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SHORT COMMUNICATION

S.-Z. Mao
X.-D. Zhang
J.-M. Dereppe
Y.-R. Du

Nuclear magnetic resonance relaxation studies of polyacrylamide solution

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S.-Z. Mao (✉) · X.-D. Zhang · Y.-R. Du
Laboratory of Magnetic Resonance and
Atomic and Molecular Physics
Wuhan Institute of Physics
and Mathematics
Chinese Academy of Sciences
P.O. Box 71010, Wuhan 430071, China
e-mail: maosz@nmr.whcnc.ac.cn
Fax: +86-27-87885291

J.-M. Dereppe
Unite CPMC
Universite de Louvain, Belgium

Abstract The cohesive interaction among polymer chains in a polyacrylamide (PAAm)–D_2O solution has been studied by NMR relaxation. The NMR relaxation times of PAAm in the good solvent D_2O 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 zhigh 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

Introduction

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 intervolve 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 cohesional entanglements of polystyrene in concentrated solution of its theta solvent and the dynamics behavior of the dissolution process by ^{13}C NMR relaxation and ^1H 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 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 1.6×10^7. D_2O was used as the solvent for the PAAm solutions and the solutions were prepared in an NMR sample tube. The deuteron content of D_2O was 99.99%. The homogeneous solutions of PAAm in D_2O 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 ^1H NMR experiments were performed on a Bruker AM-500 NMR spectrometer. The ^{13}C NMR and ^1H NMR spin–lattice relaxation times were measured by the inversion recovery method. The delay was longer than $5T_{1\max}$, 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 ^1H resonance frequency of 500.13 MHz and 32 accumulations were used. The ^1H 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].

^1H spin–lattice and spin–spin relaxations

^1H 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;

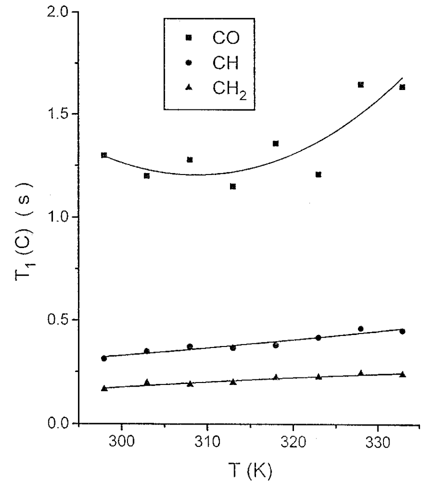

Fig. 1 The measured ^{13}C NMR T_1 values of individual carbon atoms of polyacrylamide (*PAAm*)–D_2O solution ($c = 50$ g/l) at various temperatures. Carbonyls of the side chains of PAAm (■); methine carbons of the main chain of PAAm (●); methylene carbons of the main chain of PAAm (▲)

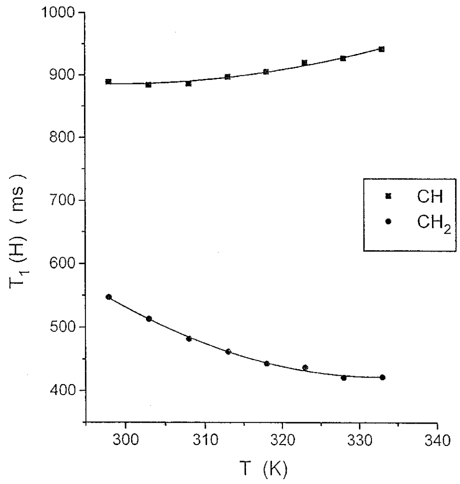

Fig. 2 The measured ^1H NMR T_1 values of PAAm–D_2O solution ($c = 50$ g/l) at various temperatures. The protons attached to the methine carbons of the main chain of PAAm (■); the protons attached to the methylene carbons of the main chain of PAAm (●)

however, it should be noted that the T_1 values of the protons linked to the methylene of the main chain decrease as the temperature increases. This unusual phenomenon will be explained in the following text.

