Proton relaxation in polystyrene in dilute solution. Application of the selective inversion technique

F. Heatley and B. Wood

Chemistry Department, University of Manchester, Manchester M13 9PL, UK
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[1]H magnetic relaxation in polystyrene in dilute solution at 300 MHz has been studied following selective inversion of backbone methine and methylene peaks. The relaxation curves are in agreement with those predicted using correlation times derived from an earlier study of backbone proton relaxation with and without saturation of the aromatic protons. Relaxation times have also been measured at 80 MHz. These too are consistent with the previous analysis.

INTRODUCTION

In a recent paper[1], a proton relaxation study of molecular motion in polystyrene in dilute solution as a function of molecular weight, concentration, solvent and temperature was described. Effective spin-lattice relaxation times for simultaneous inversion of all protons (non-selective inversion) were measured for backbone methylene and methine protons and aromatic *ortho* and (*meta* + *para*) protons at 300 MHz. In addition spin-lattice relaxation times for the backbone methylene and methine protons were measured under the influence of a continuous decoupling field saturating the aromatic resonances. The relaxation times were interpreted in terms of the diamond lattice conformation jump model of Valeur *et al.*[2-4], which gives an autocorrelation function of the form

$$G(\tau) = \exp(-|\tau|/\tau_o)\exp(|\tau|/\tau_D)\mathrm{erfc}(|\tau|/\tau_D)^{1/2} \qquad (1)$$

The correlation time τ_D characterizes three-bond conformational transitions, and the correlation time τ_0 characterizes other processes such as overall molecular tumbling and deviations from ideal lattice conditions. It was concluded that the ratio τ_D/τ_o lies in the range 0.06 to 0.3, and is more or less independent of molecular weight, solvent or temperature.

Under aromatic proton decoupling conditions, backbone proton relaxation is controlled by low frequency components of the aromatic-backbone proton interactions[1,5]. It is desirable to study low frequency components of the interaction between backbone methine and methylene protons also, in order to test the general applicability of equation (1), and to eliminate the effects of ring rotation. Unfortunately, the methine and methylene resonances are too close together to allow selective continuous saturation of one signal without seriously perturbing the other, so the decoupling technique cannot be used. However, another approach is to use a weak perturbing pulse which selectively excites only one peak[6]. The resonances coupled, in a relaxation sense, to the inverted signal show a transient nuclear Overhauser enhancement (NOE)[7,8] while the inverted signal is recovering.

The authors have therefore extended the data published previously by using this selective inversion technique to probe methine-methylene interactions by inverting only one of these and monitoring the transient NOE displayed by the other and also the aromatic protons. In addition the unperturbed spin-relaxation times of all signals, and the backbone relaxation times with aromatic decoupling, at a resonance frequency of 80 MHz have been measured in order to check the frequency variation predicted by analysis of the results at 300 MHz.

EXPERIMENTAL

Selective inversion experiments were carried out on a Varian Associates SC-300 spectrometer operating at 300 MHz on the 5% w/v solution of polystyrene of $M_w = 1.1 \times 10^5$, $M_w/M_n = 1.06$ in hexachlorobutadiene used in the earlier study[1]. The selective perturbation was obtained by pulsing the spectrometer's homonuclear decoupler with specially modified software. The decoupler power was adjusted so that pulse width for inversion of ca. 10 ms was required when set on resonance on the signal to be inverted.

Relaxation times at 80 MHz were measured on a Bruker WP-80 spectrometer on the 5% w/v solution of polystyrene of $M_w = 1.1 \times 10^5$ in $CDCl_3$ used earlier[1].

