

**STUDY OF THE EFFECT OF AGGREGATION ON THE STRUCTURE
OF SYNDIOTACTIC POLY(METHYL METHACRYLATE)
BY INFRARED SPECTRA OF ITS DEUTERATED ANALOGUES**

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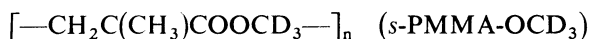
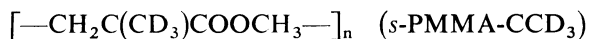
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The temperature trends of the infrared spectra of the films of some specifically deuterated analogues of syndiotactic poly(methyl methacrylate) were measured and vibrational bands sensitive to the conformational structure of the carbon backbone and to the orientation of ester groups with respect to the main chain were determined. Analysis of the spectra has confirmed that aggregated syndiotactic poly(methyl methacrylate) contains a higher population of diads in the extended chain conformation in long syndiotactic sequences as compared to the nonaggregated polymer, and has shown that in the aggregate, ordering of ester groups also takes place.

NMR studies of solutions of syndiotactic poly(methyl methacrylate) (*s*-PMMA) have shown that in some solvents (*e.g.* toluene and *o*-dichlorobenzene) associated structures of *s*-PMMA are formed^{1,2}. Aggregation of *s*-PMMA in solutions was also proved by osmometry, viscosimetry and light scattering³⁻⁵. Analysis of infrared (IR) spectra has shown that aggregation of *s*-PMMA in solution is accompanied by an increase of the population of long syndiotactic sequences in the extended chain form (corresponding to the conformation *tt* in the staggered approximation) and by ordering of ester groups^{6,7}. In samples of solid *s*-PMMA isolated at room temperature from solutions where aggregation takes place, the enhanced population of segments with the extended chain conformation and the ordering of ester groups are preserved^{6,7}. Solid *s*-PMMA prepared in this way is partly crystalline according to X-ray scattering, and exhibits fibrillar morphology in the electron microscope^{6,7}. In our previous studies^{6,7}, aggregation of *s*-PMMA was investigated by means of IR spectroscopy using samples of undeuterated *s*-PMMA (*s*-PMMA-H₈). The aim of the present study is the verification and further refinement of previous findings concerning the structure of polymer chains in the aggregates of *s*-PMMA by means of the analysis of IR spectra of the following deuterated analogues of *s*-PMMA:





EXPERIMENTAL

Samples of deuterated analogues of *s*-PMMA were prepared from the corresponding monomers by anionic polymerization initiated by triethylaluminium and TiCl_4 in toluene⁸ at -78°C . All polymers were purified by double precipitation from dry acetone into distilled water and dried for 8 h in high vacuum at 60°C .

Stereoregularity and degree of deuteration were determined from the analysis of 100 MHz ^1H NMR spectra of samples dissolved (10% w/v) in *o*-dichlorobenzene/tetrachloroethylene (molar ratio 1 : 1), measured at 135°C , using the spectrometer JEOL PS-100. The content of isotactic (*I*), heterotactic (*H*) and syndiotactic (*S*) triads was determined from the integrated intensities of the α -methyl bands, and the content of racemic (*r*) and meso (*m*) diads from the analysis of the methylene band (Table I). As all samples were prepared by the same procedure and the stereoregularities of *s*-PMMA- H_8 ⁷, *s*-PMMA- OCD_3 and *s*-PMMA- CCD_3 are practically equal, it may be assumed that also the stereoregularity of *s*-PMMA- D_8 does not deviate significantly from the determined values.

IR spectra were measured on the spectrometer Perkin-Elmer 580 B connected on-line with the multichannel analyzer TN-4000 Tracor Northern. The temperature dependences were measured in the commercial heated cell of Perkin-Elmer. The solutions of the deuterated analogues of *s*-PMMA in acetonitrile and toluene (concentration 2% w/v) were homogenized in sealed glass cells for 2 h at 120°C . After 24 h these solutions were used for the preparation of this polymer films on AgCl or KBr pellets by evaporation of solvent at reduced pressure at 25 or -40°C .