The T_1 values of protons obtained by single exponential fitting (the fitting error is less than 10%) and the T_2 values of protons obtained by biexponential fitting (the biexponential characteristic of T_2 will be explained later) of the experimental data are listed in Table 1. From Table 1 one can see that $T_1 > T_2$ in measured range of the temperature. This implies the fact that the segment motion is in the low-frequency region. The T_2/T_1 ratios are also listed in Table 1. As the temperature increases, the T_2/T_1 values of the methine proton of the main chain approaches 1, while those of the methylene protons of the main chain increase slightly. From these results and the result shown in Fig. 1 we conclude that the system is near the region of the minimum value of the characteristic curve of the relaxation time versus the correlation time. However, there is a difference: the relaxation of the methine protons of the main chains is on the left of the minimum and the relaxation of the methylene protons is on the right. The solution system has a high local viscosity and it is characteristic of the NMR relaxation of soft-solid-like materials. The methylene protons of the main chains are characteristic of the NMR relaxation of solid materials.

Biexponential behavior of ^{1}H spin–spin relaxation

The spin–spin relaxation processes of the methine and methylene protons in PAAm solution cannot be fitted well with an ordinary single exponential function (the fitting error is larger than 10%). So we tried to fit these data by using a biexponential function with the form

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

$$P_f + P_s = 1 \quad , \tag{2}$$

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

The results show that the spin–spin relaxation data of the methine and methylene protons are well fitted with the biexponential function. Figure 3 and 4 show typical simulations for protons of the main-chain methylene and methine of PAAm in solution at temperatures of 308 K ($c = 50$ g/l) and 298 K ($c = 100$ g/l), respectively. The dotted lines stand for an exponential decay

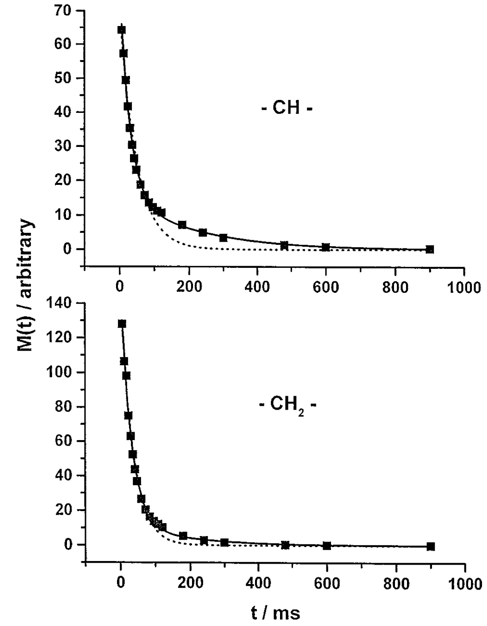

Fig. 3 Simulation of the ^{1}H spin–spin relaxation process for protons of the main-chain methylene and methine of PAAm in solution at a temperature of 308 K ($c = 50$ g/l). The *points* are experimentally measured data, the *solid line* is the curve calculated using a biexponential simulation and the *dotted line* is the curve calculated using an exponential simulation

Table 1 The relaxation times of the protons linked to carbon nuclei of the main chains of polyacrylamide (c = 50 g/l)

T (K)	CH					CH$_2$				
	T_{1H}^{a} (ms)	T_{2s}^{b} (ms)	T_{2f} (ms)	P_f (%)	T_{2s}/T_1	T_{1H} (ms)	T_{2s} (ms)	T_{2f} (ms)	P_f (%)	T_{2s}/T_1
298	889	220	27	88	0.25	547	125	26	85	0.23
303	884	209	27	83	0.24	513	153	27	94	0.30
308	886	213	28	80	0.24	482	146	28	89	0.30
313	897	292	31	89	0.33	462	138	29	81	0.30
318	905	397	31	93	0.44	443	144	28	76	0.33
323	920	562	27	94	0.61	437	164	29	77	0.38
328	927	803	26	94	0.87	421	189	30	80	0.45
333	942	1006	25	96	1.07	422	222	31	84	0.53

[a] The spin–lattice relaxation times were fitted using a single exponential function
[b] The spin–spin relaxation times were fitted using a biexponential function

