Polymer-Solvent Interactions in Thermoreversible Gels of Isotactic Poly(methyl methacrylate) as Studied by Measurement of ^{1}H NMR Relaxation of the Solvent

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SUMMARY: Dynamic structure and polymer-solvent interactions in solutions and gels of isotactic (*i*) poly(methyl methacrylate) (PMMA) in butyl acetate (BAC) were characterized by measurements of nonselective and selective ^{1}H NMR spin-lattice relaxation times of the solvent. In thermoreversible gels, the existence of *i*-PMMA-BAC complex, where the life-time of the bound solvent is ~ 100 ms or shorter, was confirmed. Although the correlation time of the solvent bound in *i*-PMMA-BAC complex is 5-10 times longer than for the free solvent, there is still a relative motional freedom for complexed solvent molecules. The same behaviour observed recently for thermoreversible gels of syndiotactic PMMA indicates the same character of polymer-solvent complexes in gels of both stereoregular forms of PMMA.

Introduction

It is well known that stereoregular poly(methyl methacrylate)s (PMMA) in solutions form ordered associated structures which are macroscopically manifested by gelation if the concentration of the polymer solution is higher than ~1 % [1)]. Both the associates and thermoreversible gels of the stereocomplex, formed by mixing solutions of isotactic (*i*) and syndiotactic (*s*) PMMA, and self-associates of *s*-PMMA have been extensively studied in the last years [1-3)]. Much less attention has been paid to association and gelation phenomena in *i*-PMMA solutions. A large amount of associated structures have been detected in dilute solutions of *i*-PMMA in butyl acetate (BAC) by NMR spectroscopy and light scattering at temperatures below -10 °C [4)]. At higher concentrations of *i*-PMMA, the formation and melting of the *i*-PMMA/BAC gel was followed by differential scanning calorimetry (DSC) [5)]. The results were consistent with the existence of a polymer-solvent complex with a stoichiometry of three BAC molecules per two *i*-PMMA monomeric units. The aim of this work was to characterize the dynamic structure and polymer-solvent interactions in solutions and gels of *i*-PMMA in BAC by NMR.

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Experimental part

Samples: *i*-PMMA was synthesized by anionic polymerization initiated with *tert*-butylmagnesium bromide in toluene at -78 °C [6]. The polymer contains 95 % isotactic, 3 % heterotactic and 2 % syndiotactic triads, as found by ^{1}H NMR analysis. Gel-permeation chromatography revealed an unimodal distribution of molecular weights with a weight-average molecular weight M_w = 21 000 and a ratio M_w/M_n= 1.15. Homogeneous solutions of *i*-PMMA in BAC were prepared in sealed 5- mm NMR tubes by heating at 80 °C. Then the samples were degassed and sealed under argon.

NMR measurements: ^{1}H NMR spectra and ^{1}H spin-lattice relaxation times T_1 were measured using a Bruker DPX-300 spectrometer operating at 300.1 MHz. The integrated intensities were determined by using the spectrometer integration software with an accuracy of ±1 %. The absolute temperature values were calibrated by using NMR spectra [7]. ^{1}H spin-lattice relaxation times T_1 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 measurements, the DANTE method was used to generate selectively the first 180° pulse [8].

Results and discussion

It has been shown for a number of systems including *i*-PMMA [1, 4, 9] that, because of the reduced mobility, the occurrence of associated polymer structures leads to the reduction in integrated band intensities in high-resolution ^{1}H NMR spectra. From a comparison of absolute integrated intensities [1, 9], the associated polymer fraction p can be determined from the relation

$$p = 1 - I/I_0 \qquad (1)$$

where I and I_0 are the integrated intensities with and without association, respectively. The temperature dependence of associated polymer fraction p obtained from measurements of the temperature dependence of integrated intensities of OCH_3 protons in NMR spectra is shown for *i*-PMMA in BAC in Fig. 1. This dependence is virtually independent of polymer concentration in the range c= 1-22 wt.-% (cf also ref. 4). The sharp transition between -10 and 0 °C indicating "melting" of associated structures is in accord with DSC results [5] where a melting endotherm of the gel was detected at -4 °C, independently of concentration. A similar transition was detected previously also for *s*-PMMA associated solutions and gels, but then, in

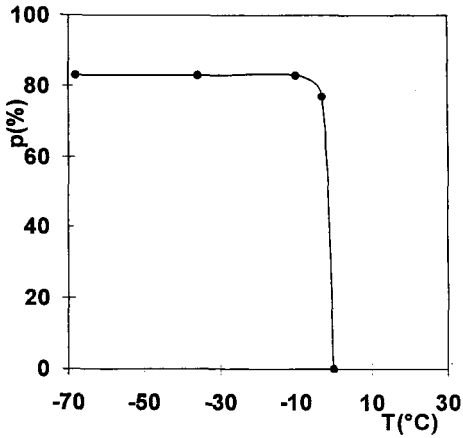

Fig. 1. Temperature dependence of associated polymer fraction p for *i*-PMMA in BAC (c = 5.38 wt.-%)

contrast to *i*-PMMA, the transition region was shifted by 60-70 °C to higher temperatures[1,4,10]. The fact that associated structures of *i*-PMMA are stable only at lower temperatures is evidently in connection with much higher segmental mobility of *i*-PMMA in comparison with *s*-PMMA. This indicates that the formation of associated structures requires relatively stiff polymer segments; for *i*-PMMA, sufficient stiffness is achieved only at lower temperatures.

