Conformation-Sensitive Infrared Bands and Conformational Characteristics of Stereoregular Poly(methyl methacrylate)s by Variable-Temperature FTIR Spectroscopy

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ABSTRACT: Variable-temperature FTIR measurements were performed on amorphous films of isotactic and syndiotactic 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}. The use of computerized FTIR instrumentation and modern methods of quantitative band-fitting analysis in combination with the recent IR and ab initio results for simple esters allowed us to achieve, for the first time, the unambiguous conformational assignment for the ester bands of PMMA. This, in turn, enabled reliable IR spectroscopic determination of conformational energies for the PMMA backbone and the ester side group. The backbone conformational characteristics for i-PMMA and s-PMMA are found to be closely similar (in the staggered bonds approximation); the trans−trans state is strongly preferred over the trans−gauche state in both polymers, and the preference is only slightly higher for s-PMMA. At the same time, the two stereoregular forms appear markedly different in the conformational characteristics of ester side group. The minimum energy conformation of the ester moiety is trans in i-PMMA but cis in s-PMMA. Moreover, the absolute value of the conformational energy difference between the cis and trans states is 1.84 kcal/mol for i-PMMA, compared with only 0.46 kcal/mol in s-PMMA. Besides, the FTIR data shows that the ester groups of i-PMMA do not contribute to the glass transition, whereas those of s-PMMA form intermolecular associates (presumably, by carbonyl−carbonyl dipole interactions) and, in this way, elevate the glass transition temperature relative to that expected from the backbone conformational energy alone. This finding discards the thesis of O'Reilly and Mosher (*Macromolecules* **1981**, *14*, 602) that the Gibbs−DiMarzio theory fails to explain the difference in T_g between i-PMMA and s-PMMA.

Introduction

The conformational characteristics of polymer chains play a key role in determining the physical properties of polymeric materials, particularly such important ones as chain stiffness,[1,2] glass transition temperature,[3,4] mobility and relaxation behavior,[5,6] and miscibility.[7,8] Historically, progress toward establishing the *general* conformation−property relationships has been made mainly by theoretical polymer science.[1,3] Experimental efforts to understand the fundamental effects of conformational structure on the polymer properties and to verify the theoretical generalizations have been confronted by interference due to chemical factors, as well as by difficulties in the determination of basic conformational characteristics among which the difference in the energy of accessible conformational states is most essential.

Stereoregular polymers may represent a unique example where the conformation−property relationships are not obscured by complicating factors of chemical origin. Indeed, since stereoregular forms of a given polymer are built with the same monomer unit and, thus, are chemically identical, any difference in their physical properties might be due solely to the difference in the conformational characteristics. In this respect, stereoregular PMMA (isotactic (i-PMMA) and syndiotactic (s-PMMA)) polymers are of particular interest, because they seem to display the strongest effect of tacticity on physical properties among all strereoregular polymers studied so far. i-PMMA and s-PMMA differ markedly in the glass transition temperature (T_g = 55 ± 5 and 125 ± 5 °C, respectively),[9] chain stiffness (characteristic ratio C_∞ = 10.2 and 7.2),[10] miscibility,[11] surface activity,[12,13] and adsorption behavior.[14] Conformational energy calculations[15−17] indicate two possible chain conformations with trans−trans (tt) and trans−gauche (tg) arrangement of skeletal bonds, both for i-PMMA and for s-PMMA. The calculated energy of the tt state, in both polymers, is significantly lower than that of tg state, leading to a strong preference for the tt conformation. This result agrees with X-ray studies on i-PMMA[18] and s-PMMA[19] which show that structures of the nearly all-trans form are most compatible with the experimental data. Besides, the theoretical values of the conformational energy difference between the tt and tg states of s-PMMA are higher than the corresponding values for i-PMMA.[16,17]

In recent years, several attempts were made to determine the conformational energy difference of stereoregular PMMAs with the use of variable-temperature IR spectroscopy.[20−24] This technique is one of the most powerful experimental tools for the conformational energy determination in polymers, provided that the conformational assignment of analytical bands is well established.[25] An overview of experimental works on the conformational energy determination and the conformational assignment of IR bands in PMMA is given below.

O'Reilly and Mosher[20] were the first to derive the conformational energy difference of stereoregular PM-

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MAs using IR spectroscopy. They employed a novel methodology consisting in the analysis of the temperature dependence of IR peaks appearing upon subtraction of the room-temperature spectrum from the spectrum measured at an elevated temperature. The spectral region of 1050−1300 cm^{-1} revealed the strongest temperature variations in the differential IR intensities and, therefore, was used in the conformational energy determination. Since the obtained values varied largely with the choice of differential peaks, it was simply assumed that the highest values represent the backbone conformational energy. However, the validity of O'Reilly's approach has been questioned by Schneider and coworkers.[26] They pointed out that the positions of IR bands in the range 1050−1300 cm^{-1} undergo pronounced temperature changes. Consequently, the differential absorbance peaks are artificially generated in the difference spectra by the temperature-induced frequency shift of actual IR bands and, thus, cannot be strictly related with the conformational states of the polymer. Nevertheless, O'Reilly's method has been adopted by others for the conformational energy determination of stereoregular PMMAs in thin films[21] and in solutions.[22]

Well before O'Reilly's work, the range 1050−1300 cm^{-1} in the IR spectra of s-PMMA was investigated by Havriliak and Roman.[27] Their approach consisted in the isolation of elementary component bands by a band fitting routine followed by the analysis of band intensities as a function of temperature. Seven component bands were identified, and four of them were grouped in pairs (1172/1192 and 1238/1268 cm^{-1}) and assigned to different rotational isomers of the ester group. Some years later, Belopol'skaya and Trapeznikova[28] applied the approach of Havriliak and Roman both to s-PMMA and i-PMMA and expanded the temperature range below room temperature. The two pairs of peaks isolated by Havriliak and Roman in s-PMMA were found also in i-PMMA. However, the temperature behavior of one pair (1172/1192 cm^{-1}) appeared more consistent with the rotational isomerism of O−CH_3 group rather than with rotation of the ester group as a whole. Despite these experimental indications that the two doublets are due to different conformational states of the *ester group*, several papers appeared recently where the bands in question were used for estimation of the *backbone* conformational energy.[23,24]

Apart from the multiple absorption bands in the range 1050−1300 cm^{-1}, the doublet at 860 and 840 cm^{-1} has frequently been used as a measure of the conformation of s-PMMA.[26,29−31] The idea of conformational sensitivity of the doublet was put forward by Schneider and coworkers.[32] The structural assignment proposed by these authors associates the bands at 860 and 840 cm^{-1} with the tt and tg conformation of polymer backbone, respectively.[26] The band at 860 cm^{-1} appears as a relatively strong peak in the crystalline or self-aggregated s-PMMA, as well as in the s-PMMA/i-PMMA stereocomplex.[26,29,33] However, it is practically absent from the spectra of amorphous s-PMMA,[33] despite the predominance of tt conformation in the amorphous state.[19] Moreover, i-PMMA does not absorb at 860 cm^{-1} at all,[26,33] though the dominant conformation of the polymer backbone is also tt.[16−18]

We may summarize that, despite the long-lasting interest and high number of studies in the infrared spectroscopic estimation of PMMA conformation and conformational energy, unambiguous conformational assignment of the IR bands possessing signs of conformational sensitivity is still lacking. Consequently, the currently available estimates of the conformational characteristics of PMMA by IR spectroscopy and the associated conclusions on the conformation−property relationships may be of limited and, sometimes, questionable value.

