Polymer Bulletin 8, 187–192 (1982)

Polymer Bulletin

Chain and Carrier Mobility in Polymer Systems as Investigated by Thermally Stimulated Current Techniques

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From the International Seminar on Polymer Physics, High Tatra, CSSR, April 1982

Summary

The results of TSC and TSD measurements carried out on polymers were analysed in terms of the influence of chain element motions on the release of charge carriers. Due to the relaxation processes occurring with increasing temperature the mobile chain elements "shake off" charge carriers leading to the charge release correlated with molecular mobility. This effect, called the "wet dog effect", was shown in TSD and TSC experiments carried out on polycarbonate films doped with different amounts of suitable additives (antiplasticizers) and it was related to the chain mobility modification of detrapping phenomena. This study shows that a correlation between particular peak positions in TSC, TSD, TL experiments and carrier motion or dipolar relaxations must be done very carefully.

Introduction

The elucidation of the mechanism of electric conductivity in polymeric materials consists in the determination of the carrier generation process and their transport in the bulk of material. In polymeric systems which belong to dielectrics there is no practical possibility for intrinsic generation of carriers. This fact is related to widely separated energy bands of saturated polymeric chains and to the weak interactions between the chain elements. The same observation is valid for many unsaturated polymers. However, in this case, a particular structure of polymer molecules makes possible narrow band formation and, if these systems show an ordered structure (partial crystallinity), an intrinsic generation of carriers is not excluded. These materials exhibit semiconducting properties especially when doped with suitable donors or acceptors. In the case of the formation of strong charge-transfer complexes or partially oxidized states one can observe a high conductivity in analogy to highly conducting low molecular weight charge-transfer complexes.

Our discussion will be mostly related to polymeric dielectrics, that is to materials in which intrinsic carrier generation can be neglected. In this case, charge carriers are injected from electrodes or generated from donor or acceptor centres, e.g. Poole-Frenkel centers. These carriers are trapped at different trapping centres and released due to illumination or heating up the specimen under study.

At temperatures below and above the glass transition there

0170-0839/82/0008/0187/$01.20

are molecular motions connected with small-chain-element, side-chain or cooperative rotations of chain segments. There arises the question how these molecular motions in polymers influence the detrapping of charge curriers. The aim of this discussion is to throw light on that matter.

General remarks on dielectric properties of polymers in the solid state and their relation to molecular mobility

Studies of dielectric loss and permittivity have become a well established and frequently used method of probing of molecular motion in polymeric systems. There are a number of excellent reviews related to this field which will be not quoted here.

The temperature dependence of tg δ or ε' provides many information on the activation enthalpy ($\Delta H^{\neq}$) and entropy ($\Delta S^{\neq}$) as well as information on the free volume. Individual processes, when resolved, are conventionally labeled α, β, γ in the order of increasing frequencies for maximum loss at constant temperature (f_{max}) or decreasing temperatures for maximum loss at constant frequency (T_{max}). Coalescence of some of these processes at certain temperatures is always observed because loss peaks obtained for solid polymers are generally much broader than for a Debye process but the use of alternative relaxation techniques such as mechanical and ultrasonic, techniques or NMR (both ^{1}H and ^{13}C) frequently helps to locate under which perturbation the relaxations are active.

Recently, the classical technique of dielectric spectroscopy at constant temperature or at constant frequency was completed by thermally stimulated depolarization (TSD) and thermally stimulated current (TSC) techniques. The basic problems related to these methods are discussed in many reviews (e.g.1). Thus, we would like to mention that TSD and TSC have a good diagnostic value in studies of molecular motions in polymeric dielectrics and in investigating the carrier release in dielectrics, semi- and photoconductors. In a particular case when carrier injection into a sample is possible and subsequent trapping of carriers occurs heating may thus result in the appearance of peaks which can be related to dipol reorientation, charge release (electrons or ions) and interfacial polarization. There are methods allowing a distinction to be made between these phenomena as they appear in TSD or TSC spectra; thus, there are possibilities to study the correlation between molecular motion and the above mentioned effects.

