

## **The Effect of Spherulite Structure of Polypropylene on the Thermally Stimulated Electret Depolarization Current**

**P. Myśliński<sup>1</sup> and M. Kryszewski**

Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies,  
90-362 Łódź, Poland

<sup>1</sup> Institute of Industrial Chemistry, 01-793 Warsaw, Poland

*Dedicated to Professor C. I. Simionescu on his 60th anniversary*

### Summary

The dependence of thermally stimulated depolarization current /TSC/ on morphological structure of polypropylene /PP/ films has been determined. Different morphologies in the investigated samples were arrived due to appropriate cooling conditions. The TSC maxima were correlated with the size of spherulites and attributed to the release of carriers trapped at the crystalline and amorphous phase borders.

### Introduction

Measurement of thermally stimulated electret depolarization current has found widespread application in studying the relaxation effects in amorphous polymers. Relatively little attention has been paid to the possibility of using this technique in studies on crystalline polymers, especially polypropylene /PP/. Publications on thermally stimulated currents in PP discuss the way of calculating the parameters of the discharge current curves obtained /activation energy, total electret charge, maximum temperature/ and the different ways of polymer charging: by corona charging (CRESWELL and PERLMAN 1971, PERLMAN 1972) and in electric field at elevated temperatures (MATSUI and MURASAKI 1973, WEBER 1979). Furthermore, comparing the results of TSC measurements for PP with those of internal friction changes in function of temperature Matsui and Murasaki have found that the maximum TSC at 80°C is related to charge release from traps situated on crystal surfaces. Explanation of the relation between the elements of PP crystal structure and the TSC would require polymer samples where only one element characterizing their structure would be different.

It has been shown (REINSHAGEN and DUNLAP 1975) that an increase in the temperature of molten PP leads, on sample cooling, to an increase in mean spherulite size, the other elements of the crystal structure remaining unchanged, possibly due to decreased number of crystallization seeds. The existence of a number of spherulites of different kinds which differ in the growth rates and melting temperatures was established (KEITH and PADDEN 1959, TURNER et al. 1964). In PP there are spherulites of four kinds: spherulites growing at temperatures below 134°C and above 138°C which melt when the temperature is raised and form again when cooled. Crystallites in these spherulites are monoclinic. Spherulites arising at 128°C and 128-132°C are metastable and are made up of hexagonal crystallites. With the temperature raise the spherulites transform into a form made up of monoclinic crystallites. In addition, it has been demonstrated (TURNER et al. 1964) that an increase of the temperature of molten PP may result in a decrease of the number of metastable spherulites during the sample cooling. The aim of this study was to establish the effect of spherulite size on TSC curves and to demonstrate the applicability of this method to show the effect of crystalline polymer morphology on its electrical properties. The samples used differed only in mean spherulite size, the other elements of their structure characterized by melting temperature  $T_t$  and density  $\rho$  of the samples being constant. X-ray large-angle scattering measurements showed no metastable spherulites. Consequently, by changing the temperature of the molten polypropylene a change of mean spherulite size was obtained.

### Experimental

Molecular weight. Isotactic polypropylene J-400 /Poland/ was used, whose viscometric mass  $M_v=300\ 000$  was calculated on the basis of the value  $[\eta]$  in decalin according to the following formula (CHIANG 1958)

$$[\eta] = k M^a \quad \text{where } k=1.0 \cdot 10^{-2}, \quad a=0.8$$

Measurement of structural parameters. The melting temperature  $T_t$  of crystallites was determined using a Perkin Elmer differential microcalorimeter DSC-1B. The density was determined at 24°C in a gradient column /alcohol/water/ and on this basis the degree of sample crystallinity was calculated according to formula

$$x = \rho_c(\rho - \rho_a) / (\rho_c - \rho_a) \quad \text{where } \rho_c = 0.936 \text{ g/cm}^3, \\ \rho_a = 0.850 \text{ g/cm}^3$$

are the density of the crystalline and amorphous phases respectively (MARK et al. 1966). The mean spherulite diameter  $R$  was defined as the inverse number of spherulite boundaries intersecting a unit

segment on optical micrographs in reflected light.

