Thermally stimulated discharge of blends of Novolac phenol–formaldehyde resin and nylon-6

M. Topić and A. Moguš-Milanković
Laboratory for Solid State Chemistry, Ruđer Bošković Institute, POB 1016, 41001 Zagreb, Croatia, Yugoslavia

and Z. Katović
Chromos, Chemical Research Centre, 41000 Zagreb, Croatia, Yugoslavia

(*Received 21 March 1986; revised 27 May 1986*)

Thermally stimulated depolarization current studies of Novolac phenol–formaldehyde (NPF) resin mixed with 10 wt % and 20 wt % nylon-6 (Ny6) were performed in the temperature range 300 to 350 K using various poling fields, E_p, and various poling temperatures, T_p. Experiments carried out with direct contacts show only a dipolar relaxation peak P_1 at $T_{m1} = 337$ K. By reversing E_p, in addition to P_1, a space charge relaxation peak P_2 is observed at $T_{m2} = 345$ K. By performing experiments at different T_ps with one electrode blocked with Teflon foil, it is possible to suppress the background current, which then allows one to separate and to identify the two relaxation processes. Addition of Ny6 to a NPF matrix increases the total depolarization current and causes electrode polarization due to the increase in heterogeneity of the blend. Ny6 also increases the maximum temperature of the two peaks but it decreases the activation energy of the dipolar relaxation process. These effects are attributed to the hydrogen bonding between functional groups from the matrix and nylon-6.

(Keywords: thermally stimulated depolarization current; phenol-formaldehyde novolac resin; nylon-6; blends)

INTRODUCTION

The thermally stimulated depolarization current (t.s.d.c.) in NPF resin has already been studied[1-3] as has the discharge in pure Ny6[4]. T.s.d.c. of NPF resin showed three reproducible current peaks. P_0 appeared at 296 ± 1 K and was assumed to be caused by a change in some detail of the resin structure[3]. P_1, which appeared at 320 ± 2 K, coincides with the glass transition, and behaves as a typical dipolar relaxation peak[2]. Such a peak is usually called the α peak[5]. The third peak, P_2, appeared at 334 ± 6 K and experimental evidence indicated that P_2 is due to the discharge of the resin. This type of peak is called the ρ peak[5]. T.s.d.c. measurements on pure Ny6 in the region from room temperature up to 473 K showed only one peak, viz. at 443 K. This peak was explained as being caused by the discharge of space charges accumulated in the electrode region. Recently, mixed heterogeneous polymer systems have been the subject of t.s.d.c. studies[6,7]. The effectiveness of storing the charge in polymer blends is more than in the individual charge-storage components.

The aim of this work was to examine how an addition of Ny6 would change the properties of the NPF resin in storing charges and to study possible consequences of the interaction between the NH groups in Ny6 and the OH groups in NPF.

EXPERIMENTAL

NPF resin was prepared by condensing phenol with formaldehyde at a mole ratio of 1:0.865 using oxalic acid as catalyst[2]. Ny6 fibres, commercial grade, were added to the NPF at 393–423 K during stirring. The blends were subsequently cooled to room temperature and pulverized. Two different blends were prepared with 10 wt % (N-10) and 20 wt % (N-20) Ny6. The samples with a Ny6 fraction above 20% were not sufficiently compact and were therefore avoided. The pulverized blend was put into a small container with silver coated brass electrodes of diameter 13.6 mm and separated by a distance of 1 mm. The blend was melted in the container which was placed in a dark shielded cell filled with dry nitrogen. The procedure for the measurements was as follows: The sample was discharged by heating up to 353 K with short-circuited electrodes. The poling was performed with a field, E_p, at the chosen temperature, T_p, for 20 min. The sample was then cooled to room temperature under the same field. After removal of E_p, the sample was held short-circuited for 30 min. The t.s.d.c. measurements were carried out with a Keithley 616 electrometer at a heating rate of 2 K min^{-1}. The cooling rate was 2–3 K min^{-1}. In some cases the poling and the measurements were performed with a blocking electrode by inserting a 130 μm thick Teflon foil between the resin capacitor and the grounded part of the cell. Other details are described elsewhere[2,3].

