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Thermally Stimulated Currents in Methacrylonitrile-Styrene Copolymer Films

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SUMMARY

Measurements are reported on thermally stimulated discharge current in methacrylonitrile - styrene copolymer films. The values of activation energy and relaxation times were calculated.

INTRODUCTION

Various kinds of polarizations are present in polymers and affect their electrical conduction and break-down properties. In this context, the experimental investigation of electrets have been confined to the study of the nature of the charge developed, its magnitude and duration, as well as to the mechanism responsible for the formation of electrets.
Last years, many researchers have used the thermally stimulated discharge current (TSC) technique for analysing the electret effect quantitatively. The most important features of TSC method were proved to be the fact that there is no applied field during the measurements and its high sensitivity.
The purpose of this paper is to present some preliminary results on TSC investigation of high molecular weight methacrylonitrile (40.83) - styrene (59.17) copolymers.

EXPERIMENTAL

The synthesis and the microstructural aspects of the copolymer were previously described (SIMIONESCU et al., 1981).
TSC measurements were performed with the experimental device presented in Figure 1. Small discs were cut out from the copolymer film (55 mm diameter, 0.9 mm thickness); the discs were coated on both sides with aluminium electrodes (50 mm diameter) in a vacuum coating unit. The sample was then introduced in a thermostating unit allowing the linear variation of temperature from liquid nitrogen temperature up to 300°C by using

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a temperature programmer and a Fe-Ct thermocouple as temperature transducer. The sample was heated, during 30 min., up to 74^{o}C, the intensity of the applied electric field being 20 kV/cm. The polarized disc was maintained at 74^{o}C during 60 min. and then cooled down up to liquid nitrogen temperature in the presence of the electric field. The sample was then short circuited for 5 min., and the circuit was closed by means of the $R=10^{12}\,\Omega$ resistence. The fall of the tension on this resistence was measured with an electrometer. The experiment was repeated three times on the same disc; by measuring the polarization current it was found that the polarization reached the saturation value.
All measurements were performed at pressures lower than 10^{-4} mmHg.

THEORETICAL

The low-temperature tail of the discharge current vs. temperature is given by (BUCCI and FIESCHI, 1966)

$$\ln I(T) = C - (W/kT) \qquad (1)$$

where C is a constant, W is the activation energy which can be determined from the straight line plot of ln I(T) versus 1/T (this is the initial rise method of GARLICK and GIBSON, 1948), k is Boltzmann's constant, and T is the temperature. The relaxation time τ_0 can be obtained from

