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NMR Evidence for Polymer/Solvent Complexes in Thermoreversible Gels

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Introduction

It is well known that some polymers form thermoreversible gels in certain solvents, usually when the concentration of the polymer is higher than ∼1%.[1] Mixtures of solutions of isotactic (i) poly(methyl methacrylate) (PMMA) and syndiotactic (s) PMMA as well as solutions of s-PMMA or i-PMMA alone give rise to gel formation.[2,3] The gelation arises from the formation of ordered associated structures. Ordered associated structures of s-PMMA are formed in some solvents (toluene, *o*-dichlorobenzene, *o*-xylene, bromobenzene, butyl acetate, CCl_4), mainly as a result of stereospecific interactions between long sequences of monomeric units forming probably double-helix structures.[2] The role of the solvent in the association process is not clear. There are some indirect indications of the formation of polymer/solvent complexes which could promote the stereoassociation and gelation of s-PMMA[2,4,5] as well as gelation of atactic (at) PMMA.[6,7] Aggregation and gelation of poly(vinyl chloride) (PVC) was also described and possible existence of solvated structures was suggested when diesters were used as solvents.[1,8,9] Very recently, the existence of the polymer/solvent complex was revealed by neutron diffraction for PVC gels in diethyl oxalate.[10]

Since at present direct evidence for polymer/solvent complexes in s-PMMA gels does not exist and to obtain further support for their existence in PVC gels, we dealt with this problem by using NMR methods. We used an approach based on measurements of nonselective and selective proton spin−lattice relaxation times T_1 of solvent which was previously applied in studies of interactions between small molecules (either solvent, i.e. water, or substrate) with biological macromolecules.[11−13]

General Analysis

It is known that both nonselective (NS) and selective (SE) proton spin−lattice relaxation times T_1 can be measured depending on the nature of the first 180° pulse in the inversion−recovery sequence used for their measurements. Assuming a dipolar relaxation mechanism, for any proton *i* its nonselective and selective relaxation rates are given by[11]

$$(T_1^{\,i})^{-1}(\mathrm{NS}) = \sum_{i\neq j}\rho_{ij} + \sum_{i\neq j}\sigma_{ij} \tag{1}$$

$$(T_1^{\,i})^{-1}(\mathrm{SE}) = \sum_{i\neq j}\rho_{ij} \tag{2}$$

In these equations, ρ_{ij} and σ_{ij} are the direct relaxation term and the cross-relaxation term, respectively, for a pair of protons *i* and *j*:

$$\rho_{ij} = \frac{\hbar^2\gamma_{\mathrm{H}}^{\,4}}{10 r_{ij}^{\,6}}\left\{\frac{3\tau_{\mathrm{c}}}{1+(\omega_0\tau_{\mathrm{c}})^2} + \frac{6\tau_{\mathrm{c}}}{1+4(\omega_0\tau_{\mathrm{c}})^2} + \tau_{\mathrm{c}}\right\} \tag{3}$$

$$\sigma_{ij} = \frac{\hbar^2\gamma_{\mathrm{H}}^{\,4}}{10 r_{ij}^{\,6}}\left\{\frac{6\tau_{\mathrm{c}}}{1+4(\omega_0\tau_{\mathrm{c}})^2} - \tau_{\mathrm{c}}\right\} \tag{4}$$

where r_{ij} is the interproton distance, ω_0 is the resonance frequency, τ_{c} is the motional correlation time, and the other constants have their usual meanings. From eqs 1−4 it follows that relaxation times T_1(SE) and T_1(NS) exhibit different dependences on the correlation time τ_{c}, as shown in Figure 1; a marked difference exists in the slow-motion region, i.e. for correlation times $\tau_{\mathrm{c}} \gg \omega_0^{-1}$.

