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Crystalline Domains as Trapping States in Amorphous Materials

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Summary

The photoconductivity and thermostimulated currents were measured on amorphous and spherulitic layers of oligo(ethyleneoxy)2,5-di(anilino)terephthalate. The crystalline domains in the amorphous phase form new traps, c. 0,6 eV deep.

Introduction

Transport levels in organic molecular substances are many-electron interaction levels and can be considered as electronic polaron states. Quasi-free charge carriers move along with their electronic polarization by noncoherent hopping. A typical charge carrier residence or localization time between separate jumps is higher by several orders of magnitude than the relaxation time for electronic polarization of surrounding molecules; hence, electronic polarization can be described in the framework of microelectronic approximation as a charge-induced dipole interaction. Since the interaction energy between a localized charge carrier and the induced dipole on the i-th surrounding molecule depends on their distance as r_i^{-4} (SILINSH 1980), the electronic polarization energy is determined by the topology of molecules in the solid. Every deviation of intermolecular distance from its mean value produces a corresponding change in energy. Local states which act as charge carrier traps in a molecular crystal may be formed in the regions of compression (SILINSH 1970, SWORAKOWSKI 1970), where the local polarization energy value (P) is higher than the polarization energy in the material situated far from the compressed region. The depth (E_t) is then equal to the energy change

$$\Delta P = E_t \approx \sum_{i=1}^{N-1} (dP/dr_i)\Delta r_i = 2e^2\alpha \sum_{i=1}^{N-1} \Delta r_i/\bar{r}_i^{\,5} ,$$

where Δr_i is the deviation of intermolecular distance from its mean value $\bar{r}_i$, e is the magnitude of the elementary charge and α is the molecular polarizability.

It may be assumed that a similar effect may be expected also in amorphous materials and polymers and that the boundary of the sites with higher density, i.e. predominantly crystalline or otherwise packed regions, would act as traps for charge carriers and excitons. The assumption was tested on thin layers of oligo(ethylenoxy)2,5-di(anilino)terephthalate(DTA), and the

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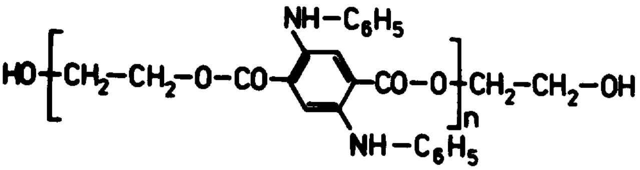
charge carrier traps which appear as a result of the formation of ordered domains in the amorphous phase were studied.

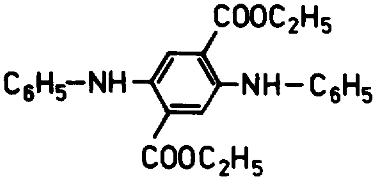


Oligo(ethyleneoxy)2,5-di(anilino)terephthalate

The depth of the traps was determined from the activation energy of photoconductivity and the isothermic photocurrent decay (IDC) and compared with the value obtained by means of the thermostimulated current (TSC) method.

Experimental

The oligomer DTA was a mixture of dimers, trimers, tetramers and pentamers in the ratio 2.0:2.0:1.6:1.0, and was prepared by a reaction of ethyl-2,5-di(anilino)terephthalate with 1,2-ethanediol in the presence of calcium acetate and antimony (III)oxide.



Ethyl 2,5-di(anilino)terephthalate

The reaction was carried out without the presence of solvent, merely by heating the compounds to the reaction temperature 470 K in a stream of inert gas.

Amorphous samples of the oligomer(DTA-A) were prepared from melt between two uviol glasses coated with SnO_2. A change in the supermolecular structure was achieved by heating them to the phase transition temperature T_g 322 K (see differential thermal analysis curve 4 in Fig.1a) followed by cooling in the vacuum 10^{-3} Pa. The procedure was repeated several times and resulted in the formation of spherulitic structures (DTA-S). The dimensions of spherulites as determined by microscopic measurements and light scattering analysis varied between 90 µm and 130 µm. The procedure was reversible: the ringlike character of structural formations disappeared when the samples were heated above T_g for a longer time.

