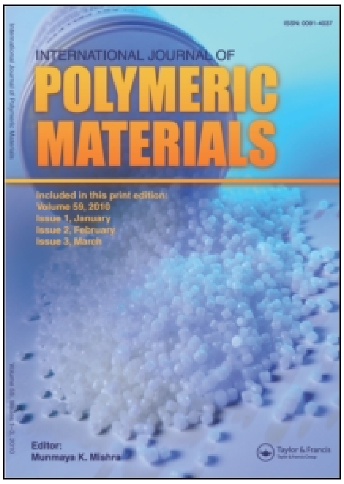

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Structural and relaxation aspects in azodye-doped abs films: TSDC study

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STRUCTURAL AND RELAXATION ASPECTS IN AZODYE-DOPED ABS FILMS: TSDC STUDY

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We utilized the thermally stimulated depolarization current (TSDC) technique for investigating the relaxation mechanism in azodye-doped ABS (acrylonitrile-butadiene-styrene) terpolymer in a wide temperature range. In contrast to the pure ABS films, the global spectra of the doped films were found to be structured. The thermal sampling (TS) technique was used in order to decompose the overlapped relaxation spectra. We verified that the compensation law is more strongly valid in case of doped samples rather than that of pure ABS samples. Moreover, this study sheds some light on the switching property of the azobenzene derivative which plays an important role in triggering the molecular orientation of the ABS host matrix, as monitored by the IR spectroscopy.

Keywords: TSDC, ABS, azodye, thermal sampling, compensation law

INTRODUCTION

ABS is a family of thermoplastics that contains three monomeric units: acrylonitrile, butadiene and styrene. It is one of the most important rubber-toughened thermoplastics and is widely used for applications where toughness and surface gloss are important [1]. The azobenzene derivative, p-hexyl-p-(10-bromodecyloxy) azobenzene (6Az10 Br), referred in this study as azodye, was selectively chosen so as to adopt three main purposes. First, the choice of the tail chain length with six carbon atoms, C6, was to prevent the formation of bilayers assemblies [2] because the aggregation of

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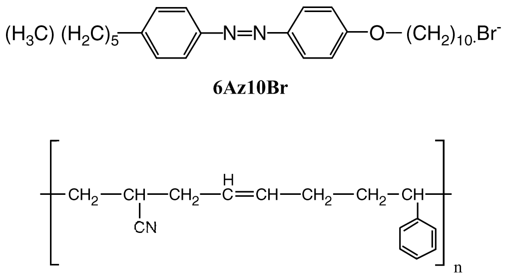
azobenzene moieties creates a high degree of inhomogeneity in the overall structure. Second, utilizing the azodye thermochromic property in order to command the contacted ABS macromolecules. Third, utilizing its electron-accepting site (CH_2Br^-) for enhancing the probability of host-guest intermolecular interaction through charge transfer complex CTC formation (will be discussed in the coming IR analysis section).

It is important to point out that the switching properties of azobenzene derivatives have been widely used in order to trigger both the optical and electrical activities of other molecular and polymeric systems attached chemically or physically to it. For instance, photoresponsive conductivity device has been designed using an amphiphilic system containing azobenzene derivatized moiety (as a photo-switching unit) connected with a TCNQ-based charge transfer complex moiety (as a working unit) through an alkyl chain (as a transmission unit) [3]. Another utility was to use the azobenzene derivative in order to photo-command nematic liquid crystals in an azo-LC-azo cell configuration for LCD applications [4, 5].

Thermally stimulated techniques have been used as powerful means of characterizing substances in various fields of science and technology. The thermally stimulated depolarization currents technique (TSDC) belongs to this family of experimental techniques and have been used to study a variety of low- and high-relative-molecular-mass materials, crystalline as well as amorphous insulators and semiconductors [6]. This technique has a particular significance due to its high resolution related to its intrinsic low equivalent frequency. On the other hand, it offers the possibility of decomposing a complex relaxation mechanism into its elementary contributions by means of the so-called thermal sampling (TS) experiments. The later allows the analysis of TSDC spectrum's fine structure known as relaxation map analysis, RMA (discussed later) which in turns enables one to select a series of signals, each of which corresponds to a specific group of dipoles. Therefore, our aim in this article is essentially oriented to investigate the structural and relaxational effects of the azobenzene moiety embedded within the ABS matrix by means of IR and TSDC spectroscopy. We have utilized the highly resolving power of the thermal sampling technique for analyzing the cooperative relaxations characterizing the TSDC spectra. Thereby, we were able to determine the role played by the dye in light of some useful models picked from the literature.

