

Thermally Stimulated Depolarization Currents in Poly(2,6-dimethyl-1,4-phenylene oxide) Films

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SYNOPSIS

Electrical properties of poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) have been studied by measuring thermally stimulated discharge currents. Depolarization behavior of poled PPO film exhibits temperature- and time-dependent single relaxation around 468 K which is attributed to dipole reorientation. The peak maxima, however, shifts from 468 K to 484 K with increasing poling temperature. This indicates that the peak has a distribution of relaxation times. The polarization in semicrystalline PPO is found to decay slowly, indicating that the overall dipoles are more stable in comparison to amorphous PPO; hence, crystalline PPO forms comparatively stable electrets. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polymers are capable of storing charges permanently when subjected to field temperature treatment. Such dielectric materials are then referred to as thermo-electrets. These polymer electrets are being used in a number of technological applications, particularly as electret microphones,^{1,2} filters,³ radiation dosimetry,⁴ and relay-type switches, transducers, and sensors.^{5,6}

Thermally stimulated discharge current (TSDC) is a sensitive technique for the investigation of the properties of polymer electrets.⁶⁻⁹ Because of the high sensitivity of the technique, it is used to investigate the effect of low concentration of dipole impurities on the dielectric behavior and relaxation processes, phase transitions, and photographic response of silver halides.⁷ The polarization in a thermally charged specimen may arise due to various mechanisms, the important among which are orientational or dipolar polarization, translational or space charge polarization, and interfacial polarization. The charge originated in TSDC due to dipole

orientation or the trapping of space charges in defect or dislocation sites is known to give rise to a uniform polarization, which is heterocharge. On the other hand, space charge buildup by migration of ions over microscopic distance gives a nonuniform heterocharge, whereas trapped injected space charge results in a nonuniform homo- or heterocharge, depending upon the work function of the metal electrodes.

The thermodynamic and relaxation properties of bulk poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) have been reported in a number of studies.⁹⁻¹⁴ Usually two molecular relaxations have been observed in PPO and are labeled as γ and α in order of increasing temperature. At high temperature, the α in order of increasing temperature. At high temperature, the α -relaxation peak observed around 503 K (at 100 Hz) has been attributed to the thermal excitation of cooperative motions in chain and identified with the glass transition temperature (T_g). The low-temperature γ -relaxation peak is observed around 157 K (at 100 Hz) and attributed to a localized vibrational mode of dipolar moiety.¹⁴ DePetris and colleagues¹¹ also observed an intermediate β -relaxation at 373 K (at 7 KHz) which they interpreted as due to oscillations of the aromatic rings around the C—O—C bond. In the dielectric mea-

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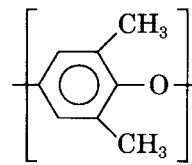
measurements Karasz and coworkers¹⁴ have reported that the magnitudes of α and γ peaks are comparable, however in the dynamic mechanical studies¹⁴ they differ by more than an order of magnitude ($\alpha > \gamma$). This may be due to the relative contributions of dipolar and mechanical motions in the respective techniques.

Alexandrovich and colleagues¹⁵ have applied TSDC technique to infer basically whether this technique can yield information on the compatibility of PPO/poly(ρ -chlorostyrene) and PPO/polystyrene blend systems. The paper also reports briefly on the TSDC data of PPO as one of the blend components. They have observed a current maximum at 179°C ($E_p = 2.5$ KV/cm) which, though it is far from the calorimetric T_g (216°C), is attributed to the relaxation of oriented dipoles. The peak is largely irreproducible due to the presence of copper salt-amine as a catalyst; related impurities are present in the commercial PPO sample used (General Electric Co., U.S.A.).

It is well established^{7,14} that the total charge stored in an impurity-free polymer electret and its relaxation mechanism are very sensitive to the electret forming parameters such as poling field (E_p), poling temperature (T_p), and poling time (t_p). With this in mind, and in view of the limited data available for PPO as electret, detailed studies were made of pure PPO. This may lead to better understanding of the influence of experimental parameters on the electret-forming properties of PPO. In continuation of our earlier attempts to investigate the electrical properties of PPO,^{16,17} an important engineering thermoplastic, the present paper reports in detail the electret properties of pure amorphous and partial crystalline PPO using TSDC technique.