Table 1. Characteristics of PMMA Samples

			tacticity (% triads)		
polymer	M_w	M_w/M_n	mm	mr	rr
s-PMMA	199 000	4.24	4	21	75
i-PMMA	208 000	3.37	91	6	3

Here, we report variable-temperature FTIR measurements made on amorphous films of isotactic and syndiotactic PMMA polymers, combined with a detailed analysis of the temperature dependence of integrated band intensities in the region 1050−1300 cm^{-1}. We adopt the strategy of the already mentioned studies of Havriliak[27] and Belopol'skaya.[28] However, contrary to these previous works, the precision of derived spectroscopic information in the current study is incomparably higher because of the use of computerized FTIR instrumentation and modern methods of quantitative band-fitting analysis in combination with the recent IR and ab initio data for simple esters. As a result, new features in the temperature dependence of component bands in the 1050−1300 cm^{-1} region are revealed, and for the first time, an unambiguous structural assignment of the bands is achieved. Using a two-state scheme of conformational states and the established structural assignment of IR bands, the difference in the energy of accessible conformational states is determined both for the backbone and for the ester group. The conformational energy results are discussed in relation with the large disparity in T_g between the two tactic forms of the polymer. Finally, our findings discard the thesis of O'Reilly and Mosher[20] that the Gibbs−DiMarzio theory fails to predict the difference in T_g between i-PMMA and s-PMMA.

Experimental Part

Materials. Characteristics of the PMMA polymers used in this study are listed in Table 1. The triad contents were determined by proton NMR. Molecular-weight distributions were measured with a Tosoh gel permeation chromatography system (HLC-8020), using polystyrene standards. s-PMMA was obtained from Polymer Laboratories (U.K.). i-PMMA was prepared by anionic polymerization initiated by phenylmagnesium bromide in toluene at 0 °C. The polymers were purified by precipitation prior to use.

Sample Preparation. The polymers were dissolved in benzene (purity ≥ 99.5%) at a concentration of 2% (w/v). Polymer films were prepared in a dust-free chamber by casting the solutions on chromic acid cleaned glass substrates (Pyrex glass Petri dishes). Film thickness was controlled by the volume of casting solution and for the s-PMMA and i-PMMA films used in the FTIR measurement reported here amounted to about 5 and 8 μm, respectively. The residual solvent was removed from the films formed at room temperature by drying films on the substrates at 70 (i-PMMA) or 130 °C (s-PMMA) for about 8 h in a clean oven. After 8 h, samples were allowed to cool to room temperature at ∼1 °C/min. The films then were scored around the edges and floated on the surface of double distilled water, from which they were picked up, blotted with filter paper, and stored over desiccant until required.

Infrared Spectroscopy. The FTIR spectra were recorded on a Nicolet 7199 FTIR spectrometer equipped with a mercury−

cadmium-telluride (MCT) detector at a resolution of 2 cm^{-1} with 32 scans. The temperature dependencies were measured in a commercial heated cell (Jasco). Temperature was controlled to ±0.5 °C during interferogram collection. The rate of temperature increase between the consequent measurements was ~0.5 °C/min. All spectra were analyzed by second derivatization in the 1050−1300 cm^{-1} region for their component compositions and peak frequencies using Omnic 3.1a software. Second-derivative spectra were smoothed with an 11-point smoothing function (10.6 cm^{-1}). Lorentzian curve-fitting[34] of the complex 1050−1300 cm^{-1} band was then performed, using Origin 6.0 (Microcal) software, on the original (nonsmoothed) spectra which were baseline corrected under assumption of zero absorbance at 1020 and 1340 cm^{-1}. The number of components and their peak positions, determined by second derivatization, were used as starting parameters. After that, a linear baseline was fitted additionally to the Lorentzian bands. This improved the fitting of wings of the complex band, leaving the integrated intensities of component bans practically not affected. In all cases, the discrepancy between frequencies obtained by second derivatization and the Lorentzian curve-fitting were below 1 cm^{-1}, except that the s-PMMA peak seen at 1061 cm^{-1} in the second-derivative spectra appeared at 1064 cm^{-1} in the curve-fitting results.

Determination of Conformational Energy Difference. The ratio of the integrated intensities of two distinct peaks centered at ν_1 and ν_2 ($\nu_1 \neq \nu_2$) and associated, respectively, with the conformational state 1 and 2 of a molecule or functional group, in a two-state scheme for the conformational states is related to the ratio of concentrations of the two states by the standard equation

$$n_2/n_1 = (\alpha_1/\alpha_2)(A_2/A_1) \quad (1)$$

where n is concentration, A is the integrated absorbance, α is the integrated absorptivity, and subscripts 1 and 2 denote states 1 and 2, respectively. On the other hand, the ratio n_2/n_1 is given by the Boltzmann relation

$$n_2/n_1 = (g_2/g_1)\exp(-\Delta E_{2-1}/RT) \quad (2)$$

where R is the gas constant, T is absolute temperature, ΔE_{2-1} is the free energy difference between the conformational states ($\Delta E_{2-1} = E_2 - E_1$), and g is the degeneracy of state. Combining eqs 1 and 2 yields an expression of van't Hoff type

$$\ln(A_2/A_1) = -\Delta E_{2-1}/RT + \ln(g_1/g_2) + \ln(\alpha_1/\alpha_2) \quad (3)$$

under the assumption that the ratio of integrated absorptivities α_1/α_2 is independent of temperature. Thus, the experimentally measured $\ln(A_2/A_1)$ as a function of $1/T$ provides the experimental value of ΔE_{2-1}.

The conformational states may, in principle, absorb at the same frequency, i.e., $\nu_1 = \nu_2 = \nu$. If the corresponding absorptivities, α_1 and α_2, differ in magnitude, the integrated intensity of the resulting band is

$$A_\nu = \alpha_1 n_1 d + \alpha_2 n_2 d \quad (4)$$

where d is the sample thickness. Accordingly, A_ν will change with the sample temperature on the account of the temperature-induced concentration change given by eq 2. After normalization of A_ν by the integrated intensity of an internal reference band ($A_{ref} = \alpha_{ref} n d$, where n is the total concentration) one obtains

$$A_\nu/A_{ref} = (\alpha_1/\alpha_{ref})(n_1/n) + (\alpha_2/\alpha_{ref})(n_2/n) \quad (5)$$

Combining eqs 2 and 5 yields a Boltzmann sigmoid dependence

$$A_\nu/A_{ref} = (g_2/g_1)(\alpha_2/\alpha_{ref} - \alpha_1/\alpha_{ref})/[g_2/g_1 + \exp(\Delta E_{2-1}/RT)] + \alpha_1/\alpha_{ref} \quad (6)$$

Thus, the experimental plot of A_ν/A_{ref} vs $1/T$ fitted to a three-parameter sigmoid of the form shown in (6) yields α_1/α_{ref}, α_2/α_{ref}, and ΔE_{2-1}. In this study, the experimental data were fitted to eq 6 by nonlinear least-squares regression analysis using Origin 6.0 (Microcal) software. No constraint was imposed on the parameters during the curve fitting.

