

Conformational Structure and Stereocomplex Formation in Poly(methyl methacrylate)[†]

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ABSTRACT: The conformational structure of the stereocomplex between i-PMMA and s-PMMA has been investigated by analysis of its vibrational spectra. The mechanism of polymerization of MMA, carried out under conditions at which stereocomplex formation occurred, is discussed.

The conformational structure of isotactic and syndiotactic poly(methyl methacrylates) (i-PMMA and s-PMMA), and of their stereocomplex was investigated theoretically^{1,2} and by X-ray diffraction.³⁻⁵ By the latter method, helical structure was observed in crystalline i-PMMA^{3,4} as well as in the isotactic sequences of the stereocomplex.⁵ In s-PMMA, a complete X-ray analysis has not been performed so far, but two possible conformations (trans chain and a conformation with a glide plane) were predicted by Gotlib¹ on the basis of theoretical analysis of conformer energies. In the stereocomplex a structure with a glide plane of the syndiotactic sequences has been proposed by Liquori,⁵ based on X-ray analysis. This structure differs from the conformation with a glide plane predicted by Gotlib.

In our previous report⁶ the conformational structure of i-PMMA and s-PMMA was investigated by analysis of CH₂ rocking vibrations in their infrared spectra. It was found that the chains of i-PMMA form a helix, whereas s-PMMA assumes a form very near to an all-trans chain. Upon stereocomplex formation a new CH₂ rocking vibration appears and it was assumed that the formation of the complex is probably connected with a change of skeletal conformation.

In the present report the conformational structure of the isotactic and syndiotactic chains in the stereocomplex was investigated by analysis of their CH₂ rocking vibrations in the stereocomplexes i-PMMA-s-PMMA-CD₂ (CD₂C(CH₃)COOCH₃) and i-PMMA-CD₂-s-PMMA.

Recently Miyamoto and Inagaki⁷ reported that the presence of i-PMMA or s-PMMA promotes the polymerization of MMA to s-PMMA and i-PMMA, respectively. In the present paper the mechanism of this polymerization is discussed as well.

Experimental Section

Methyl methacrylate-d₂, CD₂=C(CH₃)COOCH₃, was prepared from CD₂O (Isocommerz, D = 99.2%), diethylamine, and monomethylmethylenemalononic acid by Mannich's reaction.^{8,9} The monoester was obtained by partial hydrolysis of the corresponding dimethyl ester.¹⁰

Methyl methacrylate-d₃, CH₂=C(CD₃)COOCH₃, was prepared in the same manner⁸⁻¹⁰ by means of monomethylmethyl-d₃-malonic acid. Initial methyl-d₃ dimethylmalonate was prepared from dimethylmalonic acid and methyl-d₃ alcohol (Isocommerz, 99.5%).¹¹

i-PMMA samples were prepared by polymerization of purified monomers at 0° in toluene with phenylmagnesium bromide as initiator.¹² s-PMMA samples were prepared by polymerization of monomers at -78° in toluene with AlEt₃ and TiCl₄.¹³

The polymerization of MMA in the presence of i-PMMA-CD₃ or s-PMMA-CD₃ was carried out at -50° in toluene with BuMgCl as initiator and the molar ratio between monomer and polymer was 10:1, according to Miyamoto.⁷ The polymerization was terminated after 15 min by pouring into methanol.

All polymers were purified by twofold precipitation from toluene (or acetone) into methanol, followed by vacuum drying at 60°.

Stereocomplex between i-PMMA and s-PMMA (1:2) was prepared by mixing their dilute acetonitrile solutions,⁵ followed by vacuum drying at 60°.

Infrared spectra were measured on the Zeiss UR10 spectrometer in KBr. Nuclear magnetic resonance spectra were taken with a Hitachi 60-MHz spectrometer from 5 to 10% solution in CDCl₃ (at 55°) or o-dichlorobenzene (at 150°); 100% deuteration of the respective groups in PMMA-CD₂ and PMMA-CD₃ was confirmed by nmr. The tacticity of the polymers was determined by Bovey's method.¹⁴ The tacticity of the i-PMMA and i-PMMA-CD₂ was essentially 100% isotactic. The s-PMMA and s-PMMA-CD₂ contained 92% S, 8% H, and 0% I triads. It is assumed that the tacticity of i-PMMA-CD₃ and s-PMMA-CD₃ does not differ essentially from the tacticity of the nondeuterated PMMA.