RESULTS AND DISCUSSION

Effect of T_p

The experimental results for measurements carried out at different T_p values are presented in *Figures 1* and *2*. *Figure 1* shows the results for the sample containing 10% of Ny6, while *Figure 2* shows the results for the sample with 20% Ny6. The poling field was constant and

0032-3861/87/010033-05$3.00
© 1987 Butterworth & Co. (Publishers) Ltd.

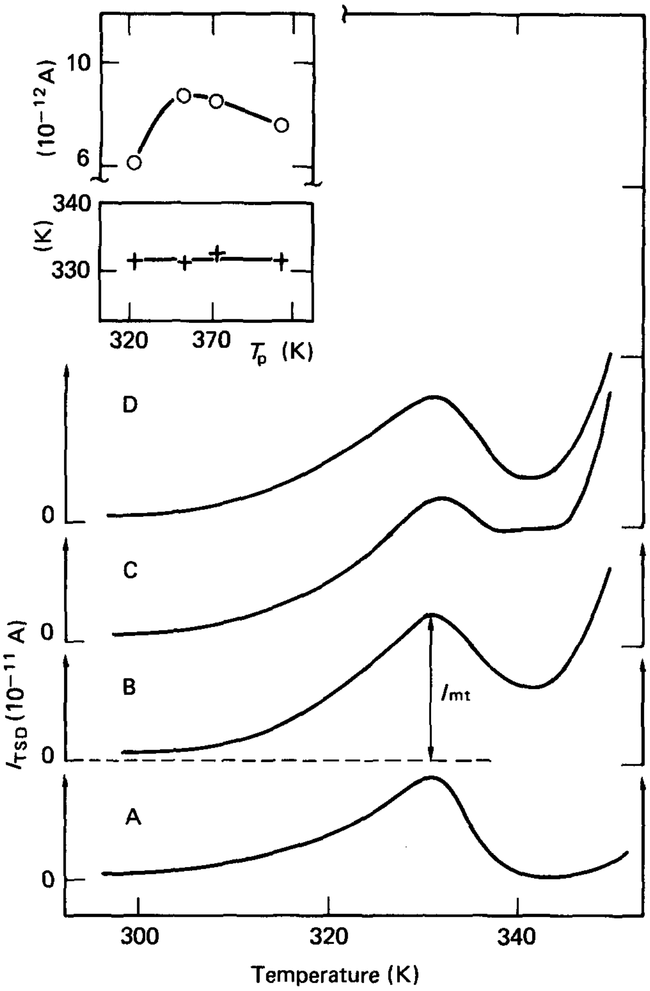

Figure 1 Thermally stimulated depolarization current, I_{TSD}, of N-10 blend vs. temperature for various T_p's: (A) 323, (B) 353, (C) 373, (D) 413 K, $E_p = 4$ kV cm^{-1}. Inset: (+) maximum temperature, T_m, (○) maximum current, I_{mt}