EXPERIMENTAL

Highly pure PPO with the following repeat unit and having T_g 483 K and molecular weight 10^5 was obtained in the form of powder from Aldrich Chemicals Company Inc., U.S.A. Before use, the PPO was further purified by dissolving in methylene chloride at room temperature (28°C) and precipitating with an excess of methanol. The purification cycle was repeated several times. Solvents used were of spectroscopic grade. The characteristic T_g of purified PPO was 483 K, obtained using differential thermal analysis technique.



Films were cast on optically plane glass plate from the solutions in spectroscopic grade methylene chloride. Evaporation of the solvent was carried out at room temperature in a dust-free atmosphere for 12 h. The films were further exposed to vacuum-drying for 48 h to remove any residual solvent. Films thus obtained were uniform in thickness (70 ± 2 μ m) and transparent.

Metal electrodes were deposited with suitable masks on the PPO films, to form a metal-PPO-metal sandwich structure by thermal evaporation of spectroscopically pure aluminium (99.999% pure; E. Merck, India). The configuration of top and bottom electrodes was such that it gave a square sandwich structure of 1 cm² crossover area. The vacuum inside the chamber during the evaporation was about 10^{-3} Torr and films were kept at a distance of 12 cm from the tungsten filament. Further electrical contacts were made by bonding copper leads to the metal films by means of an air-drying-type silver paint.

Prior to TSDC measurements, the specimens were polarized by applying a static electric field (E_p) at an arbitrary constant temperature (T_p) of 363 K, for a time (t_p) of 1.5 h. This causes an alignment of the permanent dipoles. The induced alignments of the permanent dipoles were frozen in place by gradually cooling the specimens to room temperature for another hour while the field was still on. In order to eliminate the rapid discharge of the accumulated electric charges caused by the applied field during polarization, the electrodes were short-circuited for an arbitrary time.

For TSDC measurements, the samples were heated at a uniform rate of 3 K/min⁻¹ and measured by a calibrated copper-constant thermocouple. This rate ensures good resolution of TSDC spectra without any temperature gradient across the specimen. The discharge currents, as a function of temperature, were measured by employing a Keithley electrometer (Model 610C).

Semicrystalline PPO sample films 70 ± 2 μ m thick were prepared by exposure to an atmosphere of 2-butanone (MEK) vapors for 20 and 60 h and designated as samples A and B, respectively. The crystalline films were dried under vacuum at 373 K

for 48 h. After this treatment, no residual solvent could be detected.

RESULTS

Field Dependence

The typical TSDC spectra of PPO films poled at $T_p = 363$ K for $t_p = 1.5$ h and at different poling fields (E_p) are shown in Figure 1. Curves 1 to 5 are for E_p of 14 KV/cm, 29 KV/cm, 50 KV/cm, 64 KV/cm, and 79 KV/cm, respectively. Only one peak, centered around 468 K, was obtained in each case. It is observed from these curves that although the specimens were polarized with different E_p values the positions of the current maxima characterized by T_M and corresponding to the peak remain unaltered. It can also be seen that the shapes of the spectra remain almost the same despite changes in E_p .

Figure 2 depicts the plots of the charge (Q) released to the external circuit and the peak current (I_M) as a function of E_p . It is interesting to note

