Polymer Bulletin 8, 171–177 (1982)

Polymer Bulletin

^{1}H-NMR Study of Interactions of Dimethyl Ester of 2,2,4,4-Tetramethylglutaric Acid with Stereoregular Poly(Methyl Methacrylates) in Solution

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Summary

Studies of integrated band intensities in high resolution (HR) ^{1}H NMR spectra of the dimethyl ester of 2,2,4,4-tetramethylglutaric acid (DMTMGA) in solutions containing stereoregular poly(methyl methacrylate)(PMMA) have shown that a part of the DMTMGA molecules interact with PMMA. In this interaction DMTMGA behaves similarly as syndiotactic (s) PMMA. DMTMGA can link-up in self-aggregates of s-PMMA, and also replace s-PMMA in interaction with isotactic (i) PMMA forming an analog of the PMMA stereocomplex. An analogy of the conformational structure of DMTMGA and of the s-sequences in the aggregates of PMMA is discussed.

Introduction

Stereoregular PMMAs exhibit a strong tendency to form associated structures in solution. 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, 1980b, CHALLA et al., VORENKAMP and CHALLA), associated structures are also formed in solutions of only i-PMMA or of only s-PMMA (SPĚVÁČEK and SCHNEIDER 1974b, 1975b, 1980a, SPĚVÁČEK 1978, SPĚVÁČEK et al. 1982). In all the cited cases of association of stereoregular PMMA, the mobility of segments directly participating in aggregation is limited to such an extent that the ^{1}H HR NMR signals of these associated segments escape detection. From a comparison of integrated band intensities in ^{1}H HR NMR spectra it is therefore possible to determine the fraction of associated monomer units of PMMA (SPĚVÁČEK and SCHNEIDER 1974a, 1975b, 1980a, SPĚVÁČEK 1978, SPĚVÁČEK et al. 1982).

Formation both of the PMMA stereocomplex and of the self-aggregates of s-PMMA strongly depends on solvent; in some solvents the content of associated segments is large, whereas in $CDCl_3$ no aggregation takes place. Both the stereocomplex and the self-aggregates of s-PMMA decompose at temperatures below the melting temperature of solid i- or s-PMMA. On the contrary, with self-aggregates of i-PMMA the content of associated segments is always relatively low and the aggregates exhibit high thermal stability, decomposing at temperatures comparable to the melting temperature of solid i-PMMA (SPĚVÁČEK and SCHNEIDER

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1974a,b, 1975a,b, SPĚVÁČEK 1978, SPĚVÁČEK et al. 1977, 1982). Some minimum length of the stereoregular sequences is necessary for stereoassociation. The minimum length of s-sequences necessary for the formation of the PMMA stereocomplex has been determined from ^{1}H HR NMR spectra (SPĚVÁČEK and SCHNEIDER 1974a). It was found that in some solvents this minimum length can be very small. So e.g. in dimethylformamide (DMF) and in toluene this minimum length is 3 and 4 monomer units, respectively (SPĚVÁČEK et al. 1982, SPĚVÁČEK unpublished).

In this paper we have used ^{1}H HR NMR spectra to find out under which conditions DMTMGA (the dimer model of PMMA) can undergo interactions with PMMA similar to stereoassociation of PMMA.

Experimental

DMTMGA was prepared according to MIHAILOV et al.

PMMA. Fully deuterated i-PMMA-d_8 was prepared by polymerisation of methyl methacrylate (MMA) -d_8 in toluene at 0°C, initiated with phenylmagnesium bromide. Fully deuterated s-PMMA-d_8 was prepared by polymerisation of MMA-d_8 in toluene at -78°C with triethylaluminium and titanium (IV) chloride. Details are given elsewhere (SPĚVÁČEK et al. 1977). The degree of deuteration from ^{1}H NMR spectra in both i-PMMA-d_8 and s-PMMA-d_8 exceeded 99%. The stereoregularities of the deuterated samples of PMMA were considered identical to those of the corresponding undeuterated polymers prepared analogously. By analysis of ^{1}H HR NMR spectra it was found that i-PMMA contained 91% of isotactic, 7% of heterotactic and 2% of syndiotactic triads; s-PMMA contained 85% syndiotactic, 12% heterotactic and 3% isotactic triads.

