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^{13}C Relaxation Studies of ^{13}C Enriched Polystyrene in Solution

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From ^{13}C spin lattice relaxation and Nuclear Overhauser measurements of 1wt% solutions of α-^{13}C enriched polystyrene activation energies for three bond rearrangements are found to be 27,5 ± 4kJ/mol in cyclohexane-d_{12} and 19,5 ± 2,5 kJ/mol in toluene-d_8. From these values internal energy barriers of 15 kJ/mol in cyclohexane-d_{12} and 10,5 kJ/mol in toluene-d_8 are deduced. The concentration dependence of the correlation time is characterized by a slow initial increase followed by a much steeper rise beyond a critical concentration.

Introduction

^{13}C NMR relaxation experiments have been proven to be a powerful method to study the segmental motion in polymer solutions (HEATLEY and BEGUM 1976). Because of the low sensitivity of the ^{13}C isotope with 1% natural abundance, these investigations have been limited so far to semidilute solutions at or above 10% which are not completely free from intermolecular interactions. Therefore it seemed worth while to study the ^{13}C relaxation behaviour from dilute to concentrated solutions by preparing a ^{13}C enriched polymer. We have chosen polystyrene because this polymer has been studied most extensively by other methods, such as ^{1}H (HEATLEY and WOOD 1979) and ^{19}F (MATSUO et al.) NMR relaxation, dielectric relaxation (STOCKMAYER and MATSUO) and fluorescence depolarization (VALEUR et al. 1976). Our results can be particularly compared to ESR measurements (BULLOCK et al.) which have been carried out at comparable molecular weight and concentration.

Experimental

By anionic polymerization in benzene a 50% ^{13}C enriched poly (α - ^{13}C-styrene) was prepared. The synthesis of the α-^{13}C enriched styrene monomer will be described in a separate paper (PETER and GRONSKI). The molecular weight determined by GPC was M_w = 165 000 with M_w/M_n = 1.63. The ^{13}C measurements were carried out on a Bruker WH 90 Spectrometer at a ^{13}C frequency of 22.63 MHz. Spin lattice relaxation times T_1 were determined by the inversion recovery method. Nuclear Overhauser enhancement factors were measured by the gated decoupler method (OPELLA et al.) where particular care to a sufficient dong delay of at least 10 T_1 has been taken. The concentration of the solutions is always given in weight %.

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Results and discussion

The temperature dependence for 1% and 20% solutions in toluene and for 1% solution in cyclohexane is shown in fig. 1. With increasing concentration the minimum is raised and shifted to higher temperatures. The temperature shift which starts at about 5%, reflects the reduced segmental mobility of the polymer chains with increasing concentration. In terms of a distribution of correlation times the raise of the minimum can be understood as an increase of the width of the distribution (HEATLEY and BEGUM 1976). This effect also accounts for the depression of the NOEF curve at higher concentration. In cyclohexane the T_1 and NOEF curves are steeper than in toluene as a consequence of a higher activation energy of the segmental motion in cyclohexane. Recently it has been shown (HEATLEY and WOOD 1979) by proton relaxation measurements that the effect of the solvent on the segmental motion consists mainly in a scaling of the rate of motion due to different thermal activation energies. This means that the T_1 curves for different solvents can be superimposed on a common master curve by plotting the data versus a reduced reciprocal Temperature T^{*-1} given by

$$\frac{1}{T^*}=\frac{E}{E_{ref}}\cdot\frac{1}{T}+\frac{R}{E_{ref}}\ln\frac{\tau_\infty}{\tau_{\infty,ref}} \qquad (1)$$

where E and τ_∞ are the activation energy and the correlation time at infinite temperature in the Arrhenius equation of a suitable correlation time in an arbitrary solvent and the solvent chosen as a reference solvent. Chosing toluene as the reference and substituting the ther-