Results and Discussion

In our previous report the conformational structure of PMMA was determined by means of a dimer model compound for PMMA, the dimethyl ester of 2,2,4,4-tetramethylglutaric acid.⁶ It was found that in the solid state this ester exists as one conformer A, the CH₂ rocking vibration of which absorbs at 848 cm⁻¹ (Figure 1 and Table I). In the liquid state this ester exists as two conformers: the conformer A and the less stable conformer B; the CH₂ rocking vibration of the latter absorbs at 868 cm⁻¹ (Figure 1 and Table I). Based on analysis of infrared spectra the conformational structure of conformer A was determined and the most probable structure of conformer B was proposed (Figure 2). (The real conformational structure of the conformers A and B may differ slightly from the staggered conformations, given on Figure 2. Because the values of deformation angles cannot be determined accurately from infrared spectra, small deviations from the staggered conformations cannot be detected.)

Further, only one CH₂ rocking vibration was found at 848 cm⁻¹ in the spectra of the i-PMMA as well as in the

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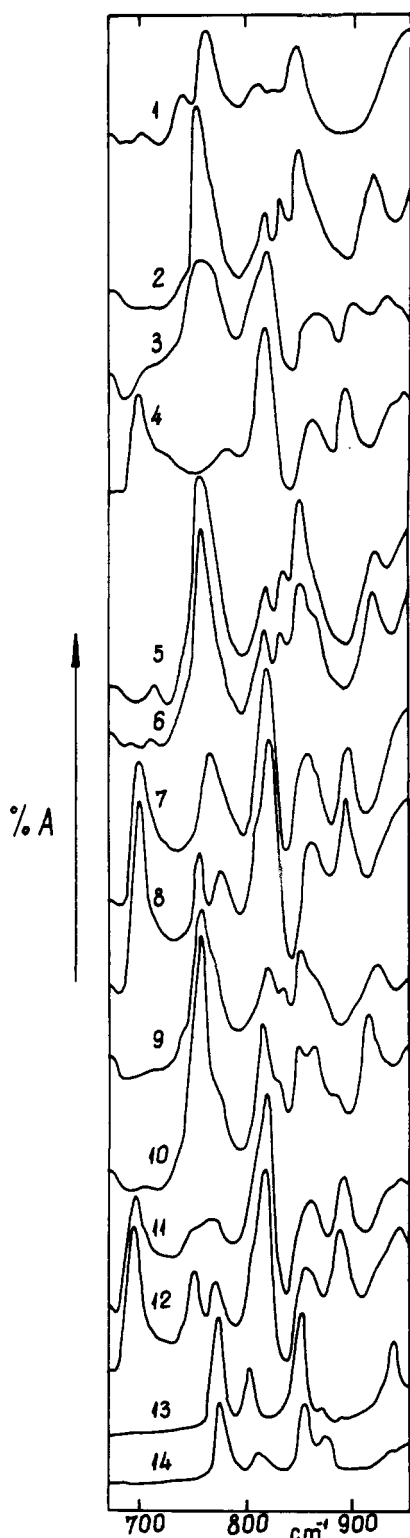


Figure 1. Infrared spectra. (1) i-PMMA, (2) s-PMMA, (3) i-PMMA-CD₂, (4) s-PMMA-CD₂, (5) mechanical mixture i-PMMA-s-PMMA, (6) stereocomplex i-PMMA-s-PMMA, (7) mechanical mixture i-PMMA-s-PMMA-CD₂, (8) stereocomplex i-PMMA-s-PMMA-CD₂, (9) mechanical mixture i-PMMA-CD₂-s-PMMA, (10) stereocomplex i-PMMA-CD₂-s-PMMA, (11) mechanical mixture i-PMMA-CD₂-s-PMMA-CD₂, (12) stereocomplex i-PMMA-CD₂-s-PMMA-CD₂, (13) dimethyl ester of 2,2,4,4-tetramethylglutaric acid in solid state, (14) dimethyl ester of 2,2,4,4-tetramethylglutaric acid in liquid state.

spectra of the s-PMMA (Figure 1 and Table I). These bands (at 848 cm⁻¹) correspond to the band at 848 cm⁻¹ in conformer A of dimethyl tetramethylglutarate. As the conformational structure of PMMA is manifested in the