Samples. Solutions were prepared directly in the measuring cells. The three-component systems DMTMGA-(i- or s- PMMA -d_8)-solvent were prepared with 20 mg of DMTMGA, 40 mg PMMA-d_8 and 0.4 ml solvent. Solutions of DMTMGA of the same concentration but without the polymer were also measured for comparison.

NMR spectra. ^{1}H HR NMR spectra were measured with the spectrometer JEOL-PS-100 at 100 MHz. Absolute temperatures in the sample were calibrated by means of NMR spectra. The integrated intensities were measured by the built-in integrator with a relative precision of ± 1%.

Results

In all the studied systems DMTMGA exhibits 3 strong bands in ^{1}H HR NMR spectra, corresponding to C-CH_3 (1.1 p.p.m. from TMS), CH_2 (2.05 p.p.m.) and OCH_3 (3.7 p.p.m.) protons (SPĚVÁČEK et al. 1977). A comparison of integrated band intensities has shown that in the systems DMTMGA-(i- or s-PMMA-d_8) -toluene-d_8 and DMTMGA-(i-PMMA-d_8)-DMF-d_7 the integrated intensities of all bands are lower than in the comparable two-component systems DMTMGA-toluene-d_8 or DMTMGA-DMF-d_7; the percentage of intensity loss is the same for all bands of DMTMGA.

This indicates that in the cited systems, a part of the DMTMGA molecules escapes detection in ^{1}H HR NMR spectra. The fraction p of these molecules of DMTMGA was determined from the relation

$$p = 1 - I/I_o \ , \tag{1}$$

where I_o is the sum of the integrated intensities of all bands of DMTMGA in a system without PMMA-d_8, and I is the sum of integrated intensities in analogous samples containing PMMA-d_8. The values of p are summarized in Table I.

TABLE I
Values of the fraction p (in %) of DMTMGA protons which escape detection in ^{1}H HR NMR spectra at 26°C in various solvents

System	Solvent		
	DMF-d_7	toluene-d_8	$CDCl_3$
DMTMGA + i-PMMA-d_8	14^a	12-15	0
DMTMGA + s-PMMA-d_8	0	11	0
DMTMGA + mixture (i/s)-PMMA-d_8	b	0	0

[a] At 0°C
[b] Not measured

The temperature dependences of the sum of the integrated intensities of the bands of DMTMGA are shown in Fig.1. The integrated band intensities of various proton groups (OCH_3, CH_2, C-CH_3) exhibit equal behaviour. The mildly convex monotonously decreasing temperature dependence of integrated band intensities seen in Figs.1a and 1d is typical for systems where the content of detected protons does not change in the whole temperature range studied. The increase of integrated band intensity with temperature as seen in Fig.1b and a concave course of the temperature dependence of integrated band intensities as seen in Fig.1c is observed in those cases where a part of the protons escapes detection in HR NMR spectra because of restricted mobility, and in the studied temperature range such restrictions are relaxed by heating (SPĚVÁČEK and SCHNEIDER 1975b). From Figs.1b and 1c it is also seen that in the systems DMTMGA-(i- or s-PMMA-d_8)-toluene-d_8, all DMTMGA is detected in ^{1}H HR NMR spectra only at temperatures above 50°C. In the systems DMTMGA-(s-PMMA-d_8)-DMF-d_7 and DMTMGA-(i- or s-PMMA-d_8)-$CDCl_3$, integrated intensities decrease monotonously with temperature similarly as in Figs.1a,d, in agreement with the finding that in these systems all DMTMGA is detected in ^{1}H HR

NMR spectra at room temperature (Tab.I).