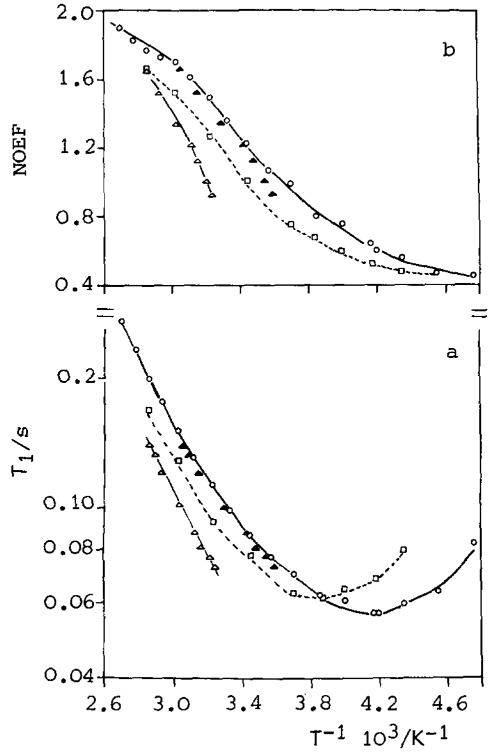

Fig. 1.: ^{13}C T_1 (a) and NOEF (b) of the CH carbon of 50% α-^{13}C enriched polystyrene in 1wt% solutions in toluene-d_8 (o) and cyclohexane-d_{12} (△) and 20% solutions in toluene-d_8 (□). (▲) represent the data in cyclohexane-d_{12} in a reduced temperature plot according to eq. 1.

mal parameters determined by the subsequent analyses into eq. 1 it can be seen by fig. 1 that the T_1 curve for cyclohexane is shifted onto the T_1 curve for toluene if the data are plotted versus the reduced temperature. Except for the two lowest temperatures near the cloud point in cyclohexane, which occurs at 31°C, a good superposition is also obtained for the NOEF curves. The effect due to different thermal activation parameters can also be eliminated by plotting the NOEF values directly versus T_1. It has been shown (GRONSKI and MURAYAMA) that this procedure yields a common master curve for solvents of different viscosities belonging to the same solvent class. However, the present results seem to indicate that this behaviour is universal for all solvents irrespective of their thermodynamical properties. This means that the general type of motion should be the same for all kinds of solvents. It is clear from fig. 1 that the attempt of shifting T_1 and NOEF curves belonging to different concentrations onto a common master curve by a similar procedure must fail because an additional vertical shift would be necessary for which no physical basis seems to be given.

The dependence of the relaxation rate T_1^{-1} and the NOEF on concentration is shown in fig. 2. For both quantities the concentration dependence tends to persist down to 1% concentration. T_1 and NOEF values of the lowest 1% con centration measured are of the order of 5% higher than those of a 10% solution. The concentration dependence becomes more pronounced above 10%.

The quantitative analysis of the experimental results was carried out on the basis of the three bond jump model for diamond lattice chains (VALEUR et al. 1975) which has been proven to be successful in the description of ^{13}C spin relaxation experiments of flexible polymers in solution (HEATLEY and BEGUM 1976, LAUPRÊTRE et al. 1977). The correlation function of this model is

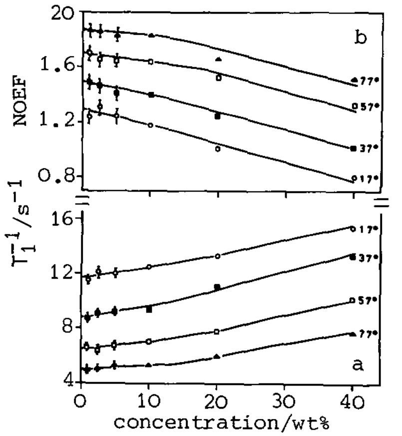

Fig. 2.: ^{13}C spin lattice relaxation rate T_1^{-1} (a) and NOEF (b) of the CH carbon of 50% α-^{13}C enriched polystyrene in toluene-d_8 in dependence on polymer concentration.

$$\Phi(t) = e^{-t/\theta} \, e^{t/\tau_D} \, \mathrm{erfc}\,(t/\tau_D)^{1/2} \qquad (2)$$

where τ_D is the correlation time associated with the three bond process and θ is an additional curve fitting parameter. The relevant formula for ^{13}C spin lattice relaxation and the ^{13}C nuclear Overhauser enhancement connected with the Fourier transformation of eq. (2) are given in the literature (LAUPRÊTRE et al. 1977).

