Influences of paramagnetic impurities on the proton spin–lattice relaxation time T_1 of siloxane polymers

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Proton spin-lattice relaxation times T_1 were measured for three poly(dimethylsiloxanes) of different molecular weight over the temperature range 3K–300K. The T_1 temperature dependence is characterized by different relaxation mechanisms due to hindered methyl group rotation, segmental motion about the Si–O bond, a motional process associated with recrystallization and molecular motions which are effective in the temperature range below the methyl group rotational minimum. None of these processes showed a molecular weight effect within the range covered by the three samples. A temperature dependent paramagnetic impurity effect was observed. It can be concluded from the experimental results that this effect is due to molecular oxygen.

INTRODUCTION

A complete characterization of siloxane polymers is desirable[1–4] because of their increasing technical importance. Nuclear magnetic spin-lattice relaxation experiments contribute to these data on a microscopic level by yielding information about the type of molecular motion, its activation energy and correlation time function. A variety of theoretical models has been proposed to calculate the motional parameters from the temperature and frequency dependence of the londitudinal relaxation time T_1 [5–7].

The present investigation has been undertaken to characterize in more detail the nature of the low temperature motions of poly(dimethylsiloxanes), in particular in the temperature range below the nitrogen boiling point. In this region the temperature dependence of the spin-lattice relaxation time is influenced strongly by paramagnetic impurities[8–11]. In order to get information about the nature and temperature dependent relaxation efficiency of paramagnetic impurities, the samples were subjected to different treatments.

EXPERIMENTAL

Measurements

Measurements of the proton spin-lattice relaxation times were performed at 60 MHz in a temperature range from 3K–300K. The experiment was carried out in a Bruker spectrometer, type SXP 4–100, using a $\pi/2$–τ–$\pi/2$ pulse sequence. Sequence control and data handling were achieved by a Nicolet processor, type NIC-1080. The temperatures were maintained by an electronically controlled Leybold–Heraeus evaporation cryostat. More detailed information about the experimental set up can be found elsewhere[12,13].

Materials

The samples were made from industrial poly(dimethylsiloxanes) (Wacker-Chemie, Burghausen) of different polymerization degree, characterized by the supplier according to their plasticity. The plasticity was measured on a Brabender–Plastograph to give 430, 620 and 900 mkp for the samples S_1, S_2 and S_3, respectively.

To remove impurities such as residual monomers and paramagnetic species inherent from the production process, the material was solved in either cyclohexane or ethylmethylketone and precipitated by propanol. The precipitate was then kept under a pressure of 1.5 μbar at 90°C for about 48 h to extract the solvent and nonsolvent and to remove molecular oxygen.

RESULTS AND DISCUSSION

The temperature dependence of the spin-lattice relaxation time of the three siloxane polymers is characterized by at least four relaxation mechanisms, two of which are well assigned as to their genuine type of molecular motion. These are related to the classical, thermally activated hindered rotation of the methyl group about the Si–O bond. Each process generates a minimum of the longitudinal relaxation time T_1 when the temperature dependent mean correlation time of the molecular motion and the inverse spectrometer frequency are of the same order of magnitude.

Figure 1 shows the T_1 temperature dependence of the sample S_2 (medium chain length). This specimen was taken from the untreated polymeric material as received from the supplier. Keeping the sample under air before measurement results in plot A. The T_1 minimum at about 85K is due to methyl group rotation. This process interferes with segmental motion about the Si–O bond with increasing temperature leading to a maximum of T_1 at about 160K.

The T_1 minimum due to the latter process which, by inspection of the plot, should occur at about 200K is inter-

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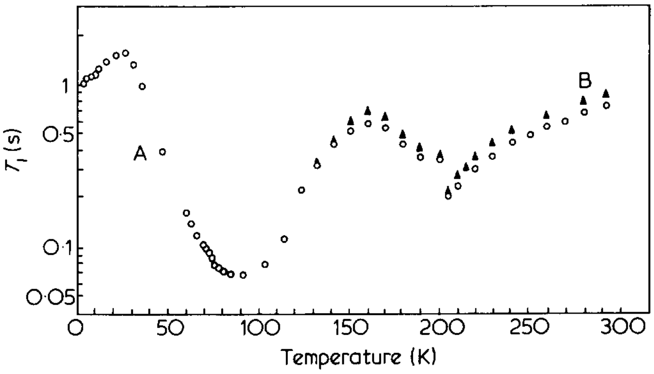

Figure 1 Temperature dependence of the longitudinal relaxation time of sample S_2. A, as received from the supplier; B, kept under inert gas atmosphere for 24 h