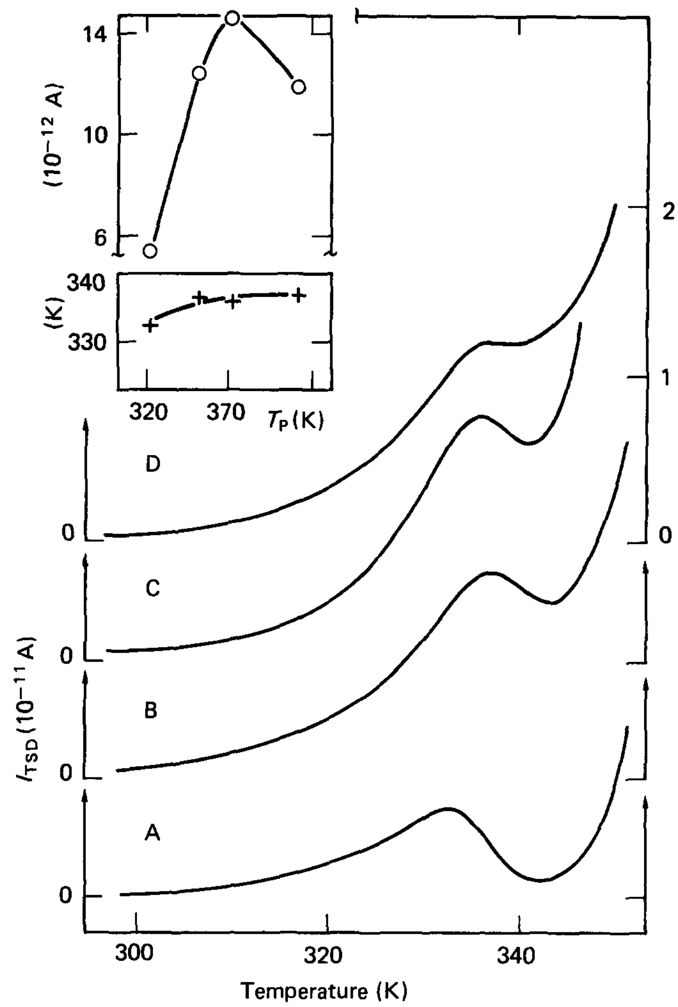

Figure 2 I_{TSD} (T) curves for N-20 blend for various T_p's: (A) 323, (B) 353, (C) 373, (D) 413 K. $E_p = 4$ kV cm^{-1}. Inset: (+) T_m, (○) I_{mt}

amounted to 4 kV cm^{-1}. The insets in *Figures 1* and *2* show the dependence of the main parameters, the maximum temperature, T_m, and the maximum current of the peaks, I_{mt}, on T_p. I_{mt} was primarily considered as the total current above the zero line without subtracting the thermally stimulated background current.

In the sample with the lower concentration of Ny6, T_m is independent of T_p and amounts to 331 ± 1 K (inset in *Figure 1*). In the sample with the higher concentration of Ny6, T_m is increased, but it becomes constant when it reaches saturation at 336.5 ± 0.5 K (inset in *Figure 2*).

The variation of I_{mt} and the appearance of a maximum in the I_{mt} (T_p) function (insets in *Figures 1* and *2*) shows the effect of electrode polarization. Such behaviour is characteristic for heterogeneous systems[7] with a high concentration of trapping sites at the bulk–electrode interface. This indicates the heterogeneous nature of the NPF–Ny6 blends which is more pronounced in the sample with the higher concentration of Ny6.

The pure NPF resin shows two peaks in the same temperature range. All the curves in *Figures 1* and *2* show only one peak. At this stage it is not possible to discuss the origin of these peaks.

Effect of E_p

The effect of E_p was investigated for the sample with the higher concentration of Ny6. *Figure 3* shows the effect of a

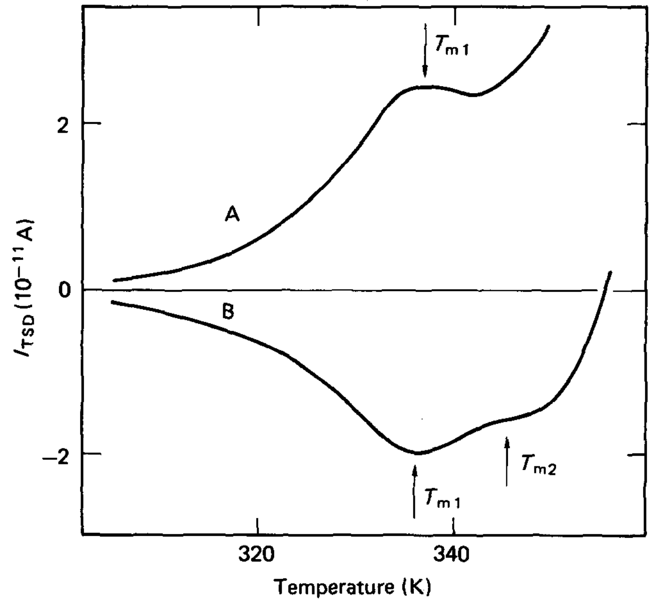

Figure 3 I_{TSD} (T) curves for N-20, $T_p = 353$ K, E_p: (A) 8, (B) −8 kV cm^{-1}, $T_{m1} = 336$, $T_{m2} = 345$ K

