Depolarization current in phenol–formaldehyde resin below the glass transition

M. Topić
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

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A thermally stimulated depolarization (t.s.d.) current study of a novolac phenol–formaldehyde resin performed using electric poling at temperatures $T \leqslant T_g$ (T_g being the glass transition temperature which equals 323 ± 2 K) shows a continuous distribution of polarizability in the range from 295 to 323 K. The efficiency of poling is found to be dependent upon the physical ageing of resin. In addition to the known current peaks P_1 and P_2, which appear at $T_{m1} = (320 \pm 2)$K and $T_{m2} = (334 \pm 6)$K respectively, a new peak, P_0, is detected at $T_{m0} = (296 \pm 1)$K. P_0 appears reversibly with the same magnitude regardless of the electrical history of the resin or the physical ageing. The activation energy determined by the initial rise method and the whole curve integration method is found to be 500 and 570 kJ mol^{-1}, respectively. It is assumed that P_0 is caused by a discrete phase transition in the resin.

(Keywords: thermally stimulated depolarization current; phenol–formaldehyde novolac resin)

INTRODUCTION

Novolac phenol–formaldehyde resins with the phenolic –OH groups which can be polarized[1,2] under the action of an external electric field represent potential electret materials. Therefore, an investigation into the polarizability and charge storage ability is a worthwhile experiment. The storage of charge in this particular resin by use of thermally stimulated depolarization current (t.s.d.c.) measurements has already been studied[3]. The samples were prepared by use of filter paper impregnated by the methanol novolac solution. The methanol was removed by heating for 24 h at 333 K and then drying in a vacuum. The t.s.d.c. curve obtained showed only one peak at 378–383 K which was explained as a possible consequence of curing. However, in the regularly prepared novolac resin the curing is excluded. The influence of the paper was found to be negligible but the traces of methanol might alter the properties of the investigated sample.

In a recent work[4] on a novolac resin the peak at 378–383 K was not confirmed. Instead, two current peaks P_1 and P_2 were found at temperatures $T_{m1} = (320 \pm 2)$K and $T_{m2} = (334 \pm 6)$K, respectively. P_1 coincided with the glass transition temperature $T_g = (323 \pm 2)$K[5] and was explained as a consequence of the dipolar relaxation. The other peak P_2 appeared to be due to the discharge of the traps in the bulk resin. Both of the peaks were induced by previous electric poling applied at $T \geqslant T_g$. The present paper describes the results of our t.s.d.c. measurements obtained with poling carried out at $T \leqslant T_g$ and in the absence of any electric poling.

EXPERIMENTAL

The novolac resin was prepared by condensing phenol with formaldehyde at the mole ratio 1:0.865 using oxalic acid as catalyst[4]. Average molecular weight determined by v.p.o. (vapour phase osmometry) was 590. The density at 298 K was (1.22 ± 0.02) g cm^{-3}.

The resin was placed in a small container with silver coated brass electrodes (diameter 13.6 mm). The thickness of the resin condenser was 1 mm. The container was placed in a shielded dark cell with a thermocouple and a heater. T.s.d.c. was measured with a Keithley 616 electrometer. The current and temperature were recorded by a dual trace chart recorder. Before starting the experiments, the samples had been heated up to 333–353 K and then cooled down to the temperature of storage, T_s, with short-circuited electrodes. The storage time at T_s, called the time of ageing, t_a, was as short as possible unless otherwise stated. The sample was then poled at the desired temperature, T_p, for 20 min and cooled down to T_s. After removal of the field the resin was kept short-circuited at T_s for 30 min up to the beginning of the t.s.d.c. measurements. The heating and cooling rates were 2 K min^{-1}. All measurements were performed in a dry nitrogen atmosphere. Other details concerning the resin container and the measurements are described in a previous paper[4].

RESULTS AND DISCUSSION

Effect of poling temperature

Figure 1a is a plot of t.s.d.c. *versus* temperature for a sample poled at different temperatures, at or below the glass transition, from 295 to 323 K. The electric field used for poling, E_p, was 4 kV cm^{-1}, and T_s was 295 K. The integrated area under the peaks representing the charge released by t.s.d. *versus* T_p is shown in *Figure 1b*.

The peaks obtained show the shift in maximum tem-

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perature, T_m, as well as the increase of the released charge, Q, by increasing T_p. Electric poling carried out at $T_p \leqslant T_g$ induces only the unsaturated peaks but the function $Q(T_p)$ tends towards saturation. The peaks from *Figure 1a* correspond to the peak P_1 identified[4] as the peak caused by relaxation of the dipolar state in the resin which was fully saturated by poling at $T_p \geqslant T_g$.

