

NMR-Study of Structure and Dynamics of Associates of Syndiotactic Poly(Methyl Methacrylate) in Toluene

Jiří Spěváček and Bohdan Schneider

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences,
162 06 Prague 6, Czechoslovakia

Summary

High-resolution ^1H NMR spectra (^1H HR-NMR) of solutions of isotactic (i) and syndiotactic (s) poly(methyl methacrylate) (PMMA) in toluene- d_8 were measured in the concentration range 0.2 to 10% w/v; for solutions of s-PMMA (10% w/v), ^1H NMR spectra with magic angle rotation (MAR-NMR) at various temperatures and ^{13}C NMR spectra with strong proton decoupling were also measured. It was found that even in very dilute solutions of s-PMMA in toluene- d_8 a considerable portion (76%) of polymer segments are associated: association is of intramolecular origin and is due to interaction of long syndiotactic sequences. From NMR spectra the motion of associated segments appears as isotropic with an effective correlation frequency $10^6 - 10^7$ Hz. A globular structure of the associates of s-PMMA is proposed.

Introduction

In the course of our NMR studies of association of stereoregular PMMA in solution we have found that besides the well known stereocomplex of PMMA formed by mixing of solutions of i- and s-PMMA (LIQUORI et al., SPĚVÁČEK and SCHNEIDER 1974a, 1975a), associated structures are also formed in solutions of only i-PMMA or only s-PMMA (SPĚVÁČEK and SCHNEIDER 1974b, 1975b, SPĚVÁČEK 1978a). Contrary to the stereocomplex, in these cases association is a consequence of interactions between sequences of equal tacticity. Associates of i-PMMA are very stable (they decompose at temperatures about 160°C) but their contents is relatively low (10-20%). Associates of s-PMMA are less stable (they practically decompose between $35-60^\circ\text{C}$), but their contents in some solvents is very high (up to 80%).

In this paper we have tried to characterize in greater detail the structure and dynamics of associates of s-PMMA in toluene- d_8 . To this end we have measured the contents of associated monomer units by means of the integrated band intensities in ^1H HR-NMR spectra (SPĚVÁČEK and SCHNEIDER 1974a,b, 1975a,b, SPĚVÁČEK 1978a),

and we have also made use of some solid state high-resolution methods: variable-temperature ^1H MAR-NMR (DOSKOČILOVÁ et al., SCHNEIDER et al.) and ^{13}C NMR with strong proton decoupling (SCHAEFER et al.).

Experimental

Conventional ^1H HR-NMR spectra were measured on the PS-100 Jeol NMR spectrometer at 100MHz. The integrated intensities were measured by means of the built-in integrator. The accuracy of determination of integrated intensities was $\pm 1\%$ for samples with concentrations above 1% w/v, and $\pm 5\%$ for the sample with the concentration 0.2% w/v.

^1H MAR-NMR spectra were measured on the JNM 3-60 Jeol NMR spectrometer at 60 MHz, using a variable-temperature MAR-NMR probe head and glass rotor-cells described elsewhere (SCHNEIDER et al.)

^{13}C NMR spectra were measured on the FX-60 Jeol NMR spectrometer at 15 MHz, with proton noise decoupling field intensity $\gamma\text{H}_2/2\pi \approx 5\text{kHz}$ was applied.

Three samples of PMMA were used. Sample i-PMMA was prepared by anionic polymerization in toluene at 0°C with initiation by phenylmagnesium bromide. Sample s-PMMA-1 was prepared by anionic polymerization in toluene at -78°C with triethylaluminium and titanium(IV) chloride. Sample s-PMMA-2 was prepared by radical polymerization in dioxane at 30°C with initiation by dibenzoyl peroxide in the presence of $[\text{RhCl}(\text{C}_8\text{H}_{12})]$ (4-methylpyridine)]. Characteristics of polymers are summarized in Table I.