#### TSC measurements and electric conductivity

Silver vacuum-deposited electrodes were used; surface area - 15.9 cm<sup>2</sup>. TSC curves for PP samples were determined using an Ekco vibrating-reed electrometer N 616 B with a Riken-Denshi X-Y recorder in the function of linearly rising temperature. The rate of temperature increase was 1°C/min. The parameters of electret formation were so selected as to prevent any changes in the sample structure at elevated temperature. For this reason the formation time  $t_0$  was 2 min, temperature  $T_p = 105^\circ\text{C}$ , and electric field strength  $E_p = 8 \text{ KV/cm}$ . Electric conductivity  $\gamma$  was determined according to the formula:  $\gamma = Il/US$  where U-voltage, I-current intensity, S-surface area of the electrodes, l-sample thickness. The samples used were 0.5 mm thick plates obtained by pressing for 30 min under 200 kg/cm<sup>2</sup> at different temperatures /190°, 200°, 220°C/ and cooling in the press down to 60°C. To obtain samples of different degree of crystallinity some of them were pressed at 260°C for 5 min, others were heat-treated at 150°C for 90 min. The measurements performed on the samples obtained in this way included the melting temperature  $T_t$ , density  $\rho$ , and spherulite diameter R. The results of these studies for samples obtained from melts of different temperatures showed that the increase of melt temperature gives rise to mean spherulite diameter only /Table 1/.

TABLE 1.

Melting temperature  $T_t$ , density  $\rho$ , spherulite diameter R for samples of PP pressed at different temperatures T.

T [°C]	R [μ]	$T_t$ [°K]	$\rho$ [g/cm <sup>3</sup> ]
190	6.94	434.3	0.9044
200	7.40	434.5	0.9044
220	8.00	434.6	0.9045

TABLE 2.

Degree of crystallinity X of samples obtained under different conditions.

formation conditions	X [%]
pressed at 260°C	0.591
annealed	0.647
annealed in electric field	0.680
pressed at 200°C	0.703

A similar result was obtained in the case of isothermal crystallization of PP at constant supercooling temperature  $\Delta T$  (see REINSHAGEN and DUNLAP 1975). The samples under study were non-isothermally crystallized in the

press. It can thus be assumed that under such conditions the crystallization occurred at a temperature similar to the highest crystallization rate temperature which, for PP, is equal to ca. 120°C (FRANK 1968). It follows from Keith and Padden studies (KEITH and PADDEN 1959) that at such high supercooling temperatures the changes in the crystal structure of polypropylene with changes in  $\Delta T$  are small. For this reason the small changes in  $\Delta T$  related to non-isothermal crystallization employed in our study did not affect the crystal structure of PP. The degrees of crystallinity of samples pressed at 200°C and 260°C and annealed at 150°C under different conditions are collected in Table 2.

### Results and discussion

Fig.1 shows the temperature dependence of TSC for samples obtained from the melt at 220°C and 190°C which, on cooling, developed spherulites of mean size of 8.0 and 6.9  $\mu$ . The discharge current after electret formation at 105°C shows two characteristic maxima at 90 and 120°C.

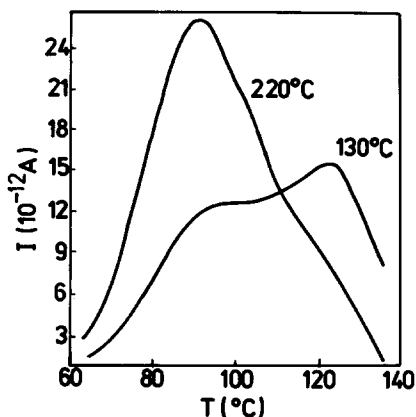


Fig.1 TSC plots for PP-samples differing in the temperature of pressing and in spherulite sizes / $T_p=105^\circ\text{C}$ ,  $t_p=2$  min.,  $E_p=8$  kV/cm/.

Changes in TSC value in the region of both maxima are related to the differences in the mean spherulite size in the sample show that structural parameter does affect the discharge current value to an appreciable manner. The increase of mean spherulite size in the sample leads to increased value of the current in the region of the 90°C maximum, and to its decrease in the region of the other maximum. This shows that spherulite size has a different effect on TSC in this two regions. The TSC curves for samples of the same mean spherulite size, i.e. 8.0 and 6.9  $\mu$  obtained after po-

-larization at 125°C are shown in Fig.2.