MATERIALS AND EXPERIMENTAL WORK

The materials used in this study are (i) p-hexyl-p-(10-bromodecyloxy) azobenzene (National Institute of Materials and Chemical Research, Tsukuba, Ibaraki, Japan) and (ii) poly (acrylonitrile-Butadiene-Styrene) terpolymers (ABS), Bayer AG, Germany. The relative compositions of ABS are (A: 24%, B: 14% and S: 62%). The chemical structure of both materials is represented below (Scheme 1).



6Az10Br

ABS terpolymer

SCHEME 1

The films of azodye-doped ABS were prepared by dissolving them in chloroform as a common solvent. The solution was continuously stirred before casting onto a glass substrate. The solvent was evaporated in an oven at 343 K. The film thickness, ranging from 20 – 30 μm, was determined by a digital micrometer (Mitutoyo No: 293 – 521 – 30, Japan). Carbon paste (Kontact chemie, Germany) was used as a conducting electrode.

FT-IR spectra has been obtained by using a Mattson 5000 FTIR spectroscopy in the range from 500 – 3500 cm^{-1}. To investigate TSDC spectrum, the samples were poled at a constant temperature (T_p) by applying an electric field (E_p) for certain time (t_p). The poled samples were then cooled from the poling temperature to room temperature while the electric field was still applied. In order to remove any surface charges, the poled samples were kept short circuited at room temperature for 15 min. Then, the samples were linearly heated to a certain temperature at a uniform heating rate $\beta =$ 3 K/min and during which, the current was measured using a Keithley electrometer 610 C.

On the other hand, Arrhenius plots or RMA could be obtained using TS technique as follows: (i) Heating the sample to a polarization temperature T_p located within the temperature domain corresponding to the global relaxation being studied. (ii) Application of poling field ($E_p = 7 \times 10^6$ V/m) for a certain time t_p (15 min). (iii) Cooling, while the field is still applied, to a depolarization temperature T_d, five degrees below T_p, ($T_p - T_d = 5$ K). (iv) Turning the field off and leaving the system at T_d for a time t_d (15 min) under short circuit condition. (v) Quenching the sample to a temperature $T \ll T_d$. (vi) Linear heating of the sample while measuring the depolarization current. Using this method at various T_p over the entire temperature range allows the complex peaks observed in TSDC global spectra to be experimentally decomposed.

RESULTS AND DISCUSSION

IR Spectrum Assignment

The IR spectra for both pure ABS and azodye-doped samples are illustrated in Figure 1. From this graph one finds that the vibrational modes (*e.g.*, symmetric and asymmetric stretching) characterizing the ABS constituents are affected by the addition of the azobenzene moiety content in light of the following two regimes: (1) Upon increasing the azo content, a strong CH_2 wagging band at $1248\,cm^{-1}$ (assigned for CH_2—Br group) grows up in expense of a significant decrease in the C—H bending (δ_{as} and δ_s CH_3) positioned at 1450 and $1378\,cm^{-1}$, respectively. This is a good evidence for some conformational changes in the ABS macromolecules owing to the intercalation of the trans-isomeric azobenzene molecules resulting in an enhancement in the orientational order of the polymeric ABS coils. (2) The sharp decrease in the band peaked at $2245\,cm^{-1}$ (assigned for the CN group in ABS) upon increasing the azodye content, is a strong evidence that a break in one of the CN triple bonds may have occurred. This might be caused by the physical attachment of azobenzene bromodecyl end group forming a new electron-donating center [7] providing an important guideline for the formation of charge transfer complex, CTC.