$$\tau_0 = kT_m^2 \,/\, hW\exp(W/kT_m) \qquad (2)$$

where T_m is the temperature at which maximum current

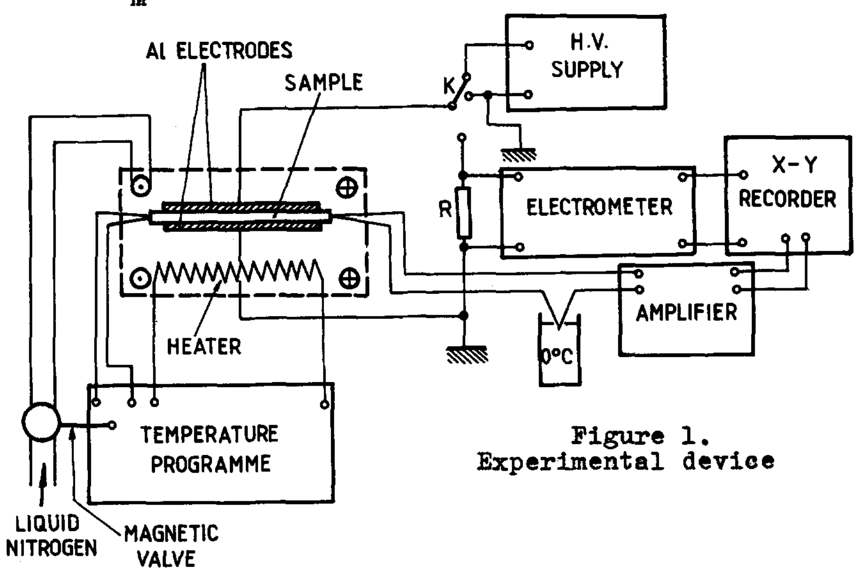

Figure 1.
Experimental device

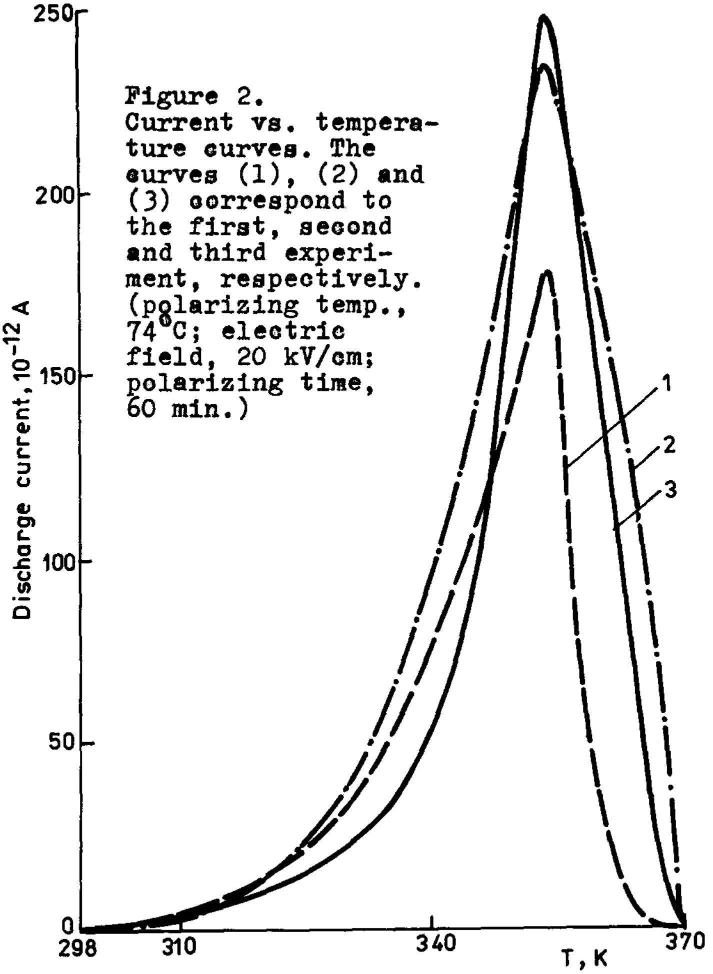

Figure 2.
Current vs. temperature curves. The curves (1), (2) and (3) correspond to the first, second and third experiment, respectively. (polarizing temp., 74°C; electric field, 20 kV/cm; polarizing time, 60 min.)

occurs and h is the heating rate.
The total charge released to the external circuit (Q) is given by

$$Q = \int_0^\infty I(T)dt \qquad (3)$$

and, on the other hand,

$$\tau(T) = \tau_0 \exp(W/kT) \qquad (4)$$

The plot of ln τ vs. 1/T should then be a straight line; the slope and intercept of this line will determine W and τ_0, respectively.

RESULTS AND DISCUSSION

To observe the modifications of the TSC curves, occuring due to the thermal treatment, the measurements were registered on the same sample; the intensity of the polarizing field was 20 kV/cm and the polarizing

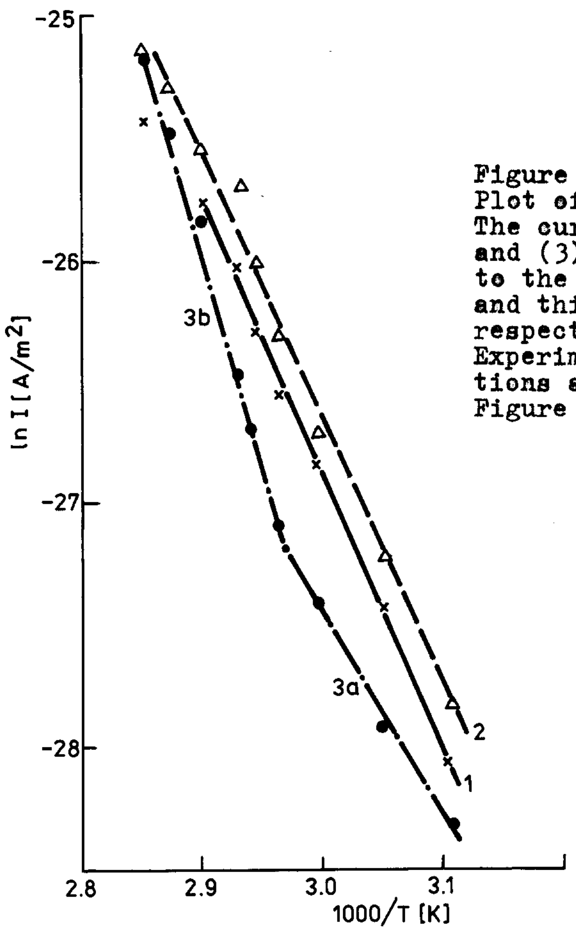

Figure 3.
Plot of lnI vs. 1/T.
The curves (1), (2) and (3) correspond to the first, second and third experiment, respectively.
Experimental conditions are given in Figure 2

