Nuclear magnetic relaxation of modified poly(*p*-phenylene sulfide)

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The influence of controlled purification and thermal treatment on the nuclear magnetic relaxation of poly(*p*-phenylene sulfide) (PPS) has been studied. The temperature dependence of spin-lattice relaxation times at 30 and 90 MHz in modified samples has been measured. High temperature annealing leads to an increase in the number of paramagnetic centres, which are most probably radical cations, and to the observed increase in molecular weight of PPS. Sustained purification and degassing of PPS causes the removal of low molecular weight oligomers and paramagnetic oxygen. This effect leads to non-exponential magnetization recovery.

(Keywords: poly(*p*-phenylene sulfide); n.m.r.; relaxation; thermal treatment)

INTRODUCTION

Poly(*p*-phenylene sulfide) (PPS) is a highly crystalline thermoplastic polymer with high thermal and chemical resistance. The glass transition temperature (T_g) of PPS is 365 K, the recrystallization temperature (T_r) is 400 K and the crystalline melting point (T_m) is 558 K[1]. The degree of crystallinity of PPS, determined by X-ray diffraction, is typically 65%[1]. A range of materials differing in degree of crystallinity and molecular weight, denoted Ryton PPS V-1, P-2, P-3, P-4 and R-6, are commercially available (Phillips Petroleum Co., USA)[2]. Depending on molecular weight, these materials are used as anti-adhesive and corrosion-resistant coatings and can be injection and compression moulded in the manufacture of machine components[2]. PPS is also used in the production of thin films on a laboratory scale.

^{1}H n.m.r. investigations were conducted mainly on pristine Ryton PPS V-1 before and after purification[3,4] and on Ryton PPS P-4 and R-6[3]. Spin-lattice relaxation times, T_1 and $T_{1\rho}$, at 15, 30, 90 MHz and 42, 45 kHz, respectively, were measured over a wide temperature range. T_1 was exponential in all cases. The activation energy (11 kJ mol^{-1}) determined from the observed temperatures of T_1 minima at 15 and 30 MHz is similar to that determined for phenylene sulfide oligomers[3]. A similar result was also determined from the linear slopes of the temperature dependence of T_1 at 90 MHz and was attributed to rotation of phenylene groups around the sulfur–phenyl–sulfur axis. Furthermore, it is suggested[4] that an additional relaxation mechanism, related to interactions of protons with paramagnetic centres, is operative in the low temperature range. The temperature dependence of the relaxation times in the thermally treated samples Ryton PPS P-4 and R-6 are alike, but they differ from the analogous response of Ryton PPS V-1[3]. After thermal treatment, the low temperature relaxation minima disappeared and the relaxation times shortened in the low temperature regime. Both these facts were attributed to an increased contribution of spin diffusion in the relaxation process[3].

The purpose of this paper is to provide a detailed analysis of the influence of controlled purification and thermal treatment on n.m.r. spin-lattice relaxation in PPS.

EXPERIMENTAL

The starting material was Ryton PPS V-1 (Phillips Petroleum Co., USA). The polymer was subjected to thermal treatment in vacuum for 6 h at 473 K (sample I). A different type of thermal treatment was used to produce thin films from PPS: the polymer powder was melted at ~580 K under a pressure of 0.03 MPa in a vacuum of ~1.3 mPa, followed by rapid cooling in a mixture of alcohol and dry ice[5] (sample II). The degree of crystallinity of this film determined by X-ray diffraction was 31%[6].

The initial polymer was also subjected to extraction in water and tetrahydrofuran on a Soxhlet column (170 purification cycles). The resulting sample was 99.19% pure with an empirical formula of $C_6H_{3.96}S_{0.95}$. The sample was then dried in a vacuum of 1.3×10^{-2} Pa for 7 days (sample III). Samples I, II and III were placed in n.m.r. tubes and sealed under vacuum.

Spin-lattice relaxation times in all cases were determined from the 90°–τ–90° pulse sequence on a home-made pulse spectrometer[7] and a Bruker spectrometer operating at 30 MHz over a wide range of temperatures. In order to compare our results with literature data[4], additional T_1 measurements exploited the 180°–τ–90° sequence applied to sample III on the Bruker pulse spectrometer operating at 90 MHz.

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RESULTS AND DISCUSSION

Exponential T_1 decay was observed for the thermally treated PPS (samples I and II) over the whole temperature range (*Figure 1*). Analogous results for Ryton PPS V-1, P-4 and R-6 are shown in *Figure 2*. Clearly, heating PPS in vacuum at 473 K results in an increase in T_1 over the whole temperature range and in a shift of the high temperature minimum towards lower temperatures. The increase in T_1 may be due to the removal of paramagnetic oxygen atoms from the sample. An analogous effect was observed for Ryton PPS R-6[3]. The shift of the T_1 minimum, mentioned above, and the noticeably smaller slope of the temperature dependence of T_1 near the minimum, indicates more facile molecular mobility in the heated and evacuated sample. This may be related to the fact that molecular structure becomes more similar to that at thermodynamic equilibrium as a result of annealing above T_r.