TSDC Spectra

Figure 2 displays the typical TSDC thermograms of pure ABS and azodye-doped ABS films (all samples were poled under identical conditions, *i.e.*, $E_p = 7 \times 10^6\,V/m$, $T_p = 373\,K$ and $t_p = 30\,min$). It is obvious that for pure ABS, the peak located at $T = 395\,K$ can be assigned as an α-relaxation or dipolar relaxation peak as reported elsewhere [8–10]. As the content of the azobenzene moiety is increased, both the peak position and intensity of the spectrum is significantly affected. It is also clear that the strong asymmetry and breadth of TSDC spectra indicates the existence of a distribution of relaxation times. Hence, the global TSDC spectrum around T_g, shown in Figure 2, reflects the so-called "cooperative α-relaxation" which possesses various dipoles with different relaxation times. Such a relaxation is characterized by maximum activation energy at the glass transition temperature [11–13]. The spectral shift mentioned here might be attributed to the intercalation of the dye long molecule within the ABS macromolecular matrix, lowering the glass transition temperature T_g, of the latter.

As one may also observe from Figure 2, the TSDC spectra of the azodye-doped samples are structured comparing with that of the pure ABS. That is to say, the α-relaxation peak is preceded by a shoulder in the temperature region 348–369 K that coincides with the temperature range of the liquid crystalline phase of the dye [judging from observation of melting point

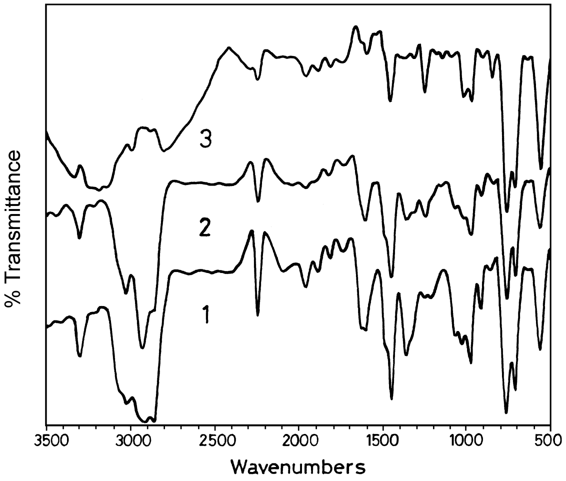


FIGURE 1 FT-IR spectra of (1) Pure ABS, (2) 1 wt% Azo-doped, and (3) 5 wt% Azo-doped.

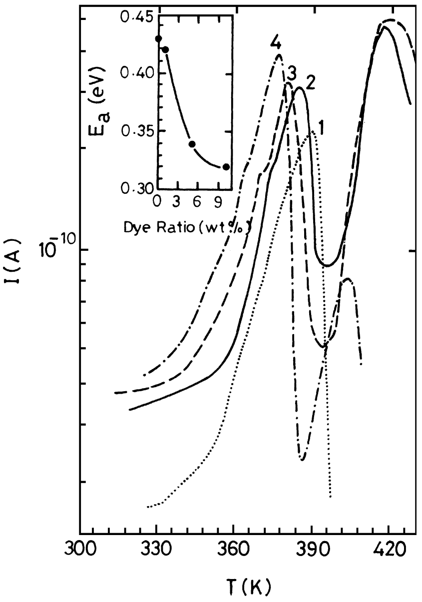


FIGURE 2 TSDC spectra of (1) Pure ABS, (2) 1 wt% Azo-doped, (3) 5 wt% Azo-doped, and (4) 10 wt% Azo-doped, $E_p = 7 \times 10^6$ V/m, $T_p = 373$ K, and $t_p = 30$ min. Carbon paste as electrode. Heating rate $\beta = 3$ K/min.

experiment by optical microscopy]. The other preceding peak could be assigned as ρ-relaxation or space charge relaxation [14]. Such a relaxation may be attributed to the existence of heterogeneities within which space charges (heterocharges) are accumulated or trapped and thereafter released or detrapped during the TSDC measurements.

The activation energy (E_a) was calculated for the α-peak using the initial rise method [15] and plotted as function of the azodye concentration (see the inset of Fig. 2). Both the peak shift towards lower temperature side and the decreasing activation energy, E_a reflect the effect of the azodye on the relaxation mechanism. This may be further understood from one of the following two possibilities: (i) The dopant may diffuse into the amorphous/crystalline interfaces of the polymer and form charge transfer complexes, CTC, as revealed by the IR spectral analysis. (ii) It may interact substitutionally in the polymer matrix in the form of hydrogen bonding intermolecular connections.