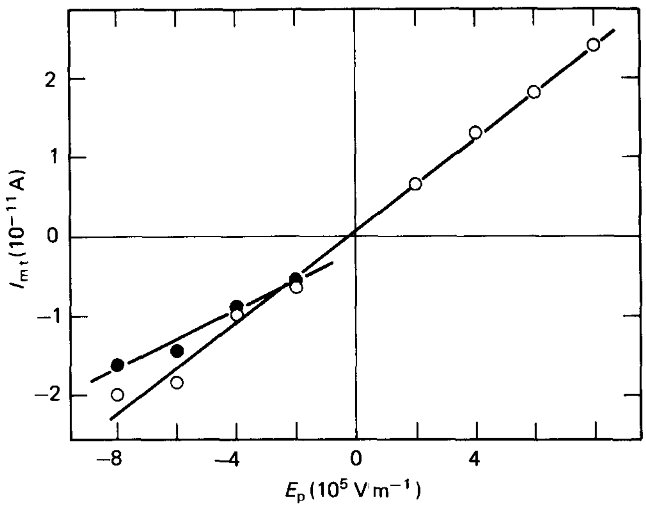

Figure 4 I_{mt} vs. E_p for N-20 blend, $T_p = 353$ K. (○) peak P_1, (●) peak P_2

reversal of E_p. Curve A in *Figure 3* was obtained with $E_p = 8$ kV cm^{-1} at $T_p = 353$ K. Curve B was obtained in the same way, only the sign of E_p was reversed. The negative curve shows one other peak.

The results for I_{mt} *versus* $\pm E_p$ for a series of measurements (T_p = constant = 353 K) are shown in *Figure 4*. The $I_{mt}(E_p)$ function for the lower temperature peak (open symbols) is more or less linear over the whole, positive and negative, E_p range. Such a behaviour is typical for the relaxation of a dipolar state. The same function for the higher temperature peak (filled symbols) is also linear but it exists only in the negative region of the applied E_p. When the poling is positive this peak does not appear, probably because it is masked by a positive background current. By analogy with the pure NPF resin, one may assume that the low temperature peak corresponds to $P_1(\alpha)$, while the peak at the higher temperature corresponds to $P_2(\rho)$.

Comparison of results

A direct comparison of t.s.d.c. results for samples with different Ny6 contents is shown in *Figure 5*. Curve A shows a measurement with the pure resin. Curves B and C are for the resin samples with 10% and 20% Ny6, respectively. All the curves were obtained under the same experimental conditions ($E_p = 4$ kV cm^{-1}, $T_p = 353$ K). The poling was carried out with a positive E_p. Therefore in the curves B and C only the dipolar relaxation peak P_1 appears. The broken lines represent the thermally stimulated background current obtained without previous polarization, which is mainly caused by the thermocurrent and by the increase of the sample conductance with temperature^5. Some other usual sources of this parasitic current are mentioned in the literature^8. However, the background obtained without poling is not real, because the poling itself may influence its level. Therefore, a more appropriate background was estimated by interpolating the exponential curve which was fitted to the first and the last part of the current peak^{9,2} (dash-dotted lines in *Figure 5*). From *Figure 5* the net maximum current, I_m, is given by

$$I_m = I_{mt} - I_0 \qquad (1)$$

where I_0 is the base current component of the total maximum current, generated by the poling field. The currents I_0 and I_m as well as T_m are shown in the inset of *Figure 5* as a function of the concentration of Ny6.

The results indicate the most remarkable change is a shift in T_{m1} for the sample containing 20% Ny6. In comparison with the pure resin, T_{m1} is shifted towards a higher temperature by 15 K. A shift of about 13 K also occurs for peak P_2 (compare T_{m2} in *Figure 5*, curve A, and in *Figure 3*, curve B). The increase in the maximum temperature caused by the addition of Ny6 can be understood as a consequence of a closer interaction between the two phases, due to the formation of hydrogen bonds between the amido groups of the Ny6 and the phenolic hydroxy groups in the NPF resin. Such an interaction can block in particular the –OH groups and this causes a slowing down of the dipolar relaxations.

The maximum current, I_m, or P_1 and the corresponding base current, I_0, are also affected by the addition of Ny6, because the new interface area in the samples gives rise to new sites for storing the charge.

