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Radiothermoluminescence Studies of Chlorinated Polyphenylmethacrylate Polymers

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SUMMARY

Radiation chemical processes in polyphenylmethacrylate and several chlorinated polyphenylmethacrylate samples are analyzed by means of radiothermoluminescence.
The spectral distribution of the luminescence was also studied in dependence on the temperature. The observed results show that the chlorine atoms play a dominating role in the radiation chemical reactions.

INTRODUCTION

The radiothermoluminescence (RTL) technique is a valuable tool for the investigation of radiation induced reactions, structural transitions and radiation damages in polymeric solids (PARTRIDGE, 1972). The RTL monitors photons as a function of the temperature (glow curves) during a thermal scan. During the low-temperature irradiation of the polymer positive ions and electrons are produced. The free electrons are trapped by structural or chemical defects of the polymer matrix. Subsequent heating releases the electrons from their traps. These electrons recombine with ions and emit light.

PARTRIDGE (1972), FLEMING and HAGEKYRIAKOU (1984) have reviewed the major developments in the study of RTL for polymeric materials.

We report RTL data on polyphenylmethacrylate (PPhMA) and polychlorphenylmethacrylate (PClPhMA). PPhMA belongs to the group of degrading polymers (RAGHUNATH, 1983), while PClPhMA with a Cl-atom on the aromatic ring in o-, m- or p-position crosslinks after irradiation with ionizing radiation.

It is assumed that the crosslinking reaction takes place through abstraction of chlorine atoms (IMAMURA, 1982).

The difference in these radiation chemical effects for PPhMA and PClPhMA should be reflected in the RTL glow curves.

EXPERIMENTAL

The polymers were dissolved in monochlorbenzene and spin-coated on a silicon or aluminium substrate and baked at 160°C for 1h. The thickness of the polymer layers was 3 µm and 0,5 µm. The experimental set-up used for the RTL measurements

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has already been described in detail elsewhere (KUNZE, 1983). The samples were irradiated with 15keV-electrons. The luminescence was measured with a photomultiplier directly after the irradiation at a constant temperature T = 80K (isothermal luminescence) and then during the thermal scan (glow curve), respectively. The spectral distribution of the RTL was recorded with a monochromator SPM 2 (Carl Zeiss, Jena).

RESULTS AND DISCUSSION

RTL glow curves of PPhMA and PClPhMA with a Cl-atom on the aromatic ring in o-, m- or p-position are shown in Figure 1. The glow curve of PPhMA has one peak around 115K and a more or less pronounced shoulder around 160K. Electron traps of the low temperature peak originate from the polymer chains themselves (FLEMING, 1968).
PClPhMA-samples have two pronounced peaks around 110K and in the range of 150K - 165K. The intensity and temperature of these peaks depend on the position of the Cl-atom on the aromatic ring. The intensity shows a strong decrease for P(o-ClPhMA) in comparison to P(p-ClPhMA) and P(m-ClPhMA). Furthermore, the spectral distribution of the RTL was investigated in dependence on the temperature for PPhMA and P(p-ClPhMA) (Figure 2). The spectrum of PPhMA reveals a maximum around $\lambda = 425$ nm, and the distribution is independent of the temperature. In the case of P(p-ClPhMA) a maximum was observed around $\lambda = 480$ nm for the low temperature range and around $\lambda = 435$ nm for the peak at 160K.
The RTL-results indicate that the chlorine atoms play a dominating role in the radiation chemical reactions and suggest that the chlorination of PPhMA changes the reaction mechanism. During the irradiation the primary reactions can be typified by:

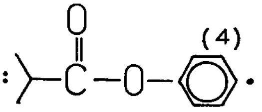
$$\mathrm{P} \xrightarrow{e^-} [\mathrm{P}]^+ + e^- \qquad (1)$$

$$\mathrm{PCl} \xrightarrow{e^-} [\mathrm{PCl}]^+ + e^- \qquad (2)$$

$$e^- \longrightarrow e^-_{tr} \qquad (3)$$

$$\mathrm{PCl} \xrightarrow{e^-} \mathrm{P}^\bullet + \mathrm{Cl}^* \qquad (4)$$

P: PPhMA, PCl: chlorinated PPhMA, $\mathrm{P}^\bullet$:



e^-_{tr} : trapped electron

Cl^* : radiation induced chlorine; $\mathrm{Cl}^\bullet$ or Cl^-

The reaction (4) is a typical process during the irradiation of chlorinated hydrocarbons (SYMONS, 1982). It is the so-called dissociative electron capture of a Cl-atom.
The luminescence in the low temperature range (around T=115K and T=110K, resp.) is the result of recombination processes between the trapped electrons being released at this temperature and the polymer cations:

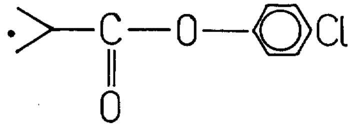
$$\mathrm{P}^+ + e^-_{tr} \longrightarrow \mathrm{P}^* \longrightarrow \mathrm{P} + h\nu_p \qquad (5)$$

$$\mathrm{PCl}^+ + e^-_{tr} \longrightarrow [\mathrm{PCl}]^* \longrightarrow \mathrm{PCl} + h\nu_p' \qquad (6)$$

