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POSITRONIUM ANNIHILATION STUDIES OF POLYCARBONATE, POLYETHERSULPHONE AND POLYSULPHONE

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Abstract—Positron annihilation studies are reported on polycarbonate polyethersulphone and polysulphone over the temperature range 260–370 K. The data were analysed into three components, the longest lifetime-*o*-component is associated with the pick-off mechanism; a linear variation of that component with temperature was observed. Using ultrasonic velocity data, the free volume distribution was calculated; its magnitude and temperature dependence are discussed in relation to the mechanical properties of the polymer.

INTRODUCTION

Polycarbonate, polyethersulphone and polysulphone are well known high temperature thermoplastics and are often given the generic name "engineering plastics". These polymers all contain *p*-phenylene structures and their relaxation properties have been investigated extensively [1–7]. The technological importance of these polymers stems from their high temperature characteristics and good impact strength at room temperature [8]. Ultrasonic and dynamic mechanical measurements have been reported [7, 9] and indicate facile molecular motions of the polymer at room temperature. It has been proposed that the high impact strength of these polymers is related to a large free volume in these polymers below their glass transition temperature T_g [10]. It was concluded from the dielectric and ultrasonic measurements [7, 9] that the beta relaxations in these polymers have a common origin and that the processes being observed can be associated with local motions of the polymer backbone and have activation energies of 40 kJ/mol for polycarbonate, 13.1 kJ/mol for polyether sulphone and 16.6 kJ/mol for polysulphone. This latter process is associated with a coupled rotation of the phenylene ring and the polar backbone link.

The positron annihilation technique has been used previously for the investigation of the glass to rubber transition in many amorphous and *p*-crystalline polymers [11]. In a recent study of supercooled *o*-terphenyl [12] and polyphenylene oxides [13], it was demonstrated that the *o*-positronium (*o*-Ps) lifetime was a function not only of the number of voids which exist in the system, but also a function of the changes in the shape of the cavity during the *o*-Ps lifetime. Studies of poly(alkyl methacrylate) [14] have further indicated how side-chain motions can influence the temperature dependence of the *o*-Ps lifetime. In this study no such side-chain motions are possible; however, the motion of short elements of the backbone can be identified with the beta relaxation.

EXPERIMENTAL

Materials

The polycarbonate–poly(4,4′-dioxydiphenyl-2,2′-propane carbonate) samples were prepared from commercial material, Bayer Makralon. The samples of polysulphone and polyether sulphone were supplied by ICI Ltd. The samples were pressed in the form of discs which were cut into squares approx. 2 cm^2 for the positronium studies. Details of the physical characteristics of the polymers have been published [9].

Positronium annihilation measurements

The positronium lifetime measurements were performed using a standard fast–slow coincidence configuration [15]. The sample was degassed and sealed with a [^{22}Na]-Kapton foil source in a Pyrex tube. The experimental system consists of two plastic fast scintillators (NE111) coupled to fast photo-multipliers (Mullard XP2230) and mounted in line on an Oxford Instruments DC-2 cryostat. This configuration allows the sample to be investigated over a temperature range 260–400K with a control of temperature of better than ±0.1K. The time resolution of the system was determined from the prompt curve of a ^{60}Co-source and was found to be better than 400 psec. The source correction was determined by measuring the positron annihilation lifetime of benzophenone crystals. Approximately 5×10^5 events were stored for analysis in each spectrum and the lifetimes were determined using the Positron Fit Extended computer program [16, 17].

Inspection of the matrix of correlation coefficients indicated that the correlation between the two shortest lifetime components (τ_1 = 125 psec and τ_2 = 430 psec) was large, indicative of strong interaction in the fitting of these data and hence resulting in a large uncertainty in the intensities. The longest lifetime component was clearly resolved at all temperatures and exhibited low correlation coefficients with the other components. The uncertainties of τ_2 and τ_3 were estimated to be ±0.01 and 0.02 nsec respectively. Within the precision of these measurements, the shortest lifetime components do not exhibit a defined temperature

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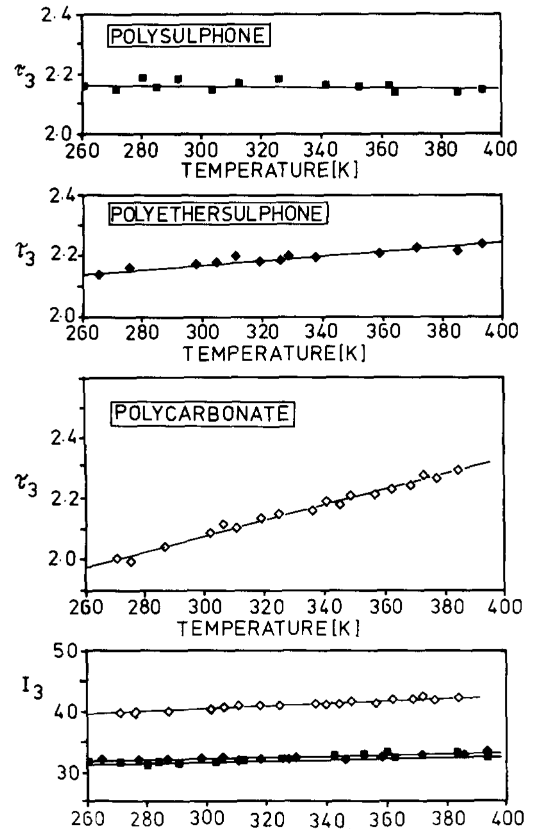

