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Conformational Structure of Ordered Forms of Stereoregular Poly(Methyl Methacrylates)

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The results of the studies of the conformational structure of stereoregular PMMA obtained by means of infrared spectroscopy, combined with NMR spectroscopic studies of the kinetics of the aggregation of s-PMMA, are described. It was found that both the aggregation of s-PMMA and PMMA stereocomplex formation lead to the generation of double helices with a large number of monomer units per turn, and that such helices also exist in all three crystalline forms of stereoregular PMMA (i-PMMA, s-PMMA, stereocomplex) in the solid state. Interactions leading to the formation of the stereocomplex can enforce this structure even in s-PMMA chains with not too high stereoregularity.

INTRODUCTION

Recent X-ray diffraction studies of crystalline isotactic (i) poly(methyl methacrylate) (PMMA) revealed that the backbone forms a double 10/1 helix.[1,2] Based on X-ray diffraction measurements and on conformational energy calculations, the structure of a double helix with a large number of units per turn was also proposed for another form of crystalline PMMA, the so called stereocomplex which is formed by mixing the solutions of i-PMMA and syndiotactic (s) PMMA in a suitable solvent and by subsequent removal of the solvent.[3] NMR measurements indicate that the double helices are already present in the stereocomplex aggregates in solution.[4] Although the quality of X-ray diffractograms of crystalline s-PMMA is not very good, even here this method indicates, together with infrared (IR) spectroscopy, that the most probable backbone conformation is the helix with a large number of units per turn.[5,6] In all the mentioned helix structures, the backbone conformation can be approximately described as tt, and according to theoretical calculations this is the energetically most favoured structure of the i- and s-PMMA chains.[7,8]

In our previous studies we have found that similarly to the PMMA stereocomplex, the existence of a preceding aggregation stage in solution is a prerequisite also for the preparation of crystalline s-PMMA.[6,9,10]

At the same time, the NMR results indicate that, though the motion of the backbone of aggregated segments in solution is strongly retarded, the aggregated segments still retain considerable mobility and, therefore, the greater part of aggregated units of PMMA in solution cannot be present in

the crystalline state.[6] For s-PMMA solutions in butyl acetate of concentration $< 60\%$, where most of s-PMMA exists in the aggregated state, actually no crystallinity was found by wide-angle X-ray scattering.[10]

In the present study we wished to supplement the existing data on the conformational structure of the crystalline forms of PMMA and to find out if the conformational structures found in the solid state are also present in aggregates of stereoregular PMMA in solution. To this end previous results obtained by IR spectra[6,9,11–13] were supplemented by IR measurements on samples of i-PMMA-α-CD_3 and samples of the stereocomplex i-PMMA-α-CD_3/ /s-PMMA-OCD_3, and by NMR measurements of the concentration-dependent kinetics of s-PMMA self-aggregate formation.

EXPERIMENTAL

Methods

Infrared spectra were measured with a Perkin-Elmer 580 B spectrometer connected on-line with a multichannel analyzer TN-4000 Tracor Northern. High resolution ^1H NMR spectra of PMMA solutions were measured with the Jeol PS-100 spectrometer at 100 MHz.

Samples

Stereoregularity and the degree of deuteration of the studied samples were determined by ^1H NMR analysis. The stereoregularity values are given in Table I. The degree of deuteration of the respective groups in samples of s-PMMA-OCD_3 and i-PMMA-α-CD_3 was higher than 98%. The films of amorphous i-PMMA, i-PMMA-α-CD_3, s-PMMA-1, s-PMMA-2 and s-PMMA-OCD_3 were prepared from

TABLE I

Stereoregularity of PMMA Samples

Sample	Diads/%		Triads/%		
	m	r	I	H	S
i-PMMA	99	1	98	2	0
i-PMMA-α-CD_3	99	1	—	—	—
s-PMMA-1	6	94	2	8.5	89.5
s-PMMA-2	19	81	3	31	66
s-PMMA-OCD_3	11	89	4	14	82

acetonitrile solutions by evaporation of solvent. The films of crystalline i-PMMA and i-PMMA-α-OCD_3 were prepared from acetonitrile solution by evaporation of solvent and subsequent annealing for 13 days at 115 °C. The films of crystalline s-PMMA-1 were prepared from toluene solutions by evaporation of solvent at room temperature.[6] The films of the crystalline stereocomplexes i-PMMA/s-PMMA-1, i-PMMA-α-CD_3/s-PMMA-OCD_3 and i-PMMA/s-PMMA-2 were prepared from acetonitrile solutions by evaporation of solvent. The crystalline (or amorphous) states for all solid PMMA samples were verified by wide-angle X-ray scattering.

