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ORIGINAL CONTRIBUTION

S.-Z. Mao
H.-Q. Feng

Study of the dissolution process of polystyrene in concentrated cyclohexane solution by MNR relaxation*

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Dr. S.-Z. Mao (✉) · H.-Q. Feng
Laboratory of Magnetic resonance
and Atomic and Molecular Physics
Wuhan Institute of Physics
and Mathematics
The Chinese Academy of Sciences
Wuhan 430071
P.R. China

Abstract ^{13}C-NMR relaxation times of polystyrene (PS) chains in its theta solvent, cyclohexane, have been measured at different temperatures. It was found that relaxation of carbon nuclei of the side-chain-phenyl groups and those of main chains have remarkably different temperature-dependent relaxation behaviors in the solvent. A two-step model for the dissolution process is proposed. According to the model, swelling of the polymer below θ temperature corresponds mainly to the gradual dispersion of the side-chain phenyl groups; while the complete dissolution above θ temperature corresponds mainly to the gradual dispersion of the main chains at a molecular level. These dispersions reflect the fact that cohesional interaction among side-chain-phenyl rings or main chains are weakened by solvent molecules, which shows the existence of the cohesional entanglements among polymer chains. The results of T_1(C) are confirmed by the biexponential dependence of ^{1}H-NMR spin–spin relaxation on temperature.

Key words NMR – relaxation time – cohesional entanglement – polystyrene – theta solvent

Introduction

Thermodynamic properties and conformation of polymer chains in solution have attracted much interest, through which one can construct the universal temperature–concentration diagram. The semidilute θ solutions and the transition from θ to good solvent system is a part of such a diagram. The study for the θ condition about polymer solution is incomplete. Many thermodynamic parameters, such as characteristic correlation length between polymer and polymer, contract factor between solvent and polymer and renormalized third virial coefficient have been obtained by theoretical calculation based on small-angle X-ray scattering and neutron-scattering data [1–8]. At the same time, a number of models were built up for treating experimental data. In these works, however, the thermodynamic properties of polymer chains in solution can be studied. For describing the motion of polymer chains at a molecular level, NMR spectroscopy may be a powerful means. With the development of NMR techniques, especially with the improvement of resolution of NMR spectra, it is not difficult to obtain the information about the motion of the segments at various positions of molecular chains by using NMR spectrometer with a high magnetic field. Therefore, now one can study in detail the motion of different groups in the molecular chains, while previously one could obtain the statistical effect of the motion of the groups only [9]. In this paper we study the motion of segment of polystyrene in solution to elucidate the dynamic behavior of polystyrene in dissolution process, through which we describe the characteristics of the θ systems of polystyrene–cyclohexane and variation at different temperatures at the molecular level.

N 937

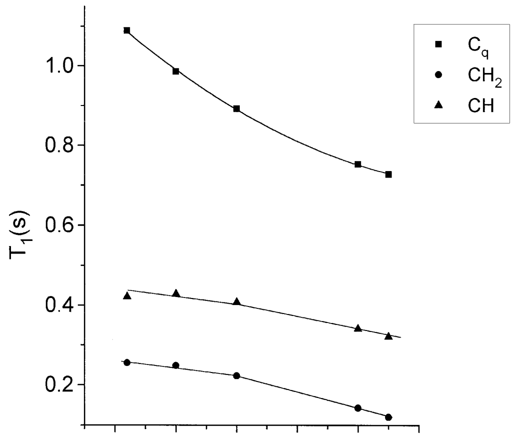
Samples and experiment

Monodispersed PS with $M_w = 1.5 \times 10^5$ (produced in Najing University) was used as experimental sample. PS solutions with cyclohexane as the theta solvent were prepared in NMR sample tubes. The concentration was 150 mg/ml. The ^{13}C-NMR and ^{1}H-NMR experiments were performed on a Bruker ARX-500 NMR spectrometer. The ^{13}C-NMR spin-lattice relaxations of each carbon atoms of PS were measured by inverse recovery method. The delay longer than $5T_{1\max}$, the range of probe temperature from 22 to 65 °C, ^{13}C resonance frequency of 125.76 MHz and 60–100 accumulations were used. The temperature stabilization was within +3 °C. The ^{1}H-NMR spin–spin relaxations were measured by spin echo method, the used ^{1}H resonance frequency was 500.13 MHz.