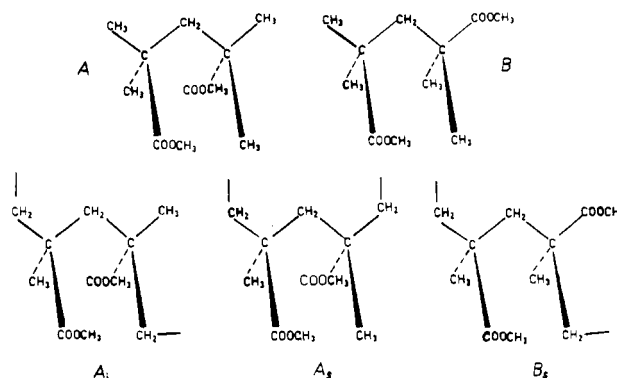


Figure 2. Conformation structure of dimethyl ester of 2,2,4,4-tetramethylglutaric acid and PMMA dyads.

CH₂ rocking vibration, the structure of the dyads in i-PMMA (A_i) and in s-PMMA (A_s) is assumed to correspond to that of the conformer A (Figure 2). For the chains of i-PMMA composed of A_i dyads this leads to the formation of a helix whereas for the chains of s-PMMA composed of A_s dyads this results in the formation of an almost trans chain. Upon stereocomplex formation between i-PMMA and s-PMMA a new CH₂ rocking vibration appears at 862 cm⁻¹ (Figure 1 and Table I). It was assumed that the formation of the complex is connected with a rotation about skeletal C-C bonds.

In order to determine the conformational structure of the isotactic and syndiotactic chains in the stereocomplex, we have studied the CH₂ rocking vibrations in the stereocomplexes i-PMMA-s-PMMA-CD₂ and i-PMMA-CD₂-s-PMMA, as described in the present report.

In both stereocomplexes studied the CH₂ rocking vibrations are overlapped by an additional weak band at about 855 cm⁻¹ which is well resolved in the spectra of s-PMMA-CD₂ and i-PMMA-CD₂ (Figure 1). This band was assigned to a vibration of COOCH₃ groups in PMMA because it was found as a band or a weak shoulder in the infrared and Raman spectra of i-PMMA, s-PMMA, i-PMMA-CD₂, s-PMMA-CD₂, i-PMMA-CD₃, and s-PMMA-CD₃, whereas it was absent in the spectra of i-PMMA-COOCd₃ (CH₂C(CH₃)(COOCd₃)) and s-PMMA-COOCd₃.⁹ By a comparison of the infrared spectra of the mechanical mixture and of the stereocomplex between i-PMMA-CD₂ and s-PMMA-CD₂ it was established that upon stereocomplex formation the band at 855 cm⁻¹ did not change its intensity and frequency (Figure 1). For this reason this band was not considered in the present studies.

First, we compared the spectra of the mechanical mixture and of the stereocomplex between s-PMMA-CD₂ and i-PMMA (Figure 1 and Table I). It was found that upon stereocomplex formation the band of the CH₂ rocking vibration in i-PMMA at 848 cm⁻¹ retains its intensity and frequency, whereas the band of the CD₂ rocking vibration in s-PMMA-CD₂ at 760 cm⁻¹ splits into two bands at 750 and 770 cm⁻¹.

Then we studied the spectra of the mechanical mixture and of the stereocomplex between i-PMMA-CD₂ and s-PMMA (Figure 1 and Table I). It was found that upon stereocomplex formation the intensity of the band of CH₂ rocking vibrations in s-PMMA at 845 cm⁻¹ strongly decreases and a new band at 862 cm⁻¹ appears. In the region of CD₂ rocking vibrations in i-PMMA-CD₂ no changes were observed.

