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Electrical Polarization Phenomena in Poly (Phenylquinoxaline) (PPQ)

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Summary

Results are described of TSD- and TSP-measurements of Poly (Phenylquinoxaline) in dependence on the degree of annealing and on the polarizing field strength. Seven relaxations regions are investigated and discussed. Electronic and ionic space charge regions are observed and discussed in detail. It is shown that dielectric losses in polymers do not result from dipolar processes only, but also from translational motion of charge carriers.

Introduction

The electrical behaviour of the highly thermostable and highly insulating Poly (Phenylquinoxaline) (PPQ) was studied by thermally stimulated depolarization (TSD), by thermally stimulated polarization (TSP) and by isothermal polarization methods. Electrical fields are able to produce several electrical polarization phenomena in PPQ. Several authors reported on this phenomena, on the synthesis, and characterization of PPQ and on other electrical properties of this substance (KORSAK et. al. 1974, HÄNSEL and KNOBLICH 1980, GRÄSSLER and KNOBLICH 1978, BÜTTCHER and NEUMANN 1978, GRÄSSLER et. al. 1980, HÄNSEL et. al. 1976, STROLOKE and NEUMANN 1980, SCHRADER 1981). The measurements were performed in function of the degree of annealing, the polarization temperature and the polarizing field strength E_p.

The aim of our researches was (i) to seperate the polarization mechanisms of PPQ, (ii) to clarify the influence of the

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thermal annealing process of the substance, and (iii) to generalize these results to other polymers.

Annealing process

The samples were annealed in vacuum at temperatures below and above the glass-transition-temperature T_g (T_g=258°C). The annealing time was many days. The characterization of the annealing process was performed by monitoring the voltage U_o and the current I_o which were measured without an external electrical field (QUELING et. al. 1981). The thermal annealing process was considered to be finished when $\sigma \sim U_o/I_o$ changed by less than 2% during the annealing time of 100 hours.

The dependence of σ on the annealing time suggests an existence of two different mechanisms of annealing. First of all, σ decreases by up to four orders of magnitude for annealing temperatures above T_g (Fig.1). We attribute this decrease of σ to crosslinking reactions. The decrease of the magnitude of the α- and β-peaks in the TSD spectrum also confirms this assumption. σ begins to increase again after annealing times longer than 60 hours. Furthermore, a strong increase of the current is observable in the TSD spectrum above T_g. We attribute these facts to the generation of ions in this annealing region, being the consequence of degradation processes in the substance. The existence of ions in the samples after enough long annealing times was also concluded from in-

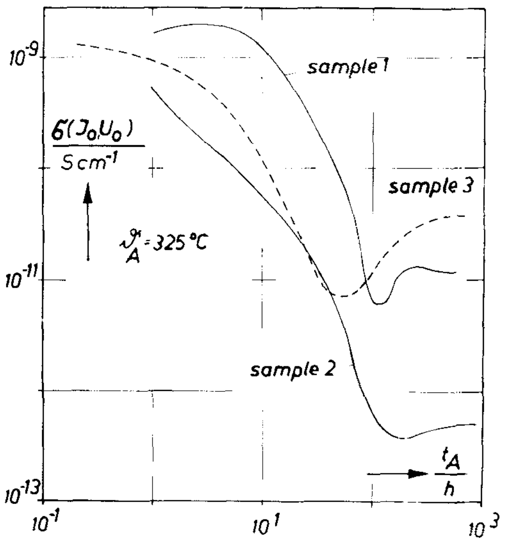

Fig. 1 A dependence of $\sigma \sim U_o/I_o$ on the annealing time t_a

vestigations of their electrical properties (QUELING et. al. 1981).

Relaxation regions

Seven relaxation regions may be distinguished in the TSD spectrum (Fig.2 and Fig.5). The possibility of observation of these regions depends strongly on the annealing degree of the samples. Three of these relaxation regions were also detected in the tanδ spectrum of PPQ by SCHLOSSER and RAUBACH and explained in the same way (SCHLOSSER and RAUBACH 1977). Two relaxation peaks are located below 0°C. Traces of water (peak about -100°C) and solvent (peak about -25°C) give rise to them. Magnitudes of these peaks differ from sample to sample. This fact shows that the water and the solvent are not homogeneously distributed in the foil from which the samples are made. The peak due to water vanishes on annealing, whereas the peak of the solvent shifts to lower temperatures (to about -40°C). The third peak charac-