The results obtained show that the process of building up the polarized state in the resin is being continuously distributed *versus* temperature when the poling is performed below T_g. Such behaviour is typical for amorphous polymers when a dipolar relaxation peak is in question[6].

Influence of ageing

To study the influence of thermal history of the sample on the t.s.d. results a series of consecutive measurements were carried out on the sample with variation in ageing time. *Figure 2* shows the results of such an investigation. After the preheating procedure as described in Experimental section, the sample was kept in the short-circuited state at $T_s = 292$–293 K. t_a varied from approximately zero to 96 h. The sample was then poled at $T_p = 292$–293 K with $E_p = 8$ kV cm^{-1}. T.s.d.c. measurements were carried out from 293 K to 334 K recording peak P_1. The results clearly show a decrease of the current peak with an increase in t_a. At the initiation of the ageing the resin is polarizable and sufficiently sensitive to the external electric field as it does retain a degree of flexibility of its constituents from the high temperature phase. This state is a non-equilibrium state which tends to assume the equilibrium[7] in essence. At T_s the structure of the resin becomes more rigid with the less-movable constituents. Therefore, the likelihood of the resin being polarized by E_p diminishes. Similar results for the t.s.d.c. measurements were obtained in investigation of the physical ageing of unplasticized PVC[8].

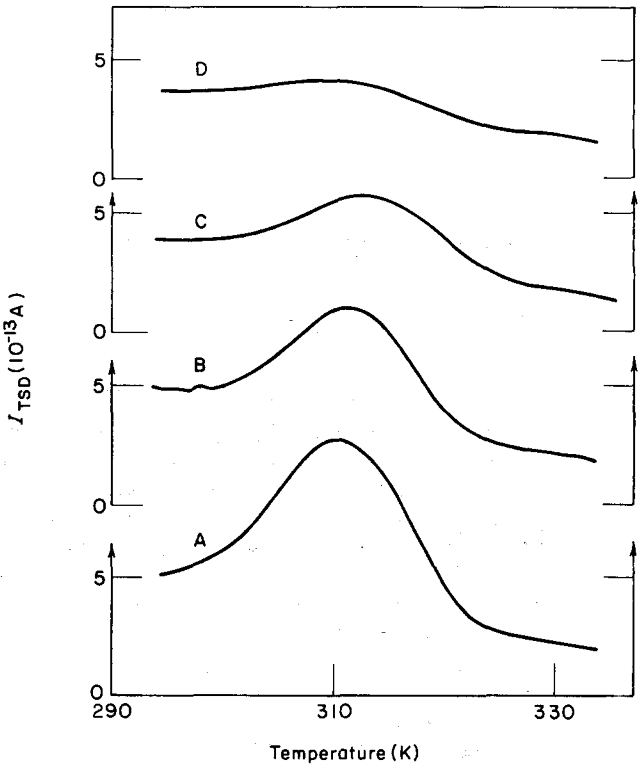

Figure 2 Thermally stimulated depolarization currents, I_{TSD}, vs. temperature for different ageing: (A) 0, (B) 1, (C) 24, (D) 96 h; $E_p = 8$ kV c,$^{-1}$, $T_p = T_s = 292$–293 K