TABLE I

Number-average molecular weights M_n and stereoregularity of poly(methyl methacrylate) samples; I, H, S: iso-, hetero-, and syndiotactic triads, respectively

Polymer	M_n	Content ^a of triads (%)		
		I	H	S
i-PMMA	13000	91	7	2
s-PMMA-1	86000	3	12	85
s-PMMA-2	45000	3	31	66

^adetermined by ^1H NMR at 160°C

Solutions of the stereoregular PMMA samples in toluene-d₈ (99.6% deuterium) were prepared directly in measuring cells for conventional ^1H -HR and ^{13}C -NMR spectra. Solutions were homogenized for two days at 100°C with constant stirring. After this procedure, all the solutions had the appearance of clear liquids at room temperature without visible indications of aggregation. The cell for the measurement of MAR-NMR spectra

was filled by the solution used for the measurement of conventional ^1H -NMR spectra.

Results and Discussion

From the values of integrated band intensities in ^1H HR-NMR spectra the contents of associated monomer units p was determined (SPĚVÁČEK and SCHNEIDER 1974a, 1975b). The obtained values p for solutions of stereoregular PMMA at various concentrations are shown in Table II. From this table it is seen that association takes place both in *i*-PMMA and *s*-PMMA-1; in *s*-PMMA-2, association does not take place. Both syndiotactic

TABLE II
Content of associated monomer units p at 27°C for solutions of PMMA in toluene- d_8

conc. (% w/v)	p (%)		
	<i>i</i> -PMMA	<i>s</i> -PMMA-1	<i>s</i> -PMMA-2
0.2	10	73	0
1	10	76	0
10	9	76	0

polymers contain very few *i*-triads, but differ in the distribution of *s*-sequences. Assuming 1st order Markov statistics, *s*-PMMA-1 contains about 80% of monomer units in *s*-sequences longer than 15 monomer units; in *s*-PMMA-2, 80% of monomer units are in sequences shorter than 15 units (SPĚVÁČEK and SCHNEIDER 1974a). The mean *s*-sequence length $\bar{l}_s = 16$ for *s*-PMMA-1 and $\bar{l}_s = 6$ for *s*-PMMA-2. This indicates that the existence of long *s*-sequences is a necessary condition for association in *s*-PMMA. In spite of the fact that the stereoregularity of the sample *i*-PMMA-1 is very high ($\bar{l}_i = 27$), the values of p are much lower than for *s*-PMMA-1.

From Table II it is further evident that the content of associated units p is independent of concentration within the range comprising two orders of magnitude. For the samples summarized in Table II we have also followed the temperature dependence of p and we have found that even this is concentration independent. The fact that associates of stereoregular PMMA in toluene- d_8 exist even in very dilute solution and that both their amount and character are independent of concentration indicates their intramolecular origin. It is interesting that *s*-PMMA-1 does not form associates in CD_3CN , even though this medium is very suitable for the formation of the PMMA stereocomplex (LIQUORI et al., SPĚVÁČEK and SCHNEIDER 1974a, 1975a).

The aggregates in a 10% w/v solution of *s*-PMMA-1 in toluene- d_8 can be directly detected in ^1H HR-NMR

spectra. They give rise to a broad base of the peak which is absent in the ^1H HR-NMR spectrum of s-PMMA-2 measured under the same conditions (Fig.1). In order to determine the width and shape of the band of associated segments, we have measured the ^1H NMR spectra of

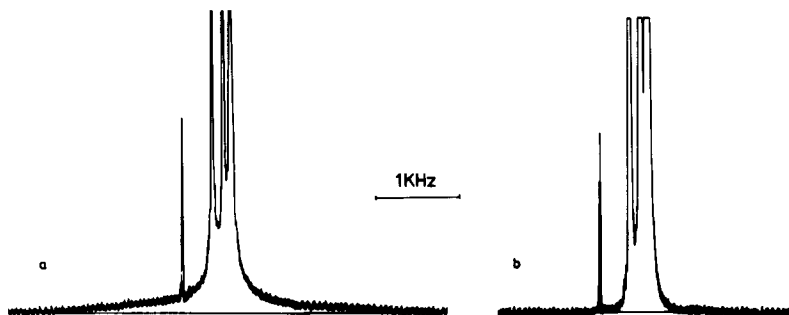


Fig. 1 ^1H NMR spectra of 10% w/v solutions of s-PMMA in toluene- d_8 at 25°C
 a) s-PMMA-1 ($p=76\%$); b) s-PMMA-2 ($p=0$)

the 10% w/v solution of s-PMMA-1 in toluene- d_8 so as to clearly reveal both the narrow and the broad component of the spectrum (Fig.2). These spectra were then analyzed with the assumption (1) that the bands of various