RESULTS AND DISCUSSION

s-PMMA

As shown in our previous paper[6], aggregates of s-PMMA in solution (in toluene, *o*-dichlorobenzene or butyl acetate) contain long sequences of diads with the tt backbone conformation (in staggered approximation). In IR spectra this is manifested by an increase of the intensity of the band at 860 cm^{-1}. Interaction of ester groups leading to aggregation is manifested in vibrational spectra by a complicated structure (splitting) of the band of the C=O stretching vibration[6,9,13], in IR spectra mainly by the appearance of a new band in this range at 1742 cm^{-1}. This range of IR spectra is shown in Figure 1 for

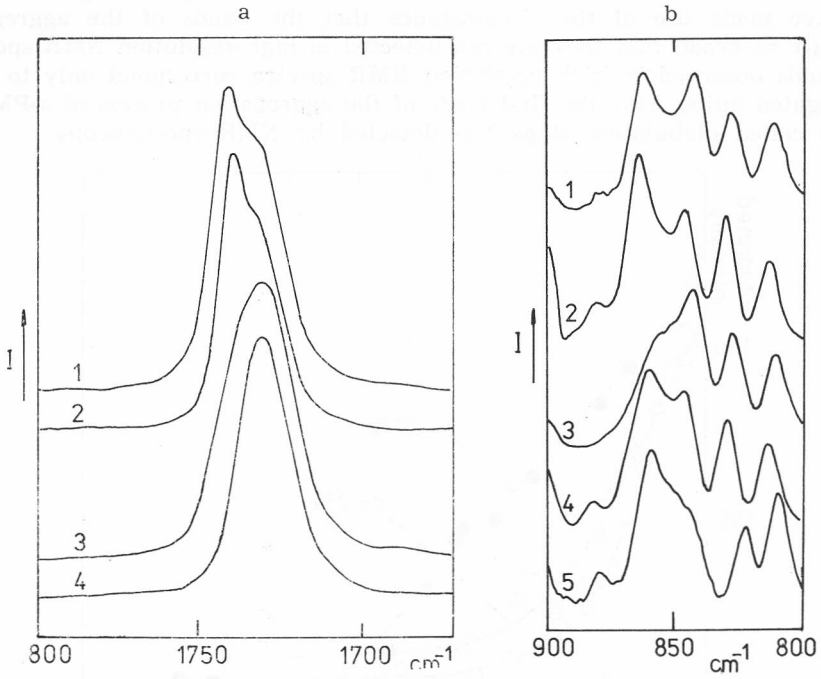

Figure 1. Two ranges of IR spectra of s-PMMA-1. Crystalline film prepared from toluene solution (1), s-PMMA-1 in toluene solution (2), amorphous film prepared from acetonitrile solution (3), s-PMMA-a in acetonitrile solution (4), s-PMMA-1 in PMMA stereocomplex film (i. e. normalized difference of the spectra of stereocomplex and i-PMMA) (5). All spectra measured at 25 °C.

samples of a crystalline film of s-PMMA-1 prepared from toluene solution (spectrum 1), of s-PMMA-1 in toluene solution where most of the polymer is present in the aggregated state (spectrum 2), of an amorphous film of s-PMMA-1 prepared from acetonitrile solution (spectrum 3), and of s-PMMA-1 in acetonitrile solution where aggregation does not take place (spectrum 4). This figure reveals that long sequences of tt conformational diads are generated during aggregation of s-PMMA, but partly already during dissolution of amorphous s-PMMA, and this even in solvents where aggregation of s-PMMA does not take place (acetonitrile). The band of the C=O stretching vibration at 1742 cm^{-1} only appears with s-PMMA aggregates in solution and with a

crystalline film of s-PMMA. The spectra also indicate, especially by the quite identical splitting of the band of the C=O stretching vibration (see also ref. 13), that the conformational structure of aggregated s-PMMA in solution and of crystalline s-PMMA is equal.