Results and discussion

The polystyrene–cyclohexane system consists of two different phases in a sample tube at room temperature, the upper part is a rich solvent and the lower part, a gel polymer, that is the so-called swelling polymer phase. The ^{13}C-NMR spin-lattice relaxation times of individual carbon atoms of the solutions at temperatures from 22 to 65 °C are shown in Fig. 1. T_1 values of the individual carbon atoms of PS in solutions (gel polymer) decrease as the temperature increases. This implies that the T_1 values decrease when the molecular motion becomes faster or when the correlation time decreases, which is just the characteristic of the NMR relaxation in a macromolecular solution [10]. However, there exists considerable difference in the variation of the rate of relaxation time with temperature between the carbon nuclei in the main chain and in the side chain. Below a certain temperature T_1 values of carbon nuclei of the main chains of PS kept nearly constant while they start to decrease significantly when the temperature rises further. The turning point at ~40 °C, is very close to the theta temperature of 34.5 °C for PS determined by light scattering measurement [11]. This phenomenon can be understood by the fact that the interaction of the main chains with the solvent molecules could not overwhelm the interaction of the main chains among themselves at a temperature below the θ temperature, although it could at higher temperatures. This interaction among main chains of polymer shows the existence of a binding state, i.e. the cohesional entanglement among main chains in the polymer system. This cohesional entanglement among main chains cannot be weakened below the theta temperature. On the other hand, the T_1 value of the quarternary carbon atom of the phenyl group, i.e. the carbon atom linked to methine carbon atom of the main chain of PS, always decreases sharply as the temperature increases even at temperatures below 40 °C, before dissolution of the polymer has started. The decrease of T_1(C) of the quarternary carbon atom before the theta temperature implies that the rotation of the phenyl group which is the main cause of relaxation of this atom is speeded up; therefore, the interaction among phenyl groups themselves has became weaker already below the θ temperature. The temperature-dependent curve of ^{13}C-NMR T_1 of PS in Fig. 1 also reflects the motion variations of the individual carbon atoms during their state transition from gel (swollen) to solution (dissolution). The above result helps to understand the mechanism of dissolution which describes the property of the static state only. From the study by conventional methods, one knows only phenomenologically that PS in cyclohexane, theta solvent, does not dissolve at temperatures lower than the theta condition, and no information about the dissolution process can be obtained while our NMR study reveals that the dissolution of PS in cyclohexane is a two-step process. Below the theta temperature, the interaction of the side-chain-aromatic rings with cyclohexane-solvent molecules has begun to weaken the cohesional interaction among phenyl rings themselves, thus making the motion of phenyl groups faster, but the interaction between the solvent molecules with the main chain is not strong enough to weaken the self-association of the main chains at temperatures below the theta condition; therefore, PS chains cannot mix with cyclohexane at a molecular level. In this case they can exist only as a gel polymer, i.e., a swollen one.

Fig. 1 The measured ^{13}C-NMR T_1 values of individual carbon atoms of PS–deuterocyclohexane solution (C = 150 mg/ml, M_w = 1.5×10^5) at various temperatures, in which C_q = quarternary carbon of the phenyl group; CH = methine carbon of the main chain; CH_2 = methylene carbon of the main chain



When the temperature is high enough so that the interaction of main chain segments with solvent molecules overwhelms the cohesional interaction among main chains, the segments of PS can move freely in the solution, the macroscopic dissolution is achieved, and the solution becomes transparent. The temperature is the theta temperature.