For the determination of the correlation times the C-H bond length was taken as 0.107 nm. The procedure employed was to fix first the ratio τ_D/θ by plotting the NOEF and T_1 data in a NOEF versus T_1 diagram in which calculated curves for constant τ_D/θ ratios were drawn and then to determine the τ_D value from a T_1 versus τ_D plot which contained the T_1 variation corresponding to the fixed τ_D/θ ratio.

In fig. 3 an Arrhenius plot of the correlation times in 1% toluene and cyclohexane solutions is presented. The plot has been limited to those temperatures where the parameters τ_D and τ_D/θ could be determined with sufficient accuracy.

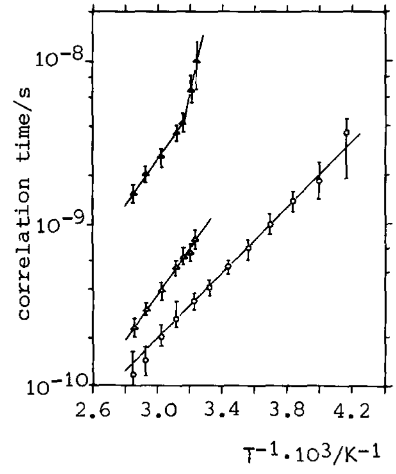

Fig. 3.: Arrhenius plot of the correlation time τ_D in toluene $-d_8$ (O) and cyclohexane-d_{12} (△) and the correlation time θ (▲) in cyclohexane-d_{12} for 1 wt% solutions.

In this range the ratio τ_D/θ has a nearly constant value of 0.15 except for the two lowest temperatures below 40°C near the critical point in cyclohexane where the τ_D/θ ratio drops to 0.08. Consequently the Arrhenius plot for cyclohexane becomes nonlinear below 40°C. A similar behaviour has been observed by ESR measurements (BULLOCK). The activation energy obtained from the linear portion of the Arrhenius plot for cyclohexane is 27.5 ± 4 kJ/mol. The activation energy of the segmental motion in toluene is 19.5 ± 2.5 kJ/mol. This value is considerably higher than the value of 10.5 kJ/mol determined by ^{13}C relaxation measurements in 15% (wt/vol) solution in toluene-d_8 on the basis of the model of isotropic segmental motion (INOUE and KONNO). The preexponential factors $\tau_{D,\infty}$ used for the calculation of the reduced temperature according to eq. 1 are $2\cdot 10^{-14}$ s for cyclohexane and $1.6\cdot 10^{-13}$s for toluene. For concentrations up to 10% in toluene no significant increase of the activation energy was found. From similar plots as in fig. 3 values of 22 kJ/mol, 23 kJ/mol and 26 kJ/mol are found for 10%, 20% and 40% solutions respectively.

In dilute solution the rate of segmental motion is determined by two factors, by the viscous drag of the solvent itself and by intramolecular energy barriers of rotation which can be modified by polymer-solvent interactions. These two effects can be separated according to KRAMERS theory for the diffusion of a particle over a potential barrier. For the limiting case of high viscous damping the theory predicts that the activation energy of the rate of motion is

