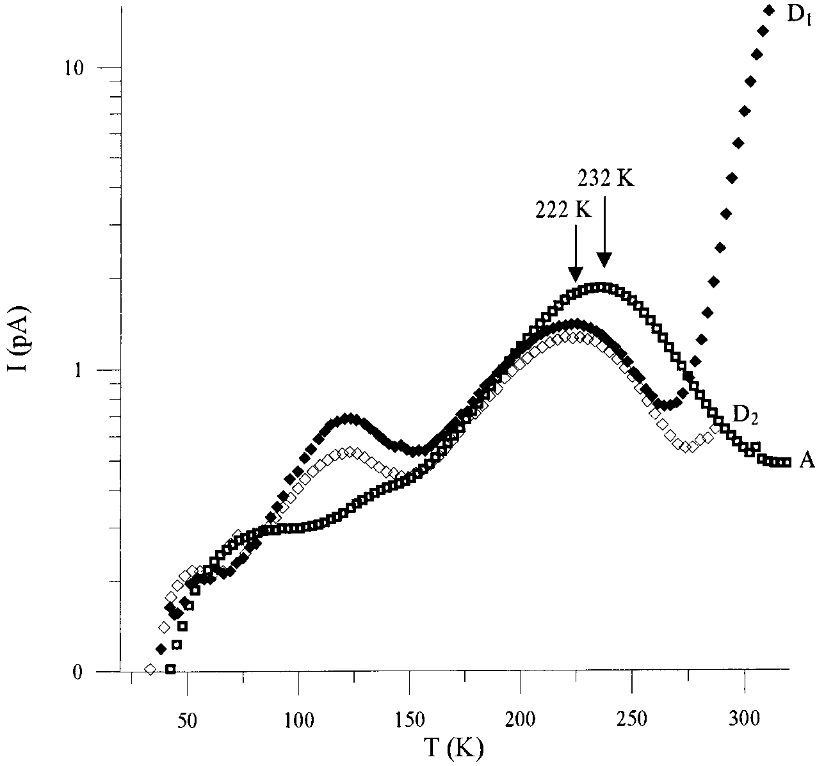


Fig. 2b: TSD current spectra of (A) pure PMMA and Rh6G+PMMA samples: D_1 is the initial spectrum and D_2 the spectrum after vacuum treatment with T_p=285 K.

The partial heating method has been applied for the entire range of materials presented in Fig. 3. Since the current rises in the temperature range of β-relaxation in PMMA were found to steepen during the series of heating, it is most likely that the dipoles are continuously distributed in E. In fact, the analysis of the initial slopes for PMMA reveals a monotonically increasing trend of the energy E vs. T_c, described by the solid line presented in Figs 3 and 4, in agreement with earlier investigations [16-17]. The energy spectrum associated with the β-relaxation in bulk PMMA is similar to that of PMMA with dispersed perylene chromophores. This observation supports a model considering the chromophores as trapped in the polymer network without strong chemical or hydrogen bonding. There is, however, a strong deviation in the case of PMMA containing the ionic rhodamine compound 6G/Cl^-, what deserves further attention. Figure 4 presents the variation of the activation energy spectrum of the secondary relaxation in the Rh6G+PMMA blend as a function of the evacuation time. The points in the $E(T_c)$ diagram show a strong dependence on the magnitude of the high temperature signals for the polarization temperature of T_p=320 K (curves a, b; Fig. 4). By applying the partial heating method with electret forming temperature T_p=285 K, and after the considerable decrease of the strength of the HT polarization signals, we observe an energy spectrum that resembles, within the limits of error, the spectrum of pure PMMA (curve c; Fig. 4).

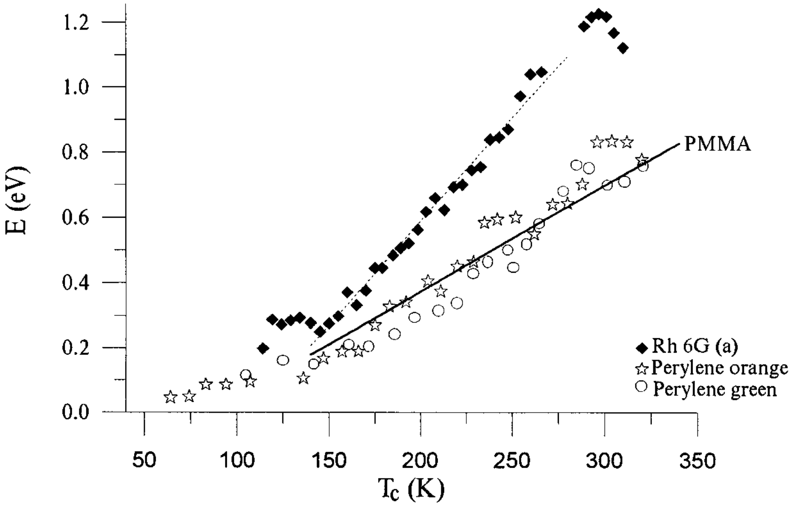


Fig. 3: Energy spectrum of PMMA blends with the Rh6G, PO and PG organic dyes. Solid line represents pure PMMA.

