Thermally Stimulated Current of Iodine-Doped Acrylonitrile–Butadiene–Styrene Thin Films

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SYNOPSIS

Structural change of acrylonitrile–butadiene–styrene (ABS) terpolymer due to iodine doping has been reported using both infrared (IR) and thermally stimulated current (TSC) techniques. IR investigation revealed the presence of a new stretching band at 640 cm^{-1} that indicates the formation of the C-I structure. The TSC spectrum consists of two different decaying charge distributions of opposite polarity, which simply superpose to yield the net current observed. The variation of the position of the negative peak relaxation and its intensity as the iodine percentages increases indicates the formation of different ionic iodine species. The induced ionic dipoles superpose the α-relaxation of ABS. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Halogen doping has been reported to produce structural changes in some polymers. One such polymer is nylon, in which iodination has been reported to produce significant structural changes in the polymer films.[1-3] Most research efforts have been devoted to the study of the nature of these halogen species[4] and to determine if charge transfer between the dopant and the donar or partial oxidation of the original material leads to an increase in the conductivity.[5-8]

Measurement of thermally stimulated current (TSC) is a useful general method for studying trapping characteristics in materials.[9,10] The TSC technique is based on the electret effect and many authors have used it to study molecular motions in polymers.[11-13] The TSC peaks obtained from such electrets have been associated with structural transitions in the polymer. In the present paper, we report results of some experiments conducted on iodine-doped acrylonitrile–butadiene–styrene (ABS) terpolymer in an attempt to elucidate the structural changes that occur during iodination of ABS. Our TSC measurements clearly distinguish between the transport due to detrapping of electronic charge and dipolar reorientation. Infrared studies revealed that iodine attacked the terpolymer.

EXPERIMENTAL

Acrylonitrile–butadiene–styrene (ABS) terpolymer (Novador PH-AT Bayer-Germany) is an amorphous material and was used without further purification.

Films of thicknesses ranging from 10 to 20 μm were formed by a casting technique. The material and the proper weight of iodine were dissolved in chloroform. The solution was dried on a glass substrate under normal atmosphere. Conducting surfaces of the sample were made by thermal deposition of silver. The specimens were polarized by an applied electric field (Ep) for a specific time (tp) at the desired temperature (Tp). The film was then cooled to room temperature under the applied field (Ep). Details of experimental arrangements and measuring techniques are to be found elsewhere.[13-15] Results were reproducible to within 10%.