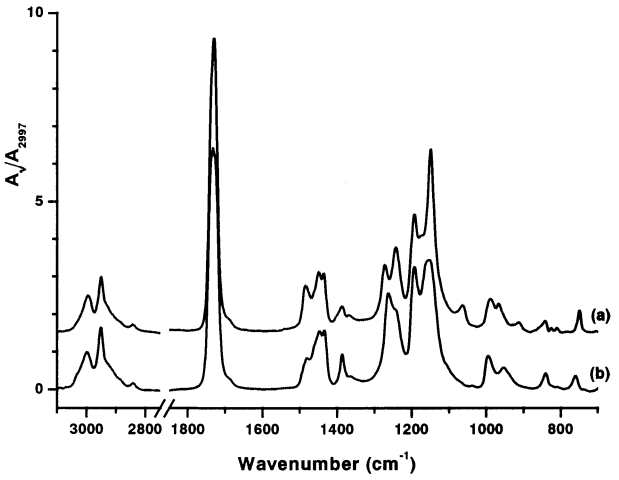

Figure 1. FTIR spectra of (a) s-PMMA and (b) i-PMMA films at room temperature. The film thicknesses were ~5 (s-PMMA) and 8 μm (i-PMMA), respectively. To compensate for the thickness difference, the spectra were normalized by the intensity of internal reference band at 2997 cm^{-1}.

Results and Discussion

1. General Observations. In the analysis of temperature dependencies of IR spectra, aimed at identifying the conformation-sensitive IR bands, one has to use amorphous samples to dismiss obscuring effects of crystallinity. The i-PMMA film appeared totally amorphous in wide-angle X-ray scattering measurements (WAXS). The WAXS diagram of s-PMMA film was almost completely amorphous, indicating that the degree of crystallinity was below 10%. One may note in Table 1 that the stereoregularity of i-PMMA (*mm* 91%) was higher than that of s-PMMA (*rr* 75%). A syndiotactic specimen of higher stereoregularity (*rr* 93%) was available, but it could not be used in this study because the crystalline content of resulting film amounted to ~30%. The WAXS data were published elsewhere.[33]

Figure 1 compares room-temperature FTIR spectra of the s-PMMA and i-PMMA films in the 700−3100 cm^{-1} region. The tacticity of the polymer backbone has a marked influence on the shape, relative intensity, and localization of IR bands in the range 700−1500 cm^{-1} as well as on the number of peaks between 700 and 1000 cm^{-1}. Many vibrational assignments for the IR bands of stereoregular PMMAs are available and those made by Nagai[35] and Willis et al.[36] are most comprehensive. The intensive multiple absorbances in the region pertinent to the current study (1050−1300 cm^{-1}) are commonly assigned to stretching modes of the ester group.

The FTIR spectra of s-PMMA and i-PMMA films in the temperature ranges 25−175 (s-PMMA) and 25−80 °C (i-PMMA) are shown in Figure 2, parts a and b, respectively, for the 700−1550 cm^{-1} region. The C−H stretching modes at 2800−3000 cm^{-1} did not reveal any appreciable changes with temperature and, therefore, were excluded for reasons of clarity. The C═O stretching at 1700−1750 cm^{-1} was also excluded, because any reliable analysis of this band was not permitted due to its high intensity in the spectra. It can be seen that the

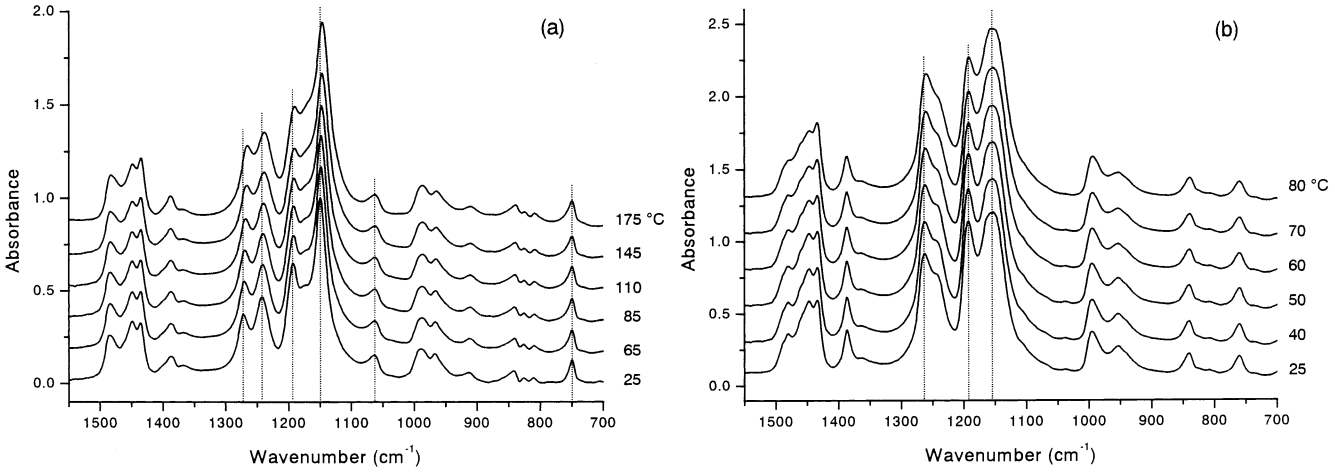

Figure 2. FTIR spectra in the region 700−1550 cm^{-1} for (a) s-PMMA and (b) i-PMMA at various temperatures indicated on the IR spectra.

increase of temperature produces the most notable spectral changes in two regions, 1400−1470 and 1100−1300 cm^{-1}. The former displays a continuous increase in the ratio of peak intensities at 1435 and 1448 cm^{-1}. This behavior was ascribed by Schneider et al.[26] to conformational transitions of ester groups, based on the dominant contribution of deformation modes of the ester CH_3 group to the spectrum in this region. As to the region 1100−1300 cm^{-1}, the temperature-induced changes are not limited to significant alterations in the relative intensities of IR peaks but include also broadening of band contours and substantial low-frequency shifts in peak positions. The profound influence of temperature on the IR spectra of PMMA in the spectral range under consideration has been observed by many authors, mostly for the band intensities. Substantial downshifts in peak positions were reported by Schneider et al.[26] and by Belopol'skaya.[28] According to our data for s-PMMA (Figure 2a), increasing the temperature from 25 to 175 °C causes a downshift of 3−4 cm^{-1} for the bands located in the room-temperature spectrum at 1149, 1193, and 1242 cm^{-1} and of 7 cm^{-1} for the band at 1272 cm^{-1}. For comparison, the position of peaks at 749 and 1061 cm^{-1}, associated with stretching modes of the polymer backbone, is constant to within ±0.3 cm^{-1}. In i-PMMA, the frequency shift of ester stretching vibrations is weaker (Figure 2b), though one has to note that the highest temperature shown is only 80 °C.