The temperature dependence of T_1 for the melted film (sample II) differs significantly from the initial material and the polymer heated at 473 K (sample I). T_1 decreases over the whole range of temperatures and the low temperature minima disappear. On the other hand, the T_1 *versus* temperature responses for the film and the thermally treated Ryton PPS R-6 are identical[3] (*Figure 2*).

Paramagnetic relaxation has been invoked before[8] in systems where T_1 values level off and do not follow the strong temperature dependence. Thus the character of T_1 *versus* temperature for the film points to a greater contribution of spin diffusion to paramagnetic centres in the process of relaxation. Since the amount of paramagnetic oxygen is inevitably less in the annealed film, the relaxation centres must be other than oxygen. In the course of the PPS polycondensation process, radical cations are formed as unstable reactive intermediates[9]. It is assumed that the reaction leading to increase of molecular weight takes place in the melted polymer[10]. In the course of this reaction radical cations must appear. Rapid cooling of the melt during film processing causes rapid termination of the reaction and results in 'freezing' of radical cations; these are the reactive intermediates. Therefore, the number of paramagnetic centres in the film increases, relative to the initial material. A similar increase in the number of paramagnetic centres, when PPS was heated, was also observed by e.p.r.[11]. By analogy one can assume that a similar process takes place in Ryton PPS R-6 during high temperature thermal treatment[2].

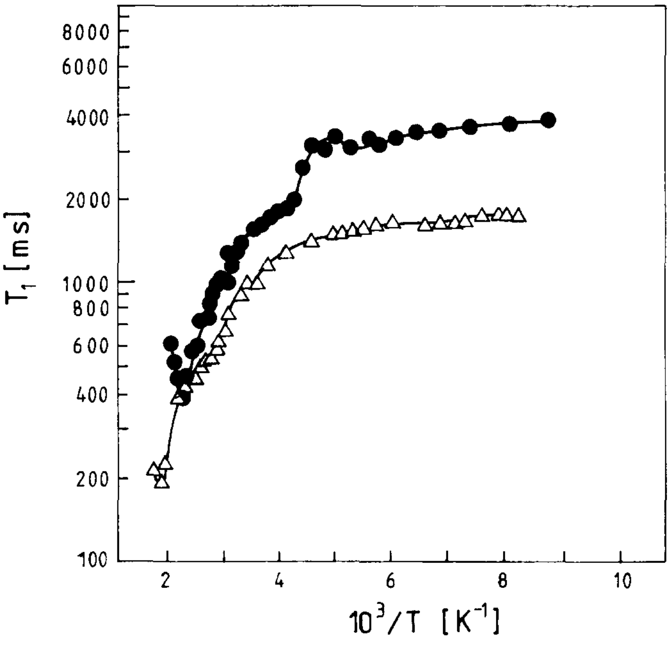

Figure 1 Temperature dependences of relaxation times: (●) Ryton PPS V-1 heated at 473 K for 6 h (sample I); (△) film obtained from Ryton PPS V-1 by means of heat treatment (sample II)

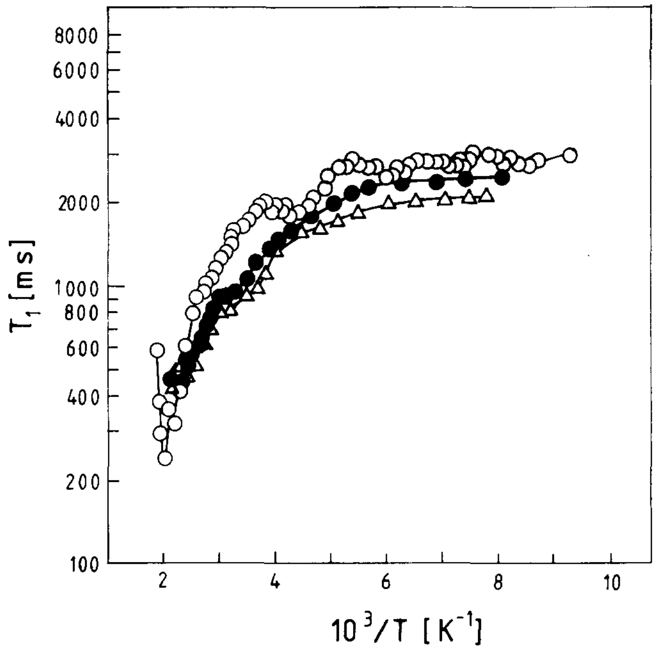

Figure 2 Temperature dependences of relaxation times[3]: (○) Ryton PPS V-1; (●) Ryton PPS P-4; (△) Ryton PPS R-6

Furthermore, it follows from a comparison of *Figures 1* and *2*, that the high temperature T_1 minimum for the film is shifted towards higher temperatures relative to that of the pristine polymer. This shift is caused by an increase in molecular weight of the polymer on annealing[12].