RESULTS AND DISCUSSION

Effect of Aggregation on IR Spectra of Deuterated s-PMMA

In our preceding study⁷ we have followed the effect of aggregation of *s*-PMMA on the IR spectra of the solutions and films of *s*-PMMA- H_8 in the range of the band

TABLE I
Stereoregularity and deuteration of samples of *s*-PMMA

Sample	Diads, %		Triads, %			Content of D, %		
	<i>r</i>	<i>m</i>	<i>I</i>	<i>H</i>	<i>S</i>	OCH_3	CH_2	CCH_3
<i>s</i> -PMMA- CCD_3	7	93	—	—	—	0	0	96
<i>s</i> -PMMA- OCD_3	11	89	4	14	82	99	0	0
<i>s</i> -PMMA- D_8	—	—	—	—	—	99	99	99

of the C=O stretching vibration and in the range of the doublet $860,843\text{ cm}^{-1}$. In the spectra of *s*-PMMA- H_8 solutions where aggregation takes place, or in films prepared from these solutions, the carbonyl band has the form of a doublet at $1741, 1731\text{ cm}^{-1}$, whereas in spectra of solvents where aggregation does not take place, a single peak appears in the range of the carbonyl vibration. The component at the higher wavenumber of the carbonyl doublet corresponds to the stretching vibration of C=O bonds in aggregated units of *s*-PMMA- H_8 . In the doublet at $860, 843\text{ cm}^{-1}$ aggregation of *s*-PMMA- H_8 is manifested by an increase of the intensity of the band at 860 cm^{-1} corresponding to an increase of the population of *tt* conformational forms of the carbon backbone.

Similarly as in the case of *s*-PMMA- H_8 ⁷, also in the spectra of the studied solutions of deuterated analogues of *s*-PMMA in toluene, and in the spectra of the corresponding films prepared from these solutions by evaporation at 25°C , a doublet is observed in the range of the C=O stretching vibrations (see *e.g.* Fig. 1). The shape of the carbonyl bands in the corresponding spectra of *s*-PMMA- OCD_3 and *s*-PMMA- -CCD_3 is similar to the shape shown in Fig. 1 for solutions and films of *s*-PMMA- D_8 . This indicates that in the solutions of the deuterated analogues of *s*-PMMA in toluene (contrary to the solutions in acetonitrile, Fig. 1), aggregation of the polymer takes

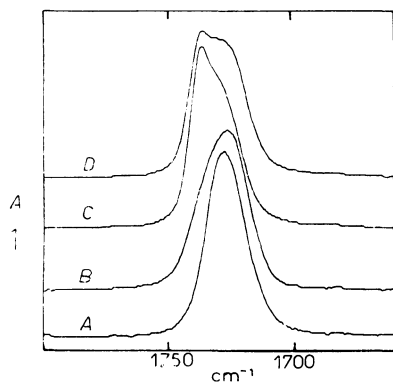


FIG. 1

Parts of IR spectra of 2% (w/v) solutions of *s*-PMMA- D_8 in acetonitrile (A) and in toluene (C) (spectra of solvents subtracted) and films prepared from the corresponding solutions by evaporation of acetonitrile (B) or toluene (D) at 25°C

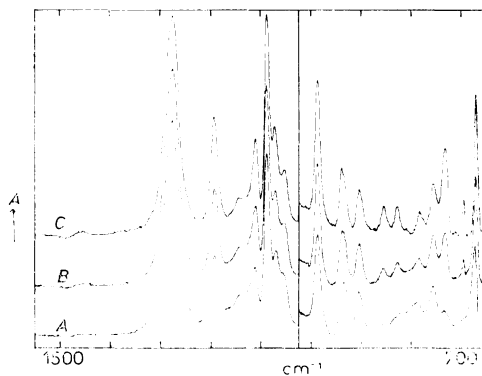


FIG. 2

IR spectra (30°C) of *s*-PMMA- D_8 films from 2% (w/v) solutions of *s*-PMMA- D_8 in acetonitrile (A), toluene (B) at 25°C , and the normalized difference of spectra B and A in the ratio 1:0 and 0:5 (C). In the range below 1025 cm^{-1} absorbance expanded four times.