2. Curve Fitting of the Complex Band at 1050−1300 cm^{-1}. The high temperature sensitivity of the bands associated with skeletal stretching vibrations of the ester group implies their sensitivity to the conformation of the ester group or polymer backbone or both of them. To identify the presence and the type of conformational sensitivity for each individual band, one has to perform a rigorous analysis of the temperature dependence of the band intensity. Since the bands under consideration undergo temperature-induced changes not only in the peak height but also in the bandwidth and position, any analysis based on peak heights would lead to erroneous results, and therefore, integrated intensities must be used instead. Thus, the complex band under consideration is to be resolved into elementary component bands by curve fitting. The number and location of individual component bands used in curve fitting were obtained from the second derivative of the original spectra. As an example, Figure 3 shows the

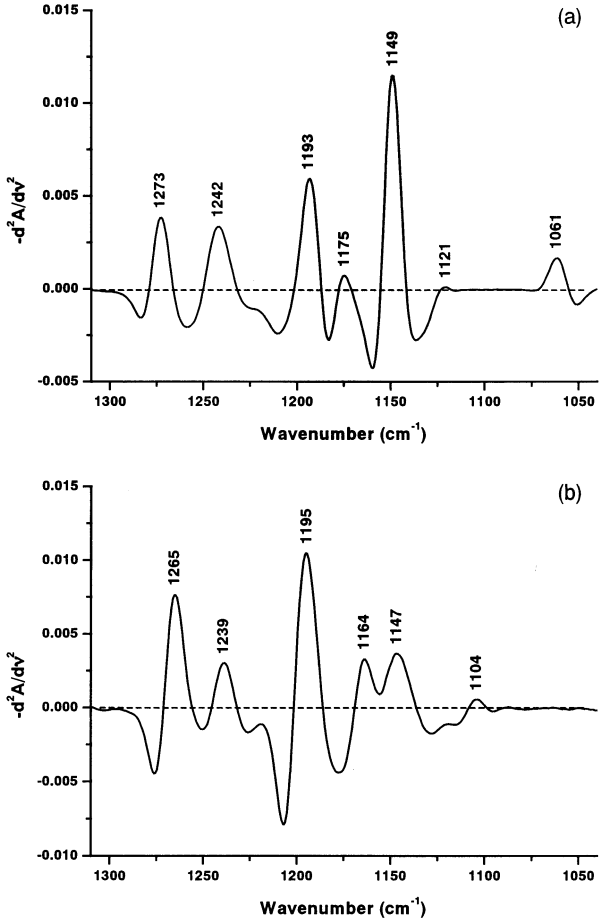

Figure 3. Second-derivative FTIR spectra in the region 1050−1300 cm^{-1} for (a) s-PMMA and (b) i-PMMA at room temperature.

second-derivative FTIR spectra (1050−1300 cm^{-1}) of s-PMMA and i-PMMA films measured at room temperature. They reveal seven component bands for s-PMMA and six ones for i-PMMA, in full agreement with the results of earlier studies.[27,28] Figures 4 and 5 show the 1050−1300 cm^{-1} region with the fitted component bands (designated as ν_1 to ν_7 inclusive in Figures 4a and 5a) of the FTIR spectra measured at 25, 115, and 175 °C for s-PMMA (Figure 4) and at 25, 55, and 80 °C for i-PMMA (Figure 5). The spectra shown represent three characteristic temperature regimes, i.e., well below T_g,

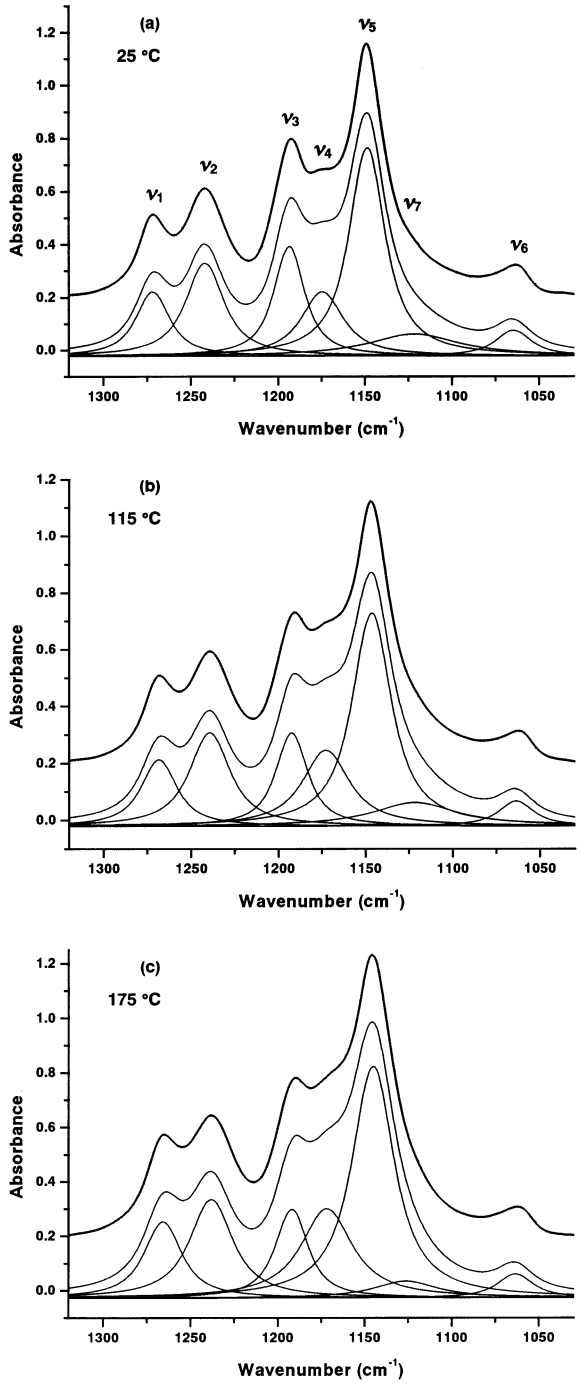

Figure 4. FTIR spectra in the region 1050−1300 cm^{-1} with fitted component bands for s-PMMA at (a) 25, (b) 115, and (c) 175 °C.

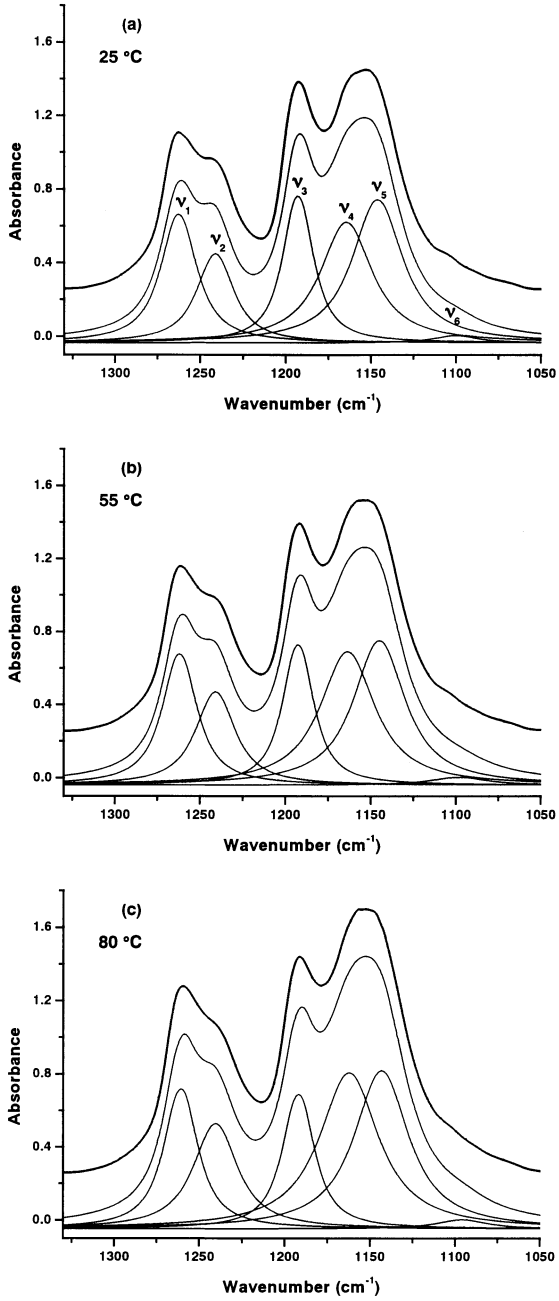

Figure 5. FTIR spectra in the region 1050−1300 cm^{-1} with fitted component bands for i-PMMA at (a) 25, (b) 55, and (c) 80 °C.

