Vibrational spectra and structure of stereoregular poly(methyl methacrylates) and of the stereocomplex

J. Dybal, J. Štokr and B. Schneider
Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06
Prague 6, *Czechoslovakia*
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Infra-red and Raman spectra of films and solutions of syndiotactic and isotactic poly(methyl methacrylate) (PMMA) and of the stereocomplex of PMMA were measured. Vibrational bands sensitive to conformational transitions were determined. Differences of band intensities in spectra of stereoregular PMMA and of the stereocomplex indicate changes of populations of conformational forms of polymer chains accompanying stereocomplex formation. For syndiotactic PMMA in the stereocomplex, the extended chain conformation predominates.

Keywords Infra-red spectroscopy; Raman spectroscopy; stereoregular poly(methyl methacrylate); conformational structure; intermolecular interactions

INTRODUCTION

The infra-red (i.r.) and Raman spectra of syndiotactic and isotactic poly(methyl methacrylate) (s-PMMA and i-PMMA) have been studied by a number of authors[1-12]. The bands in vibrational spectra of stereoregular PMMA have been assigned[2-5,9], and bands in i.r. and Raman spectra sensitive to PMMA chain stereoregularity have been determined[1,9]. Havriljak and Roman[3] used i.r. spectra in a conformational study of PMMA, and they interpreted the temperature dependence of bands in the range 1050–1300 cm^{-1} by changes in the orientation of ester groups of s-PMMA in the solid state. From analysis of bands in this range, Belopolskaja and Trapeznikova[7] concluded that conformational changes of ester groups also take place in films of i-PMMA; they also considered rotation about the CO–O bond, and determined conformational energy differences. In our preceding work[6] using i.r. spectra we have found a difference in the conformational structure of s-PMMA in a film of s-PMMA only, and in a film of the stereocomplex of PMMA prepared by mixing of solutions of s-PMMA and i-PMMA in the ratio 2:1. The effect of temperature on the band at 1450 cm^{-1} in i.r. spectra of atactic PMMA was explained by changes of linewidth due to changes of the O–CH_3 group mobility[8]. Recently O'Reilly *et al.* have measured the temperature dependences of i.r. spectra of PMMA[11] and of deuterated PMMA[12] of various tacticity, and they used band changes derived from difference spectra for the determination of conformational energies. These they assigned to various conformational forms and the results were confronted with PMMA geometries and populations as calculated by Sundararajan and Flory[13].

In the cited papers, the interpretation of the conformationally sensitive bands differs. To our knowledge, the temperature dependence of vibrational spectra of solutions of stereoregular PMMA, and the effect of various solvents on vibrational spectra of PMMA, have not been studied. In order to refine existing ideas about the conformational forms of stereoregular PMMA and about the conformational structure of PMMA chains in the stereocomplex, we have made a new series of measurements of i.r. and Raman spectra of i- and s-PMMA and of the stereocomplex in the solid state and in solutions. In our studies of the structure of PMMA we have also made use of results obtained on the conformational forms of simple esters[14], the dimer of PMMA (dimethylester of 2,2,4,4,-tetramethylglutaric acid; DMTG)[6,15], and of evidence on the existence of local order of simple esters generated by static dipolar interactions of ester groups in the liquid state[14,15].

EXPERIMENTAL

Raman spectra were measured on a Coderg LRDH-800 spectrometer connected on-line with a TN-11 multichannel data analyser (Tracor system). The 514.5 nm line of a CR-3 (Coherent Radiation) argon laser was used for spectra excitation. The spectra were measured in the 90° arrangement, and were obtained by accumulation of a larger number of scans. Infra-red spectra were measured on a Perkin–Elmer 580 B spectrometer, connected on-line with a TN-4000 multichannel data analyser (Tracor Northern). The temperature dependences were measured in a commercial heated cell (Perkin–Elmer) and in a low-temperature cell developed in this laboratory[16]. The polymer films were prepared by evaporation from acetonitrile and chloroform solutions on AgCl or KBr pellets, in some cases at reduced pressure.

Syndiotactic PMMA was prepared by anionic polymerization initiated by triethylaluminium and $TiCl_4$ in toluene at 195K. Isotactic PMMA was prepared by anionic polymerization initiated by phenylmagnesium bromide in toluene at 290K. By n.m.r. analysis, the contents of I, H and S triads was 2.0, 8.5 and 89.5% in s-PMMA, and 98.5, 1.0 and 0.5% in i-PMMA.

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RESULTS AND DISCUSSION

Infra-red spectra

Syndiotactic PMMA. We have measured the temperature dependence of i.r. spectra of s-PMMA films evaporated from a solution of s-PMMA in acetonitrile at room temperature (298K) and 200K (*Figure 1*) and i.r. spectra of solutions of s-PMMA in acetonitrile, chloroform and tetrachloromethane (*Figure 2*).

The temperature dependence of band intensities in i.r. spectra of s-PMMA films has been analysed in several papers[3,7,11,12]. Havriljak and Roman[3] and also Belopolskaja and Trapeznikova[7] interpreted the temperature changes in i.r. spectra of s-PMMA films in the range 1050–1300 cm^{-1} by changes in conformational transitions of ester groups. Their interpretation was based on the assumption that the bands observed in this range can be described as pairs of bands sensitive to the conformational structure of ester groups. Our measurements of i.r. spectra of DMTG have shown[15] that the spectrum of crystalline DMTG, with only a single conformer present, also exhibits multiplicity of ester absorption bands in this spectral range. It may therefore be expected that in the range 1050–1300 cm^{-1} of the i.r. spectrum, several bands correspond to ester group vibrations of a single conformational form.

The positions of bands in this range undergo pronounced temperature changes; for example, the band observed at 1263 cm^{-1} in the i.r. spectrum of s-PMMA at 473K shifts to 1278 cm^{-1} at 160K. From *Figure 1* it can be seen that these frequency shifts are not accompanied by any pronounced changes of the asymmetry of the bands, and it is therefore evident that a frequency shift of such magnitude cannot be explained by intensity transfer in a doublet, and that it is caused by a temperature-induced vibrational frequency shift.

Frequency shifts considerably affect the shape of difference spectra obtained by subtraction of two spectra measured at different temperatures, because in the difference spectrum a band shift appears similar to an intensity change of the components of a doublet. For illustration in *Figure 3* are shown apparent band intensities calculated from difference spectra under the assumption that the counterpeaks generated as a consequence of the frequency shift of one Lorentzian band represent an intensity change of doublet components. O'Reilly *et al.*[11,12] have used a series of difference spectra obtained by subtraction of two spectra measured at different temperatures for the determination of the temperature dependence of band intensities and of the conformational energies of PMMA-h_8 and PMMA-d_8. As the temperature shifts of band frequencies in the range 1050–1300 cm^{-1} are very pronounced, we do not consider the results of their paper to be realistic. Moreover, the situation is complicated by the fact that, for none of the bands generated in the difference spectra, can assignment to a unique conformational form be proved.

From *Figure 1* it is seen that in the whole temperature range 160–473K, the intensities of the bands at 1450 and 1194 cm^{-1} change markedly in i.r. spectra of s-PMMA films. The intensity of these bands increases with decreasing temperature, and their intensities change similarly also in the spectra of solutions of s-PMMA. If it is assumed that the intensities of these bands are not affected by Fermi resonance, then it is evident that they are either conformationally sensitive, or that their width is temperature-dependent. The temperature changes of the band at 1450 cm^{-1} in the spectra of atactic PMMA have been explained by changes of bandwidth[8]. It will be shown that a similar explanation is not suitable for the interpretation of the temperature changes of the analogous band in the spectra of i-PMMA.