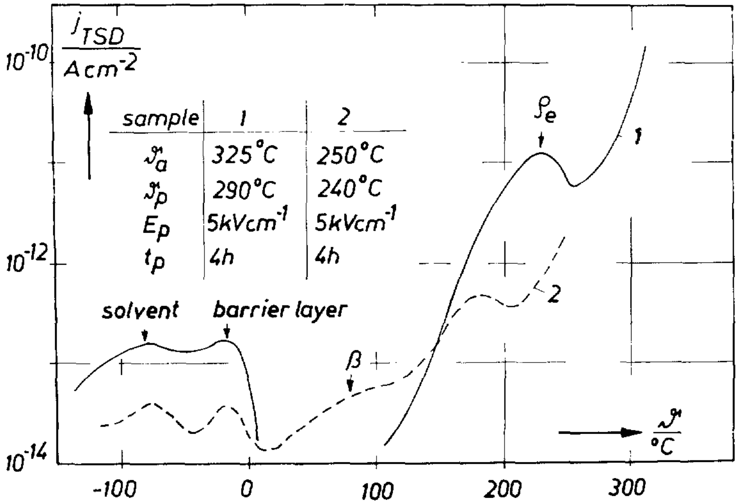

Fig. 2 TSD spectrum of PPQ (ϑ_a annealing temperature, ϑ_p polarization temperature, E_p polarizing field strength, t_p polarization time)

terizes the α-relaxation region (Fig.5). Its maximum temperature $\vartheta_{TSD,max}$ lies about 300°C. The peak shifts to lower temperatures (270°C) on annealing, whereas the charge stored derived from the integral of the current in this relaxation region decreases by up to four orders of magnitude.

A further relaxation region can be observed in some samples around 70°C. Probably a side-group β-relaxation process produces this peak, because the current $j_{TSD,max}$ in the TSD-maximum is proportional to the polarizing field E_p, a fact, which is valid for a dipol relaxation process. The magnitude of this peak decreases strongly on annealing. The β-relaxation region may be seen only for $E_p > 10^4 Vcm^{-1}$. Our interpretation of this fact is, that the annealing produces cross-linking of the substance, whereby the mobility of the side groups is hindered. Therefore the β-relaxation must vanish for low polarization fields.

Another TSD peak at about 0°C may be seen in annealed samples. We suppose barrier layer effects produce this peak, because (i) the stored charge depends on the direction of the polarizing field, (ii) the activation energy of this process depends on the field strength, and (iii) $\ln j_{TSD,max}$ is not a linear function of $\ln E_p$.

Furthermore, two space charge regions were observed produced by electronic (ρ_e-peak) and ionic (ρ_i-peak) charge carriers.

Interpretation of the space charge regions

Now we will discuss the space charge regions in detail. The investigation of the temperature and field strength dependence of the ρ_e-maximum shows, that two different processes produce this maximum. The dependence of the maximum of the depolarization current $j_{TSD,max}$ on E_p in the ρ_e-space charge region shows an ohmic, a superlinear and a saturation region (Fig.3). The transition points between these regions shift to lower values of E_p with increasing of the annealing temperature and of the polarization temperature.

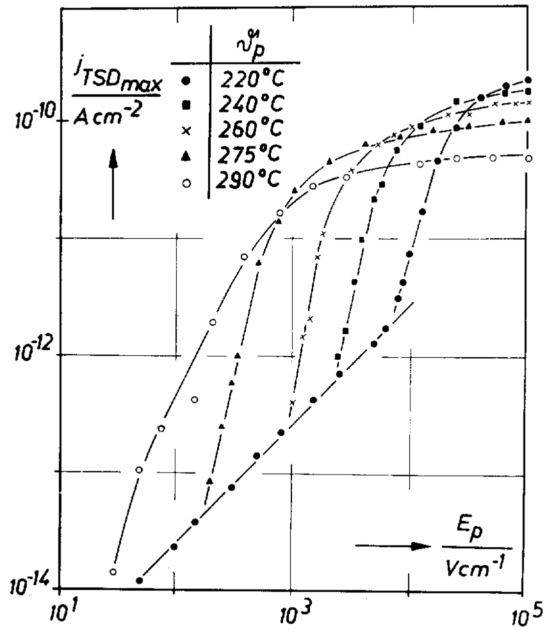

Fig. 3 $j_{TSD,max} = f(E_p)$ in the ρ_e-space-charge region for different polarization temperatures ϑ_p

The displacement of equilibrium electronic charge carriers is the reason of the ohmic range. We suppose the carriers are distributed uniformly in space in shallow transport states before the TSD measurements. This spatial distribution becomes inhomogeneous during the polarization process. This displacement of the carriers produces a maximum in the TSD, if the contacts are at least partially blocking. The permittivity ε was estimated from the charge, which is stored in the sample. ε is constant in the ohmic region. Its value ($\varepsilon = 2.85$) corresponds to the value ($\varepsilon = 3.2$) estimated from $\tan\delta$ measurements.