place, and its effect on the shape of the C=O stretching vibration is the same as for *s*-PMMA-H₈. The wavenumber changes of the C=O stretching vibration caused by aggregation are preserved in the solid polymer. In this paper, solid *s*-PMMA isolated from toluene solutions containing *s*-PMMA aggregates is designated as aggregated *s*-PMMA.

In Figs 2, 3, 4 the range 1 600–700 cm⁻¹ of the IR spectra of films of deuterated analogues of *s*-PMMA prepared by evaporation of solvent at 25°C from the solutions of the corresponding polymers in acetonitrile and in toluene is shown. In the films of *s*-PMMA prepared from toluene solutions, *s*-PMMA is present both in the aggregated, and in the non-aggregated state; in films prepared from acetonitrile solutions aggregated *s*-PMMA is not present. In the spectra of films prepared from toluene solutions of all deuterated analogues of *s*-PMMA and of *s*-PMMA-H₈⁷, the carbonyl doublet was separated into two Lorentzian components by a least-squares procedure. In all cases the ratio of the integrated intensities of both bands was equal to 1 : 1 within experimental error. From the spectra of the films of the deuterated analogues of *s*-PMMA from toluene, the normalized spectra multiplied by the factor 0.5 of the films from acetonitrile were subtracted. In spectra obtained in this way, the component at the lower wavenumber of the carbonyl doublet, corresponding

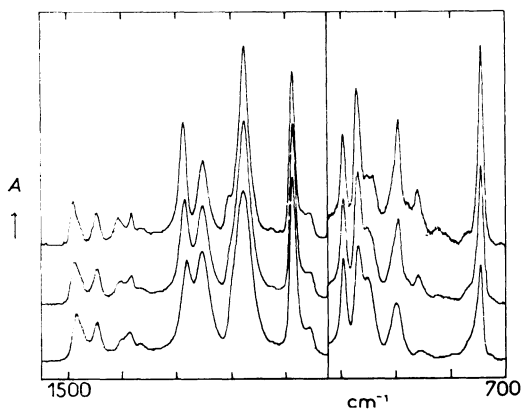


FIG. 3

IR spectra (30°C) of *s*-PMMA-OCD₃ films, prepared from 2% (w/v) solutions of *s*-PMMA-OCD₃ in acetonitrile (A) and toluene (B) at 25°C, and the normalized difference of spectra B and A in the ratio 1.0 and 0.5 (C). In the range below 1 025 cm⁻¹ absorbance expanded four times

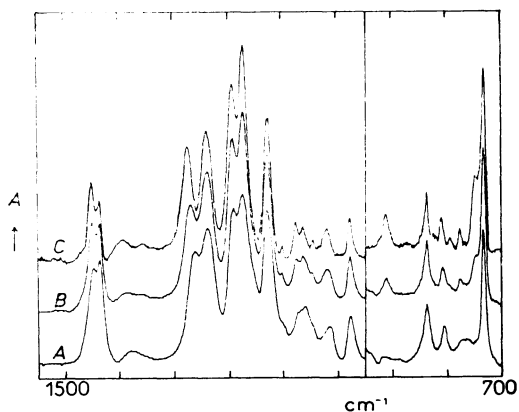


FIG. 4

IR spectra (30°C) of *s*-PMMA-CCD₃ films, prepared from 2% (w/v) solutions of *s*-PMMA-CCD₃ in acetonitrile (A) and toluene (B) at 25°C, and the normalized difference of spectra B and A in the ratio 1.0 and 0.5 (C). In the range below 950 cm⁻¹ absorbance expanded 2.5 times

to non-aggregated *s*-PMMA is compensated. These difference spectra, shown in Figs 2–4, may be regarded as spectra of the pure aggregated deuterated analogues of *s*-PMMA.