The measurements of the temperature dependences of absolute integrated intensities of the ^{1}H NMR bands of BAC have shown that in the studied *i*-PMMA gels, all the solvent is detected in high-resolution spectra; i.e., no "loss" of the solvent intensity was observed for these gels.

To characterize polymer-solvent interactions and solvent dynamics in solutions and gels of *i*-PMMA in BAC, we used an approach based on measurements of nonselective (NS) and selective (SE) ^{1}H spin-lattice relaxation times T_1 of the solvent [8, 11]. It is known that relaxation times T_1(SE) and T_1(NS) exhibit different dependences on the motional correlation time τ_c; explicit expressions are given in refs. [8, 11]. While for correlation times fulfilling the condition $\omega_0\tau_c < 1$ (ω_0 is the resonance frequency), T_1(SE) and T_1(NS) do not differ much, T_1(SE) being somewhat longer than T_1(NS), a marked difference exists for $\omega_0\tau_c > 1$ where T_1(SE) is significantly shorter than T_1(NS). For the determination of the correlation time τ_c, it is convenient to use the ratio T_1(SE)/T_1(NS):

$$T_1(\mathrm{SE})/T_1(\mathrm{NS}) = 1 + \frac{\{\ 6\tau_c/[1+4(\omega_0\tau_c)^2] - \tau_c\}}{\{3\tau_c/[1+(\omega_0\tau_c)^2] + 6\tau_c/[1+4(\omega_0\tau_c)^2] + \tau_c\}} \qquad (2)$$

The limiting values for this ratio are 1.5 for $\omega_0\tau_c << 1$ and 0 for $\omega_0\tau_c >> 1$.

We measured ^{1}H T_1(NS) and T_1(SE) relaxation times for OCH_2 protons of BAC (resonating at 4.18 ppm) in the neat solvent and in *i*-PMMA solutions and gels at several temperatures. In all cases, the relaxation curves were exponential (single T_1). In Fig. 2, a series of several partially

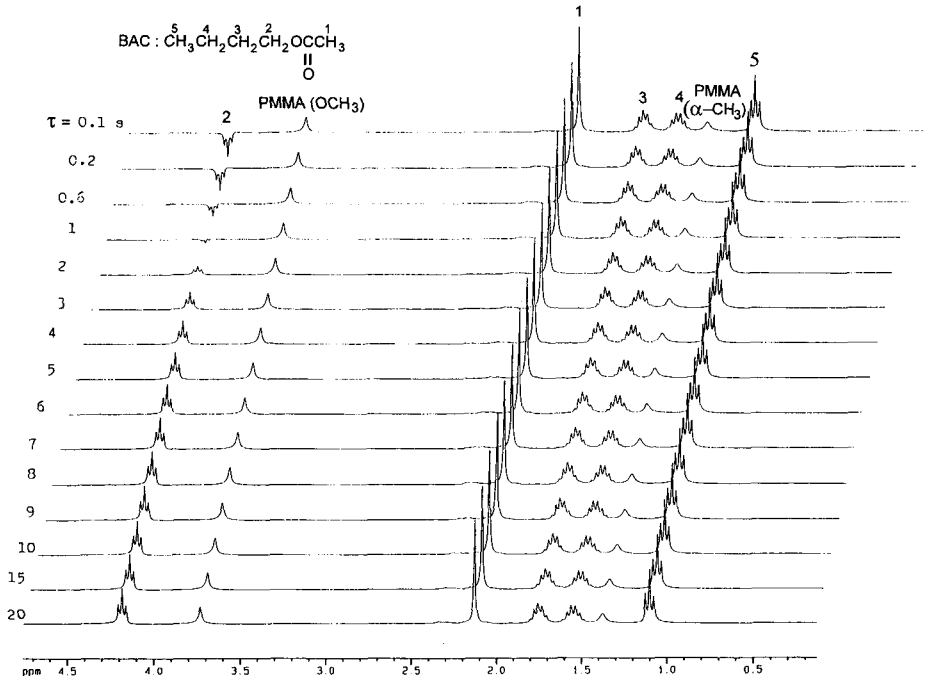

Fig. 2. Selective partially relaxed ^{1}H NMR spectra of *i*-PMMA/BAC (c = 22.1 wt.-%, 300 K)