If we assume that in a thermoreversible gel a part of the solvent molecules is bound to the polymer while the other part of the solvent is free, and if we assume a fast exchange between bound and free solvent molecules, then the observed spin−lattice relaxation rate is given as

$$(T_{1\,\mathrm{obs}})^{-1} = p_{\mathrm{F}}(T_{1\mathrm{F}})^{-1} + p_{\mathrm{B}}\,(T_{1\mathrm{B}})^{-1} \tag{5}$$

where the subscripts F and B correspond to the free and bound states, respectively, and p_{F} and p_{B} are the respective populations. If bound solvent molecules exhibit slow motions ($\omega_0\tau_{\mathrm{c}} \gg 1$), then one can expect from Figure 1 a much stronger effect on the observed T_1(SE) in comparison to T_1(NS) values.

Experimental Section

Polymers. The highly syndiotactic sample of s-PMMA was synthesized by ion-coordination polymerization initiated with triethylaluminium and $TiCl_4$ in toluene at −78 °C. The tacticity was evaluated by analysis of ^{1}H NMR spectra in $CDCl_3$. The following proportions for the syndiotactic, heterotactic, and isotactic triads, respectively, were found: S = 89%, H = 9%, I = 2%. The weight-average molecular weight $\bar{M}_{\mathrm{w}}$ = 145 000. The s-PMMA of lower degree of stereoregularity (at-PMMA) was prepared by radical polymerization in acetic acid at 30 °C initiated by dibenzoyl peroxide in the presence of $RhCl(C_8H_{12})$(4-methylpyridine). By ^{1}H NMR analysis, for at-PMMA S = 66%, H = 31%, and I = 3%; its osmometrically determined number-average molecular weight $\bar{M}_{\mathrm{n}}$ = 42 000.

The PVC sample was a commercial product (Neralit S-702); according to ^{1}H NMR analysis, this sample contains 55% syndiotactic diads.

Preparation of Solutions and Gels. Homogeneous solutions of s-PMMA in bromobenzene (c = 4.5−27.4 wt %), at-PMMA in bromobenzene (c = 12.3 wt %), PVC in dibutyl phthalate (c = 5 wt %), and PVC in diethyl oxalate (c = 5 wt %) were prepared by heating of the sealed 5 mm NMR tubes at 90 °C (PMMA) or at 130 °C (PVC). Then the samples were degassed at elevated temperature (above 70 °C) and sealed under argon. s-PMMA or PVC gels were formed at room temperature.

NMR Measurements. ^{1}H NMR spectra and ^{1}H selective and nonselective spin−lattice relaxation times T_1 were measured using a Bruker AC-300 spectrometer operating at 300.1 MHz. The same instrument was used for ^{13}C T_1 measurements of at-PMMA in bromobenzene at 75.5 MHz. The proton T_1(NS) and T_1(SE) values of the solvent were measured by using an inversion−recovery pulse sequence (180°−τ−90°) with 8 scans separated by a relaxation delay of 60−100 s; 15−20 τ values were used. In selective T_1(SE) measurements, the DANTE method[14] was used to generate selectively the first 180° pulse (typically 160 μs); the DANTE sequence consisted of 50−70 pulses separated by 200−300 μs delays. After time τ, the nonselective 90° pulse was applied.

Results and Discussion

s-PMMA Gels. By using the approach based on measurements of the temperature dependences of the

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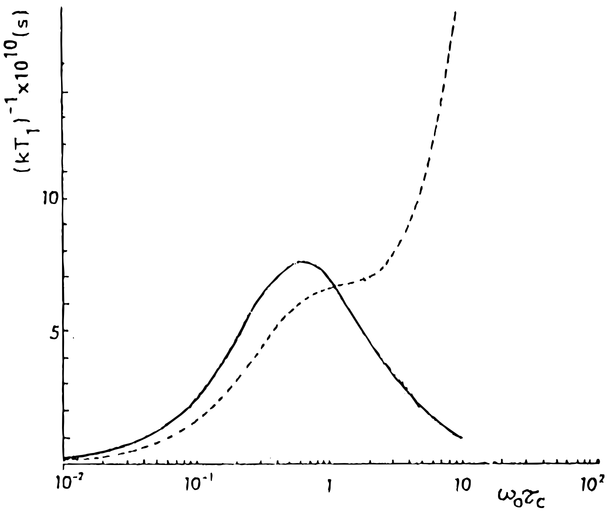
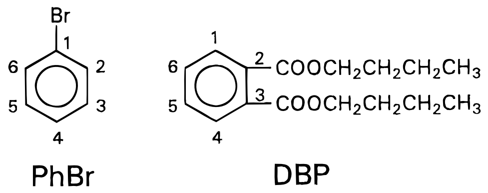


Figure 1. Selective (dashed line) and nonselective (full line) spin−lattice relaxation rate T_1^{-1} for a proton pair as a function of $\omega_0\tau_c$; $k = \gamma_H^4\hbar^2/r_{ij}^6$ (cf. ref 11).