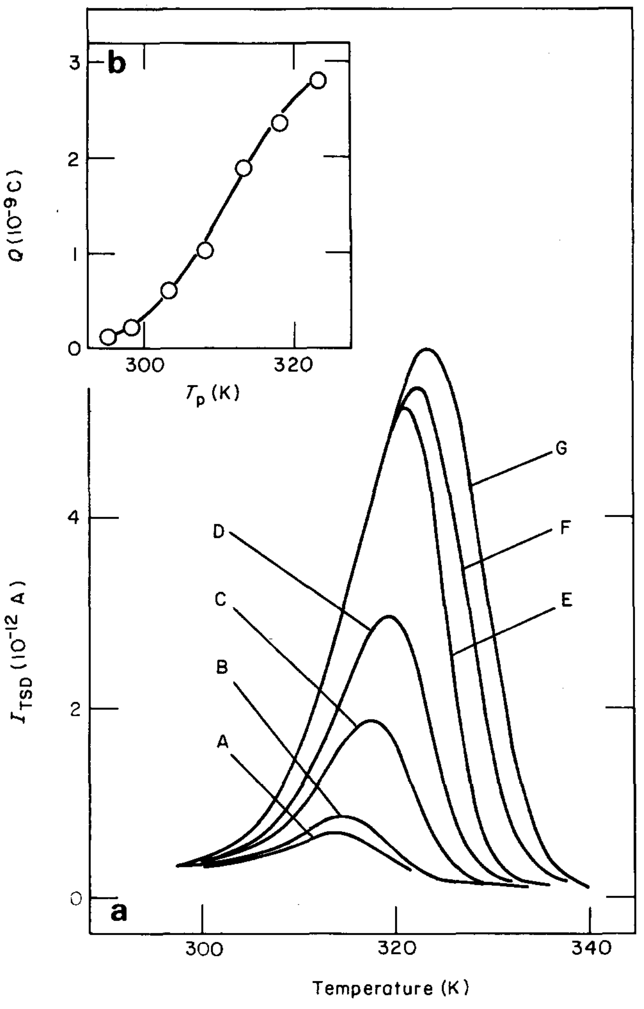

Figure 1 (a) Thermally stimulated depolarization current, I_{TSD}, vs. temperature for various poling temperatures: (A) 295, (B) 298, (C) 303, (D) 308, (E) 313, (F) 318, (G) 323 K; $E_p = 4$ kV cm^{-1}, $T_s = 295$ K. (b) Charge Q vs. poling temperature, T_p, related to the curves from (a)

Detection and behaviour of a discrete current peak, P_0

An attempt was made to shift T_s and start the measurements from a lower temperature. *Figure 3* contains three such curves obtained with $T_s = 278$ K and with relatively small $E_p = 1$ kV cm^{-1} at different T_p. In all cases, except the dominant peak P_1, it is possible to see an additional and very small peak P_0 which appears at $T_{m0} = (296 \pm 1)$ K.

In the previous experiments P_0 was not observed because it coincided with the beginning of the runs when the heating rate was not sufficiently stabilized. The recording sensitivity was not adequate and, also, a relatively strong E_p caused some overlapping. Results in *Figure 3* show that P_0 does not depend upon T_p and that its current maximum as well as the maximum temperature are practically unchanged.

In order to determine the influence of the strength and sign of E_p on P_0 several t.s.d.c. measurements were performed with variation in E_p. Curves A and B in *Figure 4* were obtained with 1 and 2 kV cm^{-1}, respectively, at temperature 295 K. The temperature of storage was

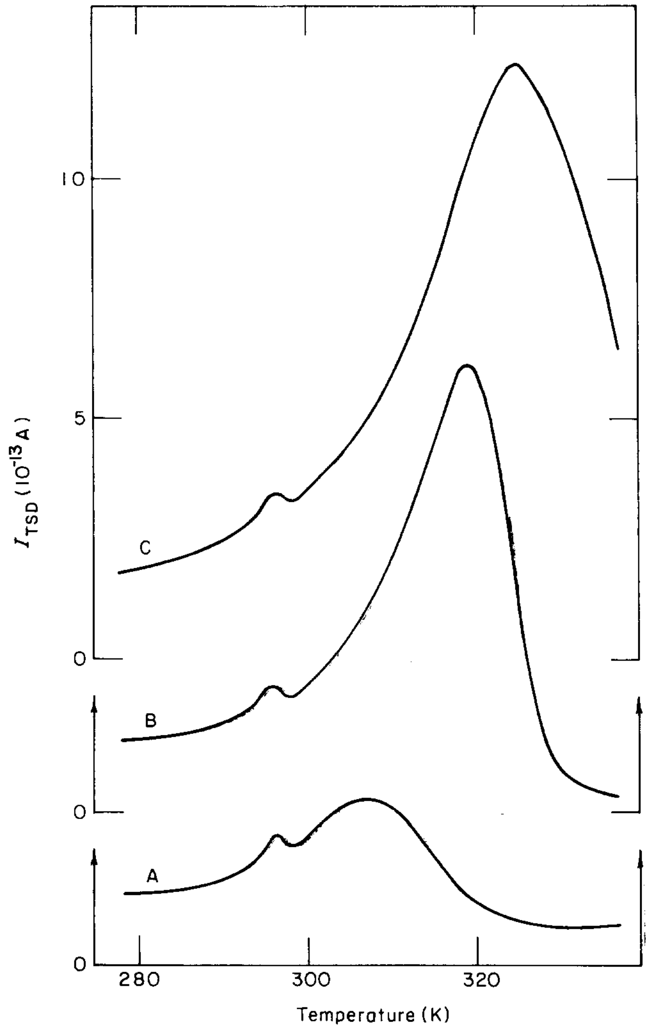

Figure 3 Detection of a new current peak. I_{TSD} vs. temperature for various T_p: (A) 295, (B) 308, (C) 323 K; $E_p = 1$ kV cm^{-1}; $T_s = 278$ K

278 K. Negative curves A′ and B′ were obtained after the negative poling of -1 and -2 kV cm^{-1}, respectively. While the maximum of the dominant peak P_1 is fully dependent upon the poling strictly following the strength and its sign, P_0 remains constant and does not change its magnitude or sign. Curve C in *Figure 4* is a blank t.s.d.c. run performed with the empty sample container without poling.