RESULTS AND DISCUSSION

At room temperature, the correlation times for polystyrene in hexachlorobutadiene conform to the condition $\omega_0^2\tau^2 > 1$, and hence strongly negative NOE's are expected. The recovery curves following selective inversion of the methylene signal, presented in *Figure 1*, show that this is indeed the case. The curves converge to a common spin temperature because of very efficient spin-spin energy exchange through $\alpha\beta \leftrightarrow \beta\alpha$ type transitions. Similar curves are obtained following selective inversion of the backbone methine proton. The transient NOE displayed by the methylene signal for this experiment is shown in *Figure 2*, together with recovery
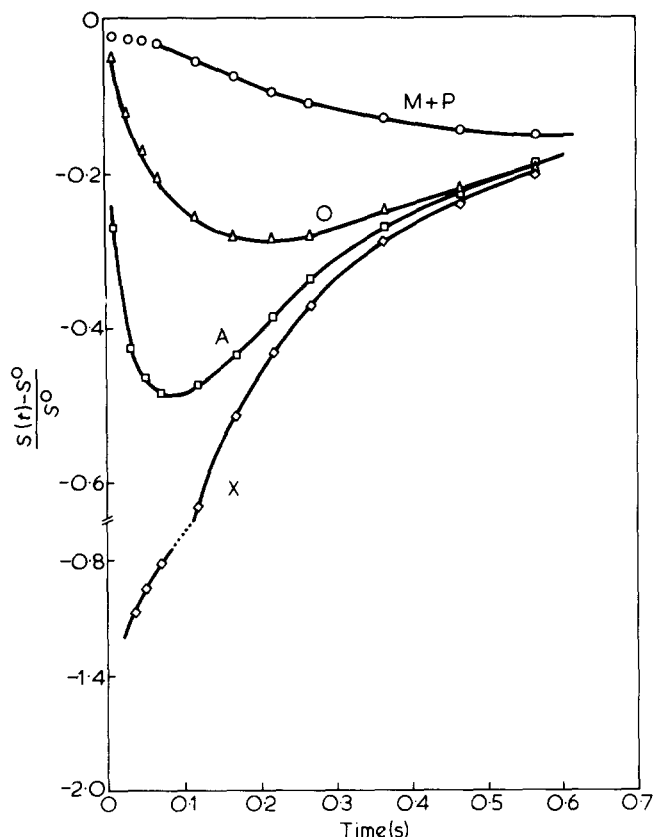
Figure 1 Recovery curves at 300 MHz following selective inversion of the backbone methylene protons. 5% w/v solution of polystyrene M_w = 1.1 x 10^5 in hexachlorobutadiene at 21°C. ○, *meta* + *para* aromatic protons; △, *ortho* aromatic protons; □, backbone methine proton; ◇, backbone methylene protons