In spectra of solutions of s-PMMA, temperature dependence is also exhibited by the doublet at 860 and 843 cm^{-1} (*Figure 2a*), in which the intensity of the band at 860 cm^{-1} increases with decreasing temperature. A comparison of spectra of solutions of s-PMMA in various solvents indicates that the intensity of the band at

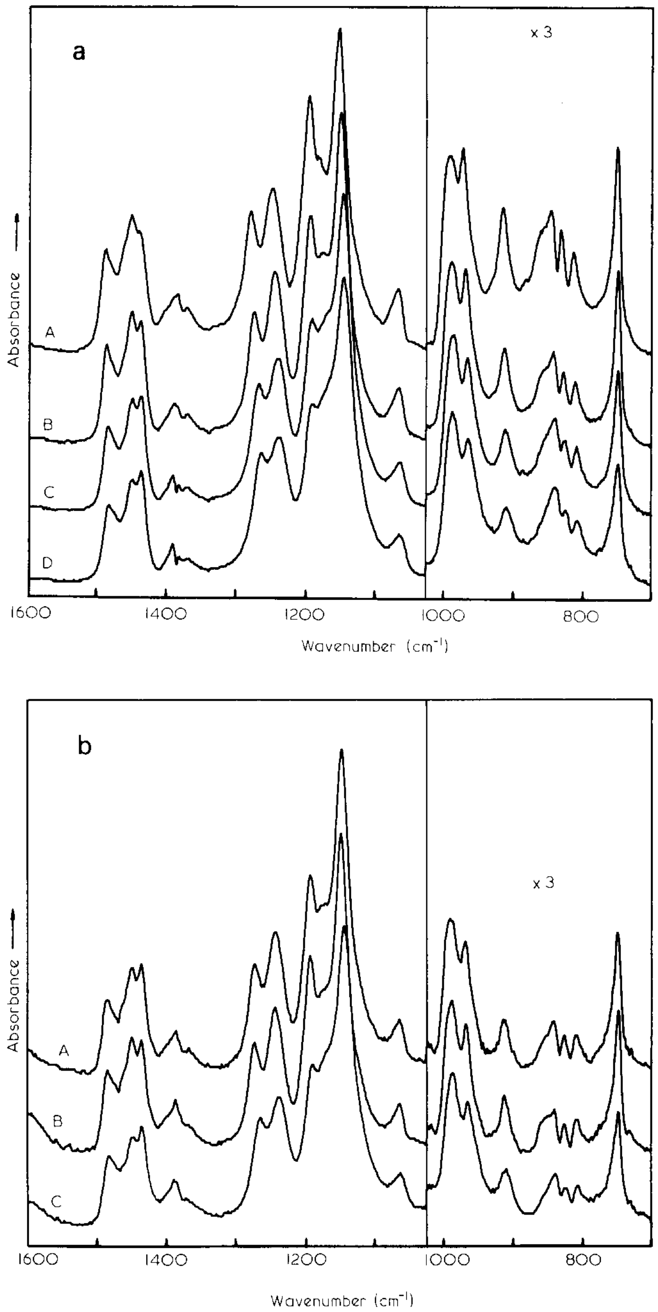

Figure 1 Temperature dependence of i.r. spectra of s-PMMA films obtained by evaporation of an acetonitrile solution of the polymer. (a) Film evaporated at 298K, spectra measured at 160K (A), 298K (B), 423K (C), 473K (D) in the sequence B, A, C, D. (b) Film evaporated at about 200K, spectra measured at 298K (A), 298K (B), 473K (C) in the sequence B, C, A. In the range below 1025 cm^{-1}, absorbance is expanded 3x

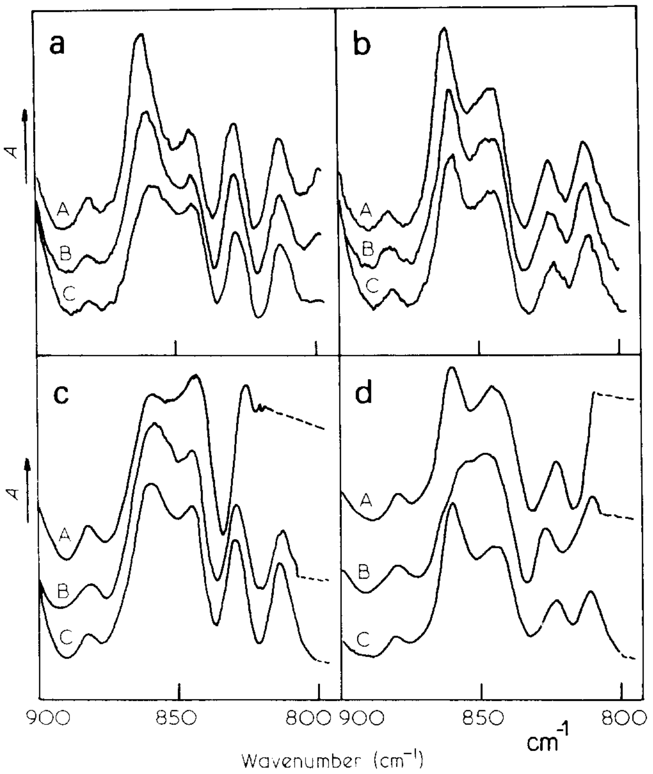

Figure 2 I.r. spectra of solutions of s-PMMA and of the stereocomplex in the range 900–800 cm^{-1}, spectra of the solvents subtracted. (a) Spectra of acetonitrile solution of s-PMMA measured at 220K (A), 260K (B), 298K (C). (b) Spectra of acetonitrile solution of the stereocomplex measured at 220K (A), 260K (B), 298K (C). (c) Spectra of s-PMMA solutions in tetrachloromethane (A), chloroform (B), acetonitrile (C). (d) Spectra of stereocomplex solutions in tetrachloromethane (A), chloroform (B), acetonitrile (C). The broken curves in (c) and (d) indicate poorly compensated strong solvent band

860 cm^{-1} also increases with increasing dielectric constant of the solvent (*Figure 2c*). In spectra of the film of s-PMMA evaporated from CH_3CN solution at 298K (*Figure 1a*) the band intensities in this doublet do not change by cooling, and in spectra measured at elevated temperatures (333, 373, 423 and 473K) changes of the intensity ratio in this doublet only occur at temperatures above the temperature of the glass transition, T_g, of s-PMMA (about 388K). I.r. spectra of films of s-PMMA prepared at 200K and 298K, when measured at normal temperature, differ only in the range of the doublet at 860 and 843 cm^{-1}, with the band at 860 cm^{-1} relatively stronger in the spectrum of the film prepared at 200K. The spectra of both films become equal after heating to 423 and 473, i.e. above the temperature T_g.