In Figs 2–4, in the spectra of aggregated *s*-PMMA most bands exhibit smaller width than the corresponding bands in the spectra of non-aggregated *s*-PMMA. From this it may be inferred that during aggregation of *s*-PMMA chains, preference of selected conformational forms takes place, whereas in non-aggregated *s*-PMMA an equilibrium distribution of all adequate conformers exists. Spectra of aggregated *s*-PMMA further exhibit shifts of some bands with respect to their positions in the spectra of non-aggregated *s*-PMMA, and a number of bands exhibit different intensities.

s-PMMA-D₈ (Fig. 2). In the spectra of aggregated *s*-PMMA-D₈, the bands at 855 and 783 cm⁻¹ exhibit higher intensity as compared to the corresponding bands in the spectrum of the film of *s*-PMMA-D₈ isolated from acetonitrile solution, and they are shifted by 3 and 6 cm⁻¹, respectively, to lower wavenumbers. In the spectrum of the film from acetonitrile, a broad band composed of two or more components corresponds to the band at 828 cm⁻¹ in the spectrum of aggregated *s*-PMMA-D₈. The relative increase of the intensity of the band at 828 cm⁻¹ by aggregation is evidently caused by an increase of the intensity of one of its components, at the expense of the others corresponding to conformers which are depleted at aggregation.

s-PMMA-OCD₃ (Fig. 3). At aggregation of *s*-PMMA-OCD₃, the intensity of the band at 859 cm⁻¹ in the IR spectrum increases. The intensity of the band at 950 cm⁻¹ decreases, and simultaneously the band at 940 cm⁻¹ becomes more prominent in consequence of width reduction. The band at 1 285 cm⁻¹ narrows and shifts to 1 287 cm⁻¹. The intensity of the band at 1 406 cm⁻¹ increases at aggregation.

s-PMMA-CCD₃ (Fig. 4). As compared to the IR spectrum of the film of *s*-PMMA-CCD₃ prepared from acetonitrile solution, the bands at 750, 775, 911, 1 075 and 1 448 cm⁻¹ exhibit higher intensity in the spectra of aggregated *s*-PMMA-CCD₃. The band at 1 263 cm⁻¹ shifts to 1 273 cm⁻¹ at aggregation, while the position of the neighbouring band at 1 240 cm⁻¹ remains unchanged.

Temperature Dependence of IR Spectra and Conformational Structure of s-PMMA

The temperature dependence of the IR spectra of *s*-PMMA-H₈ was studied in a number of papers^{9–12}. A number of bands with temperature-dependent intensities and widths were found, and these changes in the spectra were ascribed to temperature changes of conformational structures. For the conformationally-sensitive bands of *s*-PMMA-H₈ in the range 1 000–1 500 cm⁻¹ the intensities, widths and positions change both below and above the glass transition *T*_g of *s*-PMMA (about 115°C) and it is assumed that the changes are sensitive to the orientation of the ester group with respect to the backbone. The conformationally sensitive bands of *s*-PMMA-H₈, the intensities of which are temperature-dependent only above *T*_g (doublet at 860,

843 cm^{-1}) have been interpreted¹² as bands sensitive to the conformational structure of the backbone. The band at 860 cm^{-1} was assigned to the conformational structure of the backbone which in the staggered approximation can be described as *tt*. By comparison with the results of wide-angle X-ray scattering it was found⁷ that the band at 860 cm^{-1} corresponds only to sufficiently long syndiotactic sequences in extended chain conformation which can be identified with the proposed^{13,14} helical structure of *s*-PMMA with a large number of monomer units per turn (60/4). The band at 843 cm^{-1} corresponds to those segments of the *s*-PMMA- H_8 chain which do not form helical structure.