In conclusion, the blend shows two opposing characteristics. The addition of Ny6 to NPF increases the heterogeneity, but at the same time it brings about the formation of a homogeneous system through the closer interaction of the polar groups.

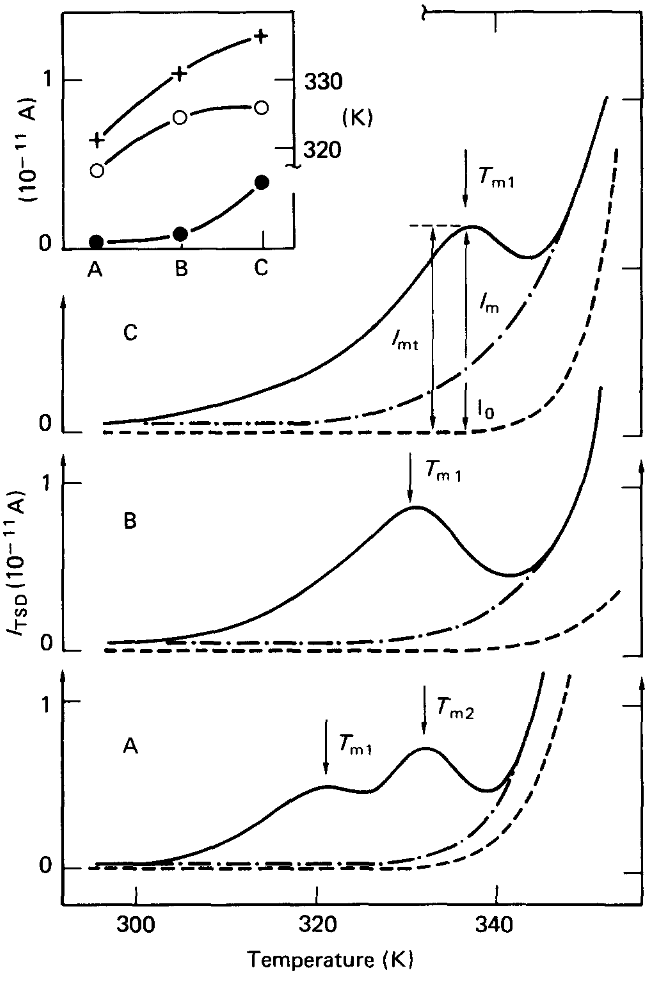

Figure 5 I_{TSD} (T) curves of various samples: (A) NPF, (B) N-10, (C) N-20, $E_p = 4$ kV cm^{-1}, $T_p = 353$ K. I_{mt}, total maximum current, I_m, net maximum current, I_0, base current, (-----) background current obtained without poling, (–·–·–) estimated background current. Inset: (●) I_0, (○) I_m, (+) T_{m1}

Table 1 Activation energy (kJ mol^{-1})

Sample	$E_{a(t)}$	$E_{a(n)}$
NPF	97	193
N-10	65	133
N-20	64	122

Activation energy

Table 1 contains the results of the activation energy, E_a, for the pure resin and for the blends. E_a was calculated for P_1 induced by $E_p = 4\,kV\,cm^{-1}$. To minimize the background current the poling was carried out at a relatively low temperature, $T_p = 323$ K. E_a was determined by the initial rise method[10]. The results for E_a can be greatly influenced by the use of an incorrect base line for the current peak. Therefore, two different methods of calculation were performed. $E_{a(t)}$ was calculated from the total current, while $E_{a(n)}$ was calculated using the estimated (interpolated), but more reliable, net current. The values obtained for $E_{a(n)}$ in comparison with $E_{a(t)}$ are significantly higher. This is probably because the total current introduces errors due to some parallel parasitic relaxations with a much lower E_a, which in turn decrease $E_{a(t)}$. However, in spite of methodology used it is clear that E_a decreases with an increase in the concentration of Ny6 in the samples investigated.

For all three experiments shown in *Table 1* the equal poling procedures used did not induce equal relaxation processes. A constant E_p at a constant T_p in samples with Ny6, induced processes with a lower activation energy. This means that, in comparison with the pure resin, the blends are less polarizable because they have less-movable constituents. This result is in agreement with the assumption concerning the interaction between Ny6 and NPF resin.