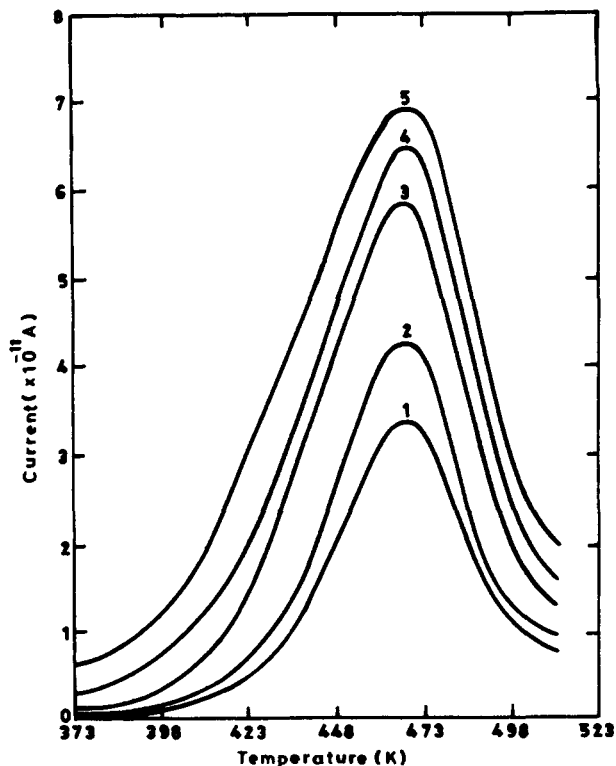


Figure 1 TSDC Spectra of PPO films poled at $T_p = 363$ K for $t_p = 1.50$ h with different poling fields (E_p); Curves 1 to 5 correspond to E_p of 14 KV/cm, 29 KV/cm, 50 KV/cm, 64 KV/cm, and 79 KV/cm, respectively.

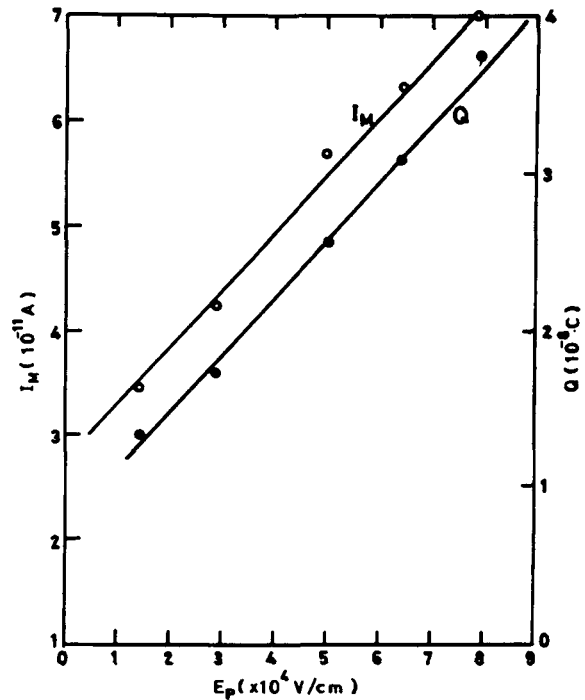


Figure 2 Plots I_M and Q versus E_p for TSDC spectra of PPO of curves 1 to 5 of Figure 1.

that when E_p was increased from 14 KV/cm to 79 KV/cm both Q and I_M , corresponding to the peak, increased linearly. The total charge, Q , released to the external circuit was obtained by integrating the TSDC spectrum with respect to time. No further appreciable changes in Q and I_M were observed with $E_p > 90$ KV/cm compared to $E_p = 79$ KV/cm.

The activation energy (E) was evaluated, using the initial-rise method of Garlic and Gibson¹⁸ from the slopes of the $I(T)$ versus $1/T$ plots (Fig. 3). The temperature-dependent relaxation times τ_T at the peak temperature (T_M) and at room temperature (300 K, τ_{300}) for the dipoles in the dielectric were calculated. The field-dependent data are summarized in Table I.

Temperature Dependence

The TSDC spectra of PPO films at identical conditions of $E_p = 29$ KV/cm and $t_p = 1.5$ h, but for different poling temperatures $T_p = 363, 398,$ and 413 K, were obtained. A single peak was obtained in each case, which shifted to a higher temperature at 484 K from 468 K with increasing T_p without any alteration in peak profile. However, with increase in T_p from 363 K to 413 K, the magnitude of peak current and the charge associated with TSDC peak were