The temperature behaviour of the band intensities at 860 and 843 cm^{-1} in i.r. spectra of solutions and films of s-PMMA indicates that the bands are sensitive to conformational structure. Because in the spectra of films their intensities only change above the temperature T_g, it is assumed that these bands are sensitive to the conformational structure of the carbon backbone of s-PMMA. We assume that the bands at 1450 and 1194 cm^{-1} which undergo intensity changes in the whole measured temperature range in the spectra of solutions and films correspond to conformational transitions of ester groups. This is in agreement with the band assignment according to which the band at 1450 cm^{-1} corresponds to the antisymmetrical bending vibration of the group $O(CH_3)$,[2] the band at 1194 cm^{-1} to the antisymmetrical vibration of C–O–C–,[3,4] and the band at 843 cm^{-1} to the rocking vibration of the CH_2 group[4]. Analysis of the conformational behaviour of DMTG[6,15], which exhibits bands sensitive to the conformations of the carbon backbone in the range 900–800 cm^{-1} of the i.r. spectrum, is also in agreement with this interpretation.

The conformational forms of PMMA considered in previous studies can be represented schematically by the structures shown in *Figure 4*, together with the designation following from their analogy with staggered conformers. These schematic figures do not show the deviations of the real forms from the staggered forms which according to calculations[13] do not exceed 20° in PMMA.

The band at 860 cm^{-1}, the intensity of which in the i.r. spectrum of s-PMMA in the temperature range above T_g increases with decreasing temperature, evidently corresponds to the energetically favoured conformational structure of the chain. In analogy with DMTG[6,15] for which the approximately *tt* structure of the carbon backbone (*Figure 4a*) is the most favoured, and in agreement with the calculations of conformer energies of s-PMMA by Sundararajan and Flory[13,17] we assume that the energetically favoured form is the extended chain form of s-PMMA with the *tt* conformation of the carbon

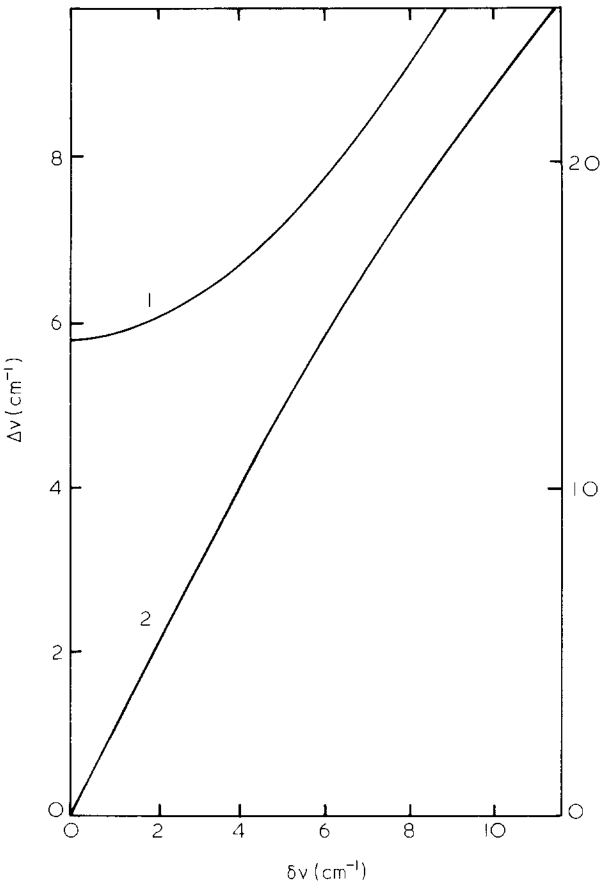

Figure 3 Illustration of the effect of band shift on the difference spectrum. Curve 1: distance Δν of two peaks in the difference spectrum. Curve 2: logarithm of the intesity ratio, log (A_1/A_2), of two bands obtained under the assumption that the peaks in the difference spectrum are caused by changes of the intensity ratio in the doublet composing the original Lorentzian band. δν is the shift of the model band with respect to its position in the reference spectrum. (The model spectrum is formed by a Lorentzian band of 10 cm^{-1} bandwidth)

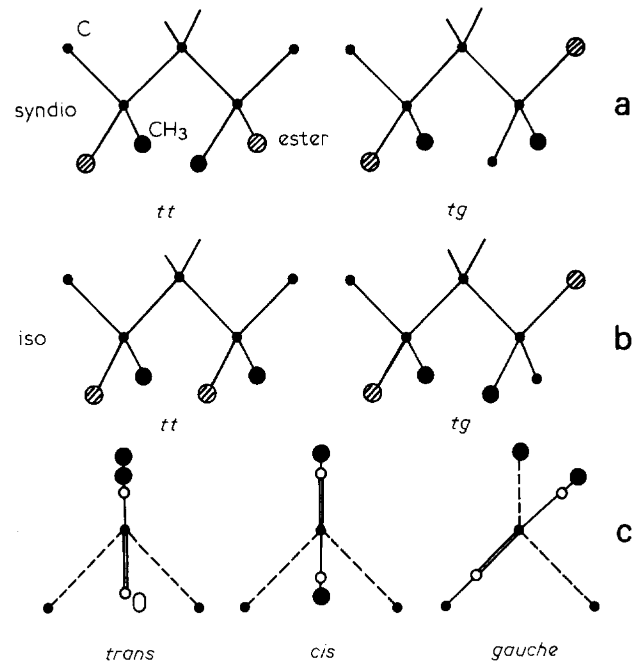

Figure 4 Considered conformational structures of stereoregular PMMA: (a) backbone conformation of s-PMMA; (b) backbone conformation of i-PMMA; (c) orientation of the ester group

backbone (*Figure 4a*). The band at 860 cm^{-1} corresponds to this form. The band at 843 cm^{-1} then evidently corresponds to the *tg* form of the carbon backbone (*Figure 4a*), generated from the *tt* structure by rotation about the C–CH_2 bond by 120° in the staggered approximation. From this interpretation it follows that with increasing dielectric constant of the solvent the population of the extended chain form of s-PMMA increases in solution, and a higher content of extended chains also appears in the film evaporated at lower temperature.

With DMTG, in the energetically most favoured structure of the ester group, the C=O and C–CH_3 bonds are in mutual *cis* orientation[15]. We assume that the s-PMMA bands at 1450 and 1194 cm^{-1}, which evidently correspond to the energetically most favoured conformational structures, should be assigned to similar orientations of the ester groups. In addition to this structure, the ester group structures with *trans*[3,13] or *gauche*[6,15] orientations of the C=O and C–CH_3 groups (*Figure 4c*) can also occur, and each of these structures should be manifested in the spectral range investigated by its own vibrational mode. As the bands at 1450 and 1194 cm^{-1}, which we assume to be sensitive to conformational structure of the ester groups, do not depend on the temperature of film preparation (the films differ by their contents of *tt* and *tg* forms of the carbon backbone), the populations of ester group structures should be approximately equal for both *tt* and *tg* forms of the backbone.

As the bands of various conformers can strongly overlap, and the number and shape of the bands are unknown, band separation necessary for reliable temperature dependence of band intensities and conformational energy determination cannot be performed. Moreover, i.r. spectra of systems with a large number of conformers, like s-PMMA, never exhibit an isolated band which would correspond to a unique conformer, and this is a further reason why conformer energies cannot be determined from i.r. spectra for systems of this type.