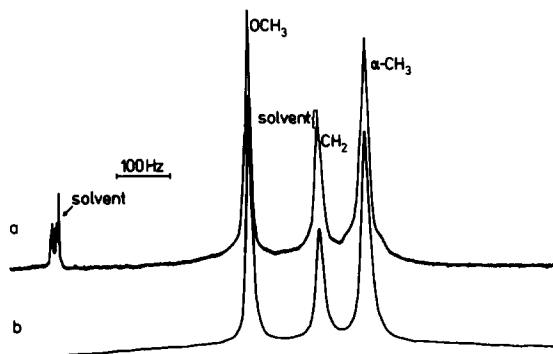


Fig. 2 ^1H NMR spectra of the solution of s-PMMA-1 in toluene- d_8 at 25°C (conc.= 10% w/v).

a) measured spectrum, b) spectrum calculated assuming Lorentzian shape of width 500 Hz for the broad component ($p = 76\%$)

proton groups are of Lorentzian shape, and (2) that these bands are of super-Lorentzian shape due to residual near -static dipolar interactions (DOSKOČILOVÁ et al.). It was found that the spectrum cannot be well described if the bands of various proton groups are each formed by either a single Lorentzian, or a single

super Lorentzian. The spectrum can be described very well if it is assumed that each band is composed of a Lorentzian line corresponding to non-associated segments (24% of monomer units, Table II), and of the line of the associated segments which is equally well fitted by a Lorentzian of 500 ± 100 Hz width, or by a super-Lorentzian with the parameter A (for definition see DOSKOČILOVÁ et al.) equal to 250 Hz. By analysis of line shapes in conventional ^1H NMR spectra it is therefore not possible to decide if near-static dipolar interactions are present in the associates. This point can be decided from MAR-NMR spectra measured with spinning frequencies ≥ 500 Hz (SPĚVÁČEK and SCHNEIDER) or from strongly decoupled ^{13}C NMR spectra measured with $\gamma\text{H}_2/2\pi \geq 500$ Hz (SCHAEFER et al.).

Therefore the 10% w/v solution of s-PMMA-1 in toluene- d_8 was measured in the ^1H MAR-NMR probe both with magic angle spinning, and with the spinning axis perpendicular to the stationary magnetic field, in the temperature range -20 to $+65^\circ\text{C}$ and at spinning frequencies 500 to 4000 Hz. It was found that both shape and intensity of the measured bands are unaffected by magic angle spinning, indicating that the shape of the broad component in ^1H NMR spectra is not determined by the presence of near-static dipolar interactions.

In order to verify this result, for the sample s-PMMA-1 in toluene- d_8 (conc. 10% w/v) we have also measured ^{13}C NMR spectra with strong proton decoupling ($\gamma\text{H}_2/2\pi \approx 5$ kHz). The bands of various carbons are shown in Fig. 3, where they can be compared with the corresponding bands of s-PMMA-1 in CD_3CN (where $p = 0$),

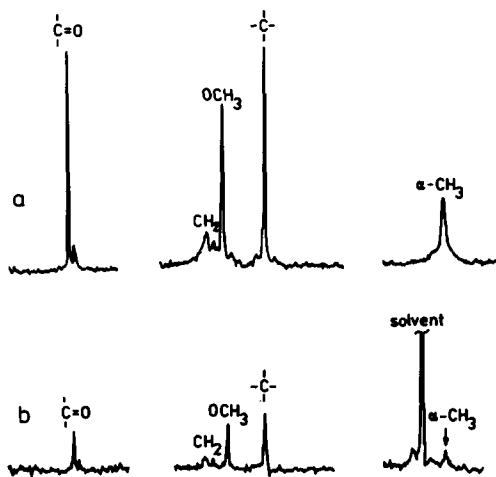


Fig. 3 ^{13}C NMR spectra of 10% w/v solutions of s-PMMA-1 measured at 15 MHz, 27°C (pulse $\pi/2$, pulse interval 2s, 3000 scans, ^1H irradiation $\gamma\text{H}_2/2\pi = 5$ kHz). a) solution in CD_3CN ($p=0$), b) solution in toluene- d_8 ($p=76\%$). Spectra a) and b) measured under identical conditions.