Already the NMR studies of the effect of the degree of stereoregularity on the aggregation of s-PMMA in solution have shown that aggregation of s-PMMA only takes place by interaction of two s-sequences of minimum length of 9 monomer units.[13] In order to verify that two chain segments actually interact during aggregation, we have measured by NMR spectroscopy the rate of s-PMMA agregation and the dependence of the rate on the concentration of the solution. Similarly as in our preceding studies[10,14] we have made use of the circumstance that the bands of the aggregated units are so broad that they are not detected in high-resolution NMR spectra; the bands observed in high resolution NMR spectra correspond only to non-aggregated units. Also, the first stage of the aggregation process of s-PMMA, the so called globulation stage,[10] is detected by NMR spectroscopy.

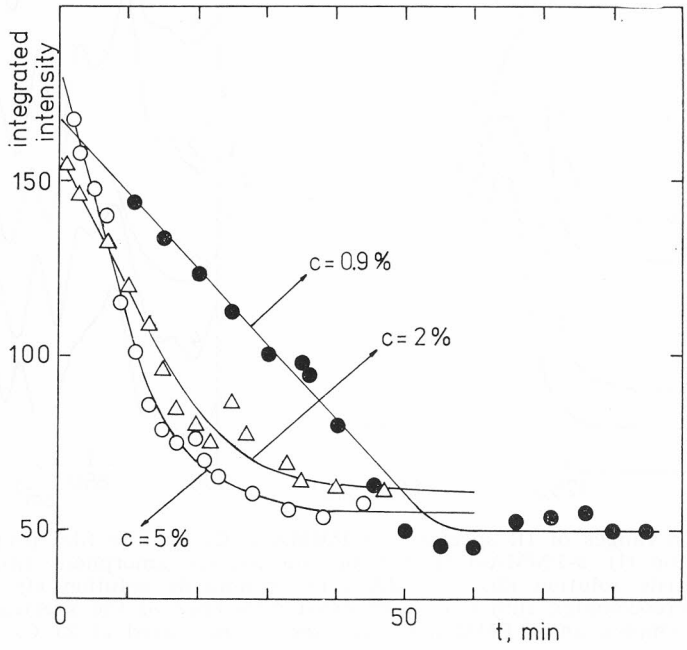

Figure 2. Time course of the integrated intensity of the OCH_3 proton NMR band of s-PMMA-1 in butylacetate solution at concentrations (w/v) 0.9% (●), 2% (△) and 5% (○), all measured at 50 °C.

Figure 2 shows the time dependences of the integrated intensity of the high-resolution OCH_3 band in ^1H NMR spectra of the sample s-PMMA-1 in butyl acetate, measured at 50 °C at three different concentrations of the solution. Prior to measurement, the studied solution was kept for 30 minutes at 80 °C (at this temperature all s-PMMA aggregates are decomposed[10,14]). Then it was placed into the spectrometer probe which was preheated to the desired temperature. A further 3—4 minutes was needed for the establi-

shment of thermal equilibrium, after which (time $t = 0$) the time dependence could be measured. The aggregation of s-PMMA in toluene at 32.5 °C was studied in a similar way.

Figure 2 reveals that the rate of aggregation increases with increasing the concentration of solution c. The rate constants k were determined from the time dependences of integrated intensity; the order n of the reaction of s-PMMA aggregate formation was determined from the ln k vs. ln c plot. For s-PMMA-1 in butyl acetate, $n = 1.7 \pm 0.2$, for s-PMMA-1 in toluene, $n = 2.0 \pm 0.4$. This confirms that there is mutual interaction of two different s-sequences during the aggregation of s-PMMA. This finding together with the results mentioned in the introduction point to the conclusion that double helices with a large number of monomer units per turn are formed in s-PMMA aggregation. Based on IR spectroscopic evidence, the same double helices are then preserved even in solid crystalline s-PMMA. The possibility that crystalline s-PMMA is formed by double helices with a large number of units per turn does not contradict the results of X-ray diffraction.[15]

i-PMMA

Having found that the IR spectra of amorphous and crystalline i-PMMA are almost identical, we paid most attention to the deuterated analogue i-PMMA-α-CD_3, the spectra of which are shown in Figure 3. Differences between the IR spectra of crystalline and amorphous i-PMMA-α-CD_3 are