So, for example, in the doublet 860 and 843 cm^{-1} in the spectrum of s-PMMA the band at 860 cm^{-1} corresponds to the backbone conformation *tt* and the band at 843 cm^{-1} to the backbone conformation *tg*. For both these backbone conformations the molecule can assume various structures of the ester group, but these are not resolved in this spectral range. For the intensity ratio of the band intensities at 860 cm^{-1} (A^{tt}) and at 843 cm^{-1} (A^{tg}) we must write

$$\frac{A^{tt}}{A^{tg}}=\sum_i \alpha_i^{tt}\exp\left(-\frac{h_i^{tt}}{RT}\right)\Big/\sum_j \alpha_j^{tg}\exp\left(-\frac{h_j^{tg}}{RT}\right)$$

where α_i are the absorbance coefficients, h_i are conformer energies and the summation is over various conformational structures of ester groups. It is evident that the conformational energy cannot be determined from the temperature dependence of the ratio of only these two bands. For the same reason, the conformer energies cannot be determined from bands sensitive to the conformational structure of ester groups.

Isotactic PMMA. We have measured the temperature dependence of i.r. spectra of an i-PMMA film evaporated from acetonitrile solution at 298K (*Figure 5*) and of i-PMMA solutions in acetonitrile (*Figure 6*) and in tetrachloromethane. Further we have measured the spectrum of an i-PMMA film evaporated from acetonitrile solution at about 200K (*Figure 5*).

Similarly as in the case of s-PMMA, the temperature dependence of band intensities in the range 1050–1300 cm^{-1} in i.r. spectra of i-PMMA films used to be explained by conformational changes of ester groups[7] or both of ester groups and the carbon backbone[11]. For the same reasons as discussed in the section on s-PMMA we consider neither band separation in the range 1050–1300 cm^{-1} nor the application of difference spectra to be suitable for the determination of conformer energies of i-PMMA.

From *Figure 5* (spectra B, C, D) it can be seen that a pronounced temperature dependence in the whole temperature range 160–473K is exhibited by the bands at 1447 and 1194 cm^{-1} in i.r. spectra of i-PMMA films. The intensities of these bands increase continuously with decreasing temperature, and they behave similarly also in spectra of i-PMMA solutions. In the spectra of i-PMMA solutions, changes of band intensities are also observed on the doublet at 967 and 954 cm^{-1} (*Figure 6*). At room temperature both bands are of roughly equal intensity, and with decreasing temperature of the solutions the intensity of the band at 954 cm^{-1} increases and the intensity of the band at 967 cm^{-1} decreases. In spectra of solutions at low temperatures, the band at 967 cm^{-1} cannot be seen because of band overlap. In i-PMMA films measured at 160–298K only the band at 954 cm^{-1} is clearly observed, but equalization of the doublet component intensities takes place at higher temperatures (in spectra measured at 333, 373, 423, 473K), i.e. above the temperature T_g of i-PMMA (about 318K). Comparison of the spectrum of i-PMMA evaporated from acetonitrile solution at 200K with the spectrum of the film obtained by evaporation of the same solution at 298K (both spectra measured at 298K) (*Figure 5*) shows clearly that the relative intensities of the bands at 1447 and 1194 cm^{-1} are lower for the film evaporated at 200K. As the band at 1447 cm^{-1} has different intensity even when the films are

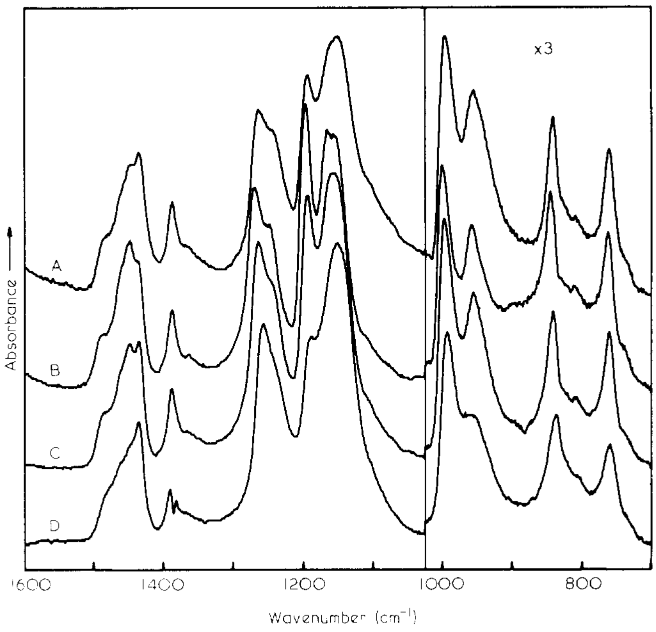

Figure 5 I.r. spectra of i-PMMA films obtained from acetronitrile solution of i-PMMA by evaporation at 200K (A) and 298K (B, C, D). Spectra measured at 298K (A), 160K (B), 298K (C), 473K (D). In the range below 1025 cm^{-1}, absorbance is expanded 3x

measured at the same temperature (298K), it is evident that the shape and intensity of this band is not determined by effects of mobility, as was assumed in a previous study[8]. Because of band overlap, the intensities of the doublet components at 967 and 954 cm^{-1} cannot be determined from the spectra of these films.

As the temperature dependence of the intensities of the bands at 1447 and 1194 cm^{-1} in i.r. spectra of i-PMMA films and solutions can be explained neither by changes of bandwidths nor by artifacts caused by relative band shifts of overlapping bands (*Figure 5*), we assume that, similarly as with s-PMMA, these bands are sensitive to conformational structure of ester groups. The temperature behaviour of the bands at 1447 and 1194 cm^{-1} indicates that they correspond to the energetically most favoured forms of ester groups; according to Sundararajan and Flory[13] this is the *cis* structure of the ester group. Analogous bands corresponding to the other forms of the ester groups cannot be detected in the spectra. This can be caused either by the presence of a larger number of minority conformers, or by lower absorbance coefficients of the bands of the additional conformers.

The bands of the doublet at 967 and 954 cm^{-1} whose temperature behaviour does not correlate with the behaviour of the bands sensitive to ester conformation (*Figure 5*), with intensities changing in i-PMMA films only above the temperature T_g, are probably sensitive to the conformational structure of the carbon backbone, with the band at 954 cm^{-1} corresponding to the energetically more favoured backbone conformation of i-PMMA. According to the conformer energy calculations of Sundararajan and Flory[13,17] the energetically most favoured structure of the i-PMMA backbone is the straight chain structure with the backbone conformation approximately *tt* (*Figure 4b*), with deviations from staggered bond angles amounting to about 15°. This result is in agreement with X-ray diffraction analysis of crystalline i-PMMA of Tadokoro *et al.*[18,19], according to which the backbone of crystalline i-PMMA forms a (10/1) helix, deviating only slightly from the extended chain structure (2° and 33°). We assume that the band at 954 cm^{-1} corresponds to this more favoured backbone structure, and the band at 967 cm^{-1} to the backbone conformation *tg* (*Figure 4b*), generated from the extended chain structure in the staggered approximation by rotation about the C–CH$_2$ bond by 120°. This form is analogous to one of the conformational structures of DMTG[15].

