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Effect of Chemical Crosslinking on Molecular Mobility in Swollen Polystyrenes

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SUMMARY

Proton relaxation time measurements of chemical crosslinked polystyrenes swollen in protonated and deuterated benzene have been done in order to get informations on the microdynamic behaviour of polystyrene as well as of benzene molecules under the influence of the polymeric network.
By means of additional T_{1d}-measurements further evidences for a slow anisotropic motion could be obtained, which cause a T_2-"plateau" in the high temperature region.
The results are compared with those of MAR-experiments.

INTRODUCTION

A great number of recent publications dealt with investigations of the dynamics of various types of motions in dissolved polystyrene (GOTLIB et al. 1975, INOUE and KANNO 1976, LAUPRETRE et al. 1977, GRANDJEAN et al. 1977, JONES 1977, GESCHKE et al. 1978, GRONSKI and MURAYAMA 1978, HEATLEY and WOOD 1978).
For the interpretation of the experimental results the intramolecular dipolar interaction has been assumed to be the predominant relaxation mechanism.
Due to the fact, that in macromolecular systems most motions are anisotropic in space, the correlation function (the Fourier transform of the spectral density) is expected to be nonexponential (VALEUR et al. 1975, JONES and STOCKMAYER 1977, BENDLER and YARRIS 1978).
Therefore a detailled study of the temperature and/or frequency dependence of the relaxation times is of great interest. In this paper we present results of ^{1}H-nmr relaxation time measurements of chemical crosslinked polystyrene swollen in protonated and deuterated benzene.
Thereby informations could be obtained on the microdynamic behaviour of macromolecules as well as of benzene molecules under the influence of the polymeric network.
In addition to this measurements of the dipolar relaxation (time constant T_{1d}) have been done in order to get further information on anisotropic motion in the systems considered.

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EXPERIMENTAL

Samples of crosslinked polystyrene were made up by suspending 20 % and 45 % by weight of PS in benzene, assuring equilibrium conditions in the gel phase. The room-temperature equilibrium swelling ratio in C_6H_6 was determined gravimetrically.
As crosslinking agent divinylbenzene (DVB) has been used.
The parallel samples of flexible polystyrene contained the same relative quantities of the polymer.
Proton relaxation times T_1, T_2 (cf. e.g. FARRAR and BECKER 1971), T_{1d} (JEENER and BROEKAERT 1967) have been measured using the BKR 322s(Bruker) spectrometer, working at 32 MHz.
For the purpose of investigations the polymer systems were purified carefully from paramagnetic spezies.

RESULTS and DISCUSSION

Fig. 1 shows the temperature dependence of the longitudinal relaxation times T_1 of crosslinked PS swollen in C_6H_6 (20 %, 45 % by weight).

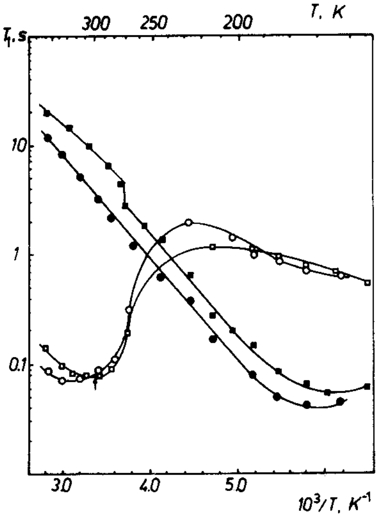

Fig. 1: Temperature dependence of relaxation times T_1 for two concentrations of systems PS(crosslinked)/C_6H_6 (20 % PS: T_{1PS}(□), $T_{1C_6H_6}$(■); 45 % PS: T_{1PS}(○), $T_{1C_6H_6}$(●)).

In such systems a two-phase behaviour of the longitudinal relaxation function has been observed and the intensities of the different components correspond to the mole fractions of polystyrene and benzene, respectively.
The results for protons of macromolecules are in good agreement with those for the systems PS/C_6D_6, which are shown in fig. 2 together with the corresponding T_2-values.

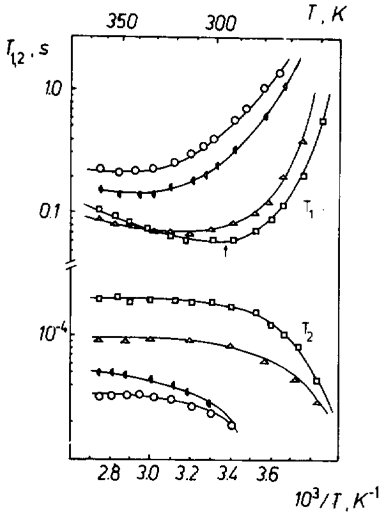

Fig. 2: Effect of crosslinking on relaxation times T_1, T_2; maximum swelling degree (DVB content: 16 % per mole (○), 12 % (◐), 6 % (△), 2 % (□)).

The results of analogous experiments, which have been done using concentrated solutions of flexible molecules, are given in fig. 3.