This two-step model for the dissolution process of PS in cyclohexane, theta solvent, is confirmed by the biexponential behavior of the ^{1}H-NMR spin–spin relaxation. The ^{1}H signals of the main chains and those of the phenyl groups are well resolved in a NMR spectrum, which enables us to study the motion of protons linked to the carbon atoms of the main chains and the side groups. The spin–spin relaxation of protons shows a biexponential behavior, i.e., it consists of a slow and a fast relaxation process. Then the spin–spin relaxation holds the relation:

$$\frac{M(t)}{M(0)} = P_f \exp\left(\frac{t}{T_{2f}}\right) + P_s \exp\left(\frac{t}{T_{2s}}\right) , \qquad (1)$$

$$P_f + P_s = 1 , \qquad (2)$$

where $M(0)$ and $M(t)$ are the magnetizations at time $t = 0$ and t, T_{2f} and T_{2s} are the fast and slow relaxation times, respectively, P_f and P_s are the relative contents of the protons which are involved in fast and slow relaxations.

The obtained T_{2f}, T_{2s}, P_f and P_s values from fitting ^{1}H spin–spin relaxation curves of main chain methylene $-CH_2-$ and side-chain-phenyl group methine –CH= of PS sample are shown in Figs. 2 and 3. The spin–spin relaxation of protons is mainly influenced by the dipole–dipole interaction of nuclear spins. The dependence of this interaction upon the distance d between two nuclei is known to be proportional to d^{-3}, and it is also related to the motion of polymer chains. The smaller the distance between protons, slower the motion of polymer chains, and the stronger the interaction of the proton–proton dipolar coupling, thus the smaller the T_2 value. The two relaxation processes suggest that there exist two independent states of the proton nuclei. Since the proton spin–spin relaxation depend indirectly on the density of protons in polymer chains, so the fast relaxation (short T_2) should be contributed by the protons with high density and those attaching to carbons in hindered polymer chain segments, while the slow relaxation (long T_2) should be contributed by protons with lower density. For this reason, fast relaxation can be considered to be contributed by the protons in polymer chains with cohesional entanglements, while the slow relaxation is contributed by those protons moving freely in the solution. From the results shown in Figs. 2 and 3, the following conclusions can be extracted. As temperature increases or as molecular motion quickens, both fast and slow relaxation times increase, but it is noticeable that P_s increases while P_f decreases. The reason is that, when the temperature increases, the polymer chains tends to separate from each other due to the thermal molecular motion, so more protons are in the low mobile state, therefore, this fraction of the free chain segments (P_s) increases. On the other hand, cohesional entanglements of main chain $-CH_2-$ and side-chain-aromatic rings –CH= (P_f) see the temperature in different senses. P_f of proton of phenyl group –CH= always decreases as the temperature increases, while as long as the theta temperature is not reached, P_f of protons of main chain $-CH_2$ will keep nearly unchanged. Remarkable decrease of P_f can be observed only when the temperature is higher than the theta temperature. This phenomenon suggests that the

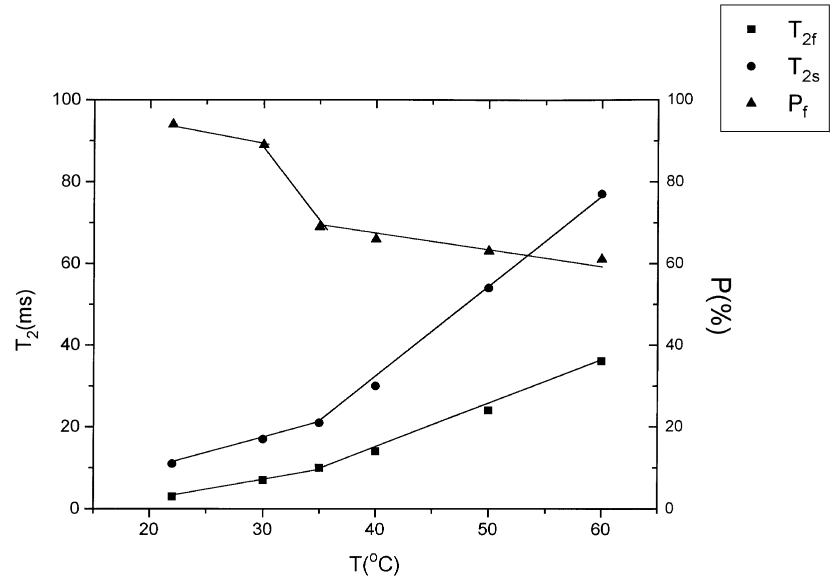


Fig. 2 ^{1}H-NMR T_2 values of the fast, slow relaxation and the fraction of the fast relaxation of the proton attached to methylene carbon of main chain on polystyrene chain in deuterocyclohexane at various temperatures