The activation energy of molecular motions responsible for the high temperature minimum was determined from the high temperature slope near the minimum for the film (*Figure 1*). It was $\sim 20\,\mathrm{kJ\,mol^{-1}}$, which is close to the energy of reorientation of phenylene rings around the sulfur–phenyl–sulfur axis near the glass transition in the amorphous region of the polymer[3].

T_1 is non-exponential in the purified sample Ryton PPS V-1 (sample III) at 30 and 90 MHz. This effect is more pronounced at lower temperature. Two components are resolved, as shown in *Figure 3*. Thus, purification and degassing as applied to sample III leads to non-exponential magnetization recovery in PPS, which has not been previously observed even for the purified sample[4].

PPS is a heterogenous system with a crystalline and amorphous phases, as confirmed by X-ray[1] and n.m.r.[3,4] methods. In the two-phase system, nuclear spin lattice relaxation can be exponential or non-exponential[13]. The relaxation is exponential when rapid spin diffusion between two phases occurs[14]. This phenomenon was observed in previous n.m.r. studies of PPS[3,4]. The impurities (oligomers, oxygen), mainly located in the boundaries between the crystalline and amorphous regions, increase the magnetic dipole interaction between protons in the two phases and promote the spin exchange

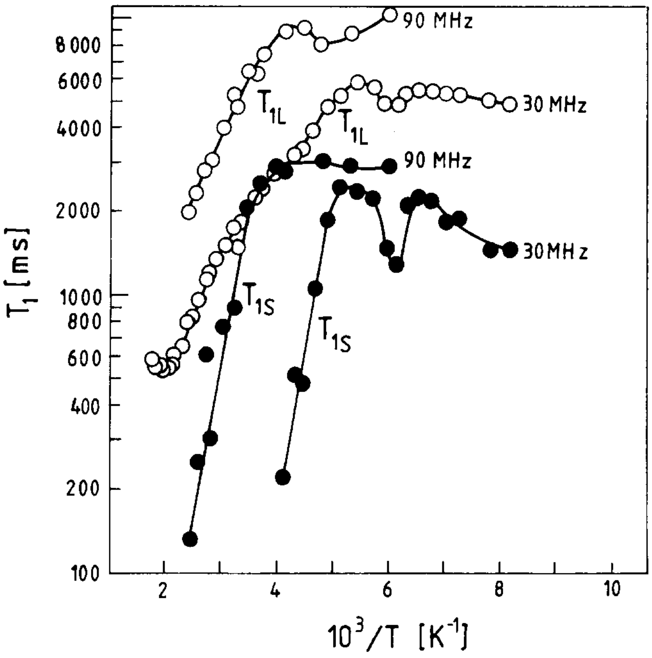

Figure 3 Temperature dependence of relaxation times for purified Ryton PPS V-1 (sample III)

between these phases. In this case a uniform spin temperature in the sample was established and only one relaxation time was observed. However, when the rate of spin exchange between two phases is lower than the highest relaxation rate of each phase, the magnetization recovery is non-exponential and two relaxation time components could be resolved[14]. This situation is observed in purified PPS (sample III). The removal of most of the impurities decreases the magnetic dipole interaction between protons in the amorphous and crystalline phases and thus the spin exchange is restricted.

The long spin lattice relaxation component, T_{1L}, is significantly higher than the T_1 for Ryton PPS V-1 observed so far, principally because care was taken to minimize paramagnetic oxygen in the polymer.

Activation energies, which are of the same order as those for the film ($\sim 20\,\mathrm{kJ\,mol^{-1}}$), were determined from low temperature slopes of the short spin lattice relaxation component, T_{1S}, *versus* temperature for both measurement frequencies. The activation energies were also determined from the low temperature slopes of T_{1L} *versus* temperature at 90 MHz and from the temperature shift of the low temperature minima at 90 and 30 MHz, as described in reference 3. The values of these activation energies are identical ($\sim 7\,\mathrm{kJ\,mol^{-1}}$). Similar magnitudes were determined for Ryton PPS V-1[3,4] and attributed to probable conformational motions of phenylene rings through the potential barrier between their equilibrium states.

CONCLUSIONS

Heating PPS in vacuum in a temperature range between T_r and T_m removes paramagnetic oxygen and the molecular structure approaches that corresponding to thermodynamic equilibrium. These effects cause T_1 to increase and the high temperature minimum to shift to lower temperatures. The activation energy of molecular motions is reduced relative to the initial polymer.

Heating PPS at temperatures higher than T_m followed by rapid cooling leads to an increase in the number of paramagnetic centres, which are most probably radical cations formed during the chain augmentation in the melt, and is reflected in the observed increase in molecular weight. These two effects cause T_1 to shorten and the high temperature minimum to shift towards lower temperatures relative to the initial polymer.

Sustained purification and degassing of PPS causes the removal of low molecular weight oligomers and paramagnetic oxygen. This effect leads to non-exponential T_1 decay due to the inability of spin diffusion to paramagnetic centres to create a uniform spin temperature throughout the sample. A significant increase in T_1 relative to the initial sample is also observed.

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