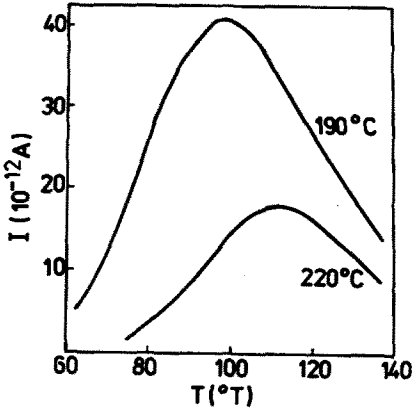


Fig.2 TSC plots for PP samples differing in the temperature of pressing / $T_p=125^\circ\text{C}$ ,  $t_p=2$  min.,  $E_p=8$  kV/cm/.

The increase in  $T_p$  effects a change in TSC values for both samples; in the case of the sample with smaller spherulite size TSC was greater than in the case of the other sample. The results of TSC measurements for PP samples differing in spherulite size /Figs.1 and 2/ show that two current maxima occur at 90 and 120°C which depend on the spherulite size in the sample under investigation and on the temperature of electret formation. The significant rise of discharge current for the sample with smaller spherulites /Fig.2/ polarized at higher temperature /125°C/ suggests that in this region TSC is related to higher electrical conductivity of the sample, during electret formation. For this reason we performed conductivity measurements for PP samples of different degrees of crystallinity /Table 2/ at different temperatures /Fig.3/. It can be seen in Fig.3 that the conductivity decreases as sample crystallinity and increases with temperature, the dependences being linear to a good approximation; the correlation coefficient is no less than 0.95 up to 100°C, which indicates linearity. At 110°C the coefficient has a smaller value /0.69/ which may be due to some changes in the crystallinity at that temperature. In order to calculate the contribution of the crystalline and amorphous phase to the measured conductivity we took advantage of the linear dependence of the logarithmic mixing rule of Lechteneker (see SAZHIN et al. 11):  $\log \gamma = -X/\log \gamma_a + X\log \gamma_c$  where  $\gamma_a$ ,  $\gamma_c$  are the conductivities of the amorphous and the crystalline phase respectively. Transformation of the above formula yields:  $\log \gamma = \log \gamma_a - X/\log \gamma_a - \log \gamma_c$ . In the coordinate system / $\log \gamma$ ,  $X$ / the above formula is represented by a straight line. Using the least squares method the parameters of that line, i.e. / $\log \gamma_a$ ,

$\log \chi_a / \chi_c /$  were calculated. On the basis of these parameters the values of electric conductivity for both phases of the polymer were calculated for different temperatures. The temperature dependence of these values is shown in Fig.4.

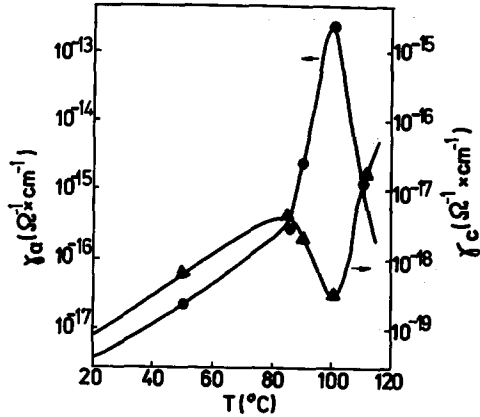
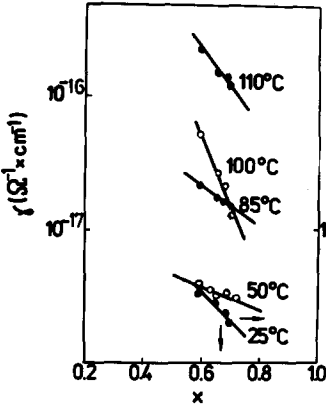


Fig.3. Electrical conductivity dependence on degree of crystallinity  $X$  for PP samples/different temperatures/. Fig.4. Temperature dependence of electrical conductivity of the amorphous and crystalline phases in PP-samples.