near T_g, and well above T_g. The effect of temperature on the integrated peak intensity is seen most clearly for the ν_3, ν_4 pair of peaks, both in s-PMMA and i-PMMA, in the whole temperature range, as well as for the peak ν_7 of s-PMMA at 175 °C. The peaks ν_1, ν_2, and ν_5 also appear to be temperature-sensitive, although the corresponding intensity changes are weaker and, hence, less obvious to the naked eye. The integrated intensity of peak ν_6 is too weak for a reliable visual examination. In what follows, the temperature behavior of the integrated intensities of peaks ν_1 to ν_7 will be analyzed quantitatively. The quantitative data will be used in conjunction with the results of recent vibrational spectroscopic and ab initio studies of methyl methacrylate (MMA) and carboxylic esters for assigning the infrared bands of PMMA.

3. Quantitative Analysis of Integrated Band Areas vs Temperature. In light of the previously published data[27,28] and our own findings disclosed below, it is instructive to divide the peaks under consideration into the groups ν_1, ν_2; ν_3, ν_4; ν_6, ν_7; and ν_5 and consider them in this same order.

3.1. Bands ν_1 and ν_2. The ν_1, ν_2 pair of peaks is located at 1273, 1242 and 1265, 1239 cm^{-1} in the room-temperature spectra of s-PMMA and i-PMMA, respectively. They are unambiguously assigned to the ν_a(C−C−O) vibration.[35,36] In 1966, Havriliak and Roman[27] showed that the splitting of this vibration into two components is a consequence of two rotational-isomeric states of the ester group, where the C═O and C$^{\alpha}$−CH$_3$ bonds are in mutual cis or trans orientation arising from

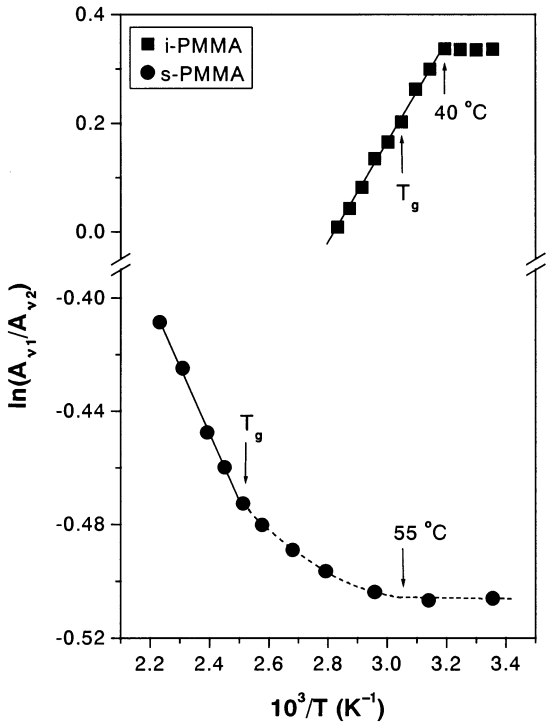

Figure 6. Logarithmic plots of the integrated intensity ratio $A_{\nu 1}/A_{\nu 2}$ against inverse absolute temperature for s-PMMA (circles) and i-PMMA (squares). The solid lines represent the fit to eq 3. The dashed line is a guide to the eye.

the internal rotation about the C$^{\alpha}$−CO bond. Though, at that time, it was impossible to associate each band with one of the two conformations, recent spectroscopic and ab initio studies of MMA, by Owen et al.[37] and Konaka et al.,[38] may allow one to do so. In the infrared spectra of MMA, the bands corresponding to peaks ν_1 and ν_2 of PMMA are located at 1325 and 1301 cm^{-1}. The frequencies of monomer bands are about 50 cm^{-1} higher than those of the corresponding polymer bands due to conjugation between the C═C and C═O bond of monomer, affecting the force constant of the C$^{\alpha}$−CO stretching vibration.[35] The ab initio results of above-mentioned research groups indicate that the high-frequency band is due solely to the trans conformation, whereas the low-frequency component is associated exclusively with the cis conformation. Thus, the corresponding polymer bands, ν_1 and ν_2, must be assigned to, respectively, the trans and cis conformation of the ester group. Accordingly, the ratio of the integrated intensities for the two peaks must be related to the conformational energy difference between the trans and cis states by the van't Hoff equation (eq 3). The corresponding van't Hoff plots are shown in Figure 6. It can be seen that the ratio of integrated intensities remains constant as the temperature increases from 25 to 55 °C for s-PMMA and to 40 °C for i-PMMA. After that, a monotonic change in the intensity ratio is observed for both polymers, indicating the occurrence of temperature-induced cis−trans rotational isomerization of the ester group. The activation temperature of this process (55 °C for s-PMMA and 40 °C for i-PMMA) falls in the temperature range of the maximum of the secondary β-relaxation in PMMA (40−60 °C at 10^2−10^3 Hz).[39,40] This fact, that the activation temperature of the cis−trans isomerization coincides with that of the β-relaxation, agrees with the recent NMR results of Schmidt-Rohr et al.,[41] which suggest that the β-process in PMMA consists of a 180° flip of the ester group about the C$^{\alpha}$−CO bond.

Comparing the van't Hoff plots in Figure 6 further, one can see that the sign of the monotonic change in the absorbance ratio of bands ν_1 and ν_2 above the respective activation temperature is different for the two polymers. That is, in s-PMMA the $A_{\nu 1}/A_{\nu 2}$ ratio increases as temperature increases, whereas in i-PMMA it decreases. In other words, raising the temperature increases the trans content at the expense of the cis content in s-PMMA, whereas in i-PMMA the cis−trans equilibrium shifts in the opposite direction. This means that the energetically favored conformation of the ester group is cis in s-PMMA and trans in i-PMMA. Furthermore, the temperature-induced change in the $A_{\nu 1}/A_{\nu 2}$ ratio for i-PMMA is nicely represented by a single straight line indicating that the conformational equilibrium is indeed controlled by the two-state Maxwell−Boltzman statistics (eq 2). The conformational energy diffrence, $(\Delta E_{t-c})^{ester} = (E_t - E_c)^{ester}$, of the ester group of i-PMMA, derived from the van't Hoff plott on the basis of eq 3, amounts to -1.84 ± 0.04 kcal/mol. Similar to i-PMMA, the temperature-induced change of $A_{\nu 1}/A_{\nu 2}$ in s-PMMA displays a linear regime in the van't Hoff plott; however, this regime takes place only above T_g (120 °C) and is preceded by a nonlinear behavior which starts at about 55 °C. There is no apparent reasons to expect that the two-state statistics confirmed above for the isotactic PMMA would not hold in its syndiotactic counterpart. Therefore, the only way to explain this specific behavior is to assume that, below T_g, only a fraction of the ester groups undergo the cis−trans isomerization and the rest are held in their low-temperature conformations by intermolecular interactions. Above T_g, the intermolecular links are broken and all the ester groups contribute to the conformational dynamics. As a result, the conformational equilibrium described by eq 2 and the corresponding linear dependency represented in the van't Hoff equation (eq 3) apply only above T_g. The linear regime yields $(\Delta E_{t-c})^{ester} = 0.46 \pm 0.01$ kcal/mol for s-PMMA.

