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Conformational Characteristics of Stereoregular PMMA and of the Stereocomplex: New Insights from FTIR Measurements

Oleg N. Tretinnikov

B. I. Stepanov Institute of Physics, National Academy of Sciences of Belarus, Prospekt F. Skariny 70, Minsk, 220072, Belarus

Summary: Isotactic (i) and syndiotactic (s) PMMA polymers differ markedly in the physical properties. The fact that these physically unlike macromolecules strongly attract each other with the resultant formation of stereocomplexes is indeed remarkable. Although stereoregular PMMAs and the stereocomplex have been studied over decades, their conformational characteristics are yet a matter of controversy. We performed variable-temperature FTIR measurements on i-PMMA and s-PMMA, followed by a detailed analysis of the temperature dependence of integrated band intensities for C–O stretching modes in the region 1050–1300 cm^{-1} and achieved, for the first time, the unambiguous conformational assignment for the C–O bands. This enabled reliable IR spectroscopic determination of conformational energies for the backbone and for the ester group. Besides, a comparative analysis of the C–O band intensities in the FTIR spectra of single-component and stereocomplex PMMA films, based on the established band assignments, revealed new features in the structure of the stereocomplex.

Keywords: conformational energy; FTIR; PMMA; stereocomplex; structure

Introduction

PMMAs are unique in the sense that they display a dramatic effect of tacticity on the physical properties. The glass transition temperature of s-PMMA is by as much as 60–70 °C higher than that of i-PMMA. The disparity in T_g or mobility is in a striking contrast with the chain flexibility: the less mobile, syndiotactic chains are more flexible than the isotactic ones! The physical origin of this behavior is not yet understood. Since the chemistry is the same, some differences in the conformational characteristics between the two tactic forms must be involved. However, the conformational characteristics have not been well understood either.

Conformational isomerism in PMMA arises from internal rotation around the backbone bonds, ester-group rotation around the C–C link between the group and the main chain, and methoxy-

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group rotation around the ester bond. *Calculations*[1–3] suggest two major backbone conformations – trans-trans (tt) and trans-gauche (tg). The tt state has the lowest energy, irrespective of tacticity. The calculated tt–tg energy difference is higher for s-PMMA. The ester group may take on cis and trans conformations, defined by the mutual orientation of carbonyl and α-methyl. The calculated energy is nearly the same or slightly lower for the cis state. The methoxy group, may in principle take on cis an trans conformations, defined by the placement of methoxy relative to carbonyl. It has always been assumed that in PMMA the methoxy trans form is prohibited.

On the *experimental* side, the available conformational data were obtained predominantly by IR spectroscopy.[4–7] This technique is one of the most powerful experimental tools for the conformational studies of polymers, *provided that the conformational assignment of analytical bands is well established.* For PMMA, however, solid conformational assignment of the IR bands possessing signs of conformational sensitivity has been absent.

As to the stereocomplex, two models have been proposed: one by Schneider et al.[8] and the other by Challa et al.[9] In both models the backbone conformation is assumed to be tt. However, the ester-group conformations differ drastically. In the first model, the iso-groups alternate in cis and trans positions and the syndio-groups are in the cis state, contrary to cis-trans alternation of syndio-groups and the the trans state of iso-groups in the second model. Besides, for the driving force of stereocomplexation, Schneider assumed dipole-dipole interactions of ester group, in contrast to sterical fit and van der Waals forces postulated by Challa.

Given this state of the art, we attempted to establish the unambiguous conformational assignment of IR bands and, on this basis, obtain reliable conformational characteristics of free and strereocomplexed PMMA. Our work is distinct from the previous ones in the use of computerized FTIR instrumentation, modern methods of band-fitting, and recent IR results for simple esters.

Experimental

Samples with the following molecular weight characteristics and triad tacticities were used. I-PMMA: $M_w = 2.08\times10^5$, $M_w/M_n = 3.37$, i/h/s = 91/6/3 %; s-PMMA: $M_w = 1.99\times10^5$, $M_w/M_n = 4.24$, i/h/s = 4/21/75 %. Each polymer was dissolved in benzene at a concentration of 2%

(w/v) and the solutions were mixed in a 1/1 ratio. The i-PMMA/s-PMMA blend film was cast on a glass substrate by slowly evaporating the solvent at 25 °C over a period of 12 h. The residual solvent was removed by drying the film at 70 °C for 20 h. Single-component i-PMMA and s-PMMA films were prepared in a similar way.[10] Wide-angle X-ray diffraction (WAXD) was measured on a Rigaku automated diffractometer using Cu K_α radiation, with a scan speed of 4°/min. The FTIR spectra were recorded on a Nicolet 7199 FTIR spectrometer equipped with a MCT detector, at a resolution of 2 cm^{-1}. Lorentzian curve-fitting was performed using Origin 6.0 software.