It can be seen that the electrical conductivity of both phases of the polymer shows maxima at  $85^{\circ}$  and  $100^{\circ}\text{C}$  for the crystalline and amorphous phases respectively. The conductivity values in the crystalline phase of PP are smaller than those in the amorphous one. The existence of conductivity maxima in the temperature scale may be related to the fact that its values were calculated on the basis of non-stationary current flowing across the sample /its values were measured 5 minutes after the application of the voltage/ thus the current may be connected with polarization processes occurring in the sample (SAZHIN et al. 1977). Consequently, the maxima of electrical conductivity can be related to accumulation of electric charge in both phases of the polymer, in the crystalline phase the maximum charge accumulates at ca.  $85^{\circ}\text{C}$ , while in the amorphous phase - at ca.  $100^{\circ}\text{C}$ . On the other hand, the TSC maxima are connected with charge release in the sample. For this reason, when comparing the conductivity values in both phases of the polymer with the TSC values one can relate the TSC maximum at  $90^{\circ}\text{C}$  to charge release in the crystalline phase, and the  $120^{\circ}\text{C}$  maximum - to charge release in the amorphous phase.

### Conclusions

The results of TSC measurements and the conductivity values obtained in this study for PP samples differing in spherulite size show that TSC curve has maxima at 90 and 120°C which are related to spherulite size in the sample. The 90°C maximum is related to charge release in the crystalline phase, the 120°C maximum - to charge release in the amorphous phase. The dependence of the TSC density in the 120°C maximum region on spherulite size shows that that maximum is connected with the conduction current flowing across the polymer during electret formation. Very likely the value of this current depends on the crystal structure of the sample. The TSC maximum at 90°C may also be correlated with the results of mechanical loss studies in PP carried out in function of temperature (MUSS and MACCRUM 1959). The determination of PP viscoelastic properties shows that the maximum at 90°C is related to the crystalline phase. On the other hand there is no maximum in loss at the 120°C region, which could be correlated with the release of carriers in the sample under study. The obtained results e.g. conductivity dependence on crystallinity /Fig.3/ and TSC current intensity dependence on PP morphology cannot fully explain the nature of charge carriers. It is connected with the fact that the conductivity measurements were carried out after short polarization times /5 min/ and for narrow range of crystallinity changes. However, it has been shown (DASGUPTA et al. 1976) that electrons are charge carriers in PP and that at temperatures above 0°C, electrons are transported by hopping from one trapping center to another. Assuming this model, it can be concluded that TSC measurements show the existence of trapping centers which are related to the borders between the amorphous and crystalline phases i.e. on the borders of spherulites and/or crystallites inside of these morphological structures.

### References

- CRESWELL, R.A. and PERLMAN, M.M.: Polym. Prepr. Amer. Chem. Soc. Div. Polym. Chem. 12, 206 (1971)  
PERLMAN, M.M.: J. Electrochem. Soc. 119, 892 (1972)  
MATSUI, M. and MURASAKI, N.: Electrets, Charge Storage Transport. Dielectr./Int. Conf./ 2nd, 1972/ (Pub. 1973)  
WEBER, G.: Prog. Colloid Polym. Sci. 66, 125 (1979)  
REINSHAGEN, J.H. and DUNLAP, R.W.: J. Appl. Polym. Sci. 19, 1037 (1975)  
KEITH, H.D. and PADDEN Jr., F.J.: J. Appl. Phys. 30, 1479 (1959)

- TURNER JONES, A., AIZLEWOOD, J.M. and BECKETT, D.R.: Makromol.Chem. 75, 134 (1964)
- CHIANG, R.: J.Polymer.Sci. 38, 235 (1958)
- MARK, H.F., GAYLORD, N.G. and BIKALES, N.M.: Encyclopedia of Polymer Science and Technology. Plastics, Resins, Rubbers, Fibers. Vol.4: New York; Interscience 1966
- FRANK, H.P.: Polypropylene /Polymer Monographs, Vol. 2/, New York; Gordon and Breach 1968
- SAZHIN, B.I. and PODOSENOWA, N.G.: Vysokomol.Soyed. 6, 137 (1964)
- SAZHIN, B.I., ŁOBANOW, A.M., ROMANOWSKAJA, O.S., EIDELNANT, M.P. and KOIKOW, C.N.: Elektriczeskije swojstwa polimierow, 2nd, Leningrad: Chimija 1977
- MUUS, L.T. and MCCRUM, N.G.: SPE.J. 15, 368 (1959).
- DASGUPTA, D.K. and JOYNER, K.: J.Phys.D. 9, 2041 (1976)

*Received June 2, 1980*

*Accepted June 6, 1980*