Experiments with a blocking electrode

Blocking electrodes have been primarily used in t.s.d.c. measurements to prevent charge injection from the electrodes into the sample and thus exclude the occurrence of space charge relaxation peaks[11,12]. In another case the blocking was applied to eliminate dipolar relaxation peaks[13]. In recent work it was shown that the blocking causes an increase of the space charge peaks[2]. This apparent contradiction concerning the proper functioning of blocking electrodes was explained as a consequence of the use of different poling temperatures[14]. Blocking applied at lower T_ps more or less decreases the dipolar peaks but eliminates the space charge peaks. The use of blocking at higher T_ps diminishes and ultimately eliminates the dipolar peaks, while the space charge peaks may be increased. Thus the blocking of both electrodes or only one electrode in t.s.d.c. measurements is useful for separating and identifying peaks.

Figure 6 shows the results of t.s.d.c. measurements performed on blend N-20. One of the electrodes was blocked during the polarization as well as during the depolarization current measurements. The applied E_p was 4 kV cm^{-1}. Curve A in *Figure 6* was obtained at low T_p (308 K), and it shows both peaks, viz. P_2 at $T_{m1} = 324$ and P_2 at $T_{m2} = 341$ K. P_1 appeared unsaturated and relatively small with a shift of its maximum towards a lower temperature (the saturated P_1 for N-20 occurs at $T_{m1} = 337$ K). This was due to the relatively low T_p and the voltage drop across the Teflon foil. P_2 was also very small, but under such experimental conditions and without blocking one would not expect it to appear at all, since T_p was too low to fill up the traps in the sample. P_2 appears to be due to the charge released by the charged Teflon while the sample was acting like a temperature switch. When the temperature reaches a point corresponding to P_2, the charge can pass through the sample and thus give a current rise in the measuring instrument. This explanation is based on measurements described elsewhere[14]. The Teflon insert also suppresses the background current making it possible to record clear thermograms.

Curve B in *Figure 6* was obtained by poling at a somewhat higher temperature, $T_p = 323$ K. Therefore P_1 is larger with a maximum at 332 K. P_2 is not observed because it is assumed to be overlapped by the reducing part of the dominant P_1. For the third experiment, curve C in *Figure 6*, T_p was increased up to 353 K. P_1 did not appear while P_2 was significantly increased.

An attempt was made to induce both of the reasonably well developed peaks during the same experimental run. Such a thermogram, curve D in *Figure 6*, was obtained by the use of a combined poling. The first poling was carried out at high temperature using a much smaller field ($T_p = 353$ K, $E_p = 1\,kV\,cm^{-1}$). The sample was then