Chart 1



absolute integrated intensities of the ^{1}H NMR bands,[2,15] we have found that in s-PMMA gels in bromobenzene at room temperature a large part of s-PMMA exists in the associated state with mobility restricted to such an extent that corresponding monomeric units escape detection in conventional high-resolution ^{1}H NMR spectra. In the studied concentration range, the values of s-PMMA associated fraction p roughly linearly increased with increasing polymer concentration, reaching the values $p = 38\%$ and 79% for concentrations 4.5 and 27.4 wt %, respectively. Similarly to other solvents,[2] the associated structures were completely decomposed (melted) at 60 °C. From previous NMR studies of s-PMMA aggregates and gels in toluene,[16,17] it follows that the motion of the associated segments of s-PMMA is spatially isotropic with effective correlation time $\tau_{eff} \sim 70$ ns. In agreement with previous results,[2] no association was detected in solutions of at-PMMA in bromobenzene. The measurements of the temperature dependences of the absolute integrated intensities of the ^{1}H NMR bands of bromobenzene have shown that similarly to pure bromobenzene and to solutions of at-PMMA, also in the studied s-PMMA gels all the solvent is detected in high-resolution spectra; i.e. no “loss” of the solvent intensity was observed for these gels.

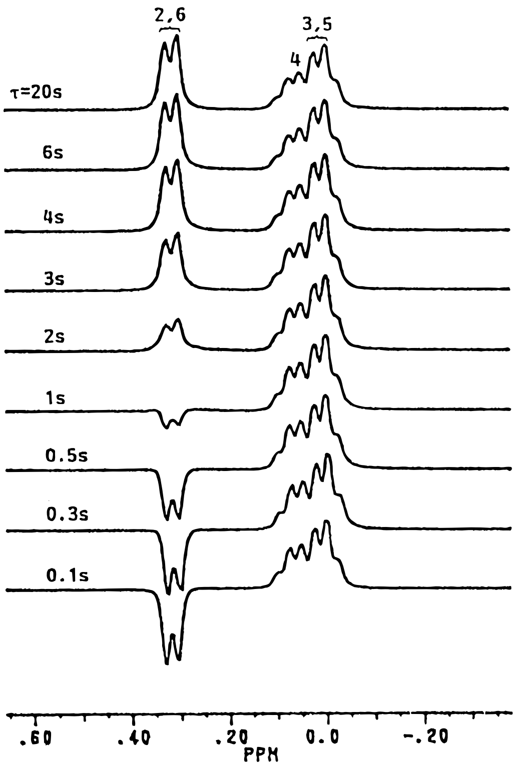


Figure 2. Selective partially relaxed ^{1}H NMR spectra of bromobenzene in s-PMMA gel ($c = 27.4$ wt %); the ppm scale in this figure is referred to the band of the 3,5-protons of bromobenzene.

Table 1. Selective (T_1(SE)) and Nonselective (T_1(NS)) Proton Spin−Lattice Relaxation Times of Bromobenzene (PhBr) (2,6-Protons) in s-PMMA Solutions and Gels at 300.1 MHz