Since TSDC spectra may be attributed either to dipolar orientation process or space charge, a distinction between them can be realized from the field dependence of TSDC properties. Hence, we selected the 10 wt.% Azo-ABS sample to be a representative sample for investigating the effect of field strength on TSDC spectra as shown in Figure 3. It is clear from the inset of the figure that the maximum current of the first peak varies linearly with field strength, whereas, that of the second peak varies nonlinearly. Moreover, the position of the first peak does not dependent on the field strength, whereas that of the second peak does. From these two arguments, one may attribute the first peak to dipolar orientation and the second peak to space charge mechanism [16].

In order to investigate the mechanism responsible for TSDC, the spectra were analyzed in terms of the theory of the initial rise method [15]. That was to calculate the activation energy from the Arrhenius plot of ln I *versus* 1/T. Thereafter, the characteristic relaxation time was evaluated and listed in Table 1. It is noticed that the activation energy values of the main peak (α-peak) are nearly independent of field strength, and their values are smaller than those corresponding to the second peak (ρ-peak). This is another evidence that the main peak originates from dipolar orientation.

Compensation Effect

One advantage of TSDC over other techniques is that the thermal sampling (TS) technique allows a very sensitive characterization of the relaxation dynamics in terms of the apparent activation energy with very high temperature resolution. Its significance stems also from the fact that the relaxation process during the glass transition is due to a number of different relaxation modes, and by isolating each relaxation mode, a true

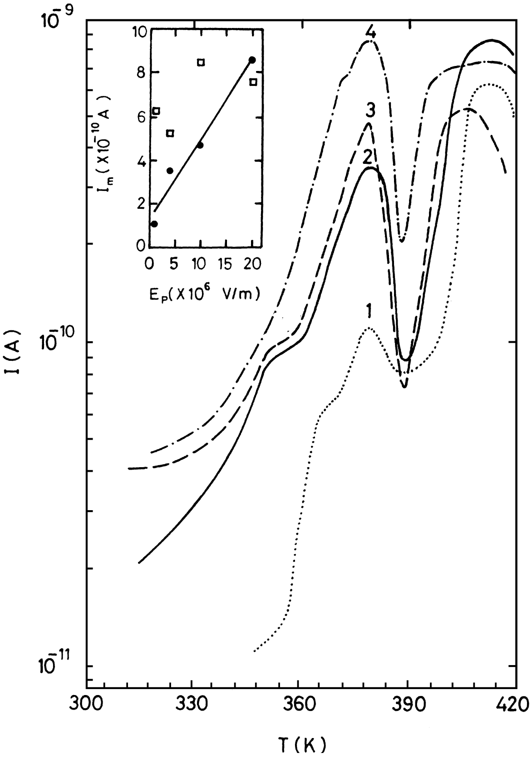


FIGURE 3 TSDC spectra of 10 wt% Azo-doped, $T_p = 373\,K$, and $t_p = 30\,min$ for various polarizing field, (1) $E_p = 1 \times 10^6\,V/m$, (2) $E_p = 4 \times 10^6\,V/m$, (3) $E_p = 10 \times 10^6\,V/m$, and (4) $E_p = 20 \times 10^6\,V/m$. Carbon paste as electrode. Heating rate $\beta = 3\,K/min$.

TABLE 1 Depolarization characteristics and relaxation characteristic parameters for α and ρ relaxations

		α-Peak relaxation			*ρ-Peak relaxation*		
$E_p\,(V/m)$	$T_p\,(K)$	$T_m\,(K)$	$E_a\,(eV)$	$\tau_0\,(sec)$	$T_m\,(K)$	$E_a\,(eV)$	$\tau_0\,(sec)$
1×10^6	373	379	0.28	1.00×10^{-05}	413	1.20	7.65×10^{-14}
4×10^6	373	379	0.41	1.87×10^{-07}	407	0.99	1.55×10^{-11}
1×10^7	373	379	0.42	1.34×10^{-07}	413	0.85	1.01×10^{-09}
2×10^7	373	379	0.41	1.87×10^{-07}	413	1.02	1.16×10^{-11}

understanding of the macroscopic properties of the material can be obtained. Figure 4 shows TS spectra of pure ABS and other azodye-doped films. On examining these figures, one can observe that the ensemble of the