P^* and $[PCl]^*$ denote the excited state of the polymers. The broad spectrum with λ_{max} = 425 nm and 480 nm, respectively, observed at low temperatures seems to correspond to the radiative transition from the triplet state of the excited phenyl or chlorine-phenyl group (phosphorescence) produced by the reactions (5) or (6).
The luminescence peak around T = 160K of the chlorinated polymers (Fig. 1) is the result of abstraction of protons (hydrogen) from the polymer matrix according to:

$$PH + Cl^\bullet \longrightarrow \bar{P}^\bullet + HCl + h\nu_p'' \qquad (7)$$

$\bar{P}^\bullet$:



The emission of λ= 435 nm (Fig. 2), however, can not be directly attributed to excited HCl-molecules (7). It is likely that the excited HCl-molecule transfers its energy to the polymer chromophores. Further investigations are in preparation. The variation of the RTL-intensity for the second glow peak can be connected with the acidity of the chlorinated phenyl cycle. The acidity rises in direction from P(p-ClPhMA) to P(o-ClPhMA). It is known that with increasing acidity of the chlorinated phenyl ring the probability of degrading reactions rises in comparison to the dissociative electron capture of the Cl-atoms.
The recombination of the polymer radical formed by the dissociation of the carbon-chlorine bond (reaction 4) and the abstraction of protons (reaction 7) leads to crosslinking reactions in chlorinated aromatic polymers (IMAMURA,1982).

The proposed crosslinking reaction is supported by further investigations on this polymer system.
The dependence of the RTL glow curves of P(p-ClPhMA) preirradiated with electron beams was investigated. The electron beam irradiations were performed with 30keV-electrons and the doses were varied between 1 x 10^{-6} $C \cdot cm^{-2}$ and 1 x 10^{-4} $C \cdot cm^{-2}$. As reported previously (WÄSCHE, 1985), ESCA investigations showed a decrease of the Cl-content of exposed samples. Analyzing the C:Cl atomic ratios, intense chlorine abstraction is found already for small irradiation doses. This effect should also be reflected in the shape of the RTL-glow curves, especially of the second peak around 160K. Fig. 3 represents the ratio of the intensity of this peak (I_2) to the intensity of the first peak around 110K (I_1) as a function of the deposited energy E_a. The deposited energy per unit volume is expressed by:

$$E_a \left[\frac{eV}{nm^3}\right] = 10^{-14} \cdot \mathcal{E} \cdot f$$

$\mathcal{E}$: energy dissipation ($\approx 1{,}8\ \frac{eV}{nm}$ for 30keV-electrons)
f : fluence [particle/ cm^2]

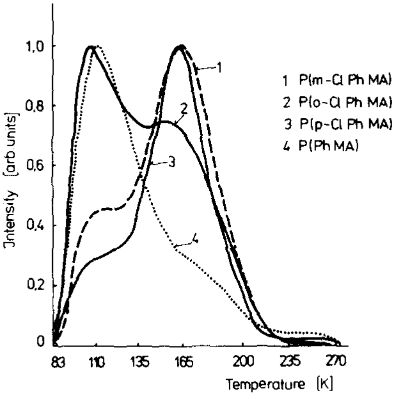


Fig.1: Glow curves of PPhMA P(o-ClPhMA), P(m-ClPhMA) and P(p-ClPhMA) (Heating rate 6 K/min)

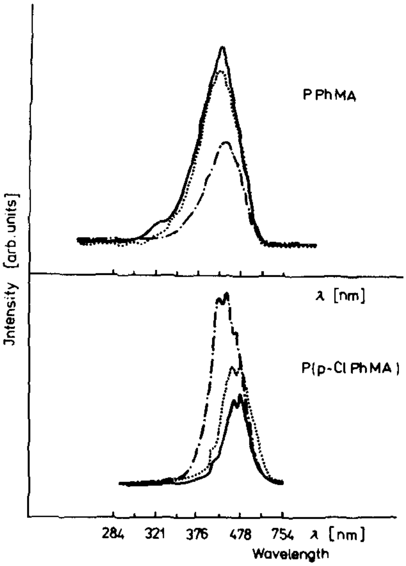


Fig.2: Spectral distribution of the RTL at various temperatures
... ITL-spectra at T = 80K
—— TL -spectra at T = 110K
—·— TL -spectra at T = 160K

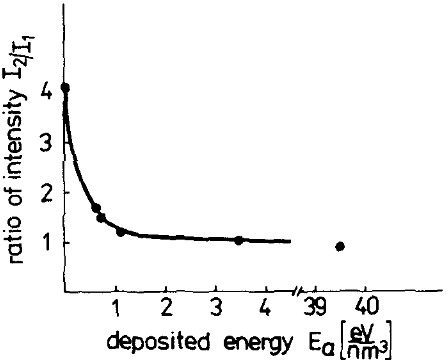


Fig.3: Ratio of intensity of the second peak (around 160K) to the first peak (around 110K) as a function of the preirradiation dose

Fig. 3 shows significantly a decreasing intensity of the second glow peak in dependence on the preirradiation dose. With increasing preirradiation dose the influence of the Cl-atoms on the RTL-process is lowered.

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