In this study we have measured the temperature dependence in the range 30 to 200°C of IR spectra of films of deuterated analogues of *s*-PMMA obtained by evaporation of solvent from acetonitrile solutions at temperatures 25 and -45°C (Figs 5–7) (where aggregation of *s*-PMMA does not take place). Similarly as in the case of *s*-PMMA- H_8 , also in the spectra of the deuterated analogues of *s*-PMMA, temperature changes of the film lead to some changes of intensity, width and pos-

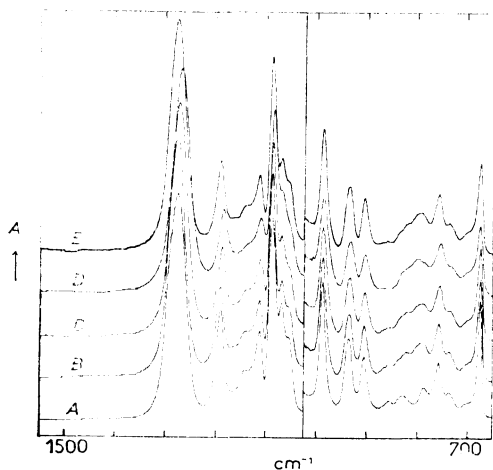


FIG. 5

IR spectra of *s*-PMMA- D_8 films prepared from 2% (w/v) solutions of *s*-PMMA- D_8 in acetonitrile by evaporation of solvent at -40°C (A) and 25°C (B, C, D and E). Spectra were measured at 30°C (A and B), 100°C (C), 200°C (D) and after cooling at 30°C (E). In the range below 1 025 cm^{-1} absorbance expanded four times

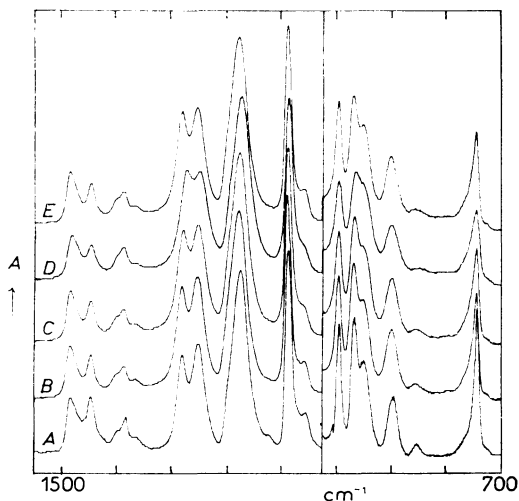


FIG. 6

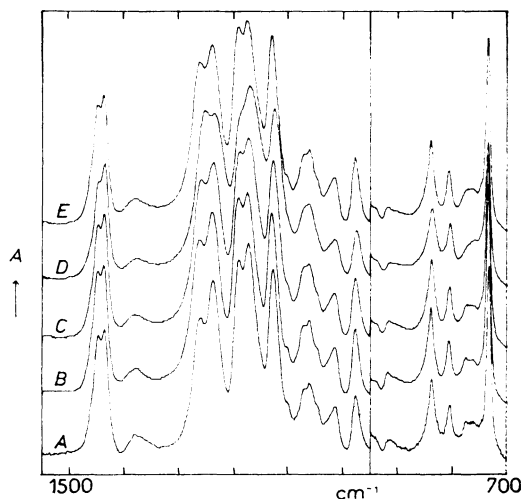
IR spectra of *s*-PMMA- OCD_3 films prepared from 2% (w/v) solutions of *s*-PMMA- OCD_3 in acetonitrile by evaporation of solvent at -40°C (A) and 25°C (B, C, D and E). Spectra were measured at 30°C (A and B), 100°C (C), 200°C (D) and after cooling of sample at 30°C (E). In the range below 1 025 cm^{-1} absorbance expanded four times

sibly even of positions of most vibrational bands. Here we shall describe only the most prominent changes which can be utilized in studies of the conformational structure of *s*-PMMA.