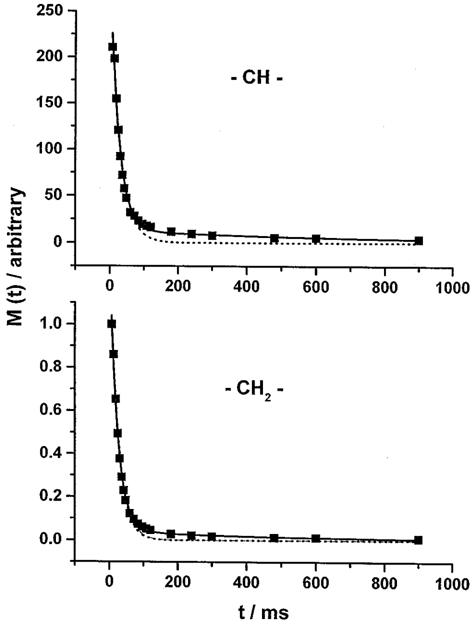

Fig. 4 Simulation of the ^{1}H spin–spin relaxation process for protons of the main-chain methylene and methine of PAAm in solution at a concentration of 100 g/l ($T = 298$ K). The *points* are experimentally measured data, the *solid line* is the curve calculated using a biexponential simulation and the *dotted line* is the curve calculated using an exponential simulation

simulation; the solid lines stand for the biexponential simulation. It is obvious that the dotted curve (exponential decay) does not fit the experimental points, but the solid biexponential curve fits them well. The T_{2f}, T_{2s} and P_s values obtained from fitting the ^{1}H spin–spin relaxation curves of protons of main-chain methylene and methine of the PAAm sample are listed in Table 1. The fitting error is less than 10%. 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 the polymer chains. The smaller the distance between the protons, the slower the motion of the polymer chains and the stronger the interaction of the proton–proton dipolar coupling, thus the smaller the T_2 value. The existence of two relaxation processes suggests that the protons have two independent states [12, 13]. Since the proton spin–spin relaxation depends directly on the distances between the protons in the polymer chains, the fast relaxation process (short T_2) should result from protons with high density or with entanglements among the polymer chains (therefore their motions are restricted), while the slow relaxation process (long T_2) should result from protons with lower density or from protons with relatively free movement among the polymer chains. For this reason, the fraction of the protons in the fast relaxation, P_f, can be considered to be the relative content of protons with entanglements. The fraction of the protons in the slow relaxation, P_s, can be considered to be the relative content of the protons moving freely among the polymer chains. As shown in Table 1, the fast-relaxing fraction is about 80% at room temperature and only about 20% of the polymer chains, which have low local viscosity, constitute the fast-moving, mobile fraction. The movement of about 80% of the polymer chains is hindered because of entanglements. This result agrees with that observed by dynamic light scattering for PAAm solutions where a slowly relaxing component of narrow distribution exists in addition to the network mode formed through interchain entanglements [18]. As shown in Table 1, with an increase in temperature, the movement of the polymer molecule speeds up and T_{2s} of the methine protons of the main chain increases, while T_{2s} of the methylene protons of the main chain and T_{2f} and P_f of both protons remain nearly constant, i.e. they are hardly affected by temperature in this temperature range. This shows that the protons in entanglements among polymer chains are not obviously sensitive as the temperature increases. The difference in temperature dependence between T_{2s} (CH) and T_{2s} (CH_2) can be explained by the difference in the degree of compensation of the following two opposing effects. Firstly, with an increase in temperature, the movement of the polymer molecules speeds up, which causes T_{2s} to increase. Secondly, the intensified thermal motion on increasing the temperature weakens the solvation; therefore, the solvent molecules break away from the polymer chains, causing the polymer chains to form curling coils, so the flexibility of the polymer chains increases. In this case the protons on the main chains become closer, leading to a decrease in the T_2 values of methine and methylene; however, the increased movement of the side group should have more influence on the proton on the methine, which is directly linked to it. For the methine proton the first effect is dominant, so T_{2s} (CH) increases, while in the case of methylene protons the formation of curling coils may make CH_2 so dense so as to restrict the movement of the CH_2 protons among main chains; the increase in thermal motion is compensated by the restriction of motion due to the increase in the proton density. This is the main reason why the $T_{2s}(CH_2)$ value did not show strong dependence on temperature as shown in Table 1 and why the T_{1H} (CH_2) value decreases as the temperature increases as shown in Fig. 2.

The temperature dependence of the ^{1}H relaxation behavior of the methylene protons of PAAm solution is different from that of ordinary polymer solution. This is due to the restricted movement of protons by forming coiled chains as a consequence of the weakening of solvation resulting from the increase in temperature.