measured under the same conditions. From Fig. 3 it is evident that the integrated intensities of all bands of s-PMMA-1 in toluene- d_8 are much lower than the

values in CD_3CN . The values p determined from the integrated intensities of the corresponding bands in these two samples are practically identical for all types of carbons (p 75%) and are equal to the values obtained from ^1H NMR spectra (Table II). From this it follows that in strongly decoupled ^{13}C NMR spectra, only unassociated monomer units are exhibited, similarly as in ^1H MAR-NMR spectra. All manifestations of associated segments in our experiments can be well described with the assumption that the motion of the associated segments is isotropic in space, with an effective correlation frequency $10^6 - 10^7$ Hz (SPĚVÁČEK and SCHNEIDER 1978b).

The observation that the associates of s-PMMA-1 in toluene- d_8 are of intramolecular nature, as well as the character of the measured NMR spectra are both compatible with the notion that the associates of s-PMMA-1 form globules with a relatively high density of interactions between syndiotactic sequences. We suppose that the bands observed in ^1H HR-NMR spectra and in ^{13}C NMR spectra correspond to polymer segments on the surface of the globules which are in good contact with the solvent. From the present results it cannot be decided, if the apparently isotropic motion limiting NMR line widths of nuclei in associated structures corresponds to overall rotation of globules, to retarded isotropic segmental motions or to some kinetic processes proceeding in these structures.

In the end it should be pointed out that for s-PMMA-1 in toluene- d_8 association takes place even in very dilute solutions, in spite of the fact that toluene (θ temper. -65°C) is considered a better solvent for PMMA than CD_3CN (θ temper. $+30^\circ\text{C}$) (ELIAS and BÜHRER), in which association does not take place. This indicates that for solutions of systems where cooperative stereospecific interactions can take place, the concepts of "good" or θ solvent may depend on stereoregularity and should be used with caution. We suppose that the different behaviour of s-PMMA-1 in toluene and CD_3CN solutions is due to the effects of these solvents upon the conformational structure of the sequences of s-PMMA (SPĚVÁČEK and SCHNEIDER 1978b, INOUE and KONNO).

References

- DOSKOČILOVÁ, D., SCHNEIDER, B. and JAKEŠ, J.: J. Magn. Res. 29, 79 (1978)
 ELIAS, H.G. and BÜHRER, H.G.: in Polymer Handbook, 2nd Ed. Ed. J. Brandrup and E.H. Immergut, New York, London, Sydney, Toronto: Wiley 1975, p. IV-163
 INOUE, Y. and KONNO, T.: Makromol. Chem. 179, 1311 (1978)
 LIQUORI, A.M., ANZUINO, G., COIRO, V.M., D'ALAGNI, M., DE SANTIS, P. and SAVINO, M.: Nature 206, 358 (1965)
 SCHAEFER, J., STEJSKAL, E.O. and BUCHDAHL, R.: Macromolecules 8, 291 (1975)

- SCHNEIDER, B., DOSKOČILOVÁ, D., BABKA, J. and RŮŽIČKA, Z.: J.Magn.Res. 36 (1979), in press
- SPĚVÁČEK, J. and SCHNEIDER, B.: Makromol.Chem. 175, 2939 (1974a)
- SPĚVÁČEK, J. and SCHNEIDER, B.: J.Polym.Sci., Polym. Lett.Ed. 12, 349 (1974b)
- SPĚVÁČEK, J. and SCHNEIDER, B.: Makromol.Chem. 176, 729 (1975a)
- SPĚVÁČEK, J. and SCHNEIDER, B.: Makromol.Chem. 176, 3409 (1975b)
- SPĚVÁČEK, J.: J.Polym.Sci., Polym.Phys.Ed.: 16, 523 (1978a)
- SPĚVÁČEK, J. and SCHNEIDER, B.: Polymer 19, 63 (1978b)

Received January 11, 1980