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Drift Mobility of Holes in Some Photoconductive Polymeric Structures in the Glass Transition Region

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SUMMARY

Drift mobility of holes in poly(N-vinylcarbazole) PVCA and its mixtures with poly(N-epoxypropylcarbazole) PEPCA was measured in a broad temperature range. Sensitivity of charge transport to the dynamic phenomena in the glass transition region was observed. Release of molecular motions near the glass transition temperature causes broadening of the transit time distribution and reversible decrease of the activation energy of drift mobility.

INTRODUCTION

Behaviour of the drift mobility of holes in the neighbourhood of the glass transition in PVCA-like polymers has been studied. Although the electric transport properties of PVCA have been investigated very intensively during the last decade, no special attention has been devoted to this particular problem. Thermally activated hopping between carbazole groups is considered to be the transport mechanism, but the role of molecular motions in transport process needs further investigation. Connection between the charge transport and segmental motions is a characteristic feature of polymeric semiconductors, which has no counterpart in inorganic photoconductive materials. In this paper we report our results of drift mobility measurement of holes in PVCA and PVCA:PEPCA mixture above the glass transition temperature. They correspond to similar results found recently by ABKOWITZ et al. (1981) for the case of some hole-transporting organic glasses.

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EXPERIMENTAL

Highmolecular Luvican M 170 from BASF was used as PVCA. Its mass-average molecular mass $M_w = 1{,}2 \cdot 10^6$ and glass transition temperature $T_g^{PVCA} = 495\text{-}500$ K (KLÖPFFER 1971, BERGFJORD et al. 1979). It had been twice purified by precipitation in methanole prior to use. PEPCA was supplied by Vilnius State University as an oligomer of about 7-10 monomer units in one molecule and its glass transition temperature $T_g^{PEPCA} = 323\text{-}328$ K (GAIDELIS et al. 1976). PVCA and PVCA:PEPCA = 1:1 mixture (molar ratio) were dissolved in toluene:cyclohexanone = 4:1 (volume ratio) and cast onto conductive substrates. Films of thickness from 3 to 6 μm were formed after the evaporation of the solvents. Semitransparent gold electrodes were evaporated on the free surface of the films in order to prepare sandwich-type structures. Both aluminium and stainless steel were used as the substrate materials, and as well as toluene:cyclohexanone mixture, tetrahydrofurane and methylenechloride were examined.

The drift mobility of holes was determined by direct method based on their transit time measurement through the polymer film. UV light source of pulse duration less than 1 μs was used for charge carrier generation and memmory oscillograph for the detection of the corresponding electric current through the sample. High UV absorption coefficient of the examined materials (KLÖPFFER 1971, GAIDELIS et al. 1976) insures surface-type generation. The whole experimental arrangement was the same as that one used by GILL (1972).

We always read the transit time directly from the oscillograph screen, which was enabled by the distinctness of the characteristic knee on the observed transient current curves. The error of its determination can be estimated not to exceed 15%. This accuracy is, however, fully sufficient because the transit time changed over three orders of magnitude in the investigated electric field and temperature ranges. Except for this, measurements on about 30 samples had been done in order to prove our results also statistically.

RESULTS AND DISCUSSION

The drift mobility of holes in PVCA was found to be thermally activated with the activation energy being temperature independent in the whole range T = 300-495 K. The corresponding transit time is characterized by a relatively small dispersion so that the drift mobility is defined well enough. The value of its activation energy decreases from 0,51 eV to 0,36 eV when increasing the applied electric field from $2{,}9\cdot10^{6}$ V/m to $5{,}5\cdot10^{7}$ V/m . These results are fully reproducible and don't depend on whether the temperature was being gradually increased or decreased during the measurements. In the glass transition region T_g^{PVCA} = 495-500 K, however, distinct change of transport properties was observed: sudden broadening of the transit time distribution made further drift mobility measurement impossible. This effect was partly irreversible - higher transit time distribution of the hole transport was observed after cooling the samples from T_g^{PVCA} down to room temperature, compared with fresh films. In spite of this it was still possible to estimate the transit time below T_g^{PVCA} and to show that it had not undergone any measurable change due to the previous heat treatment.