Thermally stimulated currents and molecular mobility of polymer chains

There are data in the literature related to thermally stimulated depolarization (TSD), thermally stimulated currents (TSC) and thermoluminescence (TL) studies in which it was shown that peak positions, activation energies etc. corresponding to the release of trapped curriers are correlated with those carriers liberated due to molecular mobility obtained by means of dielectric and mechanical measurements [1 - 4].

In the TSD experiments one often observes a "ρ-peak" which is ascribed to the release of space charge. This peak appears always near Tg and sometimes overlaps the α-peak, e.g. for PMMA [1] .

In the TSC experiment, when the temperature is increased, the trapped charge carriers are released at a certain temperature T_r, depending on the trap parameters and the heating rate. However, if the relaxation process takes place at a temperature below T_r the mobile chain segments "shake off" the carriers - - this phenomenon we call the "wet dog effect" [5] .

The frequency factors in the Arrhenius law, as determined by thermal methods (TSC, TL), are usually much lower than the theoretically predicted, being ca. 10^{12} Hz, and they are in many cases temperature-dependent which suggests the influence of molecular motion [4] .

This phenomenon can be attributed to the fact that the traps become destroyed and that the liberated carriers contribute to the TSC peak [6] . The trap depths determined at low temperature by optical bleaching or photon-stimulated current technique (PSC) are often much higher than those deduced from TSC or TL data [7,8] which also suggests that a trap destruction occurs.

Experimental

In order to study the "wet dog effect" we have investigated polycarbonate (PC) (poly/bisphenol-A/carbonate) with antiplasticizing agents: TCNQ, TCNE and chlorinated bisphenols added at different concentrations. Thin films (20 μm) were obtained by casting from a mixture of methylene chloride and ethylene chloride, dried and provided with evaporated gold electrodes (the upper one semitransparent) and a guard ring. The TSC spectra were measured after excitation at -196°C (illumination with visible light in an electric field 10^5 V/cm) and 20 min depolarization. The TSD were measured after polarization in the dark ($E=10^5$ V/cm) at 100°C, cooled to -196°C with the voltage applied and the depolarization and this temperature for 20 min. The heating rate was 5 deg/min. The details of the measuring equipment are given in [9] . Partial heating experiments were performed in the standard way.

Results and discussion

The results of the TSC and TSD studies for pure PC samples and for PC films containing 1% and 3% by weight of TCNQ are shown in Fig.1. Similar TSC and TSD spectra were obtained for TCNE and chlorinated bisphenols.

The additives used cause a shift of the β-relaxation due to their antiplastiazing effect. The T_{max} values of corresponding TSD peaks are shifted to higher temperatures than those found for pure PC samples. The TSC peaks related to the release of charge carriers shift accordingly [10] .

This shows that modifications of relaxation processes in the samples containing different amounts of additives under study, related to the β-relaxation (TSD), are connected with similar modifications of the detrapping phenomena.

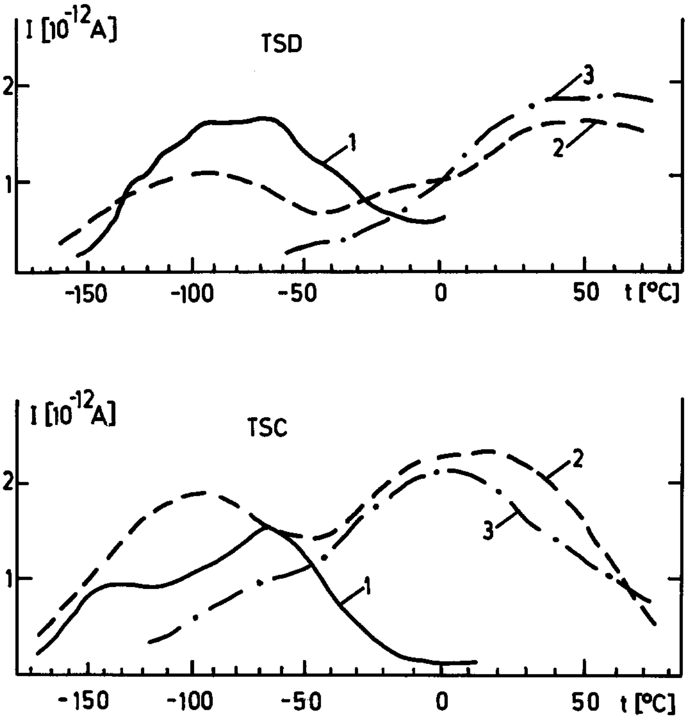

Fig.1. TSD and TSC spectra of pure and doped polycarbonate in the β-relaxation region, 1-pure PC; 2-PC+1%TCNQ; 3-PC+3%TCNQ