Infrared studies of the pure and iodine-doped ABS were carried out using a Perkin-Elmer 1430 ratio recording infrared spectrometer.
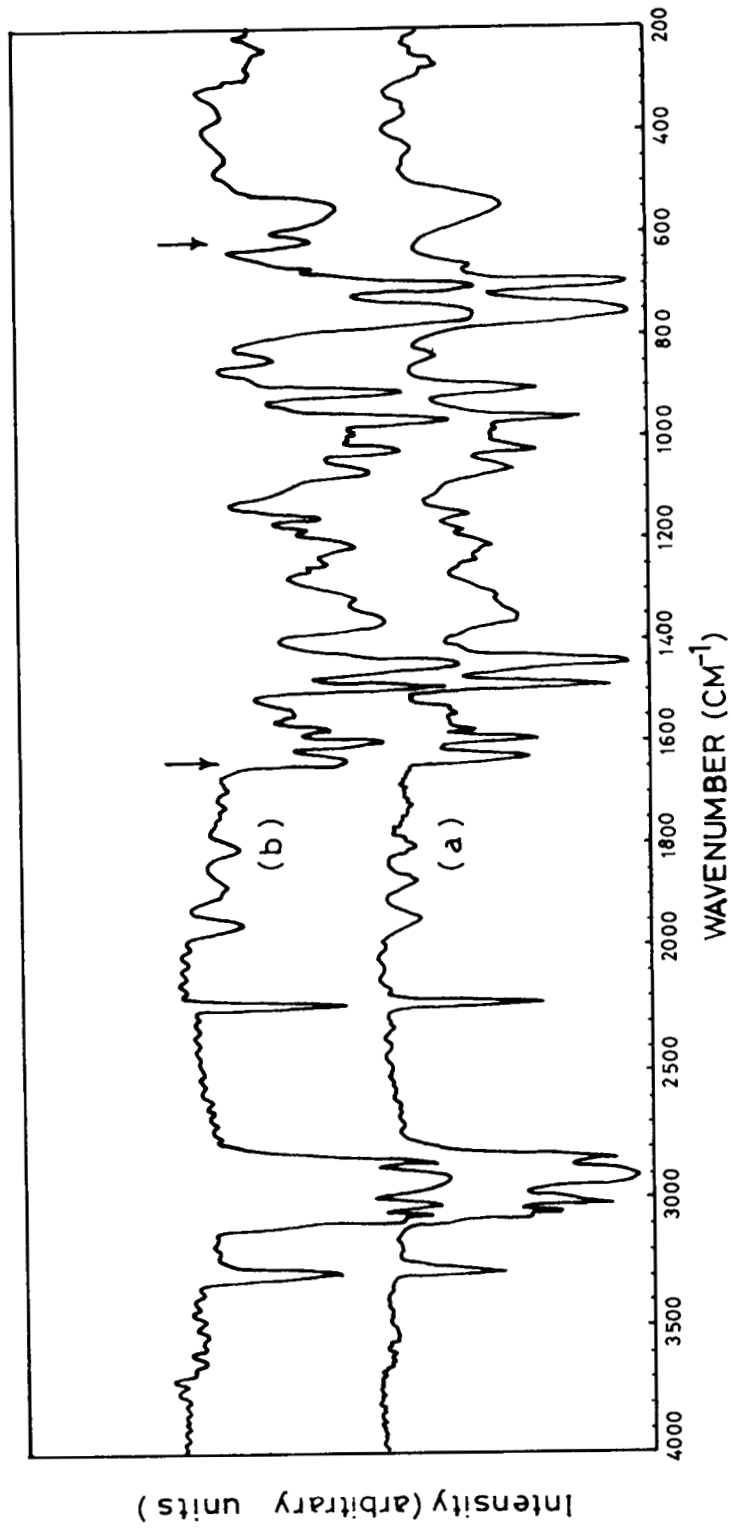
Figure 1 The IR spectral region from 200 to 4000 cm^{-1} of (a) pure ABS and (b) iodine-doped ABS.

RESULTS AND DISCUSSION

Figure 1 shows the IR spectra of pure and iodine-doped ABS in the range 200–4000 cm^{-1}. The appearance of a relatively weak band at 640 cm^{-1} in case of I_2-doped ABS is to be observed in Figure 1. This indicates that, when ABS is doped with iodine, it may go substitutionally into the polymer backbone to form a C-I structure. The intensity of this band increases as the iodine concentration varies from 0.1 to 0.5%. Beyond 0.5%, it remains constant. Further, the intensity of the band at $\sim$ 1641 cm^{-1}, which is assigned in ABS to —C═C— bending,[16] decreases as the iodine concentration increases. This can result only if iodine attacks the terpolymer and forms iodinated ABS.