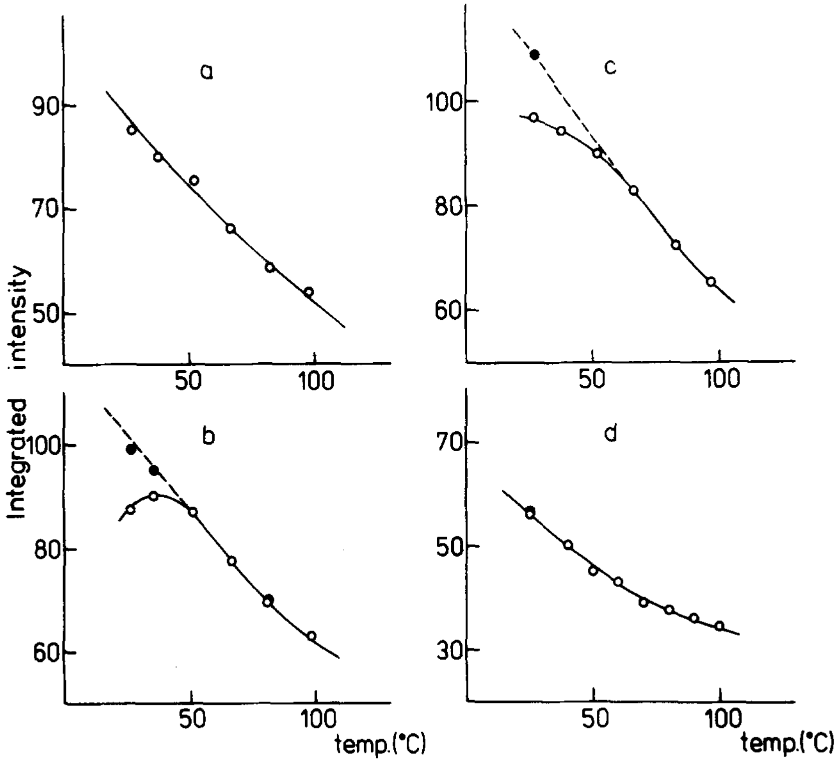

Fig.1. Temperature dependence of the sum of the integrated intensities of the bands of DMTMGA in the systems DMTMGA-toluene-d_8 (a), DMTMGA-(i-PMMA-d_8)-toluene-d_8 (b), DMTMGA-(s-PMMA-d_8)-toluene-d_8 (c), DMTMGA-mixture(i+s-PMMA-d_8)-toluene-d_8 (d). Temperature gradually increasing (○),decreasing temperature (●)

Discussion

Above it was shown that in some systems containing stereoregular PMMA-d_8 in addition to DMTMGA, the mobility of a part of the DMTMGA molecules is restricted beyond detection in ^{1}H HR NMR spectra. This can only be caused by interaction of DMTMGA with stereoregular PMMA-d_8. From Tab.II it can be seen that such behaviour is only observed in those solvents in which stereoregular PMMA is known to form aggregates with restricted mobility of the associated segments. A part of the molecules of DMTMGA escapes detection in ^{1}H HR NMR spectra of the system DMTMGA-(s-PMMA-d_8)-toluene-d_8, where s-PMMA-d_8 forms self-aggregates (SPĚVÁČEK 1978, SPĚVÁČEK and SCHNEIDER 1980a, SPĚVÁČEK et al.1982), and in the systems DMTMGA-(i-PMMA-d_8)-toluene-d_8 or DMF-d_7, i.e. in solvents where the stereocomplex is known to be formed by interaction of i- and s-PMMA (SPĚVÁČEK et al.1977, 1982, LIQUORI et al., CHALLA et al., VORENKAMP and CHALLA) (Tab.II). From this it is evident that DMTMGA can link up in self-aggregates of s-PMMA or substitute s-PMMA in its interaction with i-PMMA and form some analog of the PMMA stereocomplex.