Electric and photoelectric measurements were performed in a vacuum higher than 10^{-3} Pa by the usual electrometric techniques.

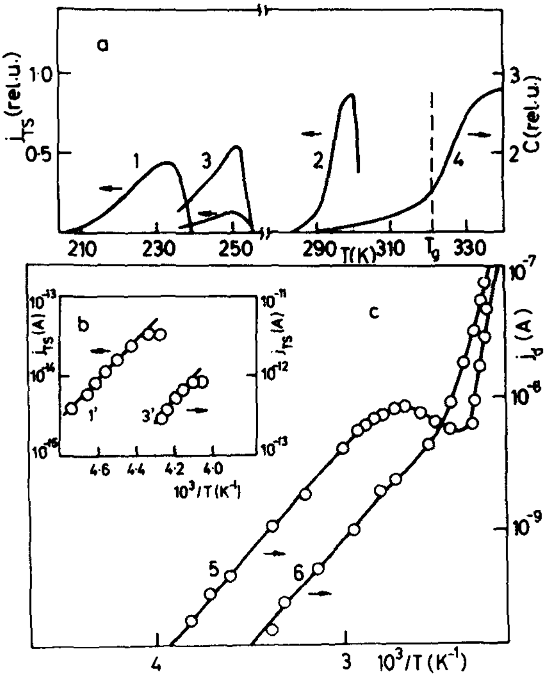


Fig.1. Thermally stimulated current curves: DTA-A - curves 1, 1´ and 2, DTA-S - curves 3 and 3´. Curve 4 - differential thermal analysis. Curves 5 and 6 are the dependences of dark current on reciprocal temperature; 5, DTA-A, heating rate 0.003 K s^{-1}, 6, DTA-A (partially DTA-S), equilibrium heating

Results

A. Amorphous DTA samples (DTA-A)

Traps were investigated by emploing the technique of thermostimulated currents. The traps were filled by irradiation at T~175 K and also by injecting charge carriers from the electrode in the regime of space-charge-limited current. The samples were subsequently heated with temperature increasing linearly with time. The thermostimulated currents possessed the usual properties which have been discussed many times in the literature (e.g. KOKADO and SCHNEIDER 1964, WOODS and NICHOLAS 1964): (i) the maximum on the TSC curve shifts to higher temperatures (T_m) with increasing rate of heating, (ii) with extended time of trap filling the number of occupied traps increases, which leads both to a rise in the magnitude of the TS current and to a shift of the position (temperature) of its maximum, (iii) with increasing voltage applied to the sample the temperature of the maximum increases but the magnitude of the activation energy remains unchanged (as derived theoretically by DEWAUX and SCHOTT (1967)). No light emission was observed during the heating process. The trap depth was evaluated by employing a method based on an analysis of the shape of the TSC peak. All the limitations of the method (GARLICK and GIBSON 1948) as well as the HAAKES (1957) assumption that TSC should be at least ten times larger than the dark current were respected.

The TSC peak was observed (heating rate $\beta = 0.011$ K s^{-1}) at a characteristic temperature $T_m^1 = 235$ K (peak 1, Fig. 1a) which belongs to traps $E_t^1 = (0.51 \pm 0.05)$ eV. The frequency factor ν calculated from the equation (HEARING and ADAMS 1960) $\nu T^{*2}/\beta E_t = \exp(E_t/kT^*)$ is $\nu^1 = 2 \times 10^{10}$ s^{-1}. The traps influence both the activation energy of photocurrent (E_{ph}) and the photocurrent dark decay. The magnitude of the activation energy of the photocurrent in the temperature range 263 $K<T<294$ K is $E_{ph}^A = (0.50 \pm 0.05)$eV and is voltage-independent. If one assumes that the temperature dependence of drift mobility is small, the temperature dependence of the space-charge-limited photocurrent may be explained by a change in the concentration of trapped carriers (MEIER 1958, NEŠPŮREK et al. 1981) and, for shallow traps, the trap depth may be determined directly as the activation energy of the photocurrent.

