High Temperature Study of Molecular Motion in Polyphenylene Sulfide by Thermally Stimulated Currents

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Thermally stimulated currents (TSC) in polyphenylene sulfide were measured in unpolarized and polarized samples. The TSC thermograms show a rapid increase in current at about 200 °C with an activation energy of about 1.6 eV. Additionally, in polarized samples a peak at about 150 °C related with the reorientational motions of the chain was found.

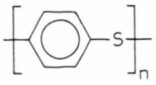
1. Introduction

Polyphenylene sulfide (PPS) is a new engineering thermoplastic of high thermal stability and outstanding chemical resistance. We attribute these properties, studied by various authors [1–3], to the structure and molecular dynamics of PPS. The elastic properties of PPS have been studied by Eisenberg and Cayrol [1] and the dielectric relaxation by Rigby and Dew-Hughes [2]. Various relaxation mechanisms have been proposed in various temperature regions and have been attributed to the rotational and torsional motion of the phenylene groups. More information on the molecular dynamics has been gained from the NMR investigation of Jurga et al. [3], who suggested to relate the relaxation process in the low temperature region with the conformational motion of the phenylene rings between two equipotential equilibrium states with an activational barrier of the order of 10 kJ/mol (0.1 eV). At high temperatures the reorientational motion of the phenylene groups seems to play a more important role. Reorientation of phenylene groups about the sulfur-phenylene-sulfur axis requires an activation energy of about 40 kJ/mol (0.4 eV).

In this paper we study the molecular motion in PPS above the recrystallization point, observed at about 150 °C as a decrease in the second moment value in NMR experiments. We studied thermally stimulated currents (TSC) for unpolarized and polarized PPS samples. This enabled us to collect information on the nature of the relaxation process and the activation energy [4]. All experiments were carried out with shortened contacting electrodes at a constant heating rate by recording the current thermograms (electric current vs. temperature). Well resolved TSC peaks were obtained, and we calculated the activation energy and the respective total charge for these thermograms [5]. We were moreover able to identify a TSC peak at about 150 °C, which appears to be related with the same process as the decrease in second moment in NMR experiments observed at 150 °C [3]. This we attributed to reorientation of PPS chains.

2. Synthesis and Properties of PPS

Polyphenylene sulfide is a crystalline aromatic polymer with a symmetrical rigid backbone chain consisting of para-substituted benzene rings connected by a single sulfur atom between the rings, as indicated below:



The preparation of polyphenylene sulfide was first described in 1897 by Grenvesse [6]. The process was investigated later by Macallum [7]. The work of Edmonds and Hill [8] enabled the manufacture of this material. The basic polymerization reaction of

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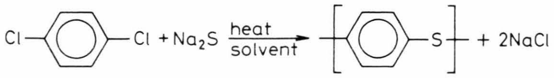
PPS takes place as follows:



Since 1969, PPS has been manufactured by Philips Petroleum Company under the name of "Ryton®" [9] in many grades. The virgin type of PPS is Ryton V-1. The other grades of PPS are obtained by annealing V-1 in air. This heating process leads to chain extension and cross-linking.

The molecular weight of polyphenylene sulfide was found to lie between 2000 and 10000 [9, 10]. The glass point (T_g), estimated by the DTA method, is 92 °C, whereas the soft point lies at 195 °C [11]. Ryton V-1 is highly crystalline. The degree of crystallinity, determined by Brady [12] by X-ray diffraction is 65%, whereas Chen Ji Zhou found 75% [13, 14]. The same degree of crystallinity was estimated by Jurga et al. applying the NMR method [3]. The crystalline melting point lies at about 295 °C [11].