The splitting of CH₂ and CD₂ rocking vibrations in s-PMMA and s-PMMA-CD₂, respectively, shows that upon stereocomplex formation the syndiotactic chains alter their conformation and a new type of dyads in s-PMMA

Table I
Methylene Rocking Vibration in PMMA and Its Stereocomplex

		CH ₂ Rocking Vibrations (cm ⁻¹)	
		Dyad A _i /Dyad A _s	Dyad B _s
i-PMMA	Solid or solution	848	
s-PMMA	Solid or solution	845	
i-PMMA and s-PMMA	Mechanical mixture	846	
	Stereocomplex	846	862
i-PMMA and s-PMMA-CD ₂	Mechanical mixture	848	
	Stereocomplex	848	
i-PMMA-CD ₂ and s-PMMA	Mechanical mixture	845	
	Stereocomplex	845	862
$\begin{array}{c} \text{CH}_3 \qquad \qquad \text{CH}_3 \\ \qquad \qquad \quad \\ \text{CH}_3 - \text{C} - \text{CH}_2 - \text{C} - \text{CH}_3 \\ \qquad \qquad \quad \\ \text{COOCH}_3 \quad \text{COOCH}_3 \end{array}$	Solid	848	
	Liquid	848	868

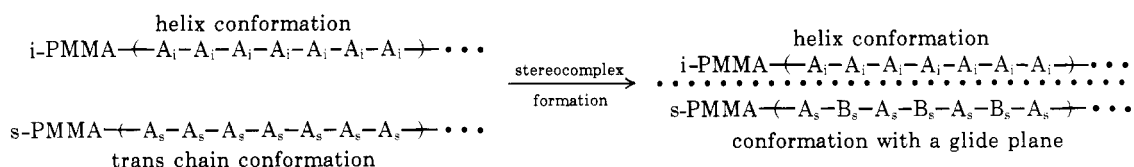


Figure 3. Mechanism of stereocomplex formation in PMMA.

Table II
Polymerization Data of MMA

Added Polymer	Added Polymer/ Produced Polymer (mol/mol)	Tacticity of Produced Polymer		
		I	H	S
i-PMMA-CD ₃	1.80	21	18	61
	0	55	10	35
s-PMMA-CD ₃	0.58	61	11	28

appears, the CH₂ rocking vibrations of which absorb at 862 cm⁻¹. This band (at 862 cm⁻¹) corresponds to the band at 868 cm⁻¹ of the less stable conformer B in dimethyl tetramethylglutarate and we assume that the structure of the new dyads (B_s) corresponds to that of the conformer B (Figure 2).

The CH₂ rocking vibrations of A_s and B_s dyads at 845 and 862 cm⁻¹ as well as their CD₂ rocking vibrations at 750 and 770 cm⁻¹ have roughly the same intensity (Figure 1) and from this it seems very probable that the content of both dyads in the complexed s-PMMA is essentially equal. Therefore it is possible that the chains of s-PMMA in the stereocomplex are composed of alternating A_s and B_s dyads and form the conformation with a glide plane theoretically predicted by Gotlib¹ (Figure 3).

In addition, it appears that upon stereocomplex formation the chains of i-PMMA retain their helix conformation whereas the chains of s-PMMA alter their trans chain conformation into a conformation with a glide plane (Figure 3).

The stereocomplex formation during polymerization of MMA was studied as well. The polymerization was carried out under conditions at which the stereocomplex formation occurred.⁷ Three types of polymerization of non-deuterated MMA were carried out: in the presence of i-PMMA-CD₃, in the presence of s-PMMA-CD₃, and in the absence of polymer. The tacticity of the PMMA obtained in this manner was established by nmr analysis of CH₃ resonance.

It was found that the presence of i-PMMA-CD₃ promotes the polymerization of MMA to s-PMMA whereas the presence of s-PMMA has only a slight effect on the tacticity of the produced polymer in comparison to that prepared in the absence of PMMA (Table II). This result is in agreement with the results observed by other authors,^{7,15,16} but the tacticity of the polymer produced in our experiment is different from that established by Miyamoto.⁷ Our data show that in the absence of PMMA the ratio between the produced i-PMMA and s-PMMA is approximately 2:1.

It was concluded that in the presence of i-PMMA the polymerization of MMA proceeds as a replica polymerization to s-PMMA.

Further, we assume that the stereocomplex formation during polymerization of MMA in the absence of a polymer proceeds in two stages. During the first stage, an i-PMMA is produced. During the second stage, the produced isotactic polymer acts as a matrix for the formation of s-PMMA.

The results obtained indicate that the syndiotactic chains do not promote the polymerization of MMA to i-PMMA because they preferably exist under the conditions of the polymerization in a near-to-trans chain conformation. Probably only the conformation with a glide plane, which the syndiotactic chains assume in the stereocomplex with i-PMMA, could be regarded as a replica conformation of the isotactic polymer or a matrix for its formation.

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