Analysis of the structure of simple esters[15,20] and conformer energy calculations of i-PMMA[13,17] indicate that, similarly as with s-PMMA, in the chains of i-PMMA the structure of the ester group with mutual *cis* orientations of C$=$O and C–CH$_3$ bonds (*Figure 4c*) is also the most favoured, with the corresponding bands at 1447 and 1194 cm^{-1} in i.r. spectra. Besides the *cis* orientation, also the *gauche* and *trans* conformations (*Figure 4c*) of ester groups may be present in i-PMMA chains. According to theoretical calculations[13] for the *tt* backbone structure, the *trans* form appears mostly next to *cis* forms where the increase of conformational energy is compensated by dipolar interactions of antiparallel dipoles of the ester groups. We assume that on a *tt* backbone, only *cis* and *trans* structures of the ester groups are present, because occurrence of *gauche* structures is limited by steric hindrance. For a *tg* backbone of i-PMMA neither the dipolar interactions favouring *trans* orientation of ester groups nor the steric hindrance limiting the occurrence of *gauche* structures are operative. Therefore we assume that, with this backbone structure, *gauche* and *cis* forms of ester groups may be present.

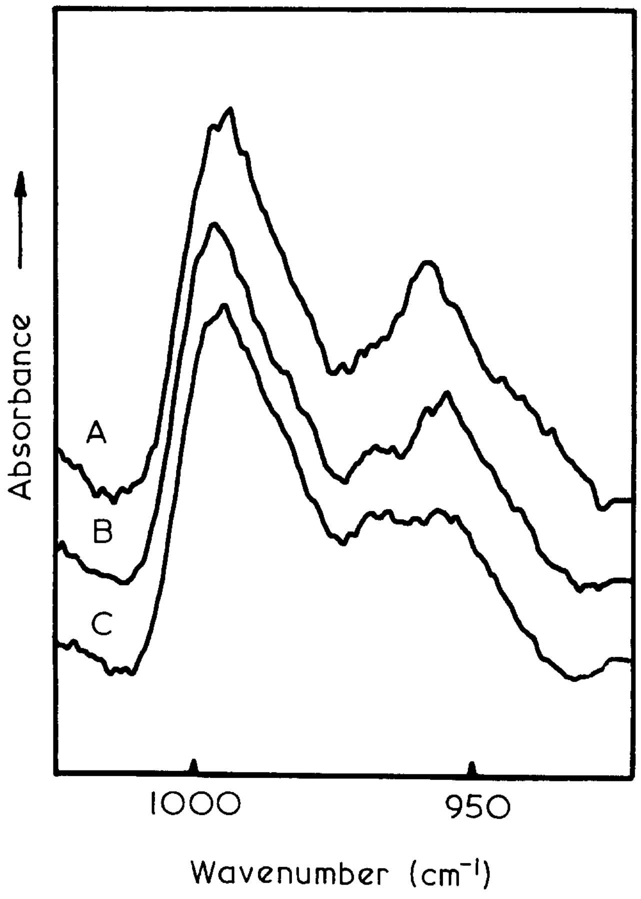

Figure 6 I.r. spectra of acetonitrile solution of i-PMMA measured at 220K (A), 260K (B), 298K (C). The depicted range does not contain solvent bands.

These structural considerations make possible an interpretation of the temperature changes of i.r. spectra of films and solutions of i-PMMA, and the effects of temperature during solvent evaporation from films (*Figure 5*). In i-PMMA films above T_g and in solutions of i-PMMA, conformer populations correspond to equilibrium states determined by the conformer energies, and this is exhibited by the temperature dependence of the bands at 1447 and $1194\,\mathrm{cm}^{-1}$, and of the doublet at 967 and $954\,\mathrm{cm}^{-1}$. At temperatures below T_g, conformational transitions between the structures *tt* and *tg* cannot take place. As the bands sensitive to conformational structure of ester groups are of different intensity in spectra of films prepared at 200 and 298K, it is evident that the populations of various ester group structures are different for *tt* and for *tg* forms of the backbone.

Stereocomplex of PMMA. The stereocomplex was prepared by mixing of solutions of i-PMMA and s-PMMA in acetonitrile in the ratio 1:1.5 and evaporation of the solvent. The sample so obtained was used for the preparation of various stereocomplex solutions and films. We have measured the temperature dependence of i.r. spectra of PMMA films prepared from solutions of the stereocomplex in acetonitrile and chloroform (*Figure 7*). We have also measured the temperature dependence of i.r. spectra of solutions of the stereocomplex in acetonitrile (*Figure 2b*), tetrachloromethane and chloroform.

In *Figure 8* is shown the i.r. spectrum of the film of the stereocomplex of PMMA prepared from a solution of the stereocomplex in acetonitrile, the spectra of the films of s-PMMA and i-PMMA prepared by room-temperature evaporation from acetonitrile solutions, as well as a computer-generated sum of the spectra of s- and i-PMMA in the ratio 1.5:1. It can be seen that in comparison to the sum spectrum, in the spectrum of the stereocomplex the bands at 1394, 880, $810\,\mathrm{cm}^{-1}$, and the component at $860\,\mathrm{cm}^{-1}$ of the 860–$843\,\mathrm{cm}^{-1}$ doublet, exhibit increased intensity (*Figure 8*), whereas for all other bands no intensity changes are observed. As all these bands occur only in the spectrum of s-PMMA, and not in i-PMMA, we assume that also in the spectrum of the stereocomplex these bands correspond to the vibrational modes of s-PMMA. The spectrum of the film prepared from the solution of the stereocomplex in chloroform does not differ practically from the corresponding sum spectrum. From the temperature dependence of the spectra of the stereocomplex film prepared from acetonitrile solution it can be seen (*Figure 7*) that at the temperatures 333, 373 and 423K the band intensities remain the same as in the original spectrum (298K). At 473K the intensity of the band at $860\,\mathrm{cm}^{-1}$ is lower than at 298K, but it still remains higher than in the corresponding sum of the spectra of heated s- and i-PMMA films. After subsequent cooling to 298K the intensity ratio in the doublet at 860 and $843\,\mathrm{cm}^{-1}$ remains practically equal to that at 473K. With the bands at 1394, 880 and $810\,\mathrm{cm}^{-1}$, intensity changes with increasing temperature cannot be followed because of band overlap. The spectrum of the stereocomplex film prepared from acetonitrile solution also exhibits a decrease of band intensities at 1450 and $1194\,\mathrm{cm}^{-1}$ with increasing temperature, but at 473K these bands are stronger in the spectrum of the stereocomplex than in the sum spectrum; after cooling of the film to 298K the i.r. intensity is lower than in the spectrum prior to heating.

Because of band overlap of s-PMMA and i-PMMA vibrations, and because of interference of solvent bands, only the doublet components at 860 and $843\,\mathrm{cm}^{-1}$ were followed in i.r. spectra of stereocomplex solutions. The band at $860\,\mathrm{cm}^{-1}$ corresponding to an s-PMMA vibration is stronger in the spectra of stereocomplex solutions in acetonitrile and tetrachloromethane than in the corresponding solutions of only s-PMMA. This follows from a comparison of the relative intensities of the bands at 860 and $843\,\mathrm{cm}^{-1}$ (*Figure 2c* and *2d*), respecting the fact that a band of i-PMMA also lies at $843\,\mathrm{cm}^{-1}$. A similar comparison of spectra of chloroform solutions shows that the relative intensity of the s-PMMA band is similar in the spectrum of the solution of s-PMMA and of the stereocomplex. An analysis of the spectra of chloroform solutions is difficult because the characteristic doublet is