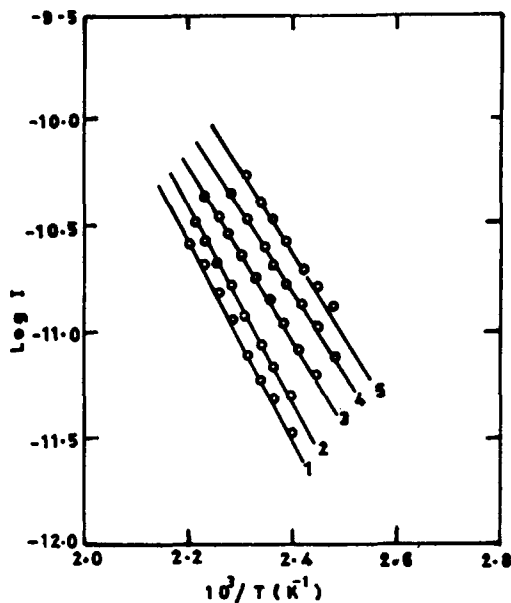


Figure 3 Log I versus $1/T$ of the TSDC curves of Figure 1; curves 1 to 5 correspond to E_p of 14 KV/cm, 29 KV/cm, 50 KV/cm, 64 KV/cm, and 79 KV/cm, respectively.

found to increase. It was observed that increasing the poling temperature further, even up to T_g (483 K), did not change the temperature at which current maxima were observed. The activation energy associated with peaks calculated from $\log I(T)$ versus $1/T$ plots increases linearly with the increase in T_p . The other electronic parameters such as τ_0 , τ_M and τ_{300} are tabulated in Table II.

Time Dependence

The TSDC spectra of PPO films poled at $T_p = 363$ K and $E_p = 29$ KV/cm but for different poling times of 1.0 h, 1.5 h, 2 h, 2.5 h, and 3.0 h were recorded. The magnitude of peak current and charge associated with it increased with increase in t_p . The position of the peak shifted from 464 K to 477 K for

maximum poling time to 3.0 h. The activation energy increased with increasing t_p ; along with other parameters for the time-dependent case, this is shown in Table III.

DISCUSSION

In the present investigation TSDC thermograms are characterized by a single peak at 468 K, as shown in Figure 1. The activation energy associated with this discharge process is 0.85 eV, which is in good agreement with the order of activation energy required for the rotation of dipoles/molecules in many long-chain polymers.¹⁹⁻²² This value of activation energy, 0.85 eV, is found to be in good agreement with the 0.91 eV value evaluated by the Bucci and Fieschi's modified method²³ (in which logarithm of the remaining charge $[Qr]$ divided by the current $[I(T)]$ at a particular temperature when plotted against the reciprocal of that temperature results in a straight line; the slope of this line gives the value of activation energy).

The magnitude of the charge corresponding to the field-independent peak, T_M , increases strictly linearly with an increase of poling field, E_p (Fig. 2).²² These characteristics clearly indicate that the observed peak can be considered to be due to the molecular motion involving the depolarization of the aligned dipoles in PPO. The possibilities, however, of the current in the external circuit being due to the release of the charge either at the T_g or through phase change are ruled out, since unpolarized PPO samples exhibit no TSD current on heating.

The repeat unit of the PPO has asymmetrical structure. According to Stockmayer's²⁴ classification, PPO belongs to the A-type polymer with dipole moment component parallel to the chain contour. In such cases the dielectric relaxation originates from the normal mode process to the fluctuation of the end-to-end chain vector, provided the polymer

Table I Depolarization Kinetics Data Calculated by the Initial Rise Method for PPO Films* of Thickness 70 μm Polarized at $T_p = 363$ K for $t_p = 5.4 \times 10^3$ s with Different Poling Fields (E_p)

Curve (Fig. 1)	E_p ($\times 10^4$ V/cm)	T_M (K)	I_M ($\times 10^{-11}$ A)	Q ($\times 10^{-8}$ C)	E (eV)	τ_0 ($\times 10^{-7}$ s)	τ_M ($\times 10^2$ s)	τ_{300} ($\times 10^7$ s)
1	1.4	468	3.36	1.31	0.85	1.21	1.70	2.28
2	2.9	468	4.25	1.68	0.84	1.57	1.72	2.01
3	5.0	467	5.83	2.59	0.85	1.15	1.70	2.17
4	6.4	468	6.45	3.14	0.85	1.21	1.70	2.28
5	7.9	469	6.90	3.81	0.84	1.64	1.74	2.10