The experimental isothermic photocurrent decay curves (Fig.2a) may be divided into three regions: (i) the initial rapid decay connected only with the recombination of free carriers, (ii) the central part, connected with the emptying of shallow traps, (iii) the slow decay process connected with the emptying of deep traps. The central part of the relaxation curves is linear when plotted as log j_{ph} vs. t providing information on the depth and frequency factors of traps which predominate in the decay process. The j_{ph} t vs. log t (IDC) curves (SIMMONS and TAM 1973) for various temperatures are given in Fig. 2b.

The $\ln\tau$ vs. T^{-1} dependence (Fig.2c) (where τ is the position of the maxima of IDC curves) has been used to determine the depth of traps, which has been found to be $E_t^A = (0.49 \pm 0.05)$eV. The frequency factor $\nu^A = 1/\tau_o$ $(1/T = 0) = 8 \times 10^8 s^{-1}$ is in good agreement with the value obtained from TSC measurements.

The traps in the amorphous phase may be characterized as chemical traps connected with impurities which however may also form structural defects acting themselves as traps. A different sort of traps probably lies behind the existence of the TSC peak 2(Fig.1), which is situated at the beginning of the glass transition (T_g) region. The peak is connected with the release of charge carriers from traps due to molecular relaxation motions. The traps are specific, occurring in polymeric and amorphous materials only and having no analogy in molecular crystals. Here, the detrapping probability can be described by a simple equation which correlates the distance between the neighbour molecules and the energy difference (trap depth) which in turn also includes the polarization energy. The mobility of the chain elements may lead to a decrease in the trap depth by changing the molecular orientation, or even traps may be destroyed and the released carriers contribute to the TSC peak.

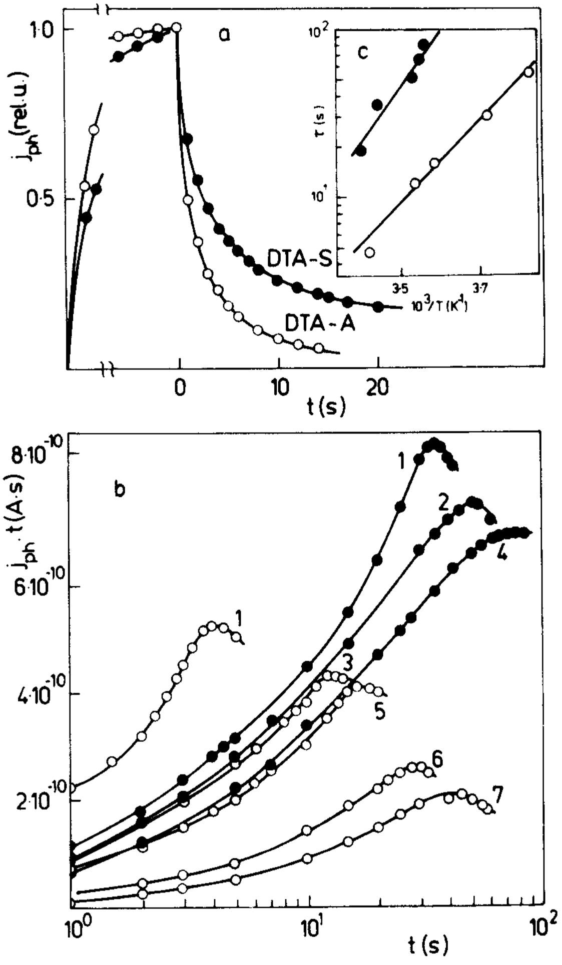


Fig.2. a - relaxation photocurrent process for DTA-A and DTA-S; λ = 625 nm, T = 219 K. b - isothermic decay current curves for DTA-A (empty circles) and DTA-S (full circles); 1 - T = 291 K, 2 - T = 283 K, 3 - T = 282 K, 4 - T = 281 K, 5 - T = 279 K, 6 - T = 267 K, 7 - T = 261 K. c - dependence of log τ on reciprocal temperature