The fractional involvement of the ester groups of s-PMMA in the cis−trans isomerization below T_g, inferred from our IR data, is in excellent agreement with the finding of the already cited ^{13}C NMR experiments[41] that only 50% of the ester groups undergo 180° flips in s-PMMA below T_g and the rest are only fluctuating around their equilibrium positions. Note that neither Havrilliak[27] nor Belopol'skaya[28] observed changes in the $A_{\nu 1}/A_{\nu 2}$ ratio for s-PMMA below T_g, most likely because of low precision and sensitivity of their measurements, arising from the use of dispersive instruments and primitive methods of curve fitting.

3.2. Bands ν_3 and ν_4. The ν_3, ν_4 pair of peaks is located at 1193, 1175 and 1195, 1164 cm^{-1} in the room-temperature spectra of s-PMMA and i-PMMA, respectively. Figures 4 and 5 show that, as temperature increases, the intensity of the peak ν_4 increases rapidly at the expense of an equally fast decrease in the intensity of the peak ν_3, both for s-PMMA and i-PMMA. The corresponding van't Hoff plots (Figure 7) reveal for each polymer a single linear dependence in the whole range of measured temperatures. The temperature-induced intensity transfer between the two peaks was reported both by Havriliak[27] and Belopol'skaya.[28] The latter author observed the phenomenon down to −173 °C for both polymers, while Havriliak could see it for

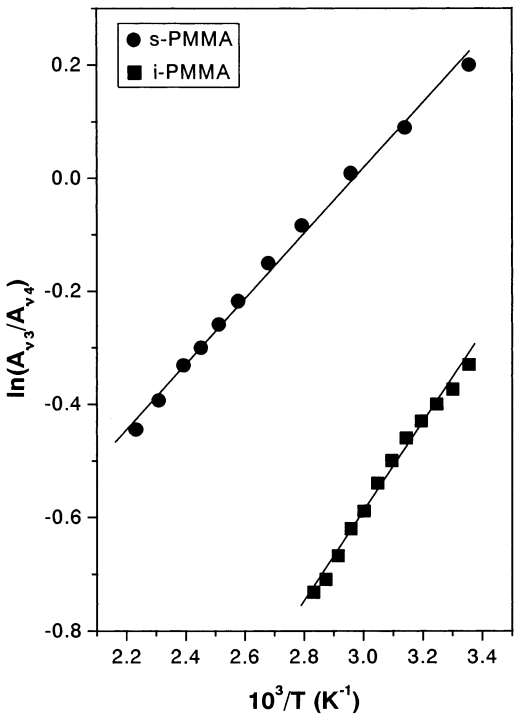

Figure 7. Logarithmic plots of the integrated intensity ratio $A_{\nu 3}/A_{\nu 4}$ against inverse absolute temperature for s-PMMA (circles) and i-PMMA (squares). The solid lines represent the fit to eq 3.

s-PMMA (i-PMMA was not studied) only above T_g. The observation of Havriliak appears to be incorrect, as the intensity change of peak ν_3 in the FTIR spectra of s-PMMA at temperatures well below T_g is evident even without the help of curve fitting (Figure 2a).

Similar to the case of the ν_1, ν_2 pair considered above, the temperature-induced intensity transfer between the peaks ν_3 and ν_4 indicates that the two bands represent the same vibration mode of the ester group, but originate from different rotational states of the latter. As the high frequency component is due unambiguously to the asymmetric C−O−C stretch [ν_a(C−O−C)],[35,36] the same must be true for its low frequency counterpart. Concerning possible rotational-isomeric states involved, we immediately exclude the rotational isomerism around the C^{α}−CO bond because the activation temperature of this transition is 40−55 °C according to the above data for the ν_1, ν_2 doublet (Figure 6), whereas the rotational relaxation reflected in the intensity change of peaks ν_3 and ν_4 does not freeze at least down to 25 °C (Figure 7). This prompts us to consider rotation of the methoxy group around the C(O)−OCH_3 bond, because this rotation represents the only remaining possibility for isomerization of the ester group.

The conformational isomerism in esters arising from rotation around the C(O)−O bond has a long history of intensive studies. It has been realized that the five heavy atoms in the ester group tend to maintain a planar configuration. The planarity is, in turn, attainable only under a cis or a trans conformation of the O═C−O−C moiety. The cis conformation has been known for many years as the major conformer for most esters[42] but evidence about the relative importance of the trans conformation has been obtained only recently.[43−45] In particular, according to recent ab initio calculations and experimental results obtained for formic acid esters,[45] the ν_a(C−O−C) band frequency is highly sensitive to the

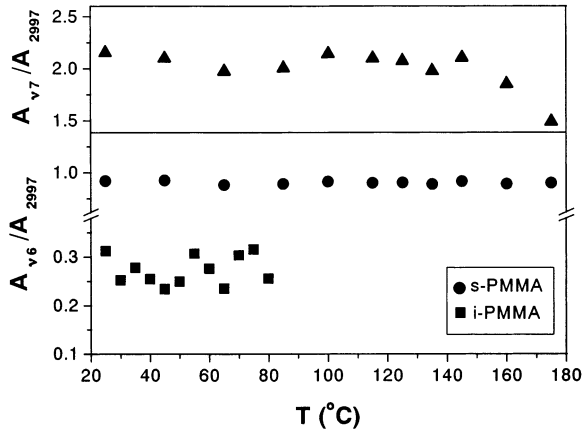

Figure 8. Plots of the integrated intensity ratios $A_{\nu 6}/A_{ref}$ for s-PMMA (circles) and i-PMMA (squares) and $A_{\nu 7}/A_{ref}$ for s-PMMA (triangles) against temperature.

conformation of the O═C−O−C skeleton. Namely, all the formates studied so far show the peak of the trans conformation at lower wavenumbers than that of the corresponding cis conformation. For example, the observed red shifts are 106 cm^{-1} for methyl formate and 29 cm^{-1} for chloromethyl formate.[45] Thus, we may confidently conclude that the peaks ν_3 and ν_4 in the IR spectra of PMMA are due to, respectively, the cis and trans conformation of the methoxy group. This same assignment was postulated by Belopol'skaya[28] as an explanation of the continuous change in the $A_{\nu 3}/A_{\nu 4}$ ratio down to −173 °C, on the basis of some experimental evidence that the low-temperature relaxation in PMMA may be associated with rotation of the methoxy group between cis and trans positions. The conformational energy difference, $(\Delta E_{t-c})^{methoxy} = (E_t - E_c)^{methoxy}$, of the methoxy group, derived from the van't Hoff plotts in Figure 7, is 1.14 ± 0.03 and 1.56 ± 0.05 kcal/mol for s-PMMA and i-PMMA, respectively. The values are comparable with the liquid-phase trans-cis energy difference of 1.66 kcal/mol reported for methyl formate.[44]

3.3. Band ν_6 and ν_7. The band ν_6 is sensitive to tacticity (1061 and 1104 cm^{-1} in s-PMMA and i-PMMA, respectively), perpendicularly polarized,[35] and relatively weak in intensity. This suggests that it is a C−C stretch of the polymer backbone.[27,35,36] Havriliak[27] in addition assumed that in s-PMMA it might be associated with the all-trans (planar zigzag) backbone conformation. However, this structural assignment disagrees with the author's own data revealing no temperature dependency for the integrated intensity of the band in question. According to our measurements (Figure 8), the integrated intensity of the ν_6 band (normalized by the intensity of the band at 2997 cm^{-1} used as an internal reference band[46]) appears to be independent of temperature for both polymers, although the scatter for i-PMMA is considerable (±15%) because of the strong overlap of neighboring bands. On this basis, we conclude that the band ν_6 does not possess any conformational sensitivity.