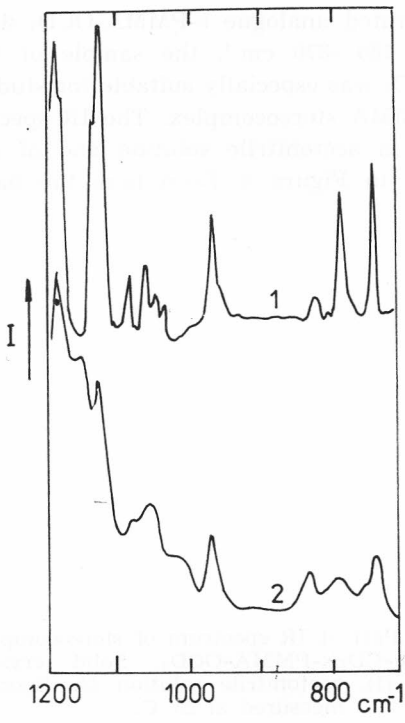

Figure 3. IR spectra of i-PMMA-α-CD_3. Crystalline film (1), amorphous film (2). Spectra measured at 25 °C.

observed in the range of about 800 cm^{-1}, where the amorphous sample exhibits a broad band with an indication of doublet structure, whereas the crystalline sample exhibits here a single sharp band at 793 cm^{-1}. Besides, crystallization leads to the disappearance of the amorphous i-PMMA-α-CD_3 band at 1157 cm^{-1}. The spectrum of i-PMMA-α-CD_3 in solution is identical with that of the amorphous film; dissolution of amorphous i-PMMA-α-CD_3 does not lead to any changes of conformational structure. As the content of i-PMMA aggregates in solution is low (~10%),[16,17] the IR spectrum of aggregated i-PMMA-α-CD_3 could not be obtained by digital treatment of the spectra. The fact that the aggregates of i-PMMA in solution decompose at temperatures above 160 °C,[16,17] i. e. at temperatures where melting of crystalline i-PMMA takes place, indicates that the aggregates of i-PMMA are probably i-PMMA microcrystallites.

PMMA Stereocomplex

The spectrum of s-PMMA-1 in the crystalline film of the stereocomplex i-PMMA/s-PMMA-1, obtained by computer as the normalized difference of the spectra of PMMA stereocomplex film and i-PMMA film, is shown in Figure 1. It is clearly apparent that the spectral range in Figure 1b is dominated by the band at 860 cm^{-1}, corresponding to long s-sequences with a tt backbone conformation, similarly as in ordered structures of s-PMMA only.

As the amorphous film of the deuterated analogue s-PMMA-OCD_3 does not exhibit any band in the IR range 780—870 cm^{-1}, the sample of the sterecomplex i-PMMA-α-CD_3/s-PMMA-OCD_3 was especially suitable for studies of the conformational structure of the PMMA stereocomplex. The IR spectra of the aggregates of this stereocomplex in acetonitrile solution and of the corresponding crystalline film are shown in Figure 4. Even here the band

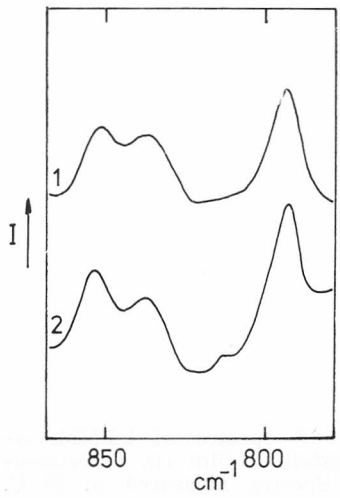

Figure 4. Part of IR spectrum of stereocomplex i-PMMA-α-CD_3/s-PMMA-OCD_3. Solid crystaline film (1), acetonitrile solution (2). Spectra measured at 25 °C.