sample	T (K)	T_1(SE) (s)[a]	T_1(NS) (s)[a]	T_1^{-1}(NS) − T_1^{-1}(SE) (s^{-1}) ($=\sum_{i\neq j}\sigma_{ij}$)
PhBr	250	5.1	4.2$_5$	0.039
	280	7.1	6.6	0.011
	290	8.6	7.6	0.016
	300	9.8	8.0	0.023
at-PMMA/PhBr	250	2.7	2.5$_5$	0.022
($c = 12.3$ wt %)	260	3.5	3.1	0.037
	280	5.5	4.8	0.026
	300	8.1	7.2	0.016
s-PMMA/PhBr	280	5.6	6.3$_5$	−0.022
($c = 4.5$ wt %)	290	8.3	8.1	0.003
	300	10.9$_5$	9.9	0.010
s-PMMA/PhBr	250	0.58	1.9	−1.198
($c = 13.7$ wt %)	280	2.3	3.5	−0.149
	290	3.7	4.2	−0.032
	300	5.3	5.9$_5$	−0.021
s-PMMA/PhBr ($c = 27.4$ wt %)	300	2.1$_5$	3.0	−0.132

[a] Standard deviation less than 0.5%.

We have applied the measurements of nonselective and selective proton spin−lattice relaxation times T_1(NS) and T_1(SE) of the solvent to find out if s-PMMA/bromobenzene complexes exist in s-PMMA gels. T_1(NS) and T_1(SE) values of the 2,6-protons of bromobenzene (cf. Chart 1) resonating at 7.49 ppm[18] were measured. In Figure 2 a series of partially selectively relaxed ^{1}H NMR spectra of bromobenzene in the s-PMMA/bromobenzene gel ($c = 27.4$ wt %) is shown to demonstrate a very good selectivity during these measurements. We measured ^{1}H T_1(NS) and T_1(SE) relaxation times of bromobenzene molecules in pure bromobenzene, in solutions of at-PMMA, and in gels of s-PMMA of high stereoregularity. In all cases the relaxation curves were exponential (single T_1). The results are shown in Table 1, together with the values of the difference T_1^{-1}(NS) − T_1^{-1}(SE), which are the cross-relaxation terms $\sum\sigma_{ij}$. From Table 1 it is clear that while in pure bromobenzene and in solutions of at-PMMA, where no associated structures exist, the values of T_1(NS) are always somewhat lower in comparison to T_1(SE), as expected from the theory for $\omega_0\tau_c < 1$ (cf. Figure 1), a reverse situation was found with bromobenzene in s-PMMA gels, i.e. T_1(NS) > T_1(SE) (except the concentration 4.5 wt % at 300 K). From Table 1 one can also see that T_1(SE) values of bromobenzene in s-PMMA gels are significantly shorter than in pure bromobenzene or in solutions of at-PMMA. Moreover, in all cases the T_1(NS) values increase with increasing temperature, confirming that also in the studied s-PMMA gels the bulk solvent molecules are on the high-temperature side of the T_1 curve, i.e. under fast-motion conditions $\omega_0\tau_c < 1$. This confirms that the reduction in T_1(SE) values in s-PMMA gels is not simply due to changed motional behavior of the bulk solvent in the gel.[13] Based on eqs 1−5 (cf. also Figure 1), all the obtained results evidence that a part of the bromobenzene molecules form a complex with s-PMMA. Such bound bromobenzene molecules exhibit a slow-motion behavior (similar to that of macromolecules) with fast exchange between bound and free sites relative to T_1 values (~1 s). The values of the cross-relaxation term in the last column of Table 1 demonstrate that the effect is larger for lower temperature and higher concentration, indicating an increase in the population of the bound solvent with increasing concentration. Such behavior is consistent with the results of the studies of association of s-PMMA in mixed solvents which also indicate the formation of a polymer/solvent complex with the estimated stoichiometry 1.4 toluene molecules per s-PMMA monomeric unit;[4,5,19] a similar stoichiometry was recently proposed from DSC results also for the polymer/solvent complex in i-PMMA gels.[20]