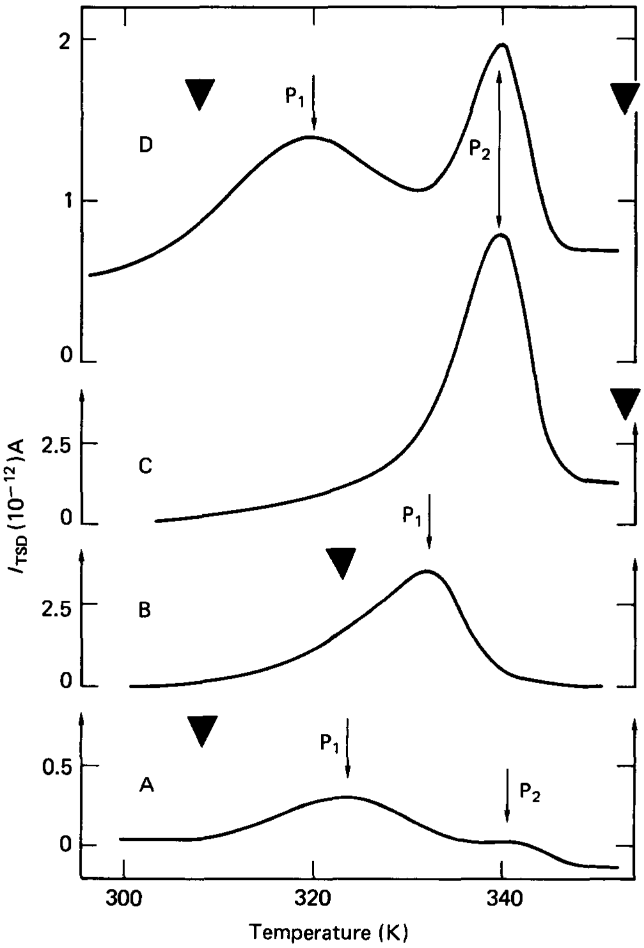

Figure 6 I_{TSD} (T) curves of N-20 blend. During poling and the t.s.d.c. measurements, one electrode is blocked with Teflon foil, $E_p = 4\,kV\,cm^{-1}$, various T_p's: (A) 308, (B) 323, (C) 353 K, (D) two polings: $E_p = 1$, $T_p = 353$ and $E_p = 6\,kV\,cm^{-1}$, $T_p = 308$ K, (▼) positions of T_p. P_1, dipolar relaxation peak, P_2, space charge relaxation peak

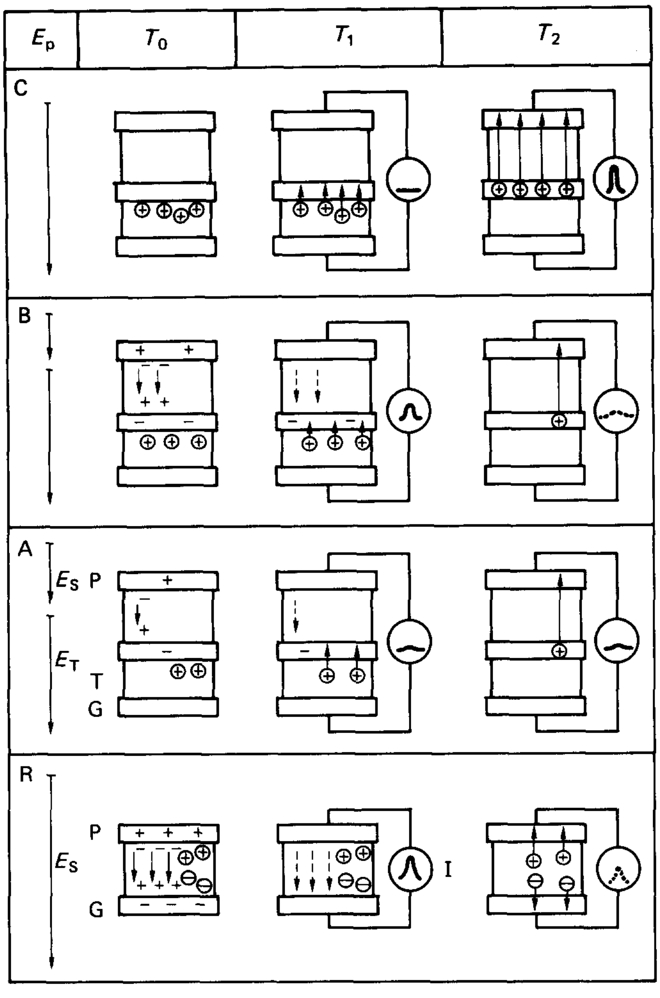

Figure 7 Simplified model for the functioning of one blocking electrode. (R) N-20 blend capacitor with normal electrodes, (A–C) N-20 capacitor with a Teflon series capacitor. Variation of T_p: (R) 353, (A) 308, (B) 323, (C) 353 K. T, 130 μm thick Teflon foil; G, grounded electrode; P, electrode for poling, and/or for electrometer input; E_p, total poling field; E_S, poling field across the sample; E_T, poling field across the Teflon; T_0, room temperature state after poling; T_1, temperature region of dipolar relaxations $P_1(\alpha)$; T_2, temperature region of conductivity relaxations $P_2(\rho)$; I, record of depolarization current. Other symbols: arrows, dipolar or displaced charges; broken arrows, relaxing dipoles; signs in electrode areas, compensation charges; signes in circles, space charges

cooled down under the same electric field. At 308 K the cooling was halted and another poling was performed with E_p increased to 6 kV cm^{-1}. In some cases, taken from the literature[5], when a wide continuous relaxation takes place, the combination of repeated poling can induce as many peaks as the number of polings performed. This was not the case in our experiments. The maximum temperature of the peaks in curve D does not coincide with the temperature of the applied poling. The peaks which appear represent two different and independent relaxation processes, $P_1(\alpha)$ and $P_2(\rho)$.