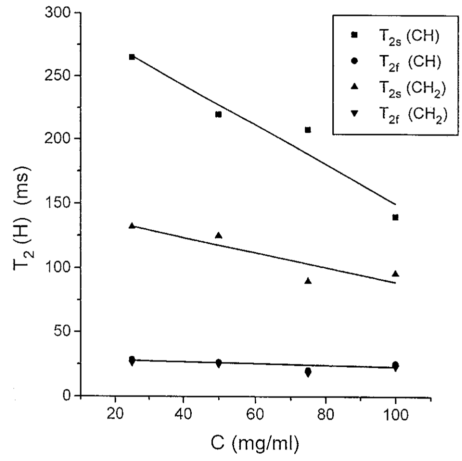

Fig. 5 ^1H NMR T_2 values of the fast and slow relaxation of PAAm–D_2O solution at various concentrations ($T = 298$ K). The slow relaxation of the protons attached to the methine carbons of the main chain of PAAm (■); The fast relaxation of the protons attached to the methine carbons of the main chain of PAAm (●); The slow relaxation of the protons attached to the methylene carbons of the main chain of PAAm (▲); The fast relaxation of the protons attached to the methylene carbons of the main chain of PAAm (▼)

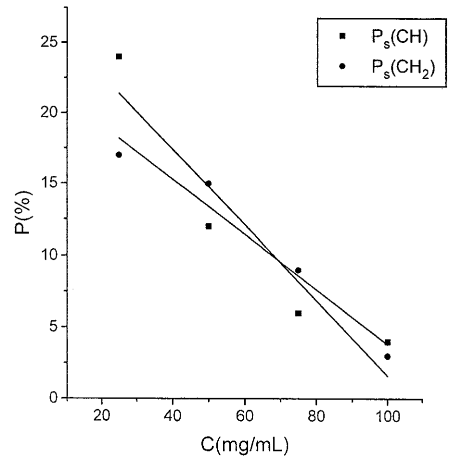

Fig. 6 The fraction of the slow relaxation of the protons attached to carbons of PAAm at various concentrations ($T = 298$ K). The fraction of the slow relaxation of the protons attached to the methine carbons of the main chain of PAAm (■); The fraction of the slow relaxation of the protons attached to the methylene carbons of the main chain of PAAm (▲)

The ^1H NMR T_{2s} and T_{2f} of the methine and methylene protons of the main chains of PAAm at concentrations from 25 to 100 g/l are shown in Fig. 5. As the concentration increases, the polymer chains tend to be closer to each other, leading to a high density and hence a short distance between protons, so macromolecular movement is retarded. This is the reason why T_{2s} of the methine and methylene protons of the main chains decrease with an increase in concentration, as shown in Fig. 5. T_{2f} remained nearly constant as the concentration of the polymer increased; this is due to the fact that the movement of protons involved in entanglements remains unchanged at the same temperature. Meanwhile, as shown in Fig. 6, P_s decreases with increasing concentration of the polymer, which implies that more and more protons are involved in the entanglement and fewer and fewer protons can move freely.

The spin–spin relaxation of PAAm protons in solution at temperatures from 298 to 333 K in a high field exhibits a biexponential relaxation, while the ^{13}C and ^1H spin–lattice relaxations exhibit a single exponential relaxation. The reason is that T_2 is very sensitive to low-frequency movement, so it exists only in a small microregion, while T_1 exists in a large microregion and the measurement of T_1 is affected by spin–diffusion interaction between phases of different movements due to entanglements, so from T_1 one cannot obtain all information about the microregion. The measurement of T_2 is not affected by spin–diffusion interaction. The movement caused by the entanglement among polymer chains is homogeneous in the region of T_1 scaling and is inhomogeneous in the region of T_2 scaling.

In conclusion, the cohesive interaction among polymer chains in PAAm–D_2O solution has been studied by NMR relaxation. The NMR relaxation times of PAAm in the good solvent D_2O were measured at different temperatures. The results show that the solution system has a high local viscosity and that the NMR relaxation characteristic is soft-solid-like. The temperature dependence of the relaxation behavior of the solution is 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 the temperature increases, the solvation is weakened, which causes polymer chains to form curling coils and so the movement of the methylene protons among the main chains is hindered. It can be expected from the existence of 80% fast-relaxing protons that there are 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.

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