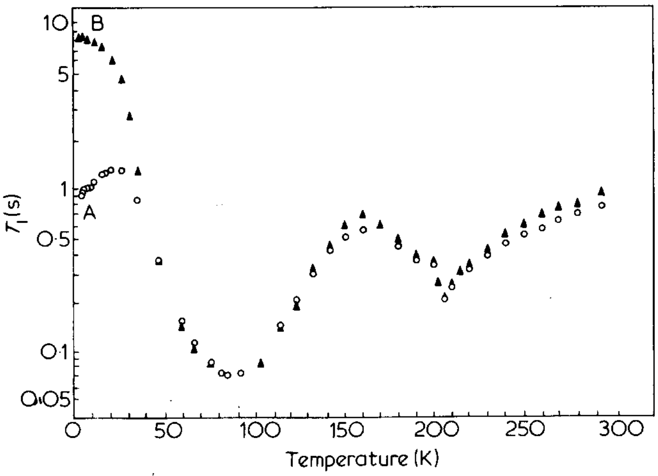

Figure 2 Temperature dependence of the longitudinal relaxation time of sample S_1. A, as received from the supplier; B, purified

sected by a discontinuity at 201K, the assignment of which to a generating motional process is not yet clear[12,14,15]. The situation is further complicated by the fact that other authors[16,17] found a minimum of T_1 in this temperature region. A paper[18] recently published reports a similar discontinuity showing further evidence of thermal hysteresis brought about by supercooling. Specific heat measurements performed in our laboratory by J. Weinberg suggest that the observed discontinuity is explained by the sudden onset of a so far unspecified type of molecular motion associated with recrystallization.

Somewhat higher T_1 values are found by keeping the sample under an inert gas atmosphere for 24 h and then starting the measurements (*Figure 1* plot B). This effect is due to a reduced concentration of paramagnetic molecular oxygen in the sample. Keeping the sample under an inert gas atmosphere more than 24 h does not enhance the T_1 values further. The influence of paramagnetic species on the longitudinal relaxation time vanishes when the spectrometer frequency is centred in the peak of the molecular motional frequency spectrum but becomes increasingly dominant with proceeding deviation from this condition. The paramagnetic impurity effect may totally mask the T_1 behaviour characteristic of the respective type of molecular motion. This case is found below 40K where the spin-lattice relaxation time of the untreated sample passes through a maximum instead of increasing monotonously with decreasing temperature due to methyl group rotation. A comparison of the longitudinal relaxation times of an untreated sample (plot A) and a sample purified according to the procedure mentioned above (plot B) is given in *Figure 2*, the sample being that of the lowest molecular weight (S_1). It shows a reasonable divergence of the T_1 curves in the lowest temperature region and a good matching in the region of a minimum.

Figure 3 shows the results of the longest chain polymer (S_3). Plot A refers to the purified specimen. Doping the purified sample with oxygen by applying a pure oxygen atmosphere of 1 bar at room temperature for 48 h yields plot B. As the doped and untreated samples exhibit the same low temperature T_1 maximum, one may conclude that the paramagnetic impurity effect is essentially due to molecular oxygen.

Contamination by free radicals, which may be inherent in the material from the production process, seems to be negligible.

The activation energy of a molecular motional process is calculated from the slope of the low temperature side of the respective T_1 minimum by applying a relaxation equation which implies a diffusion distribution function of the correlation time[7,11]. Taking the experimental results of the purified samples, this procedure yields a value of 3.9 kJ mol^{-1} for methyl group rotation and 12.5 kJ mol^{-1} for the segmental motion about the Si–O bond, both showing no molecular weight effect.

The activation energy value of methyl group rotation determined by this n.m.r. experiment lies well within a range limited by two neutron spectroscopy experiments. From incoherent inelastic neutron scattering spectroscopy data Allen *et al.*[19] arrive at a value about twice as high, whereas Anaral *et al.*[20] conclude an almost free rotation with an upper activation energy limit of 1.67 kJ mol^{-1} from neutron transmission experiments. The activation energy calculated from the slope of the low temperature side of the T_1 minimum may be considered to be slightly too small, due to the reduction of the longitudinal relaxation time by relaxation mechanisms of a different kind which become increasingly effective with decreasing temperature. This assumption is supported by the drastic failure of the classical methyl group rotational model in the temperature region below 30K.

Possible motional processes which cause this relaxation are low amplitude molecular motions, i.e. librations, and quantum mechanical tunnelling rotation of the methyl group which has already been employed to interpret the

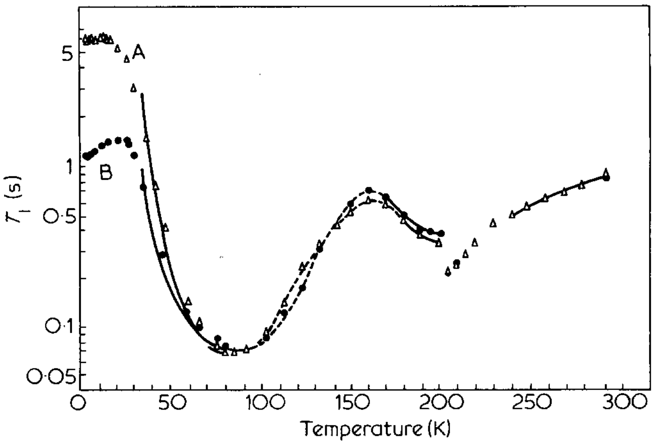

Figure 3 Temperature dependence of the longitudinal relaxation time of sample S_3. A, purified; B, contaminated with oxygen

T_1 low temperature behaviour of several organic polymers[21,22] However, it is possible that, in spite of thorough purification, small residual amounts of paramagnetic oxygen are still present in the sample.

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