The structure of crystalline poly-p-phenylene sulfide has been determined by X-ray diffraction by Tabor et al. [11]. The orthorhombic unit cell ($a = 0.867$ nm, $b = 0.561$ nm, $c = 1.026$ nm) contains four monomeric units. The space group is Pbcn-D_{2h}. Two molecular chains pass through the unit cell, one through the centre and the other through a corner. The sulfur atoms of a molecular chain are arranged zig-zag wise in the (100) plane. The planes of the phenylene groups are alternately at $+45°$ and $-45°$ to the (100) plane. The sulfur bond angle is about 110°, just as in aliphatic sulfide polymers.

The PPS-compounds have good electrical properties [9]. At room temperature, the dielectric constant is 3.10 for 10^3 Hz and 3.05 for 10^6 Hz. The dissipation factor under the above conditions is 0.00040 and 0.00075, respectively. The PPS dielectric strength is quite high, amounting to $23 \cdot 10^6$ V/m; the volume resistivity, however, is about $10^{14}\ \Omega \cdot$ m.

The latest investigations with doped PPS at high purity show a decrease in volume resistivity. For example, Showa Denko [15] has proposed a method of preparing PPS semiconductors by doping with H_2SO_4 or SO_3 radical. Abel et al. [16], by ion implantation of ^{84}Kr, ^{80}Br, ^{127}J, ^{36}Cl, ^{19}F, have succeeded in increasing the conductivity of PPS by about 14 orders. Rubner et al. [17] have formed electrically conducting polyphenylene sulfide by doping with nitrosyl salts from a solution with volume resistance equal to $10^{-1}\ \Omega \cdot$ m.

3. Methods and Results

For the investigation of thermally stimulated currents we used PPS Ryton V-1 from "Phillips Petroleum International Belgium SA". In order to eliminate the influence of low molecular impurities coming from the polymerization process, the PPS V-1 was purified by extraction in a Soxlhet column. Each sample was extracted 150 times with acetone and then with chloroform. The powder was then dried. The crystalline melting point determined with a Böthius table is about 285 °C for unpurified PPS and 293 °C for purified PPS. From extracted powder compressed under 750 MPa at room temperature, disks with a diameter of 8 mm and a thickness of about 1 mm were obtained. TSC investigations were performed both on unpolarized and polarized samples. The samples were polarized at various temperatures and electric field strengths during well defined periods of time.

Figure 1 shows the program of the polarization process. The field was applied at T_p and the sample

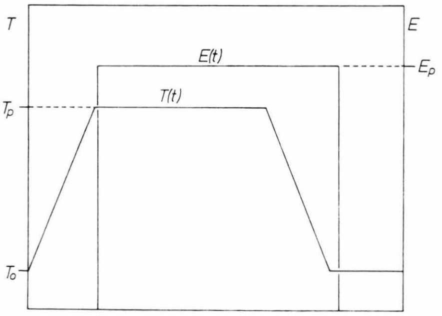


Fig. 1. Field and temperature program for the formation of polymer electrets: T_p = polarization temperature, T_0 = room temperature, E_p = polarization field strength, t = time.

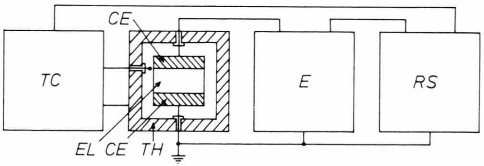


Fig. 2. Block diagram of the setup for TSC measurement: TC = temperature measurer and controller, EL = electret, CE = contacting electrode, TH = thermostat, E = electrometer, RS = recorder system.

was cooled in a field E_p applied at room temperature during about 30 min. The samples were polarized at $T_p = (20 \div 280)$ °C in fields of strength $E_p = (0.5 \div 2)$ MV/m during $t_p = (5 \div 50)$ mins. TSC measurements were carried out for samples stored during 24 h at room temperature in air. The samples were maintained in a condenser with metal electrodes placed in a thermostat (Figure 2). The electric current in a shortened contacting electrodes set-up was measured at a heating rate of 5 deg/min from room temperature up to 282 °C. Ag-Ag symmetric electrodes and Ag-Ni asymmetric electrodes were used.