Conformation-Sensitive IR Bands and Conformational Characteristics of s-PMMA and i-PMMA by Variable-Temperature FTIR

Due to the allocated size of publication, we present here only the major findings on the subject. A detailed account of the work will appear elsewhere.[10] Curve fitting of the FTIR spectra of s-PMMA and i-PMMA films reveals 7 component bands for s-PMMA and 6 ones for i-PMMA, in the 1050–1300 cm^{-1} region, designated as ν_1 to ν_7 inclusive in Figure 1.

The ν_1/ν_2 and ν_3/ν_4 doublets are known to be due to different conformational isomers of the ester group or methoxy group or both of them.[11, 12] The integrated intensity ratios, $A_{\nu1}/A_{\nu2}$ and $A_{\nu3}/A_{\nu4}$, for the two doublets display a monotonous change in the intensity ratio with increasing temperature (Figure 2), indicating the occurrence of temperature-induced rotational isomerization. The activation temperature of this process for the ν_1/ν_2 doublet (55 °C in s-PMMA and 40 °C in i-PMMA) falls in the temperature range of the maximum of the secondary β-relaxation which is known to be associated with the cis–trans rotational relaxation of ester group.[13] Therefore, the ν_1/ν_2 pair must be assigned to rotational isomers of ester group. Besides, the ab initio results for the MMA monomer[14,15] indicate that the high-frequency band (ν_1) is due to the trans conformation, whereas the low-frequency component (ν_2) is associated with the cis conformation. Unlike the ν_1/ν_2 pair, the rotational relaxation reflected in the intensity change of peaks ν_3 and ν_4 does not freeze at least down to 25 °C, indicating the involvement of rotational isomerization of the methoxy group. This finding, in combination with the recent experimental and ab initio results for simple esters,[16,17] strongly suggests that the bands ν_3 and ν_4 are due to the cis and trans state of methoxy group, respectively.