at 860 cm^{-1}, detected also with the crystalline film of s-PMMA-OCD_3, and the sharp band at 796 cm^{-1} characteristic of crystalline i-PMMA-α-CD_3, are well pronounced. The spectra of the stereocomplex aggregates i-PMMA-α-CD_3/ /s-PMMA-OCD_3 in acetonitrile solution and of the corresponding crystalline film are almost identical, indicating identical conformational structures in both cases. The conformational structure of the i-chains in the stereocomplex is very similar to the structure of crystalline i-PMMA, the conformational structure of s-chains in the stereocomplex is very similar to the structure in crystalline (or aggregated) s-PMMA. As both X-ray diffraction data and our own, above mentioned, results indicate that both crystalline i-PMMA and crystalline s-PMMA are formed by double helices with a large number of monomer units per turn, and in the PMMA stereocomplex formation interaction of at least two chains must take place (one i-PMMA and one s-PMMA), we suppose that both in the PMMA stereocomplex aggregates in solution and in solid stereocomplex samples double helices with a large number of monomer units per turn exist. The structure of the crystalline PMMA stereocomplex proposed by Bosscher *et al.*[3] is in agreement with this statement.

In our previous paper[18] we have shown, by means of NMR spectroscopy, that in acetonitrile solution the stereocomplex is formed also by interaction of i-PMMA (of high stereoregularity) with s-PMMA-2, the stereoregularity of which is appreciably lower. s-PMMA-2 did not form self-aggregates in any solvent where selfaggregation was studied,[6,14,17] with the exception of CCl_4. Parts of the IR spectra of s-PMMA-2 are shown in Figure 5. This figure reveals that the stereocomplex formation i-PMMA/s-PMMA-2 is manifested by a pronounced increase of the intensity of the band at 860 cm^{-1} which is very weak both for the amorphous film of s-PMMA-2 and

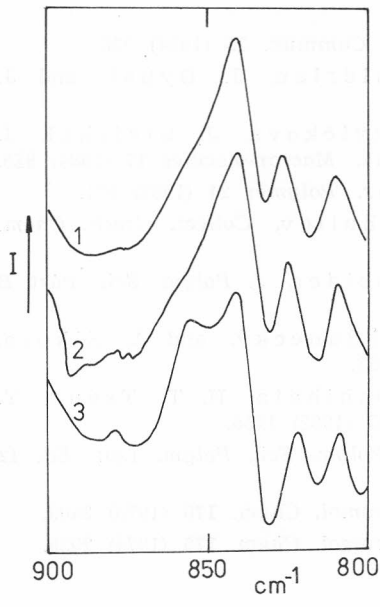

Figure 5. Part of IR spectra of s-PMMA-2. Amorphous film (1), toluene solution (2), s-PMMA-2 in the film of the stereocomplex i-PMMA/s-PMMA-2 (i. e. normalized difference of the spectra of stereocomplex and i-PMMA) (3). All spectra measured at 25 °C.

for its toluene solution. This indicates that the interactions leading to the formation of the stereocomplex are strong enough to impose the conformational structure appearing in ordered forms of s-PMMA of high stereoregularity even onto s-PMMA chain segments containing isotactic defects.

CONCLUSIONS

The conformational structure of all three crystalline forms of stereoregular PMMA (i-PMMA, s-PMMA, stereocomplex) is very similar in principle — a double helix with a large number of monomer units per turn. Our results further indicate that the same structure also exists in aggregates in solution. With s-PMMA, nuclei of long helices appear also in solutions where aggregation does not take place.

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SAŽETAK

Komformacijska struktura sređenih oblika stereoregularnih poli(metilmetakrilata)

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Opisani su rezultati ispitivanja konformacijske strukture stereoregularnog PMMA metodom infracrvene spektroskopije u kombinaciji s NMR ispitivanjem kinetike agregacije s-PMMA. Ustanovljeno je da agregacija s-PMMA i nastajanje PMMA stereokompleksa dovodi do stvaranja dvostrukih zavojnica s velikim brojem monomernih jedinica po zavoju i da takve zavojnice postoje u sva tri kristalna oblika stereoregularnog PMMA (i-PMMA, s-PMMA, stereoregularni kompleks) u čvrstom stanju. Interakcije koje dovode do nastajanja stereokompleksa mogu stvoriti ovu strukturu čak i u lancima s-PMMA, koji ne posjeduju visoku stereoregularnost.