$$E = E^{*} + E_{\eta} \qquad (3)$$

where E_{η} is the activation energy of the solvent viscosity and E* is the intramolecular activation energy. Taking the values for the undeuterated solvents E_{η} = 9.00 kJ/mol for toluene and E_{η} =12.5 kJ/mol for cyclohexane from the literature (BULLOCK) the intramolecular energies in dilute solution are 10.5 ± 2.5 kJ/mol for toluene and 15 ± 4 kJ/mol for cyclohexane. The last value is smaller than the value of 19 kJ/mol obtained recently by HEATLEY (1979) from proton relaxation measurements on the basis of the same motional model used in this work. Compared to the ESR activation energy of ca. 9 kJ/mol in toluene and of 12.6 kJ/mol in cyclohexane our values are slightly higher which may be a consequence of the use of the more realistic correlation function of eq. (2) in the description of the segmental motion. The results show that intramolecular barriers can be affected by polymer solvent interactions. The fact that the activation energy in the good solvent toluene is higher than in the poor solvent cyclohexane can be understood qualitatively by imagening that in the case of toluene solvent molecules may enter between the phenylrings providing a compensation for the rise of energy when the phenyl groups separate during three bond conformational transitions. This compensatory effect might be absent in cyclohexane where a tighter packing of the phenylgroups prevails.

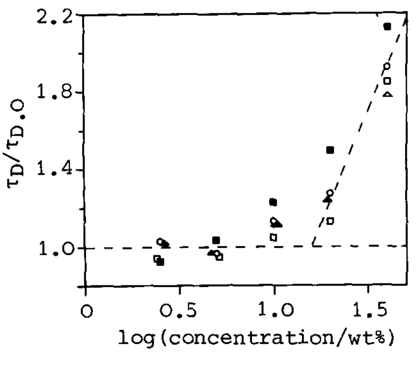

Fig. 4.: Plot of the reduced correlation time $\tau_D/\tau_{D,o}$ in toluene-d_8 at 17°C (0), 37°C (■), 57°C (□) and 77°C (△) as a function of polymer concentration in wt%.

Fig. 4 shows the effect of concentration in toluene on the correlation time τ_D. The results are presented in a similar way as for the ESR measurements of BULLOCK in terms of a reduced correlation time $\tau_D/\tau_{D,o}$ plotted against log concentration where $\tau_{D,o}$ is the correlation time obtained from the limiting values of T_1 and the NOEF in fig. 2 at zero concentration. As has been noted for the ESR correlation time the temperature has only a small effect on the reduced correlation time as compared to the concentration influence. The appearance of the curves is similar as in the case of the ESR measurements. An initial slow rise starting at about 5% is followed by a much steeper increase above 10%. If the steep rise is approximated linearly by a line drawn through the mean of the reduced correlation times at 40% and 20% and extrapolated to $\tau_D/\tau_{D,o} = 1$ a critical concentration of ca. 16% is obtained which may be regarded as the onset of the strong concentration dependence in good agreement with the ESR result.

The viscosity of concentrated polymer solutions shows a similar concentration dependence (PORTER and JOHNSON). For comparable molecular weights the critical concentration at which a change from a weak to a strong power dependence occurs falls into the same range for the viscosity and the correlation times measured by ESR and ^{13}C NMR. However, the power dependence of the ^{13}C correlation time is much weaker than measured by the other methods. It changes from zero to about 0.6 above the critical concentration wheras the power dependence of the viscosity changes from 2.3 to 5.0 (ONOGI et al.) and the ESR correlation time changes from zero to 1.8.

The existence of a critical concentration in the viscosity has been explained by the formation of an entanglement network. A similar explanation in the case of the correlation time τ_D of the present measurements seems to be in conflict with the fact that local processes as the three bond jump mechanism should hardly be effected by the creation of a low density entanglement network. On the other hand, one has to consider that these processes occur in a coupled manner along the chain. Therefore the transition rate of a given three bond segment can be affected by steric restrictions farther apart from the relaxing ^{13}C nucleus. This point is further elucidated if one considers the concentration dependence of the correlation time θ which is always longer than τ_D in the present measurements. If an average is taken over the 4 temperatures considered in figs. 2 and 4 the ratio of τ_D/θ stays nearly constant at about 0.13 - 0.15 below a polymer concentration of 10% and falls to 0.08 - 0.1 at 40%. Thus it seems that the correlation time θ has to be associated with isotropic relaxation processes involving larger parts of the chain which are more sensitive to steric restrictions imposed by the presence of other chains.

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