Fig. 1. Variation of the o-positronium lifetime and intensity for polycarbonate, polyethersulphone and polysulphone as a function of temperature. Polysulphone—■; polyethersulphone—◆; polycarbonate—◇.

dependence. The longest lifetime is, however, markedly sensitive to the temperature of observation.

RESULTS AND DISCUSSION

Temperature dependence of the o-*ps lifetime*

The observed variation of τ_3 with temperature (Fig. 1) for the three polymers is approximately linear. The temperature dependence in the case of polycarbonate is considerably greater than in either the polysulphone or polyethersulphone. It is of interest to note that lifetimes of the order of 2.0 to 2.2 nsec are very high for a polymer below its T_g. Values of τ_3 of approx. 1.0–1.2 nsec are observed for crystalline organic solids [18], whereas values of 1.2 to 1.6 nsec are typical for amorphous-glassy solids below T_g [11]. The values observed of τ_3 between 2.0 and 2.2 nsec are typical of those found above T_g. In an attempt to estimate the free volume in the materials, we use the approach of Ujihira [18]. It has been found that a strong correlation exists between the free volume and the o-positronium lifetime [18]. Using previously published data [9], the free volume radius was calculated (Fig. 2). The free volume estimated on the basis of the ultrasonic data exhibits a more marked temperature dependence in the polyethersulphone and polysulphone than in polycarbonate. This is in contrast to the temperature dependence of the o-positronium lifetime. A possible explanation is that, as the temperature is raised, the extent to which the beta relaxation can influence the distribution of cavity sizes can increase. At room temperature (298K) the beta relaxation occurs in the megahertz region [9]. Extrapolation of the activation energy plots would indicate that only at the highest temperature (360K) will the o-Ps lifetime and the molecular relaxation times become comparable. This implies that the beta relaxation processes are unlikely to influence the o-Ps data. Recent studies of the viscoelastic properties of polysulphone [19] have led to the conclusion that the polymer behaves in solution as though it were a rigid rod. The sulphone group is believed to exert strong intramolecular interactions and hence lead to the requirement that motion must involve movement of many atoms. If strong intermolecular forces are excluded, because of the observation of a low second virial coefficient in solution, then stiffness of the chain appears to be the principal source of the high T_g. The beta relaxation in these polymers may be attributed to regions in which there is less perfect packing of the chains. The slope of the temperature dependence of the o-Ps appears to correlate approximately with the difference between the temperature of observation and T_g. The glass transition in polycarbonate (PC), determined from differential scanning calorimetry, was 416K; in polyethersulphone (PES) it was 461K and in polysulphone (PS) it was 500K. The slope in PC is higher than in PES which is in turn higher than in PS, which clearly is the order of variation of T_g. This implies that the beta and alpha processes are intimately connected and that the polymer can sustain, because of the backbone rigidity, a larger free volume than found in other glassy polymers.

Intensity of o-*Ps annihilation*

The probability of o-Ps formation depends on a number of factors. The positronium on entering the solid will generate radiation damage. The efficiency of this latter process can be described by either the Orr or spur models [20, 21]. The probability of thermalization of positronium will depend on the number of

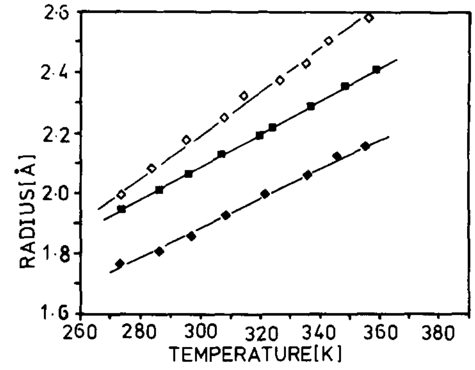

Fig. 2. Variation of the free volume radius as a function of temperature for polycarbonate, polyethersulphone and polysulphone. Polysulphone—◆; polyethersulphone—■; polycarbonate—◇.

voids present in the solid. The higher intensity in polycarbonate (Fig. 1) reflects a higher void content compared with the other polymers. This observation is consistent with the proposition that the high impact strength of polycarbonate is a consequence of a high free volume at room temperature.

CONCLUSION

The positronium annihilation studies on polycarbonate, polyethersulphone and polysulphone indicate that the mean free volume size in these polymers at around room temperature is comparable to that observed above T_g in many polymers. The *o*-Ps intensity is highest in polycarbonate; this implies a larger free volume density in this polymer which is consistent with the low density and high impact strength.

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