The band ν_7 (1121 cm^{-1}) is present only in the spectrum of s-PMMA. Its intensity is comparable with that of band ν_6 and constant up to a temperature of 160 °C which is far above T_g. This indicates that the band is not sensitive to the conformational structure. Above 160 °C, the intensity decreases. We currently have no plausible explanation for this behavior.

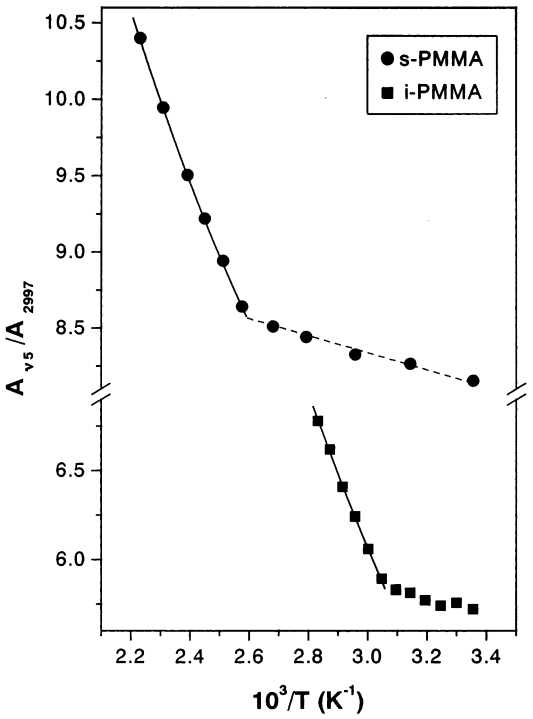

Figure 9. Plots of the integrated intensity ratio $A_{\nu 5}/A_{\text{ref}}$ against inverse absolute temperature for s-PMMA (circles) and i-PMMA (squares). The solid lines represent fit to eq 7 over the range $T \geq T_g$. The dashed line is a guide to the eye.

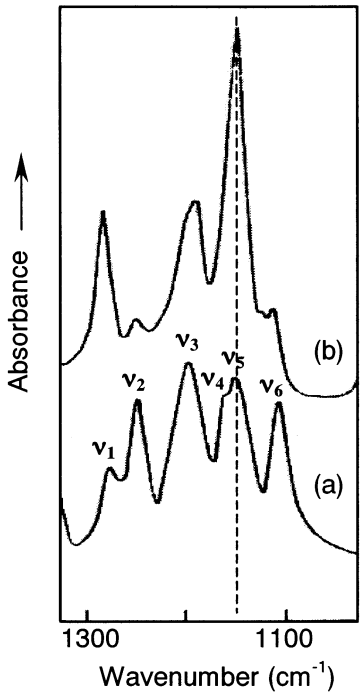

Figure 10. Room-temperature IR spectra of PMMA dimer in the crystalline (a) and amorphous state (b) (adapted from ref 49).

3.4. Band ν_5. The peak ν_5 is positioned at 1149 and 1147 cm^{-1} in s-PMMA and i-PMMA, respectively. It has a very strong intensity, which suggests its association with stretching modes of the ester group. Havriliak[27] and Willis[36] consider it as a pure C−O stretch, whereas Nagai[35] assumes essential mixing with skeletal stretching modes. Willis, in addition, assigns it as ν_a(C−O−C); this assignment must be ruled out because, according to the data discussed above, the ν_a(C−O−C) mode is associated with the ν_3, ν_4 doublet.

Before considering the temperature behavior of the band ν_5, let us first enumerate the criteria for identifying the adsorption bands of the backbone conformers in a polymer:[25]

I. The polymer chain has *two* accessible conformational states of different energy.

II. The intensities of the bands associated with the backbone conformations are independent of temperature below T_g, whereas *above* T_g the intensity of the band of the high-energy conformer increases and that of the low-energy conformer decreases as the temperature of sample is increased.

III. Conformer bands are always present *in pairs* corresponding to *the same vibration modes* in both the high-energy conformer and the low-energy conformer.

Note that the requirement imposed by the criterion I is satisfied in stereoregular PMMAs because the experimental and theoretical data indicate that the conformational characteristics are reasonably represented by a two-state scheme involving the tt and tg conformations of the polymer backbone, the energy of the tt state being lower than that of the tg state.[15−19]

The integrated intensity of band ν_5, normalized by the intensity of the internal reference band[46] at 2997 cm^{-1}, is plotted vs reciprocal temperature in Figure 9. For both polymers, the intensity is practically independent of temperature below T_g, whereas above T_g it increases monotonically as temperature increases. On the basis of this behavior and the above criterion II, it would be reasonable to assign the band ν_5 to the tg state of the polymer backbone, provided that a band of the same vibration mode, associated with the second (tt) state (criterion III), is located at a different frequency. However, as should be evident from the whole set of data considered above, 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".[48]

This finding that the integrated intensity of the band ν_5 is sensitive to the backbone conformation of PMMA is supported by the IR data of Schneider et al.[32,49] on the conformational forms of the dimer of PMMA−dimethyl ester of 2,2,4,4-tetramethylglutaric acid (DMTG). The IR spectra of the solid (crystalline) and liquid (amorphous) DMTG, measured by these authors, reveal pronounced intensity differences in the range 1050−1300 cm^{-1}, *especially* for the band at 1150 cm^{-1} (Figure 10). Notice that the number and location of ester peaks in the IR spectra of the PMMA dimer is the same as in those of PMMA polymers (cf. Figures 4, 5, and 10). Obviously, the peak assignments are also the same. Therefore, the differences in the intensity of peaks ν_1 to ν_4 between the solid and liquid states of the dimer must be due to rotational isomerism of the ester group. This explanation is not applicable, however, to the intensity change of the peak ν_5 because the peak is not found in the spectra of MMA monomer[38,39] and, thus, does not seem related to a conformation of the ester group. Moreover, the appearance of this peak in the dimer spectra, while it is absent from the spectra of monomer, strongly suggests essential mixing of this C−O stretch with skeletal C−C stretching modes. Note

Table 2. Parameters Resulting from Fitting the Temperature Dependence of $A_{\nu 5}/A_{ref}$ (Figure 9) at $T \geq T_g$ to Eq 7 with Non-Linear Least-Squares Analysis

polymer	α_{tt}/α_{ref}	α_{tg}/α_{ref}	ΔE_{tg-tt} (kcal/mol)
s-PMMA	5.27 ± 0.34	38.5 ± 3.1	2.77 ± 0.16
i-PMMA	2.96 ± 0.53	40.6 ± 8.6	2.51 ± 0.27

that the same conjecture was made by Nagai[35] on the basis of complex behavior of the band ν_5 with deuteration in the spectra of PMMA polymers. The mixing with skeletal stretches could impart sensitivity of the band ν_5 to the conformational states of the backbone. Indeed, Schreiber et al. showed that the solid DMTG contains a single conformer characterized by a tt structure of the carbon backbone, whereas both the tt and tg backbone conformers are present in the liquid state.[32,49] Thus, the enhanced intensity of the ν_5 band in the IR spectrum of the liquid form (Figure 10) should be explained, as in the case of PMMA, by the enhanced IR absorptivity of the tg state as compared to the absorptivity of the tt state at this vibrational frequency.