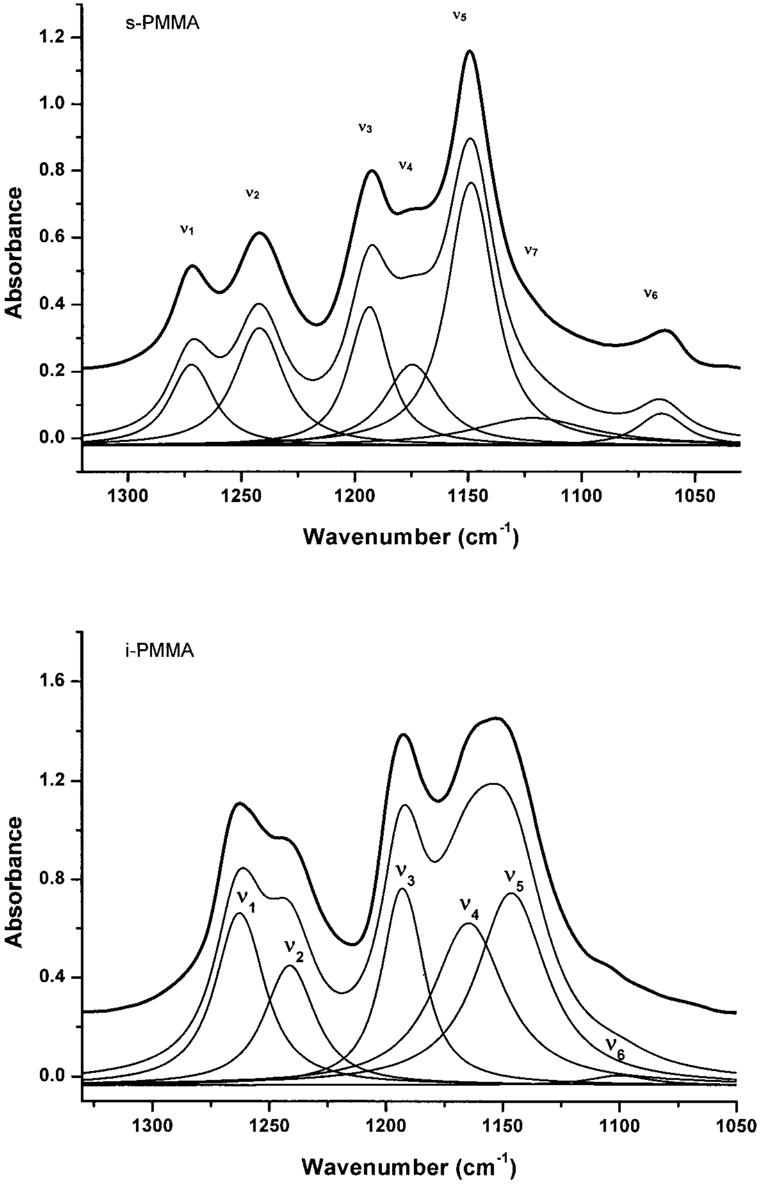

Fig. 1. FTIR spectra with fitted component bands for s-PMMA and i-PMMA at 25°C.

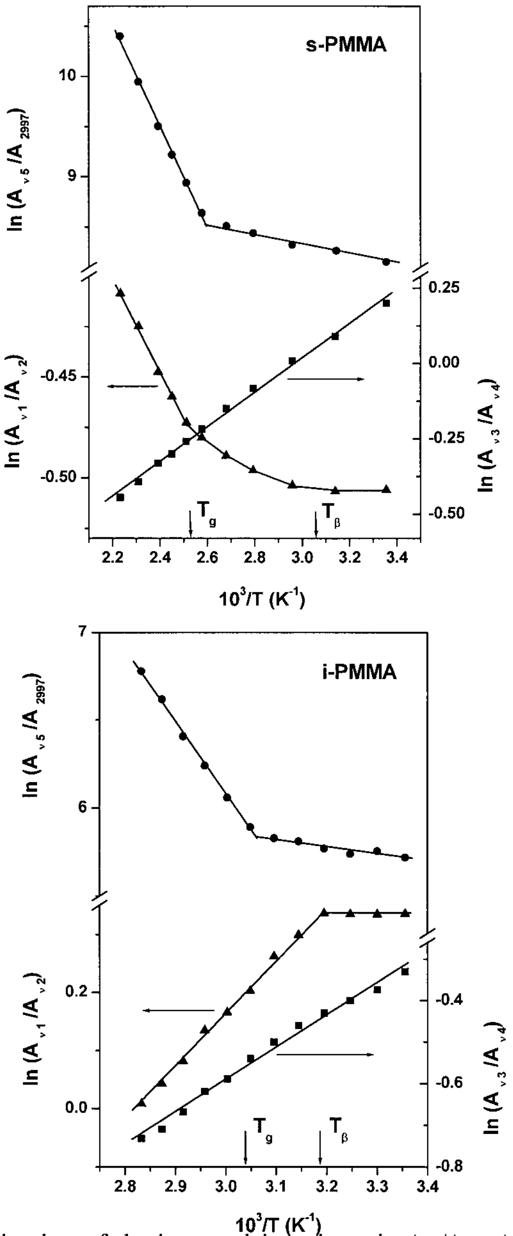

Fig. 2. Logarithmic plots of the integrated intensity ratio A_{v1}/A_{v2}, A_{v3}/A_{v4}, and A_{v5}/A_{2997} against inverse absolute temperature for s-PMMA and i-PMMA.

The bands ν_6 and ν_7 did not reveal any temperature dependence of their intensity (data not shown). On this basis, we conclude that these bands are conformation-insensitive.

The integrated intensity of the band ν_5, normalized by the intensity of the internal reference band at 2997 cm^{-1} is practically independent of temperature below T_g (T_g = 120 and 55 °C for the s-PMMA and i-PMMA sample, respectively), whereas above T_g it increases monotonously as temperature increases. Based on this behavior, it would be reasonable to assign the band ν_5 to the tg state of polymer backbone, provided that a band associated with the second (tt) state is located at a *different* frequency and decreases in the intensity with increasing temperature. However, as should be evident from the whole set of data, such a distinct band does not exist. Therefore, to explain the temperature-dependent behavior of the band ν_5, we have to conclude that the band consists of two superimposed elementary bands; one band is due to the tt conformation and the other is due to the tg conformation of backbone bonds, and the absorptivity of the "tg band" is higher than that of the "tt band".