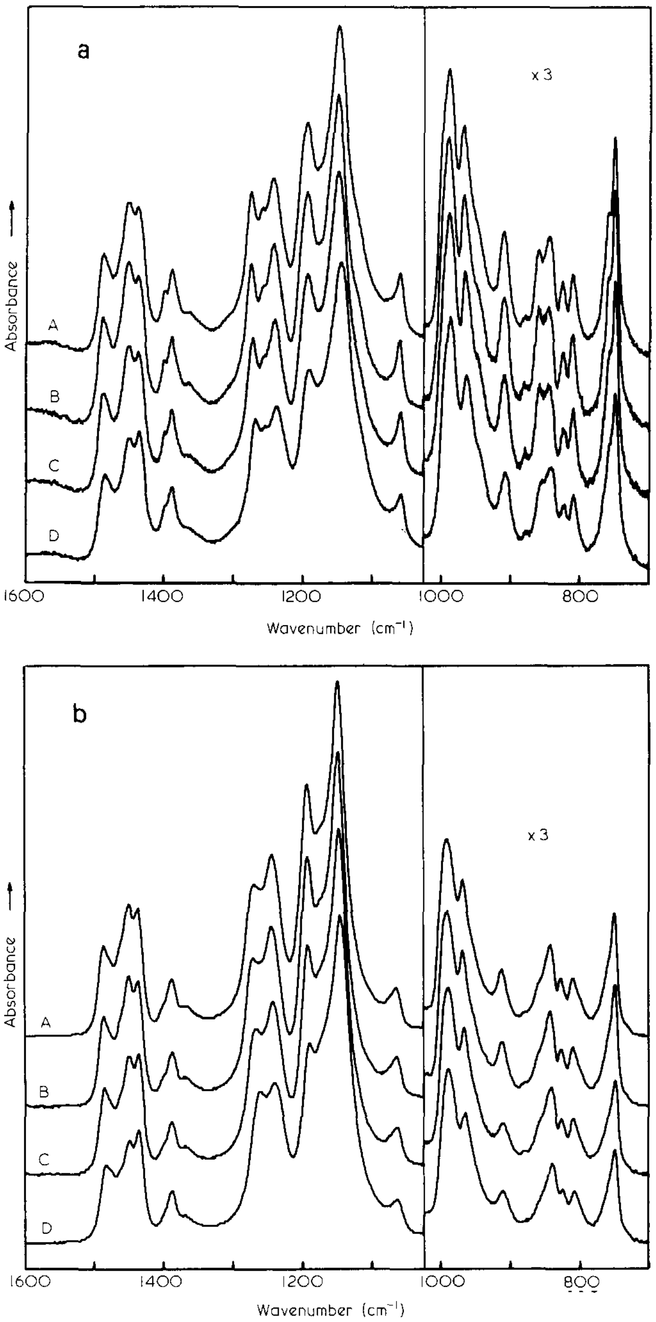

Figure 7 I.r. spectra of stereocomplex films obtained by evaporation at room temperature from a solution of the stereocomplex in (a) acetonitrile and (b) chloroform. Spectra measured at 298K (A), 298K (B), 373K (C), 473K (D) in the sequence B, C, D, A. In the range below $1025\,\mathrm{cm}^{-1}$, absorbance is expanded 3x

overlapped by a solvent band, and the solvent spectrum cannot be exactly subtracted by computer because there exist differences in band positions and widths between the spectra of pure solvent and the solvent in the PMMA solution. The temperature dependences of the spectra of the stereocomplex solutions indicate that in the solutions of the stereocomplex in acetonitrile (*Figure 2b*) and in tetrachloromethane, no changes can be observed in the doublet at 860 and 843 cm^{-1}, but in spectra of the chloroform solution of the stereocomplex, the intensity of the band at 860 cm^{-1} increases with decreasing temperature.

In the i.r. spectra of the films it can also be observed that some bands have a much smaller width in the spectrum of the stereocomplex than analogous bands in the sum spectrum (e.g. the band at 1059 cm^{-1}) (*Figure 8*). Some bands evidently undergo substantial wavenumber shifts; for example, the band at 1064 cm^{-1} in the sum spectrum corresponds to the band at 1059 cm^{-1} in the spectrum of the stereocomplex. The apparently new band at 1257 cm^{-1} in the spectrum of the stereocomplex probably represents a vibrational mode of i-PMMA, and corresponds to the band at 1263 cm^{-1} of i-PMMA film.

In the spectra of stereocomplex films and solutions, in the doublet at 860 and 843 cm^{-1} the band at 860 cm^{-1} exhibits higher relative intensity than in the corresponding sum spectra; in view of the analysis of conformationally sensitive bands of s-PMMA this indicates that the population of the segments with *tt* backbone of s-PMMA (i.e. of extended chain sequences) is higher in the stereocomplex than would correspond to the dynamic equilibrium given by conformer energies. With a solvent which does not promote stereocomplex formation (chloroform), the populations of the backbone forms of s-PMMA in the solution of a mixture of s-PMMA and i-PMMA as well as in the film prepared by evaporation of such a solution remain the same as in the solution or film of only s-PMMA. As all other conformationally sensitive bands of s-PMMA and i-PMMA overlap in the spectrum of the stereocomplex, i.r. spectra provide no evidence on the population of ester group conformers of s-PMMA, nor on the population of backbone and ester group conformers of i-PMMA in the stereocomplex. The temperature dependence of the i.r. spectra of stereocomplex film further indicates that at 473K a partial decrease of the population of extended chain sequences of s-PMMA takes place, and this process is irreversible.

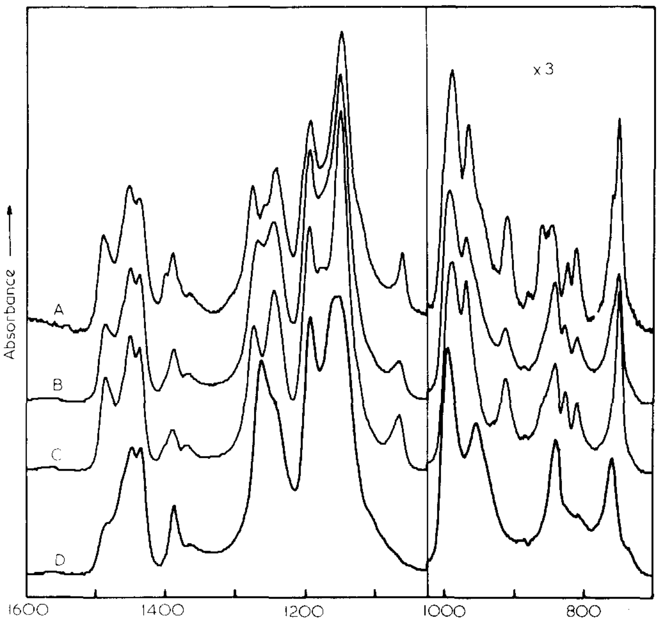

Figure 8 I.r. spectra of PMMA films evaporated at room temperature from acetonitrile solution: A, PMMA stereocomplex; B, normalized sum of spectra of i-PMMA and s-PMMA in the ratio 1:1.5; C, s-PMMA; D, i-PMMA. In the range below 1025 cm^{-1}, absorbance is expanded 3x

The smaller width of the bands in the spectra of the stereocomplex as compared to band widths in the sum spectra may be due to two effects:

(i) The bands in the spectra of i- and s-PMMA are composed of two or more components which correspond to one vibrational mode of various backbone or ester group conformers. The components differ slightly in frequency, but remain unresolved in the spectra and only lead to apparent band broadening. Because of intermolecular interactions, only selected conformers are present in the stereocomplex, and therefore the apparent band broadening is smaller.