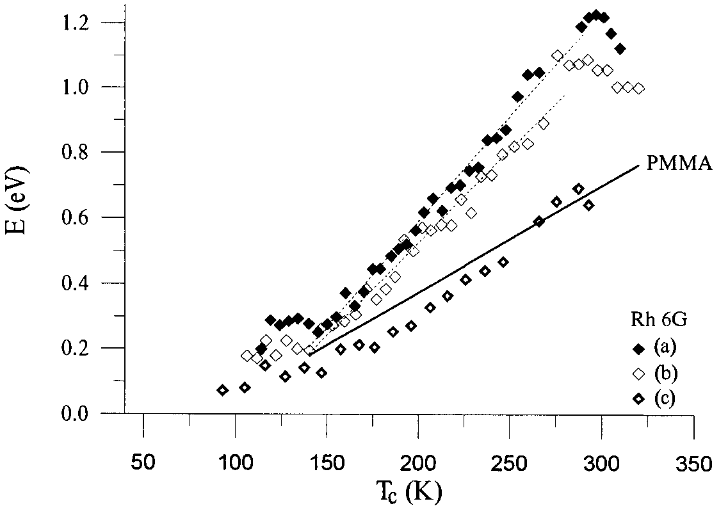


Fig. 4: Variation of the energy spectrum for Rh6G+PMMA as a function of time: (a) initial measurements, (b) after one and (c) two weeks of consecutive studies in vacuum.

An interpretation of the dissimilarities in the dielectric behavior of the Rh6G+PMMA system, on one hand, and the other materials on the other must take under consideration the presence in the untreated organic system of ethanol and water molecules, inherited from the preparation procedure. Smith and Schmitz have reviewed studies pertaining to the influence of the polar water molecules on the thermal and mechanical properties of polymers [18]. One of the models explaining the results of density measurements in the PMMA+H_2O system assumes that one water molecule effectively crosslinks two polymer chains by forming a hydrogen bond to an oxygen moiety in each of the two ester side groups. In the above context, the temporal increase of the activation energies for the ester side group (re)orientation can be attributed to the formation of hydrogen bonds between the hydrogens in ethanol and water and the carbonyl oxygen atoms. This attribution is supported by the observation that the difference between the energy parameters, before and after the sample treatment, is around 0.2 eV, which is comparable to the energy of the hydrogen bond (~ 0.18 eV). The appearance of the HT signals can be approached by two different models: either an intense structural relaxation process at the microvoids formerly occupied by water/ethanol, or a space charge relaxation involving H^+ and/or Cl^- ions. The progressive decrease can be better explained in terms of the second model if we consider the gradual desorption as an effective way for the reduction of the protonic charge carriers. The relatively high value of approximately 1.2 eV (around 300 K) could correspond to a chlorine space charge jump mechanism. Although the dye salt is fully dissociated in the polar ethanol environment, the process is expected to be, at least, partially reversed upon the removal of the polar solvents with a consecutive decrease of the relaxation strength. Another interesting point is the persistence of the band around 125 K in the Rh6G+PMMA blend, associated with the relaxation of polar H_2O and ethanol molecules. This is in contrast to the behavior observed in the other materials. The phenomenon indicates that an appreciable number of the above molecules resides in preferred positions between the predominantly syndiotactic macromolecular configuration.

The results presented above negate the existence of a strong (chemical) bonding of the chromophores to the polymeric matrix, even for the polar and highly ionic rhodamine 6G/Cl^- dye molecules. In the latter case in particular, the absence of a distinct relaxation mode associated with the chromophores, at least in the temperature range under investigation, indicates that the solid cage produced by the organic polymer molecules reduces internal rotational modes in the dye. The decrease of the maximum temperature (Fig.2b), without further changes in the smooth shape of the band, suggests that any current signal from the rotation of the polar -$COOC_2H_5$ side groups [19], in the carboxyphenyl group of rhodamine 6G, is fully integrated in the broad β-relaxation signal of PMMA. As in other rhodamine laser dyes (e.g. rhodamine 110), the carboxyphenyl substituent is held in a position nearly perpendicular to the xanthene chromophore by the bulky carbonyl group, thus allowing little, if any, mobility for the amino groups [1]. The effect is significantly enhanced in comparison to the dye solutions. As the rotational relaxation of the excited state of the laser dyes is one of the main modes of non-radiative energy loss, such a behavior is highly desired. The incorporation of the dye molecules in solid state laser matrices based on oxide glasses offers an even better solution [5].

Acknowledgements

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