The spectral positions and established conformational assignments of the ester bands ν_1–ν_5 are summarized in Table 1.

Table 1. Conformational Assignment of the Ester Bands in the Region 1100–1300 cm^{-1} for PMMA.

band designation	frequency (cm^{-1})			conformational assignment	
	s-PMMA	i-PMMA	stereocomplex	moiety	conformation
ν_1	1273	1265	1273(s), 1257(i)	ester group	trans
ν_2	1242	1239	1240	ester group	cis
ν_3	1193	1195	1194	methoxy group	cis
ν_4	1175	1164	1159	methoxy group	trans
ν_5 low absorptivity	1149	1147	1148	backbone	trans-trans
ν_5 high absorptivity	1149	1147	1148	backbone	trans-gauche

Based on the established conformational assignment of the ester bands (Table 1) and the temperature dependence of their integrated intensities (Figure 2), the conformational enrgies for the backbone, ester group, and mehtoxy group in s-PMMA and i-PMMA could be determined using standard equations,[10] and the corresponding results are summarized in Table 2.

Table 2. Backbone and Side-Group Conformational Energies (kcal/mol) of Stereoregular PMMA.

polymer	ΔE_{tg-tt} (backbone)	ΔE_{t-c} (ester group)	ΔE_{t-c} (methoxy group)
s-PMMA	2.77 ± 0.16	0.46 ± 0.01	1.14 ± 0.03
i-PMMA	2.51 ± 0.27	-1.84 ± 0.04	1.56 ± 0.05

The results indicate a strong preference of tt backbone conformation both for i-PMMA and s-PMMA; the preference is *only slightly* higher for s-PMMA. The polymers differ markedly in the conformation of ester group. That is, i-PMMA shows a strong preference for the trans conformation and, hence, a high conformational rigidity of the ester moiety, whereas the ester group of s-PMMA has a very slight preference for the cis conformation and, accordingly, a high conformational flexibility. It can be shown[10] that the marked difference in the conformational mobility of ester group is a key factor determining the difference in T_g between the two stereoregular forms. The high conformational freedom of ester groups in s-PMMA facilitates their intermolecular association (presumably, by carbonyl–carbonyl dipole interactions) and, thus, elevates the glass transition temperature relative to that expected from the backbone conformational energy alone. The intermolecular association of syndiotactic ester groups below T_g is reflected in the nonlinear temperature dependence of A_{v1}/A_{v2} ratio in the temperature range $T_\beta < T < T_g$ (Figure 2). We also note that the experimental conformational energy of methoxy group, $(\Delta E_{t-c})^{methoxy}$, indicates that the assumption of infinite $(\Delta E_{t-c})^{methoxy}$ in the previous works is not a realistic approximation.

Conformational Structure of i-PMMA and s-PMMA in the Stereocomplex

Here, we employ the conformational assignment of IR bands, established above, for a FTIR spectroscopic evaluation of the conformational structure of i-PMMA and s-PMMA in the stereocomplex.

It is yet unclear whether a single optimal i-PMMA/s-PMMA ratio for the most efficient stereocomplexation exists. The range 1/2–1/1 has been reported in the literature[18–19] as the most suitable. We selected the ratio 1/1 because it enables a much easier and more accurate analysis of FTIR data in comparison with, say, the 1/2 ratio. The formation of crystalline stereocomplexes in the bulk of the blend film prepared from the 1/1 mixture was confirmed by WAXD measurements (Figure 3). In contrast to the films of individual polymers, which appeared almost totally amorphous in the WAXD diagrams, the blend film obtained from their 1/1 mixture in the same solvent (benzene) exhibited a well-defined crystalline X-ray pattern identical to that reported by Challa et al. on solid stereocomplexes of PMMA.[20] Hereafter, the blend film under consideration will be referred to as the stereocomplex film.