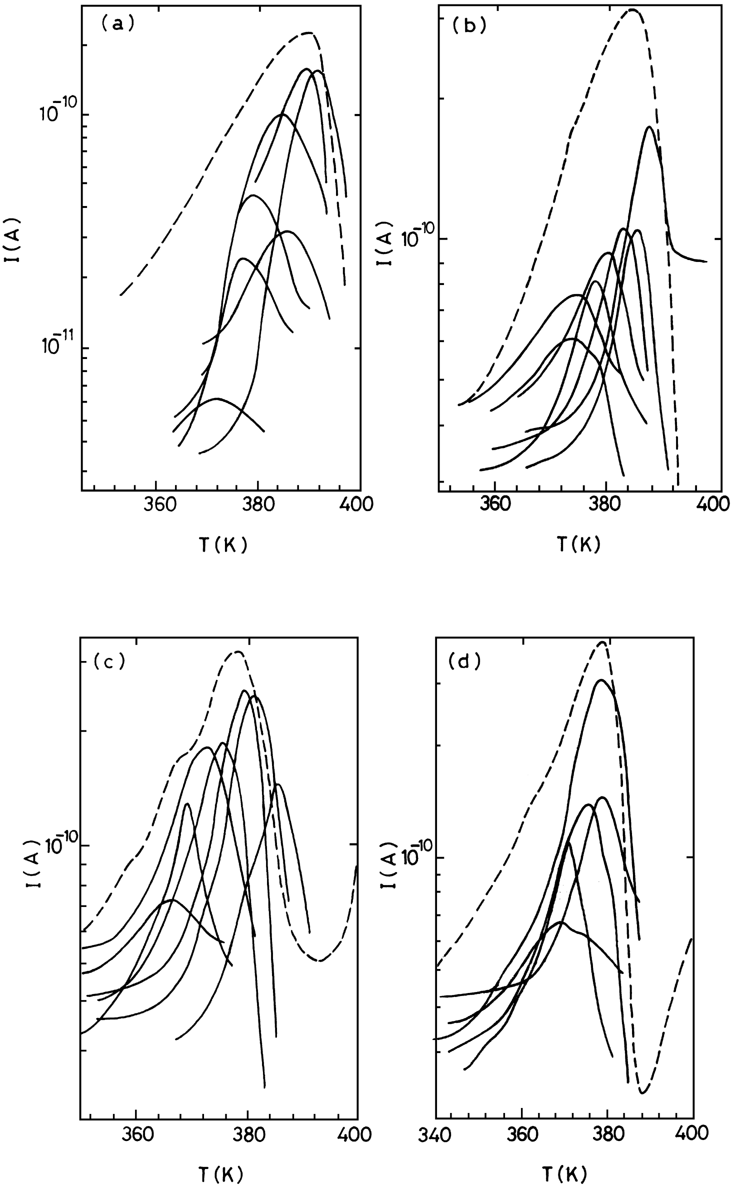


FIGURE 4 Thermally sampled spectra of (a) Pure ABS, (b) 1 wt% Azo-doped, (c) 5 wt% Azo-doped, and (d) 10 wt% Azo-doped. The global spectrum (– – –) is shown for comparison. The envelope poling conditions are $E_p = 7 \times 10^6$ V/m, $T_p = 373$ K, and $t_p = 30$ min. Carbon paste as electrode. Heating rate $\beta = 3$ K/min.

TS peaks follows the contour of the global thermogram. Another observation that could be with drown from this figure, is the enlargement of TS peaks with increasing T_p which can be understood by formally analyzing the change in the width of simple Debye peaks with increasing activation energy.