For thermograms with well resolved peaks, the activation energy and the total charge related to the peak were evaluated. The activation energy was estimated from the plot of $\ln j$ vs. $1/T$, where j denotes the current density [5]. The total charge related with the TSC peak was obtained by graphical integration.

Figure 3 shows TSC thermograms for unpolarized PPS samples with Ag-Ni electrodes. Curve (a) was obtained from an unpreheated sample, whereas curve (b) was obtained from a sample preheated at 270 °C during 30 mins. For the unpreheated sample a rapid increase in thermally stimulated current was observed at about 200 °C. For the preheated sample, this increase of the current was shifted towards higher temperatures. The activation energy estimated for this characteristic was about 1.6 eV. The value of the thermally stimulated current in this temperature region was found to be highly sensitive to the purity of the sample. For samples of lower purity the current was found to be greater. Ag-Ag symmetric electrodes were used too. The rapid increase in stimulated current at temperatures higher than 200 °C was not observed for these electrodes. Below 60 °C small TSC peaks were observed both for symmetric and asymmetric electrodes. Moreover, TSC spectra of PPS samples polarized under various conditions were taken. The samples were polarized in fields $E_p = 1.5$ MV/m during $t_p =$ 30 mins at various temperatures T_p. It was found that the TSC spectra of samples polarized at temperatures below T_g are similar to those of unpolarized samples. For samples polarized at temperatures close to T_g and higher a new TSC peak was observed. In Fig. 4, TSC spectra for samples polarized at 140 °C with Ag-Ni electrodes (a) and Ag-Ag electrodes (b) are presented. Obviously, the

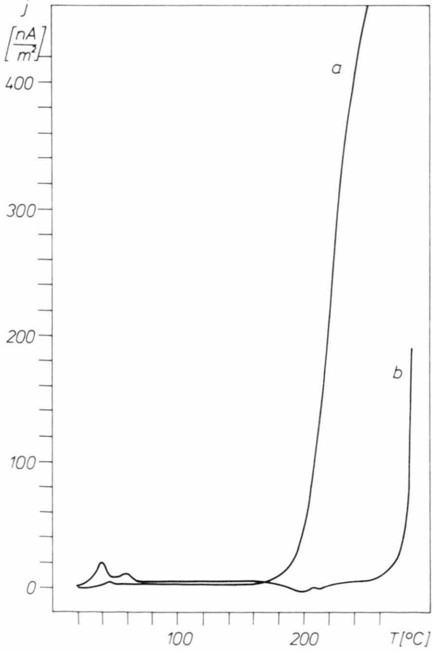


Fig. 3. TSC spectra for purified and unpolarized sample of PPS V-1 unpreheated (a) and preheated at 270 °C during 30 mins (b).

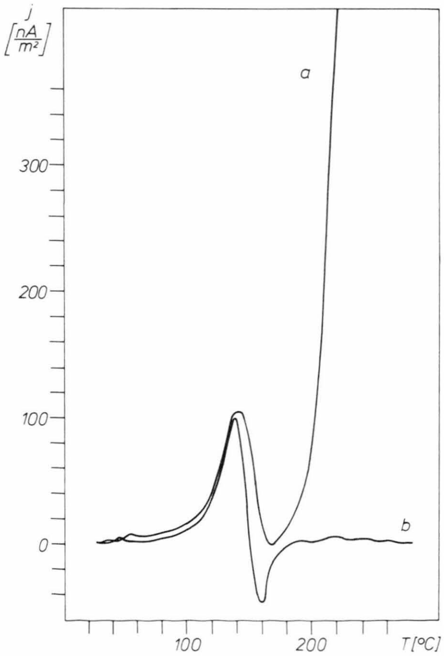


Fig. 4. TSC spectra for samples purified and polarized at temperature $T_p = 140$ °C, in a field of $E_p = 1.5$ MV/m during $t_p = 30$ mins with Ag-Ni electrodes (a) and Ag-Ag electrodes (b).