Origin of P_0

Figure 5 contains some additional results which complement the understanding of the origin of P_0. Curve A in *Figure 5* is a standard t.s.d.c. curve obtained with $E_p = 2$ kV cm^{-1} at $T_p = 295$ K and $T_s = 278$ K, measured up to 353 K. In addition to P_0 and P_1 one can also observe a trace of P_2 and under these experimental conditions P_2 cannot be found to be any higher. Curve B in *Figure 5* was obtained by the technique of blocking the ground electrode during poling and current measurements. This was done by inserting a 70 μm thick teflon foil between the sample electrode and the grounded part of the cell[4]. Other conditions were the same as for curve A. The blocking of one electrode reduces the nominal value of the applied E_p, which makes dipole alignment in the resin smaller and therefore diminishes the current peaks caused by dipolar relaxations. At the same time a filling up of the possible traps in the bulk is preferred. This method of discrimination between dipolar relaxations and real space charge moving mechanisms has been inspired by the results and discussion of L. Vescan and G. Angel[9]. Curve B from *Figure 5* corroborates this assumption. The dipolar relaxation peak P_1 is decreased while the trace of the charge releasing peak P_2 is increased but the small peak P_0 remains unchanged. The experiment performed after obtaining curve B was found to be most revealing. The sample was cooled down with the short-circuited electrodes to $T_s = 278$ K and the following run was carried out without any new poling. The resulting curve C in *Figure 5* is fully cleared of peaks P_1 and P_2 with exception of P_0. Such clearing of P_0 from other peaks enables one to determine the activation energy of the process which causes P_0. *Figure 6a* contains a typical P_0 peak separated and recorded with a higher sensitivity. The activation energy was determined by the initial rise method[10]. The corresponding plot of the logarithm of current vs. $10^3/T$ is shown in *Figure 6b*. The energy is found to be 502 kJ mol^{-1} (5.2 eV). The uncertainty in approximation of the base line of a relatively small peak might have some influence on the results. Therefore, another more reliable method of whole curve integration[11–13] was also applied. The obtained logarithm of the relaxation time $\tau(T)$ vs. $10^3/T$ is shown in *Figure 6c*. A good straight line is the evidence that a uniform process is operating. The calculated energy amounts to 569 kJ mol^{-1} (5.9 eV).