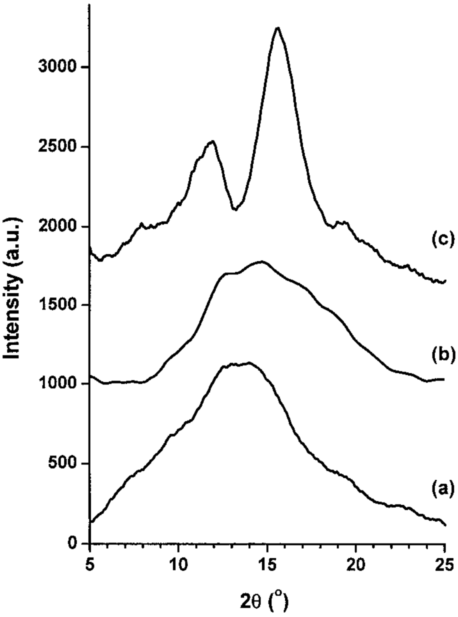

Fig. 3. WAXD patterns observed with the films of (a) i-PMMA, (b) s-PMMA, and (c) 1/1 i-PMMA/s-PMMA stereocomplex.

The FTIR spectrum of the stereocomplex films, in the 1050–1300 cm^{-1} region, with the fitted component bands is shown in Figure 4. The C–O stretching bands are designated as ν_1 to ν_5 inclusive, and their spectral positions are summarized in Table 1. It can be seen that the ν_1^{iso} peak shifts from 1265 to 1257 cm^{-1} on complexation, while the position of ν_1^{syndio} does not change. The normalized intensities of ν_1^{iso} and ν_1^{syndio} bands (relative to the internal reference band at 2997 cm^{-1})[21] are represented graphically in Figure 5(a). The band intensities in the stereocomplex film were multiplied by 2, taking into account the 0.5 weight fraction of each polymer in the film. The most striking feature of the data is a nearly 2-fold increase in the intensity of ν_1^{syndio} band on complexation, indicating a strong rise in the content of trans conformers for the s-ester groups. Unlike the ν_1^{syndio} band, the ν_1^{iso} band lowers its intensity. Since this band shifts by as much as 8 cm^{-1} upon complexation, it might be possible that the factor responsible for the band shift could also affect the absorptivity and thus the intensity.

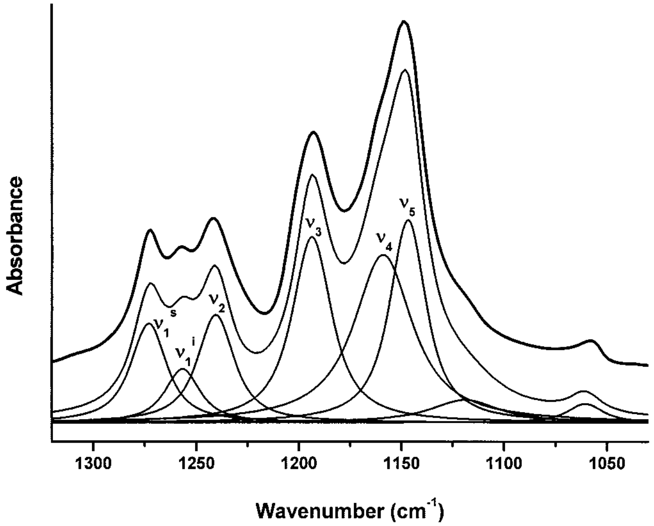

Fig. 4. FTIR spectrum in the region 1050–1300 cm^{-1} with fitted component bands for the film of 1/1 i-PMMA/s-PMMA stereocomplex.

The position of ν_2 band is nearly the same for i-PMMA, s-PMMA, and the stereocomplex. Apparently, the individual ν_2^{iso} and ν_2^{syndio} bands retain their positions on complexation and, thus, result in the single band composed of two unresolved components. Then, it is likely that not only the position but also the absorptivity of each component is practically not affected and, thus, any change in the intensity is due to a change in the ester cis content. The normalized intensities of ν_2 band for the single-component and stereocomplex films are compared in Figure 3(a). The intensity in the stereocomplex film is lower than the arithmetic mean of the intensities in the single-component films [2.5 for the stereocomplex, compared to (2.5 + 3.9)/2 = 3.2 for the mean], indicating a decrease in the overall ester cis content. From the temperature dependence of the intensity ratio of ν_1 and ν_2 bands, we know that the ratio of absorptivities $\alpha_{\nu 2}/\alpha_{\nu 1}$ in s-PMMA is 1.1. This relation and the numerical data presented in Figure 3(a) yield a value of 2.2 for the normalized intensity of ν_2 band in the stereocomplex film, under the