The decrease of intermolecular distance during molecular vibrations and rotations causes also an increase of the charge transfer probability which then competes with energy dissipation. Thus, the increase of molecular mobility due to rising temperature changes the trap structure (both trap depth and the transition probability are affected), and carriers are released simultaneously. Another posibility is the release of space charge as soon as the relaxation process appears. The mobile chain segments "shake off" the charge carriers which then contribute to the thermostimulated conductivity.

Curves 5 and 6 in Fig.1c represent the temperature dependence of the dark current (curve 5 for the heating rate $0.003 Ks^{-1}$ and curve 6 for the equilibrium heating).
The activation energy of the Ohmic dark current is $E_{a1} = (0.93 \pm 0.05)$ eV for $T<T_g$ and $E_{a2} = (2.3 \pm 0.1)$ eV for $T>T_g$. A strong change in the activation energy has been observed in the phase transition region. The dark activation energies E_{a1} and E_{a2} depend on the applied voltage and decrease if the latter rises.

B.Spherulitic DTA samples (DTA-S)

The influence of spherulitic structures in the amorphous phase on the trapping of charge carriers was investigated on DTA-S samples by the same techniques as before. A new TSC peak (3 in Fig.1a) was observed at $T_m^3 = 252$ K, characterizing traps of the depth $E_t^3 = (0.60 \pm 0.05)$ eV with the frequency factor $\nu^3 = 5x10^{-10}\ s^{-1}$. The traps may be characterized as "structural". They are influenced by the formation of spherulites and their density depends on spherulite concentration. The TSC of these trap does not form peaks in amorphous samples. Similarly as before, the traps influence both the decay and activation energy of the photocurrent. The samples with the spherulitic structure show a much longer photocurrent decay (Fig.2a). The central part of the relaxation curves is again linear in the log j_{ph} vs. t plot.

The IDC curves yield the depth of traps $E_t^S = (0.60 \pm 0.06)$ eV and the frequency factor $\nu^S = 1x10^9\ s^{-1}$. The magnitude of the activation energy of photocurrent (again voltage independent) in the temperature range $263 K<T<249<K$ was found to be $E_{ph}^S = (0.62 \pm 0.05)$ eV.

It is interesting to note that the depth of structural spherulitic traps in the amorphous phase and of traps in polycrystalline material are roughly the same. The predominant traps in the amorphous material are shallower. The energy distribution of traps is Gaussian, as follows from the space-charge-limited current-voltage curves (NEŠPŮREK and SILINSH 1976, NEŠPŮREK 1974, NEŠPŮREK and SMEJTEK 1972), with a characteristic standard deviation $\sigma = (0.10 \pm 0.03)$ eV for the DTA-A samples as determined from the dependence of photo-current on light intensity (NEŠPŮREK et al. 1981).

Conclusions

The parameters of traps were obtained by two independent measurements viz. by the method of thermostimulated currents and from the decay curves of photocurrent. Both methods yield the same values of the trap depths and frequency factors. Trap 0.51 eV deep are typical of the amorphous phase. The spherulitic ordered regions form new traps, 0.6 eV deep. Trap depth values are in agreement with the respective activation energies of photocurrent, $E^{A}_{ph} = (0.50 \pm 0.05)$ eV and $E^{S}_{ph} = (0.062 \pm 0.05)$ eV. The measurements have shown that the boundaries of the ordered or crystalline regions in the amorphous phase form traps of a new type for charge carriers.

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