Each TS curve can be mathematically mapped into its Arrhenius equation

$$\tau_0 = \tau_0 \exp(E_a/kT) \qquad (1)$$

where τ_0 is the pre-exponential factor and if the logarithm of τ_0 varies linearly with the activation energy, one can obtain a compensation law

$$\tau = \tau_c \exp(-E_a/kT_c) \qquad (2)$$

where τ_c and T_c are known as compensation time and compensation temperature, respectively. Hence Eq. (1) becomes

$$\tau(T) = \tau_c \exp\{(E_a/k)[(1/T) - (1/T_c)]\} \qquad (3)$$

Compensation phenomenon is seen most dramatically when Arrhenius relaxation curves can be extrapolated to a focus point in the temperature-frequency (or relaxation time) space [7, 17, 18]. Figure 5 displays the Arrhenius lines or RMA of pure ABS and azodye-doped ABS samples in the vicinity of the glass transition temperature. As shown in the figure, the linearity of $\ln \tau$ *versus* $1/T$ was observed even in the high temperature region near T_g. One can observe that the extrapolating lines in the set of graphs are focused through a specific compensation point. At such a compensation point, all the discrete processes that map the broad relaxation near the glass transition have the same relaxation time [10]. The most striking point is that the compensation phenomenon is much more pronounced for the azodye-doped films than that for pure ABS film. This is a good evidence for the role played by the azobenzene moiety in the organization of the molecular dynamics and, hence, the dipolar disorientation of the ABS macromolecules. From Figure 5, the values of T_c and τ_c were estimated and listed in Table 3. Another observation residing here is that the compensation temperatures are near the glass transition temperature of ABS and decrease as the dye content increases. At this temperature all dipoles are assumed either to have zero moment or become energetically indistinguishable. We may point out that Peacock-Lopez and Suhl have assumed that a compensation law must exist in any system containing elements moving with different energy barriers and coupled to a thermal bath with the same coupling function [19]. Thus, the compensation temperature would be related to this transfer mechanism and T_c is a characteristic of the heat transfer between the thermal bath and the polymer chain.

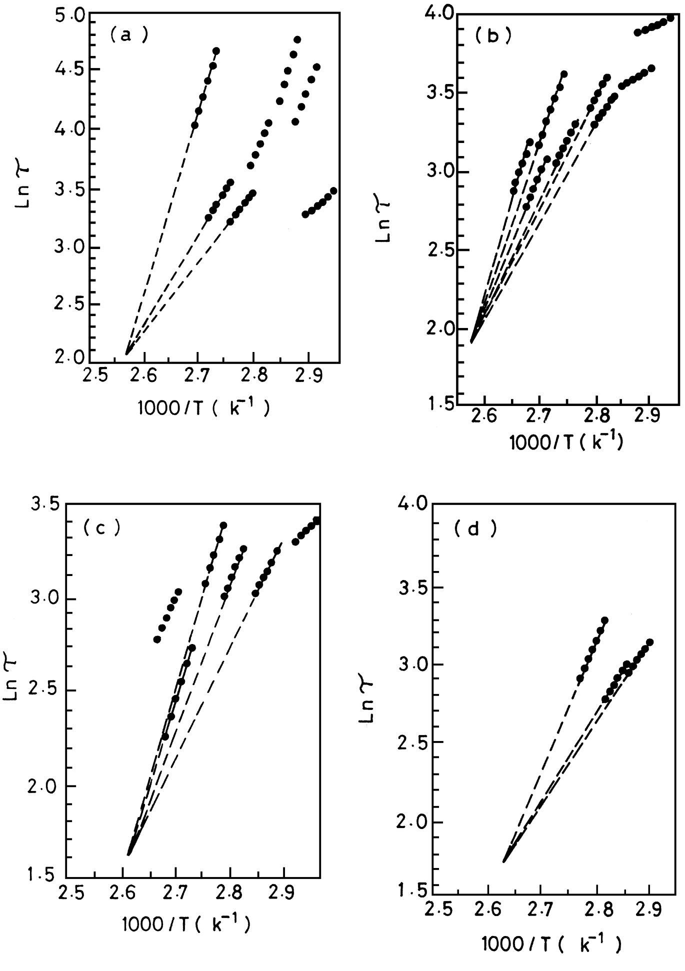


FIGURE 5 Relaxation map analysis illustrated as a ln τ *versus* 1/T plot for different azodye content: (a) 0 wt%, (b) 1 wt%, (c) 5 wt%, and (d) 10 wt%.

Another important argument which underlines the structure regularity of the system under investigation is the density of disorder (DOD). This parameter could be calculated using the compensation coordinates T_c and τ_c as follows [7, 17]:

$$\mathrm{DOD} = 100 - 2[\ln(T_c\tau_c) + 23.76] \tag{4}$$

The number 100 is arbitrarily added to shift all values to the positive side. DOD values for all investigated samples cover a narrow range as seen in Table 3.