TABLE II

Correlation between interactions of DMTMGA with stereoregular PMMA and aggregation of stereoregular PMMA

Type of interaction	Solvent		
	DMF-d_7	toluene-d_8	$CDCl_3$
Interaction of DMTMGA with i-PMMA-d_8	yes	yes	no
Formation of the stereocomplex of PMMA (interaction of i- and s-PMMA)	yes	yes	no
Interaction of DMTMGA with s-PMMA-d_8	no	yes	no
Self-aggregation of s-PMMA	no[a]	yes	no

[a] Negligible

Interactions between DMTMGA and PMMA-d_8 are disrupted at temperatures below 50°C (Fig.1b,c), similarly as in sections of PMMA stereocomplex formed by short s-sequences (SPĚVÁČEK and SCHNEIDER 1974a). In the systems DMTMGA-(i- or s-PMMA-d_8)-toluene-d_8 at temperatures below 50°C, the values of integrated band intensities measured after cooling from higher temperatures are higher than the values measured during gradual heating of the sample, and this indicates (Fig.1b,c) that the formation of the complexes of DMTMGA with i- or s-PMMA-d_8 requires some time, similarly as the formation of the PMMA stereocomplex and the formation of self-aggregates of s-PMMA (SPĚVÁČEK and SCHNEIDER 1974a, SPĚVÁČEK et al.1982). In the system DMTMGA-(mixture i-/s-PMMA-d_8)-toluene-d_8, where practically all s- and i-PMMA-d_8 participates in stereocomplex formation (SPĚVÁČEK et al.1982), interaction between DMTMGA and PMMA-d_8 leading to substantial restriction of the mobility of a part of DMTMGA molecules does not take place (Tab.1, Fig.1d). All the cited results support the notion that in interaction of DMTMGA with PMMA, DMTMGA molecules behave similarly as short s-PMMA sequences.

Analysis of the NMR spectra of PMMA stereocomplex and studies of simple esters have shown that the stereocomplex is formed through dipolar interactions of ester groups (SPĚVÁČEK and SCHNEIDER 1975a, 1980b, DYBAL et al.,a). The parallel chains of i- and s-PMMA described for the stereocomplex (SPĚVÁČEK and SCHNEIDER 1974a, 1975a, 1980b, VORENKAMP and CHALLA) are formed by practically linear chains of s- and i-PMMA, with the conformational structure of s-PMMA (DYBAL et al.,b) as shown in Fig.2a. Also the self-aggregates of s-PMMA in toluene were shown to be formed by linear chains of s-PMMA of the same conformational structure (ŠTOKR et al.).

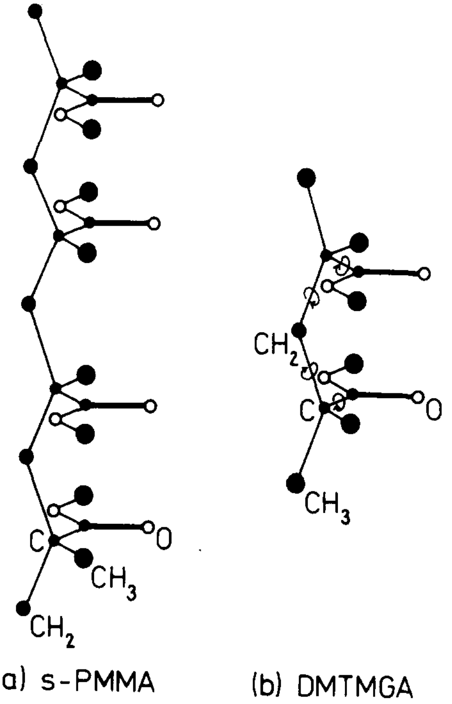

Fig.2
Conformational structure of s-PMMA in the PMMA stereocomplex and self-aggregates of s-PMMA(a), and the energetically most favoured conformer of DMTMGA(b)