Interesting is the fact that nothing indicates the formation of polymer/solvent complexes in solutions of at-PMMA; as shown in Table 1, at all temperatures $T_1(\mathrm{NS}) < T_1(\mathrm{SE})$ and the values of the cross-relaxation term do not differ significantly from the corresponding values in pure bromobenzene. At the same time, also in this system segmental motions of at-PMMA are in the slow-motion region ($\omega_0\tau_c \gg 1$), as confirmed by the ^{13}C T_1 measurements. Thus, e.g., an increase in the ^{13}C T_1 values with decreasing temperature was observed for quaternary carbons of at-PMMA in bromobenzene (T_1 = 1.51 s at 300 K, and T_1 = 3.41 s at 250 K). From the T_1 values of the methylene carbons of at-PMMA (e.g. T_1 = 112 ms at 300 K) and assuming an isotropic motional model with a single correlation time τ_c,[21,22] we obtained τ_c = 6 ns and $\omega_0\tau_c = 10$ at 300 K; $\omega_0\tau_c \approx 40$ at 250 K. Although there is still a difference in the rate of the polymer segmental motions for at-PMMA in bromobenzene and s-PMMA gels, the fact that the T_1(NS) and T_1(SE) values do not indicate any specific polymer/solvent interactions in the solutions of at-PMMA suggests that the regular conformation of s-PMMA of high stereoregularity capable of accommodating bromobenzene molecules (e.g. in cavities formed by side groups[1]) is a prerequisite to the formation of PMMA/bromobenzene complexes. Such behavior is also consistent with the finding that a part (~15−20 mol %) of the solvent remains bound even in solid s-PMMA samples obtained from s-PMMA gels by evaporation of solvent at room temperature, while no residual solvent remains in solid at-PMMA obtained in analogous way.[19]

PVC Gels. The results obtained with PVC gels in dibutyl phthalate or diethyl oxalate are very similar to those described above for s-PMMA gels. Also here the measurements of the temperature dependences of the integrated intensities of PVC lines in ^{1}H NMR spectra revealed that 40−50% of monomeric units exist in the aggregated state and therefore are not detected in high-resolution ^{1}H NMR spectra (cf. also ref 15). At the same time, these measurements confirmed that all the solvent is directly revealed in the spectra. The results of T_1(NS) and T_1(SE) measurements for the 1,4-protons of dibutyl phthalate (Chart 1) in pure solvent and in PVC gel are shown in Table 2. These results, similarly to those discussed above for s-PMMA gels, reveal the existence of PVC/dibutyl phthalate complexes in PVC gels. The existence of PVC/diethyl oxalate complexes was shown from T_1(NS) and T_1(SE) measurements of CH_2 protons of diethyl oxalate in a similar way. In both cases the exponential relaxation curves indicate that the lifetime of PVC/solvent complexes is shorter than 1 s, as found also for s-PMMA/bromobenzene complex.

Table 2. Selective (T_1(SE)) and Nonselective (T_1(NS) Proton Spin−Lattice Relaxation Times of Dibutyl Phthalate (DBP) (1,4-Protons) in PVC Gels at 300.1 MHz

sample	T (K)	T_1(SE) (s)[a]	T_1(NS) (s)[a]	T_1^{-1}(NS) − T_1^{-1}(SE) (s^{-1}) (=$\sum_{i\neq j}\sigma_{ij}$)
DBP	290	0.98	0.94	0.044
	300	1.25	1.03_5	0.166
	310	1.49	1.16_5	0.187
PVC/DBP	290	0.47_5	0.83	−0.900
(c = 5 wt %)	300	0.72	0.91_5	−0.296
	310	0.94_5	1.14_5	−0.185

[a] Standard deviation less than 0.5%.

Conclusions

On the basis of measurements of selective and nonselective ^{1}H spin−lattice relaxation times of the solvent, the existence of polymer/solvent complexes (probably of the inclusion type) was evidenced for thermoreversible gels of s-PMMA in bromobenzene and for PVC gels in dibutyl phthalate or diethyl oxalate. The bound solvent molecules exhibit a slow-motion behavior ($\omega_0\tau_c \gg 1$) similar to that of associated polymer segments, with fast exchange between bound and free sites relative to T_1 values (~1 s). Such polymer/solvent complexes can contribute to the stabilization of the overall associated structure and in this way to promote association and gelation of s-PMMA and PVC. In our opinion and in accord with DSC and neutron diffraction results on gels of isotactic polystyrene,[1] similar polymer/solvent complexes may exist also in thermoreversible gels of other polymers.

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