The non-linear characteristics $j_{TSD,max} = f(E_p)$ result from the movement of the electronic carriers in the electrical field produced by an ionic space charge at the electrodes. The electronic carriers are generated from Poole-Frenkel-centres during the TSD. The energetic depth W_{PF} of the Poole-Frenkel-centres and the Poole-Frenkel-constants β_{PF} estimated from the TSD and TSP measurements ($W_{PF} = (1.45 \pm 0.06)$eV, $\beta_{PF} = 3.96 \cdot 10^{-4}$eV cm$^{1/2}$ V$^{-1/2}$) correspond to the values estimated from the electrical conductivity ($W_{PF} = 1.45$ eV, $\beta_{PF} = 3.1 \cdot 10^{-4}$eV cm$^{1/2}$ V$^{-1/2}$) (HÄNSEL and KNOBLICH 1980).

The permittivity ε increases (Fig.4) with E_p in the superlinear region. Its order of magnitude corresponds to the values estimated from the results obtained from electrical measurements (QUELING 1981). This fact shows that dielectric losses in polymers result not only from dipolar processes but also from the translational motion of electronic and (or) ionic charge carriers. Therefore one cannot automatically estimate the dipole density in the sample from measurements of its permittivity. Till now this fact was noted only theoretically by few authors (STOLL et. al. 1976, WEBER 1978, HILL and JONSCHER 1979).

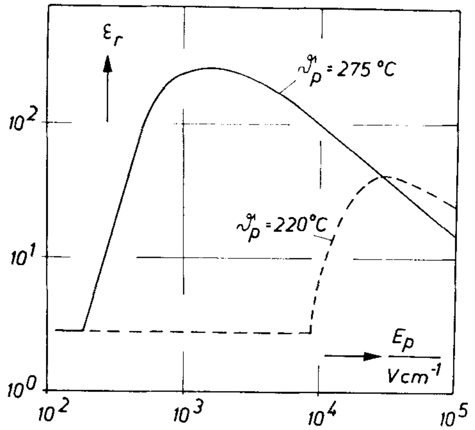

Fig. 4 $\varepsilon_r = f(E_p)$ for two polarization temperatures ϑ_p

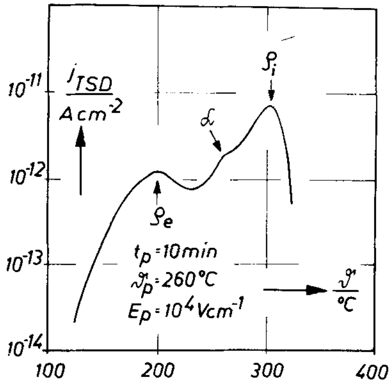

Fig. 5 TSD spectrum obtained by applying a polarization time of 10 min

The ρ_e-peak was found at lower temperatures than the α-peak (see Fig.1). This fact is contrary to the results for all other polymers. However an analysis of these works shows that the ρ_e-peaks were found in the TSD spectra at these temperatures, where σ reaches the magnitude of 10^{-14} .... 10^{-15} S cm^{-1} . PPQ has a very high glass transition temperature. Therefore, the electrical conductivity attains this value already below T_g. For that reason the hitherto existing assumption $T_\alpha < T_{\rho e}$ is not valid automatically.

We have found that the TSD spectrum includes either the α-relaxation region or a strong increase of the current covering the α-peak, depending on annealing above T_g. The analysis of the TSD spectra shows that, depending on E_p, a further polarization of the sample exists (ρ_i-peak) which is not removed on a TSD run. The sample possesses a residual polarization, which increases with increasing E_p. This polarization is due to ions generated by the degradation of PPQ on annealing. This polarization can be hindered by application of very short polarization times (<10 min.). Than the α- and ρ_i-peaks are separated in the TSD spectrum (Fig.5).

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