Figure 3 Comparison of experimental and predicted relaxation times at 80 MHz for a 5% w/v solution of polystyrene M_w = 1.1 x 10^5 in CDCl$_3$. Open symbols are experimental unperturbed relaxation times: ○, *meta* + *para* protons; △, *ortho* protons; □, methine protons; ◇, methylene protons. The solid symbol is the experimental methylene relaxation time with aromatic proton decoupling. The lines are simulations as described in the text. (———) unperturbed relaxation times; (— — — —) methylene relaxation time with aromatic decoupling
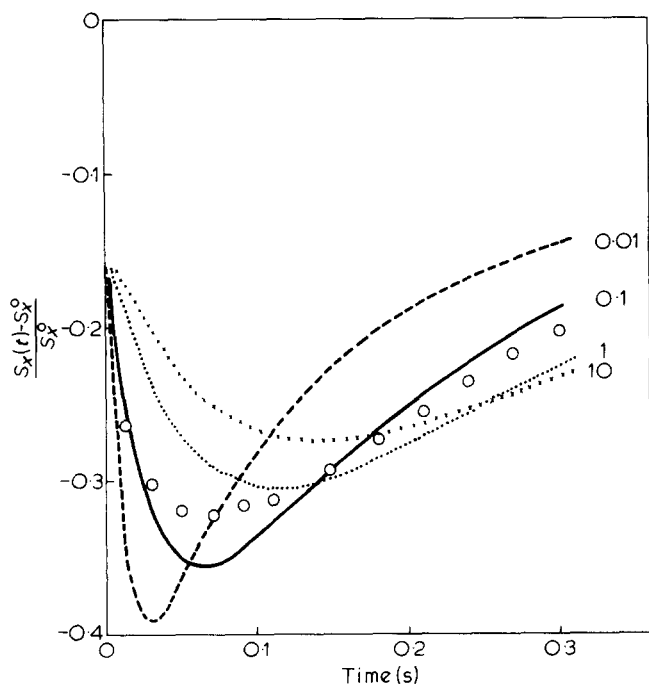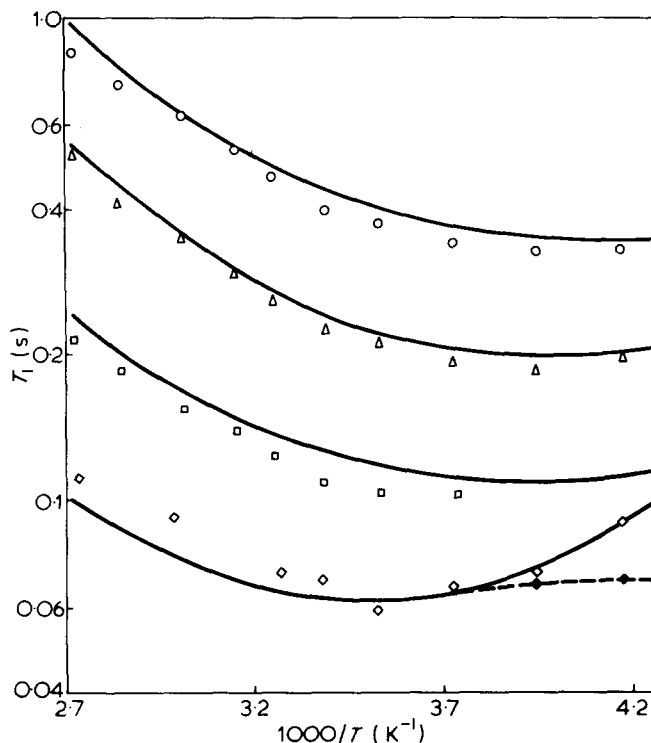

Figure 2 Recovery curve at 300 MHz of the backbone methylene protons following selective inversion of the backbone methine proton. Sample and temperature as in *Figure 1*. The circles are experimental points. The curves are simulations for the τ_D/τ_0 ratio indicated, calculated as described in the text

curves simulated using the correlation function in equation (1). These curves were calculated for the value of the ratio $\bar{\tau}_D/\tau_0$ indicated, together with the value of τ_D reproducing the observed value (1.0 s) of the unperturbed effective relaxation time of the methylene signal for that ratio. The method of calculating proton relaxation in polystyrene was fully described in the previous paper. The major problem in carrying out the simulations was in determining the initial conditions. Because the methine and methylene signals are fairly close, the unirradiated signal is slightly perturbed by the selective decoupler pulse. The extent of this effect was estimated by offsetting the decoupler an equal extent on the other side of the peak and repeating the experiment. The aromatic protons are too distant to be affected. Furthermore because of the width of the methine and methylene signals arising from unresolved tacticity effects and spin-spin coupling, and also because of short spin-spin relaxation times, it was impossible to obtain exact inversion of the irradiated signal. The simulated curves in *Figure 2* were calculated for initial normalized deviations from equilibrium $[S(t) - S^0]/S^0$ of −1.4 for the irradiated methine signal and −0.2 for the adjacent methylene signal. Fortunately, calculations show that the time at which the transient NOE passes through a minimum, t_{min}, is more or less independent of the initial degree of inversion, though naturally the minimum value of the NOE is strongly dependent on the initial conditions. Judging by the observed value of t_{min} in *Figure 2*, the best-fit value of τ_D/τ_0 is ca. 0.1 to 0.2, in satisfactory agreement with the range of values reported earlier[1].

Finally, *Figure 3* shows the relaxation times measured at 80 MHz for the CDCl$_3$ solution, together with the expected

values calculated using a τ_D/τ_O ratio of 0.1 and the values of τ_D reported previously[1]. At the higher temperatures, the τ_D values were taken at the lower end of the range quoted[1] to give the best agreement. The consistency of predicted and experimental values is quite satisfactory.

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