DMTMGA can form conformational isomers by rotation about the C-C bonds (C-CH$_2$ and C-CO). Analysis of vibrational spectra has shown that the energetically most favoured form is that given in Fig.2b (DYBAL et al.,a). In this conformer, the ester groups of DMTMGA have the same geometrical arrangement as in the s-sequences of PMMA stereoassociates (Fig.2a,b). A conformer of DMTMGA with ester group arrangement such as that assumed for the i-sequences in PMMA stereocomplex has not been detected in studies of rotational isomerism of DMTMGA (DYBAL et al., a,b). The similarity of the geometrical arrangement of ester groups in the most favoured conformer of DMTMGA and in s-sequences of PMMA stereoaggregates probably is the reason why in interactions with PMMA, DMTMGA behaves similarly as sequences of s-PMMA.

The results obtained in studies of DMTMGA with i-PMMA-d$_8$ indicate that in the so called replica polymerization of MMA performed in the presence of i-PMMA (CHALLA et al., CHALLA and TAN) it may be expected that even very short oligomers of the growing chain (dimers, trimers etc.) in s-configuration are capable of close and stable (on the NMR time scale) contact with i-PMMA. This circumstance, together with a certain arrangement of MMA molecules about the PMMA chains (SPĚVÁČEK et al. 1977) favours growth of the nascent chain about the i-PMMA matrix.

References

CHALLA,G. DE BOER,A. and TAN,Y.Y.: Intern. J. Polymeric Mater. 4, 239 (1976)
CHALLA,G. and TAN,Y.Y.: Pure Applied Chem. 53, 627 (1981)
DYBAL,J., ŠTOKR,J. and SCHNEIDER,B.: Coll.Czech. Chem. Commun., in press (a)
DYBAL,J., ŠTOKR,J. and SCHNEIDER,B.: Polymer, to be published (b)
LIQUORI,A.M., ANZUINO,G., COIRO,V.M., D´ALAGNI,M., DE SANTIS,P. and SAVINO,M.: Nature 206, 358 (1965)
MIHAILOV,M., DIRLIKOV,S., SCHNEIDER,B. and ŠTOKR,J.: Dokl.Bolg. Akad.Nauk 24, 1333 (1971)
SPĚVÁČEK,J. and SCHNEIDER,B.: Makromol. Chem. 175, 2939 (1974 a)
SPĚVÁČEK,J. and SCHNEIDER,B.: J.Polym.Sci., Polym.Lett. Ed. 12, 349 (1974 b)
SPĚVÁČEK,J. and SCHNEIDER,B.: Makromol.Chem. 176, 729 (1975 a)
SPĚVÁČEK,J. and SCHNEIDER,B.: Makromol.Chem. 176, 3409 (1975 b)
SPĚVÁČEK,J., SCHNEIDER,B., MIHAILOV,M. and DIRLIKOV,S.: Eur. Polym. J. 13, 625 (1977)
SPĚVÁČEK,J.: J.Polym.Sci., Polym.Phys.Ed. 16, 523 (1978)
SPĚVÁČEK,J. and SCHNEIDER,B.: Polym.Bull. 2, 227 (1980 a)
SPĚVÁČEK,J. and SCHNEIDER,B.: Colloid Polym.Sci. 258, 621 (1980 b)
SPĚVÁČEK,J., SCHNEIDER,B., BOHDANECKÝ,M. and SIKORA,A.: J.Polym. Sci., Polym.Phys.Ed. 20, No.9 (1982)
ŠTOKR,J., DYBAL,J. and SCHNEIDER,B.: Polym.Bull., to be published
VORENKAMP, E.J. and CHALLA,G.: Polymer 22, 1705 (1981)

Received August 14, accepted August 17, 1982