choice of electrodes does not affect the TSC peak. This peak was found to be shifted towards higher temperatures for samples polarized at higher temperatures. This is shown in Fig. 5a, where the temperature T_m of the current maximum is plotted vs. the temperature of polarization. The effect is more pronounced in the temperature region (80 ÷ 160) °C. It was found that the total charge related with the TSC peak depends on the temperature of polarization (Fig. 5b) and the total charge and TSC current dependent on the polarizing field strength. Figure 6 shows TSC spectra obtained for PPS samples polarized at $T_p = 200$ °C during $t_p = 30$ mins in fields of $E_p = 0.5$ MV/m (a) and $E_p = 2$ MV/m (b). It was found that the TSC spectra of samples polarized at temperatures higher than 200 °C show additionally a TSC peak in the temperature range (172 ÷ 184) °C, which can be assigned to the homocharge injected during polarization, and that the total charge and TSC current depend on the polarizing field strength (Figure 6). Moreover, reversal of the polarity of E_p causes an inversion of the TSC peak (Figure 7).

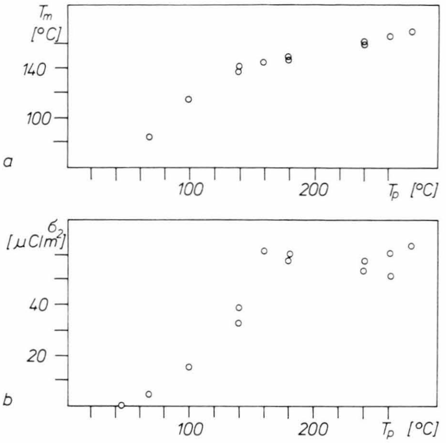


Fig. 5. Temperature T_m of the current maximum (a) and total charge density σ obtained from the TSC peak (b) as functions of the temperature of polarization for purified PPS V-1 polarized in a field of $E_p = 1.5$ MV/m during $t_p = 30$ mins.

4. Conclusions

1. TSC thermograms for unpolarized PPS samples show a rapid increase in current at about 200 °C for virgin samples and about 280 °C for samples preheated for 30 mins at 270 °C. This current was observed with asymmetric electrodes only and was found to be affected by the degree of purity of the

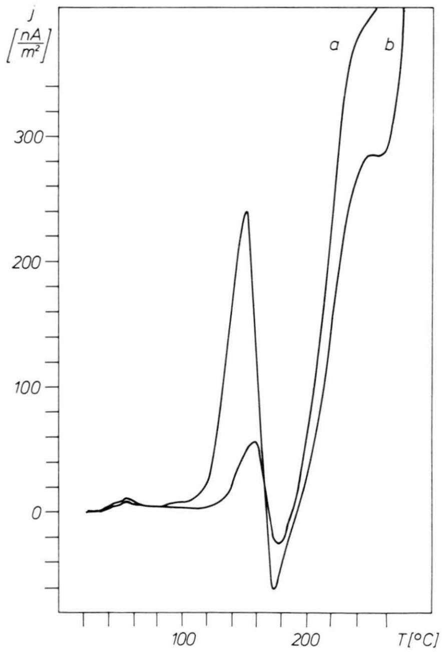


Fig. 6. TSC spectra obtained for purified PPS samples polarized at $T_p = 200$ °C during $t_p = 30$ mins in fields of $E_p = 0.5$ MV/m (a) and $E_p = 2$ MV/m (b).