TABLE 2 The peak parameters, I_m, E_a and τ_0 with the peak maximum T_m

Sample	T_p (*K*)	T_m (*K*)	I_m (*A*)	E_a (*eV*)	τ_0 (*sec*)
Pure ABS	348	371	6.07×10^{-12}	0.18	6.70×10^{-02}
	353	375	2.38×10^{-11}	0.93	1.22×10^{-12}
	358	379	4.80×10^{-11}	1.10	7.85×10^{-13}
	363	385	1.05×10^{-10}	1.02	1.68×10^{-13}
	368	387	3.10×10^{-11}	0.49	2.90×10^{-06}
	373	389	1.58×10^{-10}	0.46	1.05×10^{-05}
	378	391	1.35×10^{-10}	1.55	2.45×10^{-20}
1 wt% Azo	348	373	6.10×10^{-11}	0.14	3.20×10^{-01}
	353	375	7.55×10^{-11}	0.16	1.50×10^{-01}
	358	379	9.15×10^{-11}	0.28	2.60×10^{-04}
	363	381	8.05×10^{-11}	0.42	2.05×10^{-05}
	368	383	1.05×10^{-10}	0.51	1.46×10^{-06}
	373	387	1.05×10^{-10}	0.81	1.28×10^{-10}
	378	389	1.75×10^{-10}	0.67	1.04×10^{-08}
5 wt% Azo	348	367	7.25×10^{-11}	0.18	6.40×10^{-02}
	353	369	1.30×10^{-11}	0.41	2.00×10^{-05}
	358	373	1.80×10^{-10}	0.39	5.00×10^{-05}
	363	375	1.85×10^{-10}	0.51	1.24×10^{-06}
	368	379	2.55×10^{-10}	0.72	1.32×10^{-09}
	373	381	2.50×10^{-10}	0.78	2.90×10^{-10}
	378	385	1.45×10^{-10}	0.62	5.11×10^{-08}
10 wt% Azo	348	369	6.75×10^{-11}	0.15	2.00×10^{-01}
	353	371	1.10×10^{-10}	0.41	3.00×10^{-05}
	358	375	1.40×10^{-10}	0.48	2.94×10^{-06}
	363	377	3.05×10^{-10}	0.50	1.63×10^{-06}
	368	379	1.46×10^{-10}	0.38	8.00×10^{-05}

TABLE 3 The values of T_c, τ_c and DOD

Sample	T_c (*K*)	τ_c (*sec*)	*DOD*
Pure ABS	389.71	2.06	36.24
1 wt% Azo-ABS	388.65	1.92	36.71
5 wt% Azo-ABS	382.84	1.62	37.34
10 wt% Azo-ABS	380.80	1.73	37.13

Furthermore, the compensation phenomenon is a well known behavior observed in TSDC experiments, namely during the glass transition relaxation of amorphous materials. This is because of the increase in E_a near a glass transition or some other cooperative transition. This is more or less analogous to the chemical kinetics, where the rate constants characterized by a rapid change in E_a with temperature are the ones that compensate [20]. This behavior yields a linear relationship between ln τ_0 and E_a for the various individual components of the relaxation. This behavior is

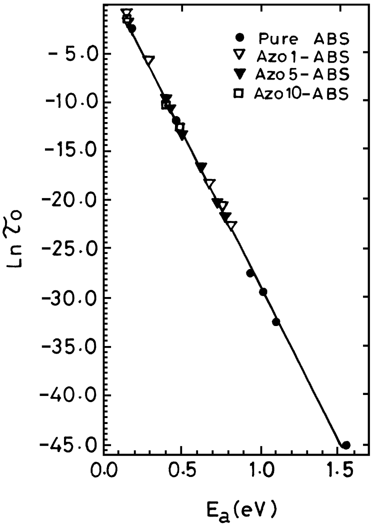


FIGURE 6 Variation of $\ln \tau_0$ *versus* activation energy for the elementary process for all azodye-doped films.

characteristic of our study as illustrated in Figure 6, which depicts such a linear relationship for all samples and assures the validity of the compensation phenomenon in our samples [21, 22].