(ii) It has been shown[21,22] that the linewidths in i.r. spectra are determined predominantly by relaxation times of vibrational and reorientation processes in the measured system. Restriction of the intermolecular resonance vibration and restriction of skeletal and ester group mobility in the stereocomplex lead to longer relaxation times and result in a decrease of bandwidths.

We suppose that both these effects are operative to some extent in the measured spectra.

Raman spectra

We have measured the Raman spectra of s-PMMA, i-PMMA and of the stereocomplex of PMMA in the solid state; the samples were prepared from acetonitrile solutions of the polymers (*Figure 9*).

A comparison of the Raman spectra of the PMMA stereocomplex in the solid state with the corresponding sum of the Raman spectra of s-PMMA and i-PMMA in

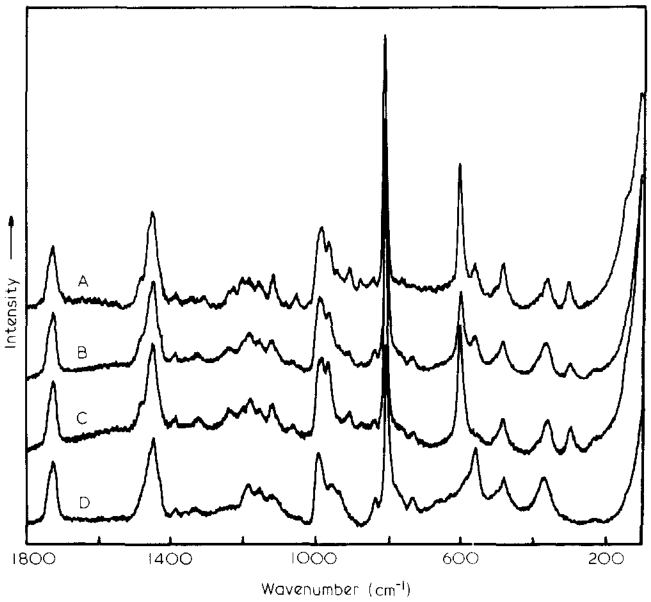

Figure 9 Raman spectra of solid PMMA samples obtained by room-temperature evaporation from acetonitrile solution: A, PMMA stereocomplex; B, normalized sum of the spectra of i-PMMA and s-PMMA in the ratio 1:1.5; C, s-PMMA; D, i-PMMA

the ratio 1.5:1 (*Figure 9*) indicates that in the spectrum of the stereocomplex the bands at 1204, 1084, 1055, 945, 910, 880, 764 and 303 cm^{-1} exhibit higher intensity and the bands at 1185 and 732 cm^{-1} exhibit lower intensity. These differences in band intensities do not contradict the conclusions drawn from analysis of i.r. spectra, namely that the population of conformational forms of s- and i-PMMA in the stereocomplex differs from that observed in samples containing only s- or i-PMMA.

Similarly as in i.r. spectra, in Raman spectra the widths of a number of bands in the spectrum of the stereocomplex are also evidently smaller than in the sum spectrum. This may also be the reason why the broad band at 1238 cm^{-1} in the sum spectrum is substituted by two narrower bands at 1229 cm^{-1} in the spectrum of the stereocomplex. Some bands in the spectrum of the stereocomplex exhibit wavenumber shifts with respect to analogous bands in the sum spectrum; so, for example, the bands at 1062, 840 and 298 cm^{-1} in the sum spectrum correspond to bands at 1055, 845 and 303 cm^{-1} in the spectrum of the stereocomplex.

We have also followed the wavenumbers of the carbonyl band in the isotropic and anisotropic components of Raman scattering of solutions of s- and i-PMMA and of the stereocomplex in acetonitrile. It has been observed that for a number of compounds there exists a difference in the positions of the isotropic and anisotropic components of Raman bands corresponding to strongly absorbing vibrations, e.g. carbonyl bands in carbonyl compounds[23,24]. Fini and Mirone[23,25] have interpreted this effect as a consequence of resonance transition dipole–transition dipole interaction made possible by local order caused by strong interactions between permanent molecular dipoles. Wang and McHale[26] have shown that $\nu_{\mathrm{aniso}} - \nu_{\mathrm{iso}}$ can be non-zero also in systems without local order, provided an angular dependence of the interaction potential exists. By analysis of the concentration dependence of the position of the carbonyl band in Raman and i.r. spectra of simple esters[14], including DMTG[15], we have detected molecular local order for these substances, probably as a consequence of dipolar interactions. Therefore we have studied the effect of chain arrangement in the PMMA stereocomplex on the positions ν_{iso} and ν_{aniso} of the carbonyl band. However, we have found that both for the solutions of i- and s-PMMA in acetonitrile, and for the solution of the stereocomplex in acetonitrile, the value of the difference $\nu_{\mathrm{aniso}} - \nu_{\mathrm{iso}}$ does not exceed 1 cm^{-1} and therefore lies within experimental error. This result does not contradict the proposed model of the stereocomplex, with mutually ordered ester groups of i- and s-PMMA, because the resonance transfer of vibrational excitations by means of transition dipoles can occur only in molecules with equal frequencies of the corresponding vibrations. In the case of the PMMA stereocomplex, the resonance transfer is considerably limited by a the difference of the carbonyl band wavenumbers for s-PMMA (1731 cm^{-1}) and i-PMMA (1733 cm^{-1}).

Structure of the stereocomplex

Considerations about the structure of the stereocomplex have to be based on the following experimental findings:

(a) The ratio of s-PMMA and i-PMMA sequences bound in the stereocomplex has been given as 1:1[27,28], 1.5:1[29,30] and 2:1[31,32].

(b) Concerning their ability to promote stereocomplex formation, three groups of solvents have been defined: strongly complexing (e.g. acetonitrile and tetrachloromethane), weakly complexing (e.g. benzene) and non-complexing (e.g. chloroform)[29,33].

(e) The mobility of ester groups bound in the stereocomplex is strongly limited[34,35].

(d) An isotactic PMMA chain can form the stereocomplex with syndiotactic chains of PMMA or poly(isobutyl methacrylate) (PiBMA), but isotactic poly(ethyl methacrylate) does not form the stereocomplex with syndiotactic PMMA or PiBMA[36].

(e) In this paper it was shown that the extended chain form of s-PMMA is preferred in the stereocomplex, and that probably all segments of s-PMMA participating in stereocomplex formation have a *tt* conformation of the carbon backbone.

There exist several explanations why stereocomplex formation takes place in PMMA. Both interactions of α-methyl groups of i- and s-PMMA[31] and interactions of ester groups of i- and s-PMMA[34,35] are cited. According to Challa *et al.*[36,37] the chains of i- and s-PMMA in the stereocomplex form a double helix, in which the radius of the i-PMMA helix is smaller than the radius of the s-PMMA helix, in agreement with the composition 1:2; the double helix is formed as a consequence of van der Waals interactions between the ester methyl groups of i-PMMA and the α-methyl groups of s-PMMA.