Figure 2 represents the TSC spectra for pure as well as for iodine-doped ABS poled at constant field strength $Ep = 1 \times 10^6$ V/cm for 1 h at 120°C. Curve 1 corresponds to the undoped ABS and curves 2–7 correspond to doped films with iodine concentration ranges from 0.1 to 10% wt. Curve 1 includes a peak at about 110°C. This peak was termed α-relaxation and has been proved to be due to dipolar relaxation.[13,17,18] The position, the intensity, and the shape of this peak is changed on doping ABS with iodine. The TSC spectra exhibit two currents of opposite polarity. A negative current in the diagrams 5–7 corresponds to one that flows in a direction opposite to that of charging current. On the other hand, the behavior and the intensity of the positive currents of curves 2–4 depend on the iodine concentration.
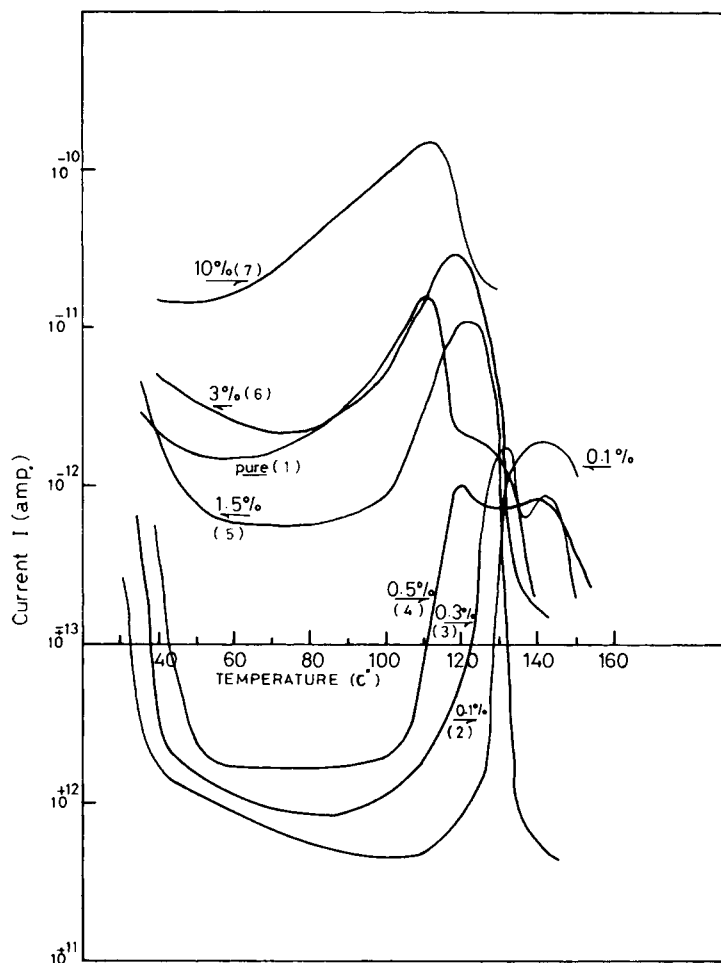

Figure 2   TSC spectra of iodine-doped ABS films (thickness 10–20 μm) polarized under identical conditions of $Ep = 1 \times 10^6$ V cm^{-1}, $Tp = 393$ K, and $tp = 1$ h. Curves 1–7 correspond to iodine concentration of 0, 0.1, 0.3, 0.5, 1.5, 3.0, and 10.0% by weight, respectively.

The occurrence of TSC spectra is generally interpreted in terms either of detrapping of electronic charge or of dipolar reorientation, including annihilation of dipoles due to ionic motion. Hence, the complex current spectrum of iodine-doped ABS is due to the existence of two different decaying charge distributions of opposite polarity that simply superpose to give the net current.[19] Assuming, for a first-order approximation, that the relaxation is governed by a single relaxation time[20,21] that obeys an Arrhenius equation with an activation energy independent of temperature, one obtains the TSC as $J(T)$, i.e.,

$$J(T) = \frac{P_0}{\tau_0} \exp\left[-\frac{H}{KT} - \frac{1}{\beta \tau_0} \int_{T_0}^{T} \exp\left(\frac{-H}{KT}\right) dT \right] \quad (1)$$

where P_0 is the initial amount of charging; τ_0, the relaxation time extrapolated to infinite temperature T; K, the Boltzmann's constant; and β, the heating rate. By differentiating eq. (1) with respect to T and equating the result to zero, τ_0 can be expressed in terms of the peak temperature (T_{max}) at which the maximum current occurs, i.e.,

$$\tau_0 = KT_{max}^2 / \beta H \exp(-H/KT_{max}) \quad (2)$$

Activation energies for the negative current peak can be calculated applying the initial rise method[22] to the TSC curves obtained under iodine-doping concentration conditions.

Figure 3 illustrates a semilog plot of the current against $(1000/T)$ for different iodine concentrations according to the initial rise method. The activation energy values for pure and 1.5, 3, and 10% iodine-doped ABS have been calculated and are listed together with T_{max} in Table I. Moreover, the relaxation time values have been calculated according to eq. (2) and are given also in Table I.