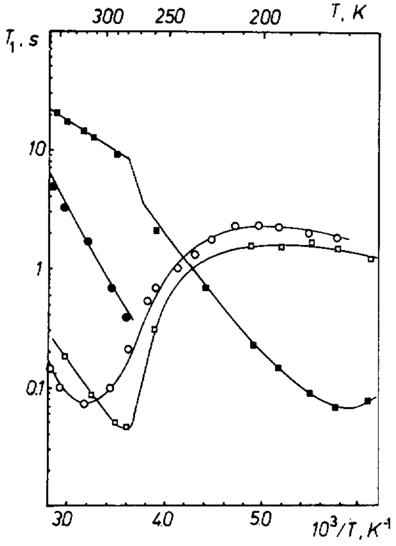

Fig. 3: Temperature dependence of relaxation times T_1 for two concentrations of systems PS/C_6H_6 (20 % PS: T_{1PS}(□), $T_{1C_6H_6}$(■); 45 %: T_{1PS}(○), $T_{1C_6H_6}$(●)).

For an unambigious identification of the relaxation times PS-d8 has been used as well as perdeuterated benzene besides the customary products.
In fig. 4 the results of preliminary T_{1d}-measurements for one of the systems mentioned above are demonstrated (45 % by weight PS, 16 % DVB, cf. fig. 2, sample (O)).

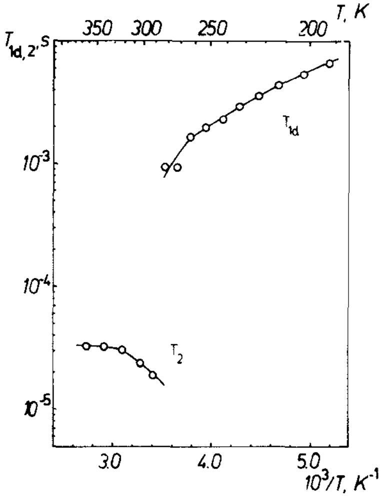

Fig. 4: Temperature dependence of relaxation times T_{1d} and T_2 of PS, crosslinked with 16 % DVB, swollen in C_6D_6.

Figs. 1 and 3 show the influence of the benzene molecules on the position of the T_{1min}-values of the polymer protons.
With higher content of $C_6H_6(C_6D_6)$ the minima in T_1 are shifted to lower temperatures. That means, that the possibility of reorientation of the polymer segments increases as a result of a modulation effect of the swelling material.
Similar phenomena appear in the temperature dependence of the longitudinal relaxation times of the benzene protons.
Under the influence of the polymeric network the minima positions deviate to higher temperatures compared with the free liquid, but they exist at much lower temperatures than those of the polymer. One has to assume, that these minima are due to the anisotropic rotation of the benzene molecules around the sixfold axis of symmetry, and it is seen, that this motion must be hindered to some extent.

Informations on the influence of crosslinking can be obtained from fig. 2 and by comparing the results with those for the flexible materials. The T_1-minima are shifted to higher temperature with increasing number of crosslinks. This corresponds to decreasing possibilities of reorientation of the polymer segments caused by the fact, that the network becomes more and more inflexible. Besides this a broader T_1-dispersion is recognizable in the case of crosslinked polystyrene, which is to be explained by a larger width of the distribution function of the correlation times.

The temperature dependence of T_2 is significantly characterized by a "plateau" in the high temperature region, which is assumed to arise from a superposition of a fast isotropic and a slow anisotropic motion; last one caused by longer chain parts fixed in the network points of the polystyrene. Thus the "plateau" can be explained with the rigid lattice behaviour of the slower motion. Because of the anisotropy the dipolar fields are not averaged completely, which enables us to observe the relaxation process of the dipolar energy. Similar conclusions could be drawn by DOSKOCILOVA et al. 1978, who investigated analogous crosslinked systems using the MAR (Magic Angle Rotation)-technique.They found a disappearence of crosslinking effects on nmr line widths by MAR at spinning speeds of the order of 1 kHz, which indicates, that the broadening investigated is due to essentially "static" dipolar interactions modulated by motions with a correlation time longer than 10^{-4} s. If line-narrowing by MAR is observed in a proton nmr spectrum, then the motion in the measured systems must be anisotropic as has been shown by the same authors.

We describe the temperature dependence of T_{1d} using the model of GOTLIB et al. 1976, which has been developed in order to explain the anisotropy of motion in crosslinked polystyrene systems.

For the second moment one gets

$$\langle \Delta H^2 \rangle = \langle \Delta H_o^2 \rangle \ (3/5z)^2 \qquad (1)$$

where $\langle \Delta H_o^2 \rangle$ means the second moment of the rigid lattice and z the number of free connected chain elements, which is given by

$$z = 1/ns \qquad (2)$$

n: mole part of crosslinks
s: number of monomeric units in a chain element.

Assuming for the resonance line a truncated Lorentzian one it can be shown that the T_2-values in the "plateau"-region are connected with the number of crosslinks by the following equation

$$T_2 \simeq 3.3z/\gamma \langle \Delta H_o^2 \rangle^{0.5} \qquad (3)$$

Experimental and theoretical results are in good agreement. By means of the BPP-formalism (FARRAR and BECKER 1971) and using the second moment (1) it was possible to give a rough relation between the temperature-dependent T_{1d}-values and the corresponding correlation times τ_c of the anisotropic motion:

$$1/T_{1d} \simeq \gamma^2 \langle \Delta H^2 \rangle \tau_c / (1 + \omega_d^2 \tau_c^2) \qquad (4)$$

where ω_d is the frequency of the local dipolar fields. Thus τ_c -values could be obtained equal to the measured relaxation times.

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