temperature 74°C. TSC curves are presented in Figure 2. These curves were used to calculate, with equations (1) and (2), the relaxation time and the activation energy. The obtained results are presented in Figure 3. One can see that for the first two experiments only one activation energy, as well as one relaxation time for experiment are yielded; the values differ only slightly from the first registration to the second one.
Maximum currents appear for all three curves at 81°C. As concerns the maximum values of the intensity of the current, an important increase for the second registration as compared to the first one has to be noted. This increase is important from the practical point of view, for the obtention of electrets with as high as possible electrical charge.
The activation energies were also determined according to equation (4), following the whole curve method.
For the first two registrations the obtained values are

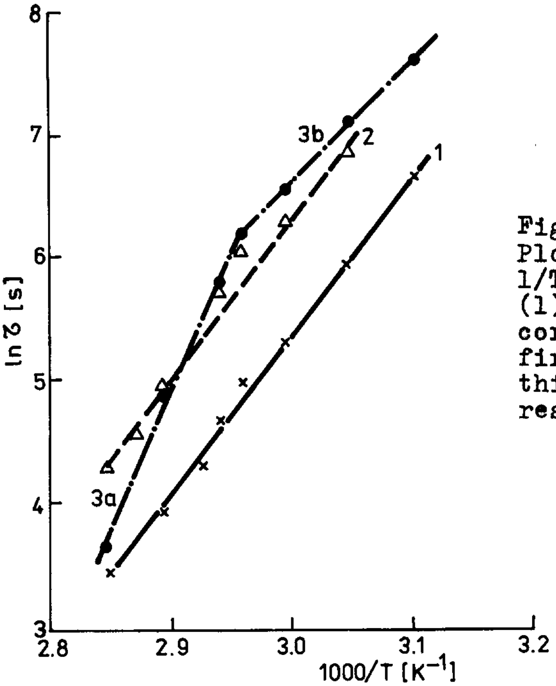

Figure 4.
Plot of ln vs. 1/T. The curves (1), (2) and (3) correspond to the first, second and third experiment, respectively

in good aggreement with those resulting from equation (1); lnτ vs. 1/T curves are presented in Figure 4. The use of the two calculation methods yielded, in other cases, distinct results (PILLAI et al., 1973; NEAGU et al., 1979).

As concerns the third experiment, the intensity of the current increases unsignificantly as compared with the second one, this evidencing a stabilizing tendency of the internal structure of the sample. The plots corresponding to the third experiment (Figures 3 and 4) show two distinct parts, with distinct activation energies, all of them being different from those determined for the first two experiments. Data are given in Table 1.

TABLE 1.
Summary of results

Sample	Temp. corr. to peak (K)	Garlick's method		Whole curve method	
		W(eV)	τ_0(sec)	W(eV)	τ_0(sec)
1	354	0.938	$1.51 \cdot 10^{-11}$	1.10	$4.4 \cdot 10^{-15}$
2	354	1.057	$8.21 \cdot 10^{-10}$	1.12	$4.4 \cdot 10^{-15}$
3a	354	0.760	$3.75 \cdot 10^{-7}$	1.94	$2.5 \cdot 10^{-27}$
3b	354	1.440	$3.03 \cdot 10^{-17}$	0.80	$5.8 \cdot 10^{-10}$

From both plots of the third experiment, one can note that the intersection point of the two lines appears at the same temperature, 337 K.
Research in progress in this field will be published soon.

REFERENCES

BUCCI,C. and FIESCHI,R.: Phys.Rev. 2, 148 (1966)
GARLICK,G.F.J. and GIBSON,A.F.: Proc.Phys.Soc.(London) 60, 574 (1948)
NEAGU,E., LEANCA,M. and NEAGU,R.: Bul.Inst.Polit.Iaşi XXV (XXIX) 1-2, 109 (1979)
PILLAI,P.K.C., JAIN,K. and JAIN,V.K.: Indian J.Pure& Appl.Phys. 11, 597 (1973)
SIMIONESCU,B.C., NATANSOHN,A., LEANCA,M., ANANIESCU,C. and SIMIONESCU,C.I.: Polymer Bull. 4, 569 (1981)

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