A simplified model for the functioning of the blocking electrode under different E_p and T_p can be seen in *Figure 7*. Scheme R is a reference and is related to the normal t.s.d.c. measurement carried out for blend N-20 without blocking. Schemes A to C are related to the experiments from *Figure 6*, curves A to C. The broken peaks represent the supposed but non-observed peaks.

The most important factor for the differences in t.s.d.c. results of the blocked system is the partition of E_p which strongly depends on T_p. During poling the total E_p is divided,

$$E_p = E_S + E_T \qquad (2)$$

where E_S is the effective field which polarizes the sample, and E_T is the field across the Teflon. An exact experimental determination of E_S and E_T is not possible. Therefore, it is necessary to make some approximations. Knowing that:

$$\frac{E_S}{E_T} = \frac{R_S}{R_T} \qquad (3)$$

where R_S is the resistance of the sample and R_T is the resistance of the Teflon, the effective field is

$$E_S = \frac{E_T}{R_T} \times R_S \qquad (4)$$

If one takes into account that the decrease of R_T vs. T is much slower than that of R_S vs. T, in the experimental temperature region, one can approximate:

$$E_S = \text{constant} \times R_S \qquad (5)$$

The background current of blend N-20 (curve C in *Figure 5*) shows a significant rise at temperatures above ~330 K. This indicates that R_S also decreases rapidly. Therefore, E_S at $T_p > 330$ K becomes too small for activation of the dipolar states in the resin. The estimation of E_R and E_T from E_p in *Figure 7* is obtained from the fact that $R_T > R_S$ and using equation (5).

The experiments with the Teflon inserted corroborate that in the blends as well as in the pure resin, $P_1(\alpha)$ and $P_2(\rho)$ relaxations exist. During the regular experiments peak P_2 was not always observed because it was shifted towards the higher temperature and thus overlapped with the background current.

ACKNOWLEDGEMENT

We are indebted to Dr S. Popovic for valuable discussions.

REFERENCES

1 Vasudevan, P., Viswanathan, P. S. and Taneja, K. L. *J. Electrochem. Soc.* 1980, **127**, 691
2 Topić, M., Moguš-Milanković, A. and Katović, Z. *Phys. Stat. Sol. (A)* 1984, **86**, 937
3 Topić, M. and Katović, Z. *Polymer* 1985, **26**, 1141
4 Nakamura, S., Sawa, G. and Ieda, M. *Jpn. J. Appl. Phys.* 1981, **20**, 47
5 van Turnhout, J. in 'Topics in Applied Physics', (Ed. G. M. Sessler), Springer-Verlag, Berlin, 1980, Vol. 33
6 Pillai, P. K. C., Gupta, B. K. and Goel, M. *J. Polym. Sci., Polym. Phys. Edn.* 1981, **19**, 1461
7 Pillai, P. K. C., Narula, G. K., Tripathi, A. K. and Mendiratta, R. G. *Phys. Rev. B* 1983, **27**, 2508
8 Reboul, J. P. and Toureille, A. *J. Polym. Sci., Polym. Phys. Edn.* 1984, **22**, 21
9 Pillai, P. K. C. and Mollah, M. *J. Macromol. Sci.-Phys.* 1980, **B17**, 69
10 Garlick, C. F. J. and Gibson, A. F. *Proc. Phys. Soc.* 1948, **60**, 574
11 van Turnhout, J. 'Thermally Stimulated Discharge of Polymer Electrets', Elsevier, Amsterdam, 1975
12 Pissis, P., Apekis, L., Christodoulides, C. and Boudouris, G. *J. Phys. D: Appl. Phys.* 1982, **15**, 2513
13 Vescan, L. and Angel, G. *Rev. Roumaine Phys.* 1981, **26**, 31
14 Topić, M., submitted to *J. Polym. Sci., Polym. Phys. Edn.*