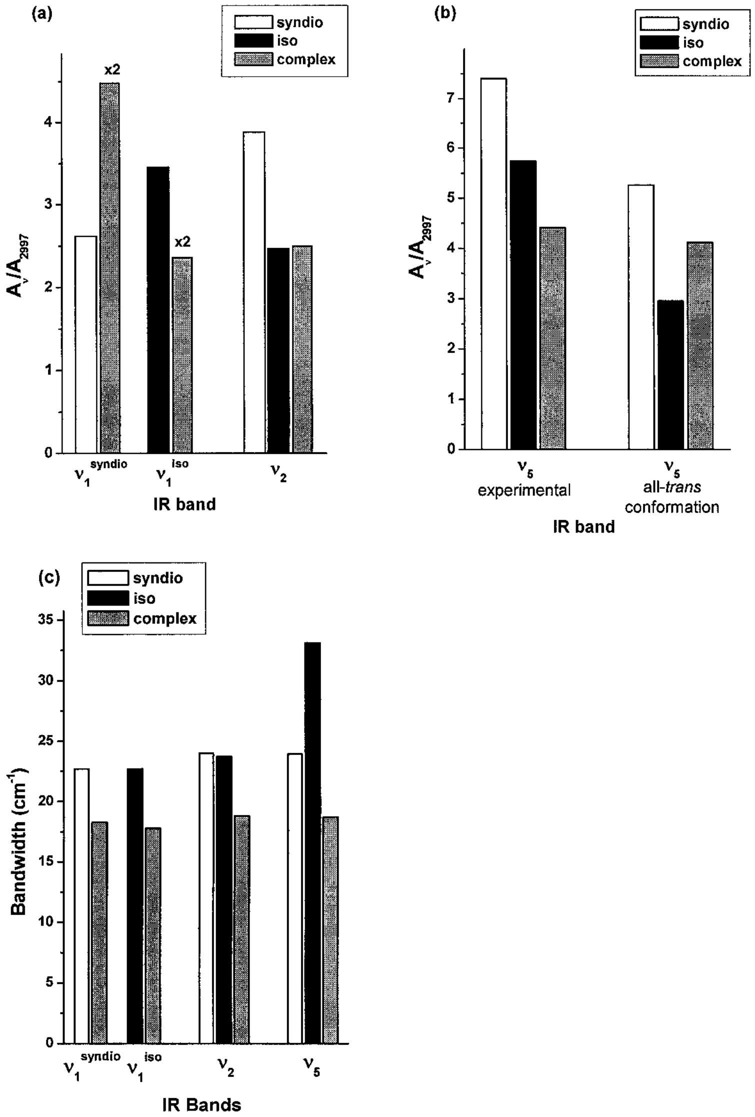

Fig. 5. Comparison of the normalized intensities of bands (a) ν_1, ν_2 and (b) ν_5, and (c) the bandwidths of ν_1, ν_2, and ν_5 bands in the FTIR spectra of i-PMMA, s-PMMA, and stereocomplex films. In part a, the intensity of ν_1^{iso} and ν_1^{syndio} bands in the stereocomplex film was multiplied by 2, taking into account the 0.5 weight fraction of each polymer in the film. Also shown in part b are the normalized intensities of ν_5 band for the limiting case of all-trans backbone conformation.

assumption that *only s-ester groups change the conformation on complexation.* As the calculated value differs from the experimental one by only 12%, the assumption certainly reflects the actual situation. Besides, the numerical data for the intensity of syndiotactic ν_1 and ν_2 bands yield a value of 0.73 for the trans fraction of s-ester groups in the stereocomplex, compared with only 0.35 in the "free" s-PMMA.

Likewise the ν_2 band, the position of ν_5 band is nearly the same for i-PMMA, s-PMMA, and the stereocomplex, indicating that the ν_5 bands of individual polymers retain their positions on complexation. The normalized intensity of this band, $A_{\nu5}/A_{2997}$, in the stereocomplex film equals 4.41 [Figure 3(b)]. This is by 30% lower than the arithmetic mean of $A_{\nu5}/A_{2997}$ in the individual films, (5.75 + 7.40)/2 = 6.58, indicating an increase in the overall tt content. Furthermore, one can calculate $A_{\nu5}/A_{2997}$ for a hypothetical stereocomplex film consisting solely of all-trans chains, by averaging the known values of $A_{\nu5}/A_{2997}$ for the all-trans i-PMMA and s-PMMA,[10] and obtain (2.96 + 5.27)/2 = 4.12 which is by only 7% lower than the experimentally observed value. This result represents a solid experimental evidence that the main-chain structure of both polymers in the stereocomplex approximates very closely to the all-trans conformation.