The results of partial heating experiments show that β-relaxation in PC consists of several distinct processes. The activation energies E_a were found to be 0.12, 0.25 and 0.36 eV. The partial heating technique applied to TSC experiments leads to similar values of activation energies, but they are somewhat lower being equal to 0.11, 0.17, 0.35 eV, respectively. It is interesting to note that the temperature ranges at which straight lines in the E_a vs. T plots obtained from TSD and TSC partial heating experiments are similar (those for TSC are a little shifted to higher temperatures).
The TSD and TSC spectra for samples containing 1% and 3% by weight of TCNQ, which is an antiplasticizing agent, are shifted towards higher temperatures and the maxima are now above 0°C. The activation energies E_a derived from TSD partial heating experiments are higher for doped samples, while the E_a values for TSC remain almost unchanged. The important fact found in partial heating TSC studies is that the temperature ranges, at which straight lines in the E_a vs. T plots occur, are shifted to higher temperatures, e.g. from -50°C to 20°C for E_a=0.35 eV. Similar shifts were observed for the lower E_a values in accordance with the shift of the corresponding

relaxation processes found in TSD.
The results of TSD and TSC investigations of PC films doped with TCNE and chlorinated bisphenols have a similar character; thus, they will be not discussed here in detail [6,9,11].

The above mentioned effects can be discussed from the viewpoint of activation energy change and detrapping probability modification both related to the variation of chain mobility.

The detrapping probability v_{ij} can be expressed by a simple formula:

$$v_{ij} = v_o \exp (- \gamma R_{ij}) \exp \left[- \frac{E_{ij}}{kT} \right] \qquad (1)$$

where R_{ij} denotes the distance to the neighbour molecule, E_{ij} the energy difference (trap depth) which includes polarization energy, v_o is the frequency factor and γ a factor depending on intermolecular overlap integrals.

It follows from this equation that the detrapping process occurs when the trapped carrier is excited to a sufficiently high energy level which is greater than the trap depth and that the transfer of charge carriers in the excited state must be fast to compete with the energy dissipation processes. Otherwise, the excitation energy will be dissipated and carriers will be still fixed in the trap.

The mobility of chain elements may lead to a decrease of the trap depth by changing the molecular orientation which yields high polarization energy. This effect seems to be of some importance. It is due to the fact that in the case of structural defects as well as chemical defects (additives with different ionisation energies or different electron affinities or dipol moments in comparison with matrix molecules) the changes of E_{ij} values, in the range of the electrical fields usually applied, cannot be neglected. However, it seems that the decrease of the intermolecular distance during molecular vibrations and rotations causes first of all an increase of the charge transfer probability influencing mainly the first exponential term in eq.1. In this case charge transfer can be more probable than energy dissipation. In the literature there are data on the increase of charge transfer probability with the change of intermolecular distance, based on approximate calculations made for very pure crystals. Petelenz [12] has shown that for antracene decrease of intermolecular distance by 10% causes an increase of charge transfer probability by an order of magnitude.

To conclude, one can say that, when the molecular mobility increases due to arise in temperature and when the trap structure is affected (both trap depth and transition probability), then carriers will be released simultaneously. This effect can also influence the results of dielectric measurements usually interpreted in terms of dipolar relaxation only, but the role of carrier release from traps may also be important in such experiments. On the other hand, relaxation phenomena related to the increase of the mobility of chain elements (also in nondipolar solids) can influence the charge carrier release thus appearing in electrical measurements.

Studies of these effects can furnish important information on the electrical behaviour of polymer materials when modified by additives and/or thermal treatment.

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Received May 17, accepted after revision August 9, 1982