We have attempted to propose a structure of the stereocomplex in view of the fact that the only interaction proved so far between ester groups is dipolar interaction[14,15]. In the proposed structure which is shown in *Figure 10*, the chains of s-PMMA have the extended chain structure with an approximate *tt* conformation of the carbon backbone and *cis* orientation of the ester groups. The chains of i-PMMA also have a near to extended chain form, with the ester groups alternating in *cis* and *trans* orientations. The extended chain form of s-PMMA chains follows from analysis of i.r. spectra. The reason for proposing an extended chain form also for the chains of i-PMMA is the fact that the alternative model of an i-PMMA helix wound around the straight s-PMMA chain is at variance with the molar composition found for the stereocomplex.

In the proposed structure of parallel straight chains of i-PMMA and s-PMMA, repeating units of both chains are in regular contact, which cannot be realized in any type of double helix. Therefore we assume that the proposed structure is the most favourable for the stereocomplex, irrespective of which groups of i- and s-PMMA are most important for stereocomplex formation. From *Figure 10* it is evident that one chain of i-PMMA can bind one or two chains of s-PMMA, probably depending on tacticity and molecular weight of the chains and on the type of solvent; this is in agreement with the cited values 1:1 to 1:2 for the mole ratio of i- and s-PMMA sequences in the stereocomplex.

In the stereocomplex the chains of s- and i-PMMA have a defined conformational structure, and for a number of substances a dependence of conformational energies on dielectric constant of the solvent has been proved[38]; therefore the tendency to stereocomplex formation in various solvents is evidently dominated by the values of the energies of all conformational states of s- and i-PMMA in the solution. This can explain the differences in the complex-promoting ability of various solvents: in

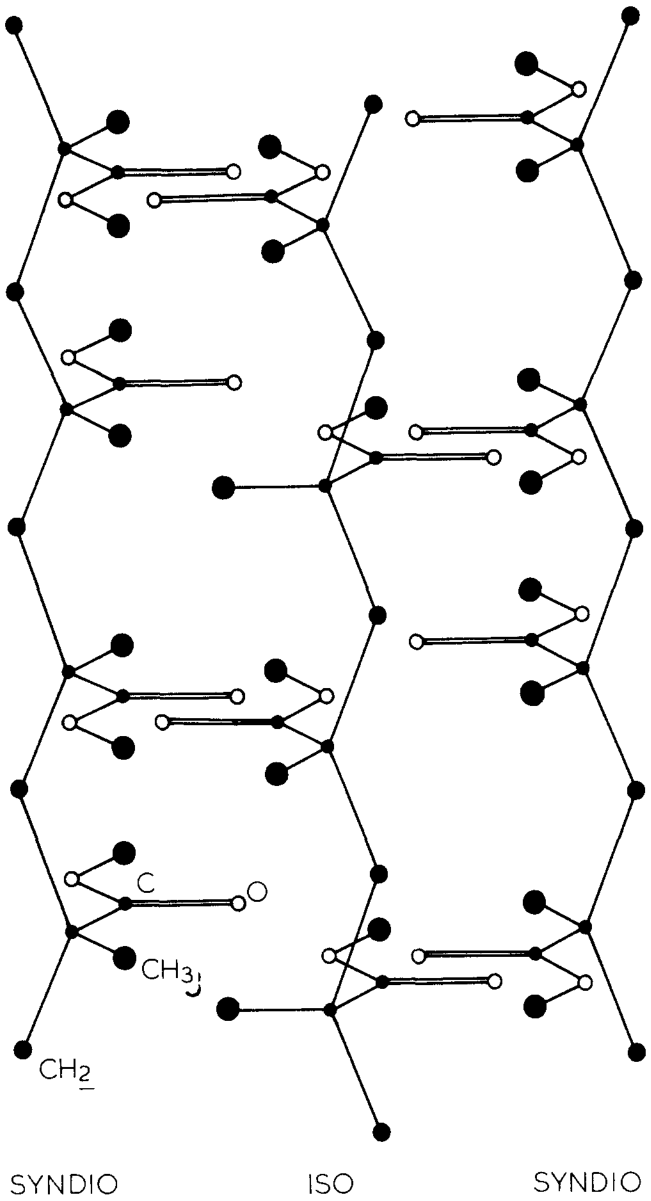

Figure 10 Proposed structure of PMMA stereocomplex

addition to the interaction energy leading to stereocomplex formation, the energy differences between conformational states are also of importance, and these depend on the type of solvent. In the case of chloroform, where stereocomplex formation does not take place, the energy of the specific interaction between the chloroform molecule and the carbonyl group of PMMA is evidently larger than the energy of mutual interaction of the ester groups.

In the proposed structure of the stereocomplex, the cited results on the formation of the stereocomplex between stereoregular chains of various poly(alkyl methacrylates) can be explained by steric hindrance affecting the contact between the ester groups of the isotactic and the syndiotactic chains. The limitation of the contact of the ester groups is severe only when methyl is substituted by ethyl in the ester group in the isotactic chain in which the neighbouring ester groups in the *tt* backbone conformation are oriented in the same direction with respect to the backbone.

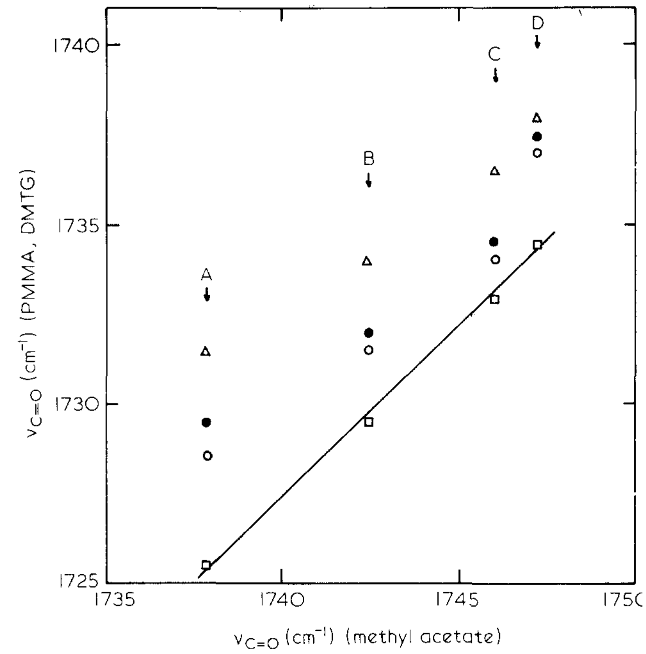

Figure 11 Wavenumbers of the carbonyl band of i-PMMA (△), s-PMMA (●), PMMA stereocomplex (○), DMTG (□) vs. wavenumber of the carbonyl band of methyl acetate in i.r. spectra of chloroform (A), acetonitrile (B), benzene (C) and toluene (D) solutions

As the position of the carbonyl band in vibrational spectra is very sensitive to the effects of the surrounding medium[14], we have used this band to investigate whether, even in stereocomplex solution, the solvent molecules penetrate into the immediate vicinity of PMMA chains. In *Figure 11*, the wavenumbers of the carbonyl bands of i-, s- and stereocomplex PMMA and of DMTG are plotted against the wavenumbers of the carbonyl band of methyl acetate in i.r. spectra for several solvents. It appears that similarly to the case of DMTG, the points corresponding to s-, i- and stereocomplex PMMA lie approximately on a straight line of 45° slope, and that the formation of the stereocomplex has no effect on the wavenumber of the carbonyl band. This result is in agreement with the proposed model according to which the stereocomplex is formed by 'fibres' containing a limited number of parallel polymer chains and surrounded by solvent molecules[35,37].

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