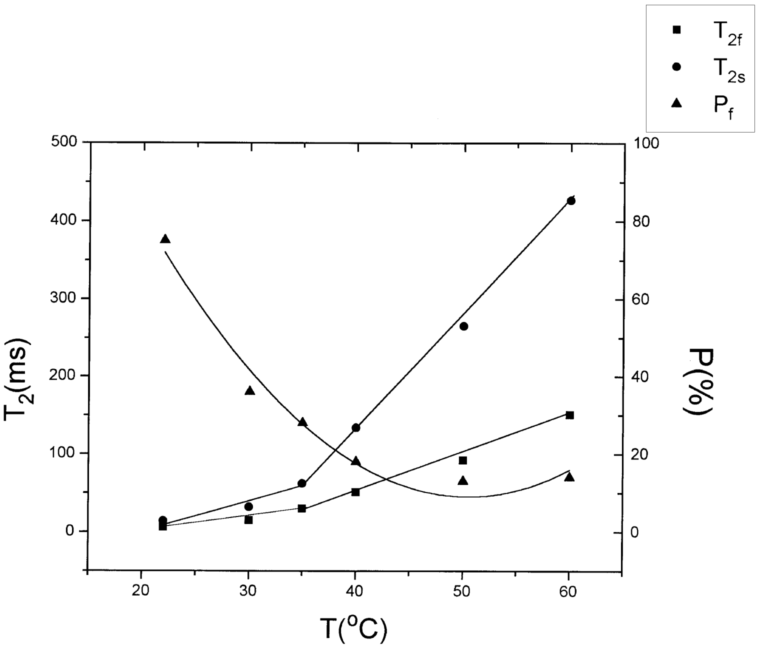


Fig. 3 ^{1}H-NMR T_2 values of the fast, slow relaxation and the fraction of the fast relaxation of the proton attached to methine carbon of phenyl group on polystyrene chain in deuterocyclohexane at various temperatures

cohesional entanglements among side-chain aromatic rings begin to be weakened at a temperature considerably lower than the theta temperature, but the cohesional entanglements among main chains can be disentangled only when the theta temperature is reached. These cohesional entanglements among aromatic rings correspond to the interaction among aromatic rings introduced by the large π bonds, which is referred to the result of T_1(C) mentioned above, in fact, they are the interlocking structures of aromatic rings [12–13]. From Figs. 2 and 3 one can see that there is an abrupt change in the vicinity of the theta temperature for both fast and slow relaxation times of protons of side-chain aromatic ring and main chain. This phenomenon shows that the phase transition from a swollen polymer to a dissolved one in PS solution takes place at the theta temperature. According to the two-step model, the dissolution of PS in its cyclohexane solvent can be explained as swelling below the theta temperature and complete dissolution above the theta temperature. The former corresponds mainly to gradual dispersion of the side-chain aromatic rings, and the latter corresponds mainly to gradual dispersion of main chains at the molecular level.

In conclusion, the relaxation behavior of polystyrene in cyclohexane solvent has been studied by NMR spectroscopy. The results of the ^{13}C-NMR spin-lattice relaxation time of individual carbon atoms of PS in solution is further confirmed by the biexponential behavior of ^{1}H-NMR spin–spin relaxation process. The dissolution of PS in cyclohexane is a two-step process. When the temperature is below the theta temperature, the polymer swells, i.e. the side chain-aromatic rings are gradually solvated by cyclohexane-solvent molecules. While above the theta temperature, conventional dissolution occurs, i.e. the main chains are gradually dispersed at a molecular level in the solvent. The interaction produced among aromatic rings by large π bonds or those among the main chains shows the existence of the cohesional entanglements.

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