selectively relaxed ^{1}H NMR spectra of i-PMMA/BAC solution is shown to demonstrate T_1(SE) measurements. The results are collected in Tab. 1. While in the neat solvent or in BAC solution of *i*-PMMA, measured at 300 K where associated structures completely melted, we observed somewhat lower values of T_1(NS) in comparison with T_1(SE), as expected for $\omega_0\tau_c < 1$, a reverse situation was found with solvent in *i*-PMMA gels (temperatures ≤ 270 K), i.e. T_1(NS) > T_1(SE). At the same time, T_1(SE) was significantly shorter in gels than in previous two cases and T_1(NS) always increased with increasing temperature, confirming that the reduction in T_1(SE) values in gels is not simply due to a changed motional behaviour of the bulk solvent in the gel [8]. These results evidence that in gels of *i*-PMMA in BAC, a part of solvent molecules form a complex with *i*-PMMA. Bound solvent molecules (possibly

accommodated in cavities formed by side groups [2, 5, 8]) can contribute to the stabilization of the overall asscociated structure. That the relaxation curves in *i*-PMMA gels are exponential indicates fast exchange between bound and free BAC molecules, regarding T_1 values (~ 1 s), i.e. the life-time of the bound solvent molecule is significantly shorter than 1 s.

Tab. 1. Selective and nonselective ^1H spin-lattice relaxation times and correlation times of butyl acetate (BAC) (OCH_2 protons) in *i*-PMMA solutions and gels

System	T (K)	T_1(SE)(s) [a]	T_1(NS)(s) [a]	T_{1B}(SE)/T_{1B}(NS)	τ_c (ns)
BAC	300	6.77	5.57	-	0.36
	270	4.52	3.98	-	0.43
	237	2.38	1.98	-	0.37
	205	0.522	0.49	-	0.52
i-PMMA/BAC	300	5.26	4.52	-	0.41
(c = 5.38 wt %)	270	1.13	2.45	0.253	2.3 [b]
	237	0.264	1.50	0.059	5.25 [b]
	205	0.178	0.482	0.052	5.63 [b]
i-PMMA/BAC	300	4.48	3.92	-	0.44
(c = 14.56 wt %)	270	0.75	2.19	0.226	2.47 [b]
	237	0.197	1.38	0.071	4.72 [b]
	205	0.132	0.486	0.086	4.25 [b]

[a] Frequency 300.1 MHz; standard deviation less than 0.5 %.
[b] τ_c values of the bound butyl acetate

For quantitative characterization of the motional behaviour of the solvent molecules bound in a polymer-solvent complex, we used the following relation for the observed T_1:

$$(T_{1,\mathrm{obs}})^{-1} = (1-f)\,(T_{1F})^{-1} + f\,(T_{1B})^{-1} \qquad (3)$$

where subscripts F and B correspond to free and bound states, respectively, and f is the fraction of bound solvent molecules. For T_{1F} values, we took the T_1 values found for neat solvent. The fraction f of bound solvent is given as

$$f = (\alpha\, p\, c)/(1-c) \qquad (4)$$

where α is the stoichiometric weight ratio (weight of the solvent/weight of *i*-PMMA in the polymer-solvent complex), p is the associated polymer fraction (cf. Fig. 1) and c is the

polymer concentration. Based on DSC results [5], we assumed $\alpha = 1.7$ (corresponding to molar stoichiometry 1.5 BAC molecules per monomeric unit). Using eq. (3), the relaxation times T_{1B}(NS) and T_{1B}(SE), and correspondingly the ratio T_{1B}(SE) / T_{1B}(NS), have been calculated for BAC in *i*-PMMA gels (see Tab. 1). Correlation times τ_c were then determined using eq. (2) (cf. last column in Tab. 1).

For the neat BAC, τ_c = 0.36 - 0.52 ns in the studied temperature range. Similar values (τ_c =0.41 and 0.44 ns) were obtained also for BAC in *i*-PMMA solutions (at 300 K). For *i*-PMMA gels, the correlation times of bound solvent are τ_c = 2.3 - 5.6 ns. Although 5-10 times (depending on temperature) longer than for the free solvent, the correlation time of the bound solvent is at least one order magnitude shorter than the effective correlation time of the motion of associated segments of *i*-PMMA (^{1}H NMR linewidth at least several hundreds Hz [1]), indicating a relative motional freedom for complexed BAC molecules. The same behaviour was recently observed also for thermoreversible gels of *s*-PMMA in bromobenzene [12], indicating the same character of polymer-solvent complexes for both stereoregular forms of PMMA.

Acknowledgement

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