Table II Depolarization Kinetics Data Calculated by the Initial Rise Method for PPO Films of Thickness 70 μm Polarized with $E_p = 2.9 \times 10^4$ V/cm for $t_p = 5.4 \times 10^3$ s at Different Poling Temperatures (T_p)

T_p (K)	T_M (K)	I_M ($\times 10^{-11}$ A)	Q ($\times 10^{-8}$ C)	E (eV)	τ_o ($\times 10^{-7}$ s)	τ_M ($\times 10^2$ s)	τ_{300} ($\times 10^7$ s)
363	468	4.27	1.69	0.82	2.62	1.77	1.56
383	473	5.10	2.22	0.85	1.54	1.74	2.90
398	479	5.93	2.69	0.87	1.24	1.76	5.06
413	483	6.45	3.03	0.89	0.95	1.75	8.39

is free of impurities. Therefore, in the present case the observed TSDC peak is associated with the relaxation process arising from the randomization of the aligned dipoles of the main polymer chain. Furthermore, in the present case the activation energy associated with the TSDC peak is quite large compared to that required for local motion/rotation of methyl and phenyl groups (0.20 eV and 0.46 eV).²⁵⁻²⁷ This rules out an effect caused by a freedom of these individual groups alone. Thus it may be concluded that the present TSDC peak originates from cooperative movement of the phenyl groups with the molecular motion of the methyl groups in the PPO backbone chain.

The shift in temperature, T_M , toward the higher temperature side with increase in poling temperature, T_p , can be explained by considering a continuous spectrum of relaxation times and activation energies. T_M in the depolarization current spectrum is given as:^{28,29}

$$T_M = (b \cdot E \cdot \tau_M / k)^{1/2}$$

This shows that, for a single relaxation process of fixed activation energy and a fixed rate of heating, T_M is independent of T_p and t_p . However, in the present case, the observed shift in T_M toward higher temperature and increase in I_M with the increase in t_p support the fact that there is a continuous distribution of relaxation times.³⁰ The linear increase of

activation energy with increase in T_p further supports our results of the distribution of relaxation times.^{31,32} The absence of wide-angle X-ray diffraction (WAXD) profiles, due to crystalline PPO (results now shown), at $2 = 8^\circ$, 13° , and 22° reveals that PPO is an amorphous polymer.³³ As a result, dipoles are randomly distributed in amorphous polymer affecting their relaxation and activation energies.³⁰

It is evident from Tables II and III that the dipole relaxation time (τ_{300}) at room temperature in the PPO electrets increases with increasing poling temperature and time. This may be due to the effect of extending the dipole polarization further into the material. As a result the steric arrangement of the dipolar groups may be hindered by the internal rotation of the methyl and phenyl groups, thus markedly increasing the dipole relaxation times with increasing poling temperature and time. It seems, thus, that the PPO electrets polarized at higher temperature with longer poling time decay slowly and may form stable electrets.

Most of the electrets are made of amorphous or semicrystalline polymers, with a high degree of morphological disorder in the bulk phase and a high number of deep traps.⁷ With this in view it was thought to create morphological disorder by inducing crystallization in present amorphous PPO. It is, however, well known that the bulk PPO cannot be thermally crystallized but that it crystallizes fairly

Table III Depolarization Kinetics Data Calculated by the Initial Rise Method for PPO Films of Thickness 70 μm Polarized with $E_p = 2.9 \times 10^4$ V/cm at $T_p = 363$ K for Different Poling Times (t_p)

t_p ($\times 10^3$ s)	T_M (K)	I_M ($\times 10^{-11}$ A)	Q ($\times 10^{-8}$ C)	E (eV)	τ_o ($\times 10^{-8}$ s)	τ_M ($\times 10^2$ s)	τ_{300} ($\times 10^7$ s)
3.6	464	2.53	1.33	0.84	12.9	1.70	1.65
5.4	468	4.28	1.67	0.87	7.19	1.69	2.93
7.2	472	5.31	2.32	0.89	5.25	1.66	4.64
9.0	476	6.05	2.68	0.91	3.85	1.65	7.38
10.8	477	6.78	2.97	0.93	2.44	1.62	10.1