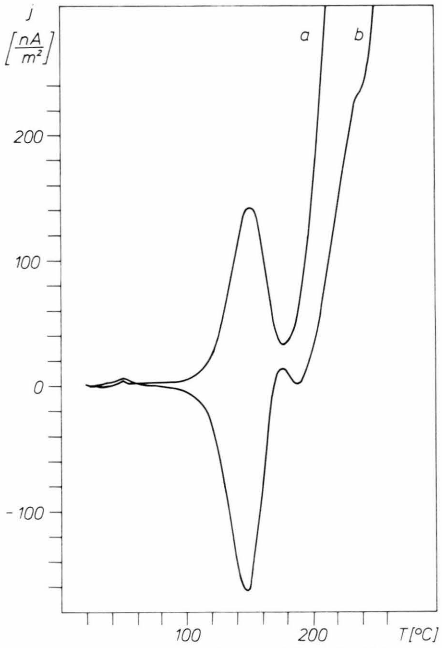


Fig. 7. TSC spectra for purified PPS V-1 samples polarized at $T_p = 180$ °C during $t_p = 30$ mins in a field of $E_p = 1.5$ MV/m: (a) for negatively charged sample, (b) for positively charged sample.

sample. The activation energy was evaluated to be of 1.6 eV.

2. In the temperature region below T_g small TSC peaks were observed and found to be unsensitive to the heating procedure and polarization reversal. In the same temperature region, dispersion of T_1 and $T_{1\varrho}$ values independent of frequency was observed in NMR investigations [18].

3. The TSC thermograms for polarized PPS samples show independently of the rapid increase in current mentioned above a well resolved TSC peak which can be reversed by polarization reversal and is found to be highly sensitive to the strength of the polarizing field. This peak is independent of the choice of electrodes, the temperatures of the current maximum T_m depends on the temperature of polarization (this peak was present only in samples polarized at temperatures close to T_g and higher) and the peak is most pronounced for samples polarized at 150 °C and at higher temperatures. We relate this peak to the same process as that observed in NMR experiments at 150 °C [3], namely the appearance of reorientational motions of the chains or their segments.

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[1] A. Eisenberg and B. Cayrol, J. Polym. Sci. **35,** 129 (1971).
[2] S. J. Rigby and D. Dew-Hughes, Polymer **15,** 639 (1974).
[3] J. Jurga, H. Eckert, and W. Müller-Warmuth, Z. Naturforsch. **34 a,** 1216 (1979).
[4] J. Van Turnhout, Thermally Stimulated Discharge of Polymer Electrets, Elsevier Sci. Publ. Co., Amsterdam 1975.
[5] R. A. Creswell, M. M. Perlman, and M. Kabayama, Dielectric Properties of Polymers, Plenum Press, New York 1972.
[6] P. Grenvesse, Bull. Soc. Chim. France **17,** 599 (1897).
[7] A. D. Macallum, J. Org. Chem. **13,** 154 (1948).
[8] Pat. USA 2354129 (1967).
[9] "Ryton®" Polyphenylene Sulphide Resins, New Product Information Phillips Petroleum Company, Bartlesville (Okla.) 1968.
[10] V. A. Sergeiev, V. K. Shitikov, and B. J. Nedelkin, Uspiekhi Khimii **11,** 2065 (1978).
[11] B. J. Tabor, E. P. Magré, and J. Boon, J. Europ. Polym. **7,** 1127 (1971).
[12] D. G. Brady, J. Appl. Polym. Sci. **20,** 2541 (1976).
[13] Chen Ji Zhou, Jiang Shi Cheng, and Hua Hsueh Hsueh Pao **37,** 101 (1979).
[14] Chen Ji Zhou, Jiang Shi Cheng, and Hua Hsueh Hsueh Pao **38,** 50 (1980).
[15] Pat. Jap. 8221456 (1982).
[16] J. S. Abel, H. Mazurek, D. R. Day, E. W. Maby, S. D. Senturia, G. Dresselhaus, and M. S. Dresselhaus, Mater. Res. Soc. Symp. Proc. **7,** 173 (1982).
[17] M. Rubner, P. Cukor, H. Jopson, and W. Deits, J. Electron. Mat. **11,** 261 (1982).
[18] J. Jurga, unpublished data.