Shift Factor

It has been demonstrated that when the volume is in thermal equilibrium at a temperature above T_g of an amorphous polymer, the α-relaxation time follows the William-Landel-Ferry (WLF) equation written below [23]. According to this equation, the *i*th relaxation times at temperatures T and T_0 take the values τ^i and τ_0^i, so that

$$\tau^i = a_T \, \tau_0^i \tag{5}$$

$$\log a_T = -\frac{C_1(T - T_0)}{C_2 + (T - T_0)} \tag{6}$$

where C_1 and C_2 are constants. The quantity a_T reflects primarily the temperature dependence of the friction coefficient of the chain segments, on which the rate of conformational rearrangement depends.

On the other hand, the Kovacs-Hutchinson-Aklonis (KHA) equation is very useful for studying the kinetics of the α-relaxation process for

$T < T_g + 10\,K$ [24]. The temperature and structure dependence of the *i*th process is given by

$$\tau^i = A\exp\left(\frac{\Delta H^i}{kT} + \frac{b}{f_T}\right) \tag{7}$$

in which ΔH^i is the activation enthalpy of the *i*th process, f_T is the fractional free volume, A and b are characteristics material constants. For $T < T_g$ it is presumed that the structure does not change, in this case at temperatures T and T_0 below T_g

$$\ln a_T = \frac{\Delta H^i}{k}\left(\frac{1}{T} - \frac{1}{T_0}\right) + b\left(\frac{1}{f_T} - \frac{1}{f_{T_0}}\right) \tag{8}$$

Here, the temperature T being in the denominator affects $\ln a_T$ directly through the first term on the right-hand side and indirectly through its control of the structure as represented by the free volume f_T in the second term. The relaxation times were calculated according the Eq. (1). Then, the ratios a_T of the electrical relaxation times at temperature T to their values at some reference temperature, $T_0 = T_m \sim T_g$, were evaluated. The value of T_m (385 K) was taken from the TS data. Figure 7 displays the dependence of shift factor a_T on the temperature for α-relaxation distribution in all samples according to Eq. (8). It is obvious from the graph that all the curves

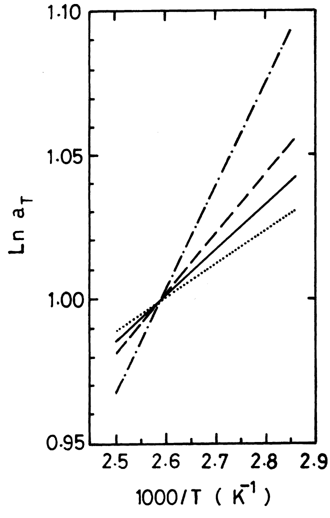


FIGURE 7 Illustration of the temperature dependence of the shift factor a_T (see text).

intersect at a common temperature matching the maximum temperature, $T = T_m$, although they originated from different structures. That is to say, the molecular distribution adopts its shape so that at the emergence point, all the relaxation times τ take the same value at T_g. So to speak, all the processes have the same relaxation time at T_g and hence all the molecules of every component have the same average configuration [11].

CONCLUSION

The global TSDC spectra of the azodye-doped samples exhibit two different modes of relaxation, namely the dipolar relaxation (structured α-relaxation) and the ρ-relaxation. Whereas, only one structureless broadened relaxation occurred in case of the pure ABS. In the former case, both the peak and its shoulder positions (assigned to the liquid crystalline phase of the azodye) were verified to be lowered with increasing the dopant concentration. That is to say, the glass transition temperature, T_g, of the copolymer decreases as the content of the liquid crystalline phase increases where the molecular flexibility is optimized. The thermal sampling technique together with the shift factor analysis demonstrated that the dipolar relaxation is organized in the dye-doped samples where the compensation phenomenon persist. That was in contrast to the results shown by the pure ABS samples, which exhibited a weak validity of the compensation law. Consequently, it is important to conclude that the azobenzene derivative has a strong effect on the orientational order of the host ABS macromolecular structure (as also revealed by the IR spectroscopy) and hence its dipolar disorientation throughout the TSDC experiment. However, the ρ-relaxation which occurred in case of doped samples was explained as an event caused by the space charges accumulating at the heterogeneities or by the charge injected from the electrodes during the poling process.

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