well in the presence of solvent.³³ The semicrystalline PPO film samples A and B were prepared by exposure to an atmosphere of 2-butanone vapors for 20 h and 60 h, respectively. The WAXD curves of these two samples (not shown here), were obtained. Inspection of the intensity of the samples' WAXD haloes reveals that the induced crystallinity in sample B is of a higher order than in sample A. The post-treated PPO films were checked for possible entrapped butanone using Fourier transform infrared spectroscopy. The total absence of C=O (1705–1712 cm⁻¹) absorption in the spectra of these films (results not shown) suggests that the samples are free from any trace of the residual butanone, which shows that the observed process is in partially crystallized PPO being intrinsic rather than extrinsic. Here again, both the unpolarized A and B samples exhibit no TSDC on heating.

Figure 4 shows the TSDC thermograms of A and B specimens. Prior to TSDC measurements both specimens were polarized with identical conditions ($E_p = 79$ KV/cm, $T_p = 413$ K, and $t_p = 3.0$ h). It is seen from these curves that with decreasing magnitude of the charge associated with the peak, the position shifts towards higher temperature ($T_M[A] = 490$ K and $T_M[B] = 496$ K) with increasing crystallinity in PPO ($B > A$).

The activation energies and the corresponding relaxation times (Sample A: $E[A] = 0.90$ eV, $\tau_M = 1.83 \times 10^2$ s, $\tau_{300} = 12.42 \times 10^7$ s; sample B: $E[B] = 0.92$ eV, $\tau_M = 1.89 \times 10^2$ s, $\tau_{300} = 12.51 \times 10^7$ s) corresponding to T_M ($T_M[A] = 490$ K and $T_M[B] = 496$ K) have been found to increase accordingly. This morphology-dependent shift of the charge decay onset to higher temperature is attributed to hindered dipole relaxations in the crystalline phase or in the intermediate region between the crystalline and amorphous phases. However, as the peak appears above T_g with broadening profiles at higher temperatures, it may also partially contribute to overall net uniform hetero charge polarization from the Maxwell-wager type of destruction of space charging at crystalline–amorphous phase boundaries. However, no separate peak or clear shoulder appears in TSDC spectra. Moreover, the TSDC peak becomes broader with increasing crystallinity in PPO and therefore involves a distributed polarization with the foot being truncated comparably to amorphous PPO, indicating enhanced storage time. Thus it seems that the crystalline PPO electret forms a stable electret in comparison to amorphous PPO. These inferences are well supported by the longer relaxation times observed for crystalline PPO.

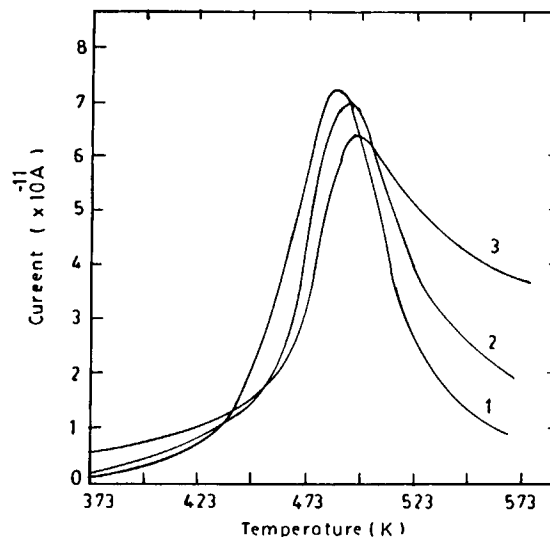


Figure 4 TSDC spectra of semicrystalline PPO films poled with $E_p = 79$ KV/cm at $T_p = 413$ K for $t_p = 3.0$ h; curves 1 to 3 correspond to nontreated amorphous PPO ($T_M = 486$ K), solvent-vapor-treated (for 20 h) film (sample A, $T_M = 490$ K), and solvent-vapor-treated (for 60 h) film (sample B, $T_M = 496$ K), respectively.

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