It may be seen from Table I that both τ_0 and H are iodine-concentration-dependent. Further, the position of the peak (see Fig. 2) shifts toward lower temperature side as the iodine concentration increases. These results reveal the presence of different types of ionic iodine species and the relaxation results from the annihilation of dipoles due to ionic motion. These species may serve as electron supply during discharge. This is confirmed by the existence of the positive current component in TSC. Hence, the increase in the dc conductivity of iodine-doped ABS compared with pure ABS that we have observed is due to the charge transfer mechanism.
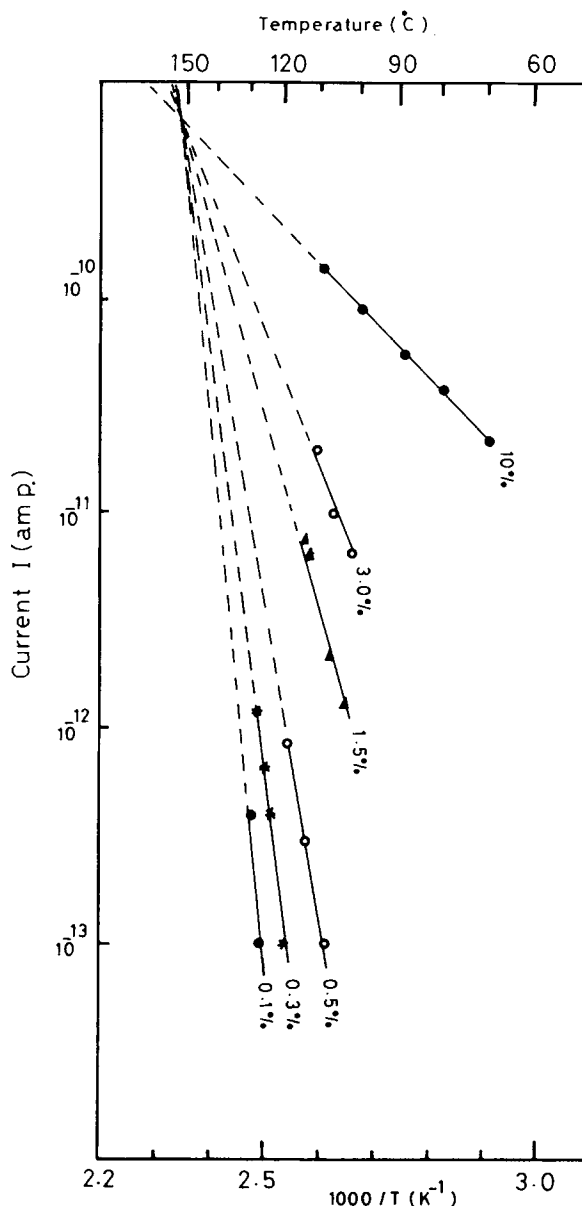

Figure 3 Arrhenous relationship of ln I vs. 1000/T for iodine-doped ABS.

CONCLUSION

The TSC technique has been used to investigate the influence of iodine on the TSC in ABS. The TSC of iodine-doped ABS consists of negative and positive components. The major part is probably related to the rearrangement of dipoles or ions, and the minor part, to the discharge of injected carriers from traps. It could also be shown that the peak intensity of the relaxation as well as its position depend on

Table I   The Values of the Activation Energy (H), the Maximum Peak Temperature (T_m), and the Relaxation Time (τ_0) for Pure and Iodine-doped ABS Films

C (%)	H (eV)	T_m (K)	τ_0 (s)
0.0	1.04	383	$0.7836502 \times 10^{-13}$
1.5	1.98	393	$0.8073714 \times 10^{-25}$
3.0	1.30	391	$0.5466622 \times 10^{-16}$
10.0	0.59	386	0.1383203×10^{-6}

the iodine percentage. Hence, the relaxation is due to induced ionic dipoles, and, in conclusion, the fact that iodine induces structural changes of polymers is consistent with our investigation.

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