s-PMMA-D₈ (Fig. 5). A pronounced temperature dependence is exhibited by the intensities of the weak bands in the range 770–870 cm⁻¹. In the spectra of the film prepared at 25°C the bands in this range are relatively broad and strongly overlapping. In the doublet at 800, 789 cm⁻¹ the intensity of the band at 800 cm⁻¹ increases with increasing temperature, whereas the intensity of the band at 789 cm⁻¹ decreases. However, intensity changes are only observed after heating of the film to the temperature of *T*_g. At subsequent decreasing of the temperature of the film from 200°C to lower temperatures, changes of line intensities are only observed at temperatures above *T*_g, at further cooling of the film the intensities of these lines do not change. In the spectrum measured after cooling of the film to 30°C the intensity of the band at 789 cm⁻¹ is lower than in the same spectrum measured at the same temperature before heating of the film. In the spectrum of the film prepared at -45°C and measured at 30°C, the intensity of the band at 789 cm⁻¹ is higher. A similar behaviour is observed with the band at 858 cm⁻¹. The temperature trends of line intensities indicate that these bands are sensitive to conformational transitions which take place only above the glass transition temperature of *s*-PMMA, *i.e.* to conformational changes of the carbon backbone. The bands at 858 and 789 cm⁻¹ correspond to the energetically favoured conformer, *i.e.* to the form *tt*^{12,15,16}. Except for the shift of the band from 1 277 to 1 270 cm⁻¹ in the IR spectra of *s*-PMMA-D₈ films, no pronounced changes take place in the measured temperature range between 900–1 300 cm⁻¹.

s-PMMA-OCD₃ (Fig. 6). Very pronounced changes of line intensities and positions (reversible in the whole measured temperature range) take place in the spectral range 900–1 400 cm⁻¹. In the doublet at 968, 950 cm⁻¹, the intensity of the band at 950 cm⁻¹ increases with increasing temperature of the film. By heating of the sample from 30 to 200°C, the intensity of the band

FIG. 7
IR spectra of *s*-PMMA-CCD₃ films, prepared from 2% (w/v) solutions of *s*-PMMA-CCD₃ in acetonitrile by evaporation of solvent at -40°C (A) and 25°C (B, C, D and E). Spectra were measured at 30°C (A and B), 100°C (C), 200°C (D) and after cooling of sample at 30°C (E). In the range below 950 cm⁻¹ absorbance expanded 2.5 times



at $1\,285\text{ cm}^{-1}$ increases, and simultaneously its peak is shifted to $1\,273\text{ cm}^{-1}$. At the same time the band at $1\,254\text{ cm}^{-1}$ is shifted to $1\,249\text{ cm}^{-1}$. All these reversible changes in the spectrum correspond to conformational changes of *s*-PMMA-OCD₃ which can take place in the whole studied temperature range, and therefore they must be ascribed to conformational changes of ester groups^{11,12}. The intensity of the band at 857 cm^{-1} decreases with increasing temperature, but intensity changes only take place above T_g . From Fig. 6 it can be seen that in the spectra measured at 30°C , the intensity of this band depends on the temperature of film preparation and further heat treatment of the sample. This band is analogous to the band at 858 cm^{-1} in the spectrum of *s*-PMMA-D₈ and it corresponds to the energetically more favoured *tt* form of the carbon backbone.

s-PMMA-CCD₃ (Fig. 7). With increasing temperature of the film, a decrease of the intensities of the lines at $1\,448$, $1\,193$ and $1\,073\text{ cm}^{-1}$ is observed. With increasing temperature, line positions in the doublet at $1\,263$, $1\,240\text{ cm}^{-1}$ change considerably, shifting to $1\,254$ and $1\,234\text{ cm}^{-1}$, respectively. The intensities and positions of all the cited bands do not depend on the temperature of film preparation, the changes take place in the whole temperature range and they are reversible. This indicates that they correspond to changes of populations of ester group conformations. A decrease of intensity with increasing temperature is also observed for the weak band at 775 cm^{-1} ; due to the overlap of this band with neighbouring bands it cannot be decided if it is sensitive to conformational changes of ester group or of the carbon backbone.