A previous IR study of PMMA stereocomplex revealed narrowing of several IR bands upon complexation, which was ascribed to restricted skeletal and ester-group mobility.[8] In the case of ν_1-ν_5 bands studied here, the narrowing was observed for the bands ν_1, ν_2, and ν_5 [Figure 5(c)]. The width of ν_1 and ν_2 bands decreased by 4-5 cm^{-1}. Since a comparable decrease of 3-4 cm^{-1} was observed on cooling the individual polymers from above T_g to room temperature, it is reasonable to ascribe the narrowing of bands ν_1 and ν_2 in the streocomplex to a decrease in the molecular mobility. As to the ν_5 band, its bandwidth is 33, 24, and 19 cm^{-1} for the i-PMMA, s-PMMA, and streocomplex film, respectively. These values, taking into account that the width of individual ν_5 bands in the stereocomplex may somewhat differ from that of the resultant band, imply the narrowing of roughly 14 and 5 cm^{-1} for the stereocomplexed i-PMMA and s-PMMA, respectively. A decrease of 4–5 cm^{-1} in the width of ν_5 band was observed in the individual polymers on cooling them from above T_g to room temperature. Thus, the complexation-driven band narrowing is comparable to the temperature-induced one for s-PMMA. However, the respective values for i-PMMA differ strikingly, indicating that the molecular mobility is *not* the major factor of the reduced bandwidth for the stereocomplexed i-

PMMA. At this point, it should be noted that the bandwidth is sensitive not only to the molecular mobility but also to the structural regularity. Note also that the ν_5 band is associated with the conformational states of backbone. This implies an increased regularity of backbone trans states in the stereocomplexed i-PMMA as a likely reason of the greatly reduced width of isotactic ν_5 band. The increase in the regularity can be regarded as a minimization in the irregular displacement of torsion angles from the perfect (lowest energy) trans state.

Table 3. Predominant Backbone and Ester-Group Conformations (and their Fractions) of i-PMMA and s-PMMA Chains in the Individual Polymers and in the 1/1 Stereocomplex.

	Backbone		Ester group	
	Individual polymer	Stereocomplex	Individual polymer	Stereo-complex
i-PMMA	tt (~0.9) irregular *tt* sequences	tt (~1.0) highly regular *tt* sequences	trans (0.9)	trans (0.9)
s-PMMA	tt (~0.9)	tt (~1.0)	cis (0.65)	trans (0.73)

This FTIR study revealed significant changes in the conformational characteristics of i-PMMA and s-PMMA chains, occurring on complexation (Table 3). Both polymers take on all-*trans* backbone conformations. This observation is an experimental proof of the previously postulated main-chain structure of stereocomplexed chains.[8,9] Besides, new important details are disclosed. Namely, complexation causes a significant increase in the regularity of torsion angles for trans states in i-PMMA and cis → trans isomerization of ester groups in s-PMMA. The breadth of the transitions implies that the involved forces may be stronger than van der Waals interactions, and the conformational transition of s-ester groups suggests that dipole-dipole interactions of ester groups may play an important role. Based on these findings, we suggest a model of 1/1 i-PMMA/s-PMMA stereocomplex depicted in Figure 6. The two parallel chains are in all-trans backbone conformations, the ester groups are in the tran*s* states, and the complex is stabilized by carbonyl-carbonyl dipole interactions between the i- and s-ester groups. The model ignores possible deviations from the staggered approximation (because these are not accessible by FTIR) and therefore is open for further refinement by, e.g., X-ray diffraction and molecular modeling.

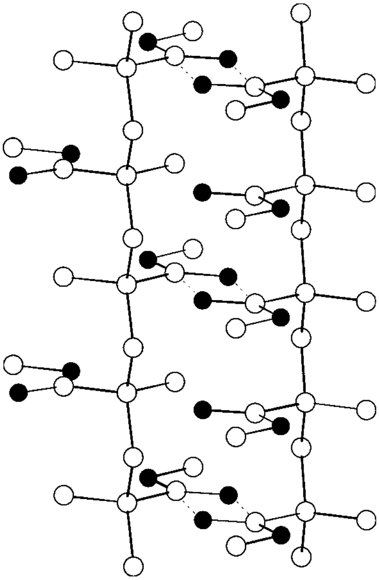

Fig. 6. Proposed model of 1/1 i-PMMA/s-PMMA stereocomplex.

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