The properties of polymer materials closely relate to entanglements and therefore much attention has been paid to macromolecular entanglements [1–7]. According to recent studies, entanglements among polymer chains can be divided into topological and cohesional entanglements [8]. The topological entanglement corresponds to the intertwine or intertwist part among polymer chains. On the other hand, the cohesional entanglement corresponds to the mutual contact or the short-range-order interaction part among polymer chains. Thus, the entanglement has a strong effect on the rate of molecular motions of chain segments, so NMR relaxation, generally used to characterize molecular motions, seems to be a useful means to study entanglement of polymers [6, 7].

Entanglements have a wide range of applications. For example, when a single surfactant is used as a displacement fluid in petroleum recovery, the remnant petroleum is usually distributed in small pores of rocks. When a surfactant mixed with polyacrylamide (PAAm) is used, however, it provides much better mobility control than a single surfactant. Obviously, the polymer viscosity plays an important role in the displacement fluid. Entanglements directly affect polymer viscosity. The authors studied the cohesive entanglements of polystyrene in concentrated solution of its theta solvent and the dynamics behavior of the dissolution process by $^{13}$C NMR relaxation and $^1$H NMR microimaging in a relatively high magnetic field [9–11] and found evidence for the existence of cohesional entanglements of polystyrene in concentrated solution. We also studied the cohesive interaction among polymer chains in a polyacrylamide (PAAm)–D$_2$O solution has been studied by NMR relaxation. The NMR relaxation times of PAAm in the good solvent D$_2$O were measured at different temperatures. The results show that the solution system has a high local viscosity and that its relaxation characteristic is soft-solid-like. The temperature dependence of the relaxation behavior of the solution is obviously different from that of ordinary polymer solutions. The difference lies in the relaxation behavior of the methylene protons in the main chain of PAAm, as shown by analyzing the relaxation process with single exponential and biexponential decays. As the temperature increases, the solvation is weakened, leading polymer chains to form curling coils, thus hindering the movement of the methylene protons among the main chains. It can be expected from the existence of 80% fast-relaxing protons that there are a high number of entanglements among the polymer chains in PAAm solution. The information about entanglements among the polymer chains can be deduced from the biexponential dependence of the spin–spin relaxation on the concentration of the polymer solutions.

**Abstract** The cohesive interaction among polymer chains in a polyacrylamide (PAAm)–D$_2$O solution has been studied by NMR relaxation. The NMR relaxation times of PAAm in the good solvent D$_2$O were measured at different temperatures. The results show that the solution system has a high local viscosity and that its relaxation characteristic is soft-solid-like. The temperature dependence of the relaxation behavior of the solution is obviously different from that of ordinary polymer solutions. The difference lies in the relaxation behavior of the methylene protons in the main chain of PAAm, as shown by analyzing the relaxation process with single exponential and biexponential decays. As the temperature increases, the solvation is weakened, leading polymer chains to form curling coils, thus hindering the movement of the methylene protons among the main chains. It can be expected from the existence of 80% fast-relaxing protons that there are a high number of entanglements among the polymer chains in PAAm solution. The information about entanglements among the polymer chains can be deduced from the biexponential dependence of the spin–spin relaxation on the concentration of the polymer solutions.

**Key words** Polyacrylamide · Nuclear magnetic resonance · Relaxation · Cohesional entanglement
biexponential dependence of the spin–spin relaxation of the protons in the polymer solution on temperature. The results showed that the behavior of the cohesional entanglements varies with the environment [12, 13]. Recently, we studied the dynamics behavior and entanglements of PAAm solutions by NMR relaxation measurements in a relatively high magnetic field; here, we report the main results.

**Experimental**

The PAAm used was PAAm 35305 produced by Pfizer. The degree of hydrolysis of the sample was 29.2% and the molecular weight was $1.6 \times 10^7$. D$_2$O was used as the solvent for the PAAm solutions and the solutions were prepared in an NMR sample tube. The deuterium content of D$_2$O was 99.99%. The homogeneous solutions of PAAm in D$_2$O were prepared by supersonic wave vibration for 35 days at ambient temperature. The concentrations of the four PAAm solutions were 25, 50, 75 and 100 g/l. The $^{13}$C NMR and $^1$H NMR experiments were performed on a Bruker AM-500 NMR spectrometer. The $^{13}$C NMR and $^1$H NMR spin–lattice relaxation times were measured by the inversion recovery method. The delay was longer than $5T_{1\text{max}}$, the range of probe temperatures was from 25 to 60 °C, a $^{13}$C resonance frequency of 125.76 MHz and 128 accumulations were used and a $^1$H resonance frequency of 500.13 MHz and 32 accumulations were used. The $^1$H NMR spin–spin relaxation times were measured by the spin-echo method.

**Results and discussion**

$^{13}$C relaxation

The $^{13}$C NMR spin–lattice relaxation times of individual carbon atoms of PAAm in solutions at temperatures from 298 to 333 K were obtained by single exponential fitting. The results are shown in Fig. 1. The $T_1$ values increase as the temperature increases; this behavior is similar to the NMR relaxation characteristic of liquid molecules with fast movement. However, there is a difference in the variation of the relaxation rate between the carbon nuclei on the main chains and on the side chains of PAAm: the $T_1$ values of the carbon nuclei on the side chain increase slightly faster than those of the carbon nuclei (methine and methylene) on the main chain. This phenomenon is due to the fact that the mobility of the side group is more sensitive to temperature than that of the main chain. The $^{13}$C NMR relaxation characteristic of this polymer is similar to that of ordinary polymer [14–17].

$^1$H spin–lattice and spin–spin relaxations

$^1$H NMR spin–lattice relaxation times obtained by single exponential fitting of protons linked to the carbon atoms of the main chain of PAAm in solution at temperatures from 298 to 333 K are shown in Fig. 2. The $T_1$ value of a proton linked to the methine increases as the temperature increases, similar to the variation of the $^{13}$C $T_1$ of methine in the main chain given in Fig. 1. The result in Fig. 1 reveals the relaxation characteristic of the skeleton structure of the polymer, which depends on the intramolecular interactions [14–17], while the result in Fig. 2 reveals the relaxation characteristic of protons linked to the carbon nuclei of skeleton structures of the polymer, which is also related to the intermolecular interactions. Since they are both related to the motion of the skeleton structure, theoretically they should have similar temperature dependence. From this point of view, the result for methine is reasonable;

![Fig. 1](image1.png)  The measured $^{13}$C NMR $T_1$ values of individual carbon atoms of polyacrylamide (PAAm)-D$_2$O solution (c = 50 g/l) at various temperatures. Carbonyls of the side chains of PAAm (■); methine carbons of the main chain of PAAm (▲); methylene carbons of the main chain of PAAm (●).

![Fig. 2](image2.png)  The measured $^1$H NMR $T_1$ values of PAAm–D$_2$O solution (c = 50 g/l) at various temperatures. The protons attached to the methine carbons of the main chain of PAAm (■); the protons attached to the methylene carbons of the main chain of PAAm (●).