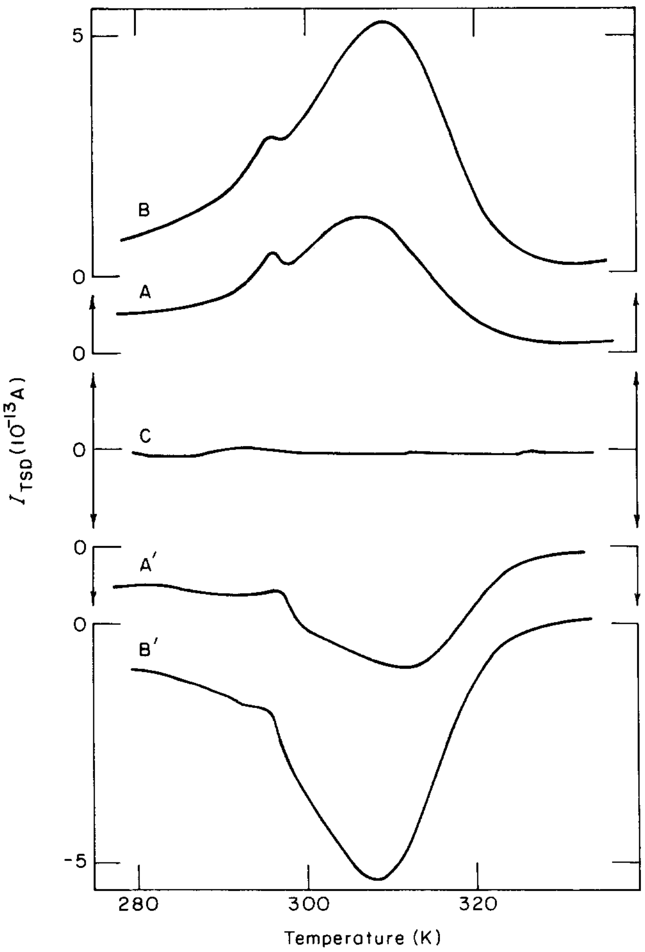

Figure 4 I_{TDS} vs. temperature for various E_p: (A) 1, (B) 2, (A′) -1, (B′) -2 kV cm^{-1}; $T_p = 295$ K, $T_s = 278$ K, (C) empty resin container without poling

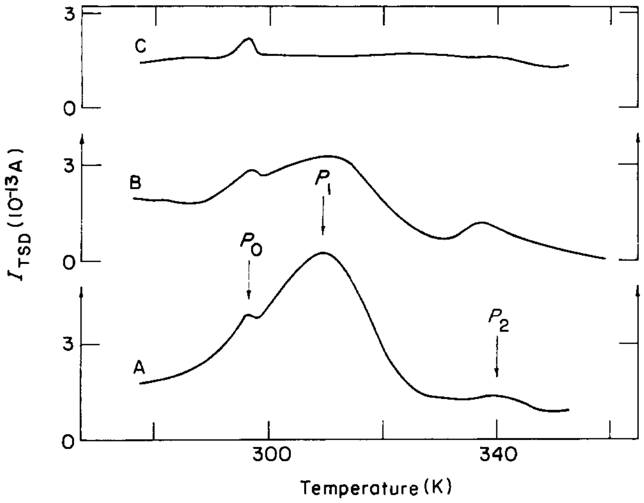

Figure 5 Different effects on $I_{TSD}(T)$ curve, $E_p = 2\,\mathrm{kV\,cm^{-1}}$, $T_p = 295$ K, $T_s = 278$ K. (A) regular curve, (B) one electrode during poling and measurements blocked with a teflon foil, (C) without poling. P_0, reversible peak, P_1, peak caused by a dipolar relaxation, P_2, peak caused by a space charge relaxation

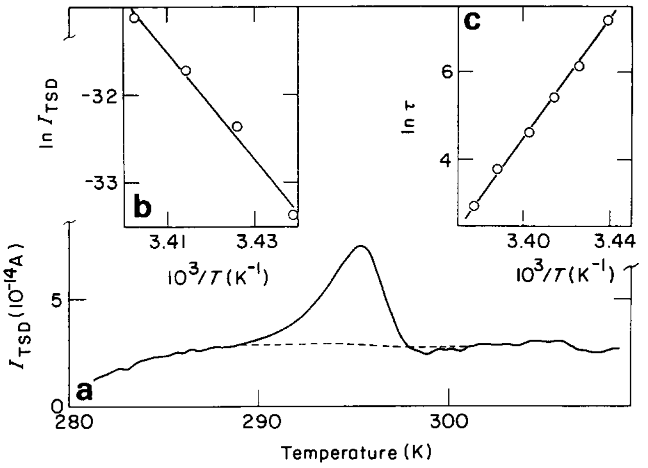

Figure 6 (a) $I_{TSD}(T)$ curve with a cleaned up current peak P_0, (b) logarithm of I_{TSD} vs. $10^3/T$ for P_0, (c) logarithm of relaxation time, τ, vs. $10^3/T$ for P_0

Besides the above described experiments the effects of some other influences on P_0 were also examined. The use of various electrode materials, such as brass and stainless steel, did not make any difference to the results. An attempt was made to apply a stronger poling of the opposite sign of $-4\,\mathrm{kV\,cm^{-1}}$ at 323 K. The curve obtained was separated from the overlapping part of P_1, and the isolated P_0 remained as a standard magnitude and Physical ageing of 120 h at 295–297 K did not alter the parameters of P_0 either. The appearance of P_0 was also verified with different batches of the resin.

Generally, P_0 appears to be reversible with the constant maximum at the constant temperature in spite of the electrical history of the sample or the physical ageing. Clearly P_0 is not caused by the discharging processes from the electrode–bulk interfaces. Discharge processes from the bulk are also excluded as well as the relaxation of the induced dipolar states. Taking into consideration all the results in the present work it is possible to conclude that P_0 is caused by a reversible process in the resin being dependent upon temperature. One may assume the existence of a phase transition which is related to a change of some details in the structure of resin.

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