Drift mobility of holes in PVCA:PEPCA = 1:1 mixture is characterized by one value of activation energy E from room temperature up to 335 K. This activation energy depends on the electric field intensity and changes from 0,52 eV at $5{,}3\cdot10^{6}$ V/m to 0,43 eV at $3{,}5\cdot10^{7}$ V/m, as shown in Figure 1. When reaching the temperature 335 K, which is about 10 K above the glass transition region T_g^{PEPCA} of PEPCA, sudden broadening of the transit time distribution appears. But in the case of high electric field intensity $F \gtrsim 1{,}5\cdot10^{7}$ V/m, the drift mobility remains still measurable up to 390 K when the characteristic knee on the transient current curves completely disappears. The activation energy of the drift mobility of holes in the temperature interval from 335 K to 390 K is more than two times smaller than in the temperature region $T < 335$ K. These results are also reproducible except for the case of heating the samples over 390 K, which results

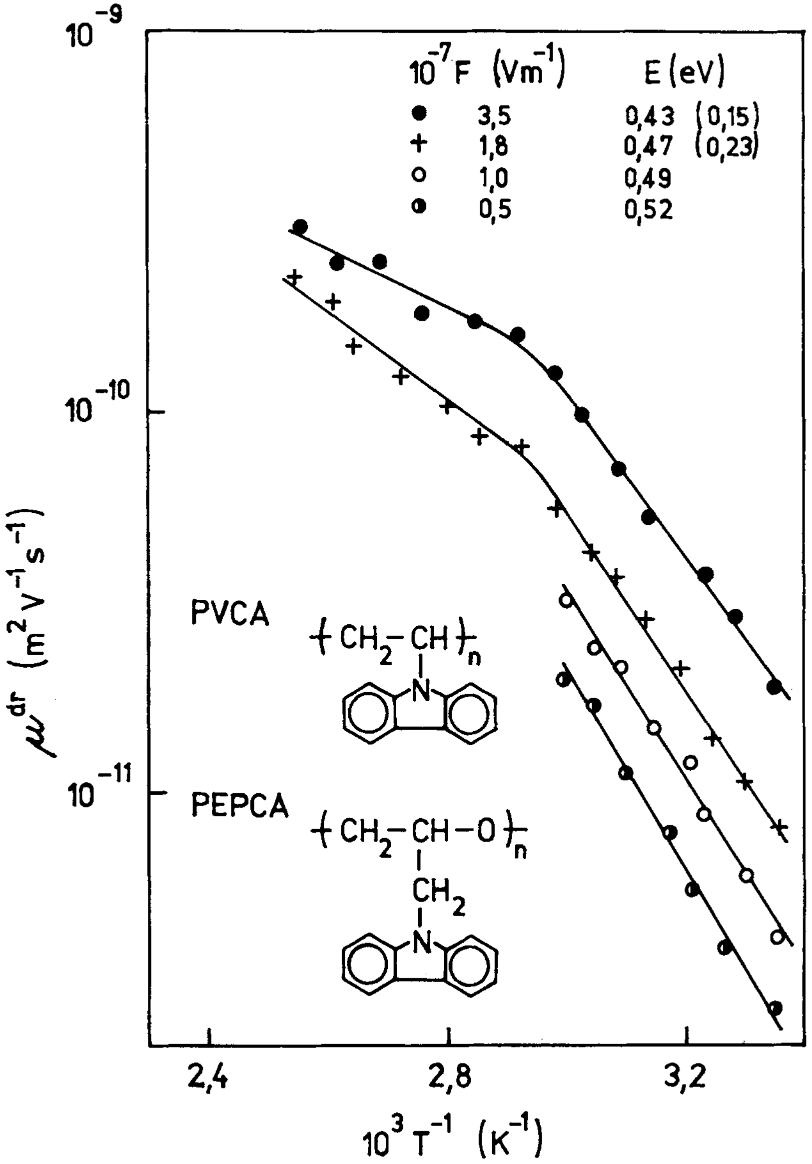

Figure 1 . Temperature dependence of the drift mobility μ^{dr} of holes in PVCA:PEPCA = 1:1 molar ratio mixture. F represents the applied electric field intensity and E is the activation energy of μ^{dr}

in irreversible increase of the transit time distribution, similar to the case of PVCA samples.

It follows from the above given experimental facts that the charge transport in polymeric semiconductors can be strongly influenced by dynamic disorder - fluctuating local potentials due to molecular motions. Especially layers of PVCA:PEPCA = 1:1 mixture are convenient for the illustration of this phenomenon, because PVCA and PEPCA each other strongly differ in the value of the glass transition temperature. The glass transition temperature T_g^M of their 1:1 molar ratio mixture can be calculated according to the simplest method (POCHAN et al. 1979), which gives $T_g^M = 390$ K. This is just the temperature at which sudden broadening of the transit time distribution was found. As we also observed distinct reversible change of the activation energy of drift mobility of holes when heating the samples above 335 K as shown in Figure 1, we can conclude that some molecular motions are released at 335 K, that means closely above T_g^{PEPCA}. If their period is comparable to or shorter than the residence time of a carrier on a particular site, they can partially cancel the omnipresent static disorder potential. This is manifested in the decrease of the activation energy of drift mobility of charge carriers. Trap-controlled hopping mechanism is suitable for the explanation of these phenomena (ABKOWITZ et al. 1981).

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