The above analysis of IR spectra of deuterated analogues of *s*-PMMA in the nonaggregated state shows that the temperature changes of line intensities and positions correspond to changes of conformer populations. With some bands, temperature changes of line intensities below and above T_g can be used to decide if these lines are sensitive to changes of orientation of ester groups or to conformational changes of the carbon backbone (Table II).

Calculations of conformer energies of *s*-PMMA¹⁵, analysis of the conformations of the dimer model of PMMA^{16,17} and analysis of the dipole moment of *s*-PMMA¹⁸ all indicate that in the energetically most favoured orientation of the ester group with respect to the carbon backbone, the bonds C=O and C—CH₃ are in *cis* orienta-

TABLE II

Conformationally sensitive bands in IR spectra of *s*-PMMA, with intensity increasing (\uparrow) and decreasing (\downarrow) at increasing temperature (ν , cm^{-1})

Polymer	Backbone	Ester group
<i>s</i> -PMMA-H ₈ ^a	860 \downarrow , 843 \uparrow	1 450 \downarrow , 1 194 \downarrow
<i>s</i> -PMMA-D ₈	858 \downarrow , 800 \uparrow , 789 \downarrow	
<i>s</i> -PMMA-OCD ₃	857 \downarrow	950 \uparrow
<i>s</i> -PMMA-CCD ₃		1 448 \downarrow , 1 193 \downarrow , 1 083 \downarrow

^a From ref.¹².

tion. In refs¹⁵⁻¹⁸ it is also assumed that the second non-negligibly populated form is the structure with the bonds C=O and C—CH₃ in *trans* orientation. This indicates that the bands in IR spectra sensitive to the orientation of ester groups with a negative temperature trend of intensity evidently correspond to *cis* structures. (Table II). However, a continuous temperature shift of line position observed with some of these bands indicates that besides the considered *cis* and *trans* forms, the ester groups may also form some further structures (*e.g.* *cis* and *trans* orientation of C=O with respect to C—CH₂, and *gauche* structures).

Structure of Aggregated *s*-PMMA

Similarly as in the case of *s*-PMMA-H₈⁷, the formation of the aggregate of *s*-PMMA-D₈ and of *s*-PMMA-OCD₃ is manifested in IR spectra by an increase of the intensity of those bands which correspond to the energetically most favoured tt form of the *s*-PMMA chains, according to the analysis of temperature dependences. We assume that in the spectra of the cited deuterated analogues of *s*-PMMA, similarly as in *s*-PMMA-H₈, these bands correspond to long syndiotactic sequences with extended chain conformation.

Besides these changes, in all deuterated analogues of *s*-PMMA as well as in *s*-PMMA-H₈, the formation of aggregates is accompanied by changes of intensities of bands which are sensitive to the orientation of ester groups with respect to the backbone. As aggregation is also accompanied by changes of line width a comparison of line intensity changes at aggregation with the changes induced by heating or cooling of the films is difficult. However, in all cases temperature changes in the spectra suggested that bands corresponding to the structure of the ester group with *cis* orientation of C=O with respect to C—CH₃ become more prominent at aggregation. This interpretation of the changes of spectra of *s*-PMMA at aggregation is in agreement with the observation that line shifts at aggregation occur similarly as during cooling of the films. The above analysis of IR spectra of deuterated analogues of *s*-PMMA together with the results of the IR study⁷ of *s*-PMMA-H₈ indicates that the aggregates of *s*-PMMA observed in IR spectra contain only long tt sequences. According to X-ray analysis¹³, *s*-PMMA in aggregates exhibits helical structure with a large number of monomer units per turn which can be approximated as tt. The generation of long tt sequences during aggregation of *s*-PMMA evidently corresponds to the formation of this helical structure.

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