Since the band ν_5 consists of the "tt" and "tg" components that coincide in the frequency but differ in the absorptivity, the temperature dependence of the relative band area $A_{\nu 5}/A_{ref}$ must relate to the conformational energy difference between the skeletal tg and tt states, ΔE_{tg-tt}, by eq 6. The latter, taking into account the 4-fold degeneracy of the tg state (tg^+, tg^-, g^-t, and g^+t), assumes the form

$$A_{\nu 5}/A_{ref} = 4(\alpha_{tg}/\alpha_{ref} - \alpha_{tt}/\alpha_{ref})/[4 + \exp(\Delta E_{tg-tt}/RT)] + \alpha_{tt}/\alpha_{ref} \quad (7)$$

where α_{tt} and α_{tg} are the integrated absoptivities of the band ν_5 for the backbone tt and tg states, respectively. The parameters α_{tt}/α_{ref}, α_{tg}/α_{ref}, and ΔE_{tg-tt} were derived from fitting the experimental data at $T \geq T_g$ to eq 7 with nonlinear least-squares analysis. Table 2 summarizes the results. Attention is attracted by the fact that the integrated absorptivity of the tt state is by an order of magnitude higher than that of the tg state. The difference is striking and, therefore, must be verified by an independent estimate. For this purpose, we separated the overlapped ester bands in the already discussed spectra of amorphous and crystalline DMTG (Figure 10) using a simple graphical method[50] and found the ratio of the areas under the peak ν_5 between the two spectra to be ~4. According to Schneider,[32,49] the crystalline DMTG consists solely of the tt conformer which also dominates in the liquid state. A simple calculation based on the above ratio of ν_5 band areas and the 100% tt content in the crystalline form yields, in the case of 60−80% tt content in the amorphous state, $\alpha_{tg}/\alpha_{tt} \approx 8-16$. These values are comparable with the ratios α_{tg}/α_{tt} of 7.2 and 13.7 resulting from the fitting analyses for s-PMMA and i-PMMA, respectively. Additionally, we have to test for reasonableness either α_{tt}/α_{ref} or α_{tg}/α_{ref}. α_{tg}/α_{ref} cannot be tested because the "pure" tg state is practically unachievable. As to α_{tt}/α_{ref}, from the literature IR spectra of highly crystalline i-PMMA,[51] we estimated the value of α_{tt}/α_{ref} at ~3.5 which is comparable with the value of 2.96 ± 0.53 that emerged from our fitting analysis. It is impossible, however, to get an estimate of α_{tt}/α_{ref} for s-PMMA in the same way because obtaining a highly crystalline form of this polymer remains a challenge. On the other hand, i-PMMA and s-PMMA cocrystallize in approximate all-trans conformations by stereocomplexation when mixed together. We analyzed the spectrum of 1:1 stereocomplex film from our previous work[13,33] and found that the relative intensity of ν_5 band ($A_{\nu 5}/A_{ref}$) amounts to 4.41. This value, in combination with the already confirmed $\alpha_{tt}/\alpha_{ref} = 2.96 \pm 0.53$ for i-PMMA, yields $\alpha_{tt}/\alpha_{ref} = 5.86 \pm 0.53$ for s-PMMA, which indicates reasonableness of the value 5.27 ± 0.34 emerged from the fitting analysis. Having the values of the two parameters proved for reasonableness, we may conclude that those of the remaining one, i.e., the conformational energy, are also correct.

We complete this major part of our study by summarizing the vibrational and conformational assignments of bands $\nu_1-\nu_7$ in Table 3 and the values of conformational energies in Table 4.

4. Comparison with Theoretical Results. Because of imperfections in the previous IR spectroscopic determinations of PMMA conformational energy, outlined in the introductory part and highlighted further by the above IR findings, we will compare our data (Table 4) only with the theoretical results, namely with those of Vacatello and Flory[16] and Sundararajan[17] (hereafter V−F and PRS, respectively). The calculated energy difference between the tg and tt states of backbone, ΔE_{tg-tt}, is on average 3.2 (V−F) and 1.1 kcal/mol (PRS) for s-PMMA, and 1.3 (V−F) and 0.8 kcal/mol (PRS) for i-PMMA. These values are considerably lower than the respective experimental quantities shown in Table 2, except for the V−F result on s-PMMA. Besides, there is a significant discrepancy in the results between the two theoretical studies. Nevertheless, both the experiment and the calculations reveal the same *qualitative* trend—the backbone conformational energy of s-PMMA is higher than that of i-PMMA. The difference amounts to only 0.26 kcal/mol in the experimental results, indicating that the preference of tt conformation is *only slightly* stronger for s-PMMA in comparison with i-PMMA. As to the conformational energy of the ester group, $(\Delta E_{t-c})^{ester}$, both theoretical works suggest a strong dependence of $(\Delta E_{t-c})^{ester}$ on the conformation of backbone. This is not supported by the experiment, where a clear linear behavior with a *single* conformational energy is observed in the van't Hoff plot for the temperature-induced cis−trans isomerization of ester group above T_g (Figure 6). This would not be the case if $(\Delta E_{t-c})^{ester}$ were a function of the backbone conformation. In this respect, the behavior of i-PMMA is most convincing; i.e., the slop of the van't Hoff dependence is the same below and above T_g (Figure 6). V−F did not isolate the ester-group energy out of the overall chain energy, while PRS did so and found $(\Delta E_{t-c})^{ester} \approx 1$ kcal/mol in both tactic forms, except for a value of 1.9 kcal/mol in the tt state of s-PMMA. These results bear neither qualitative nor quantitative comparison with the experimental data. The experimental value $(\Delta E_{t-c})^{ester} = -1.84$ kcal/mol for i-PMMA implies a strong preference for the trans conformation and a *high conformational rigidity of the ester group in the isotactic polymer*. On the contrary, $(\Delta E_{t-c})^{ester} = 0.46$ kcal/mol for s-PMMA indicates a very slight preference for the cis conformation and a *high conformational flexibility of the ester group in the syndiotatctic polymer*. As we shall show below, the marked difference in the conformational freedom of the ester group is a key factor determining the difference in T_g between the two stereoregular forms. We also note that the experimental values of the

Table 3. Vibrational and Conformational Assignments of the IR Bands in the Region 1050−1300 cm^{-1} for Stereoregular PMMA

band designation	frequency (cm^{-1}) *s*-PMMA	frequency (cm^{-1}) *i*-PMMA	vibrational assignment	conformational assignment: moiety	conformational assignment: conformation
ν_1	1273	1265	ν_a(C−C−O)	ester group	trans
ν_2	1242	1239	ν_a(C−C−O)	ester group	cis
ν_3	1193	1195	ν_a(C−O−C)	methoxy group	cis
ν_4	1175	1164	ν_a(C−O−C)	methoxy group	trans
ν_5 low absorptivity	1149	1147	ν(C−O) + skeletal ν(C−C)	backbone	trans−trans
ν_5 high absorptivity	1149	1147	ν(C−O) + skeletal ν(C−C)	backbone	trans−gauche
ν_6	1061	1104	skeletal ν(C−C)	conformation-insensitive	
ν_7	1121		?	conformation-insensitive	

Table 4. 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

conformational energy of methoxy group ($(\Delta E_{t-c})^{methoxy}$ = 1.14 and 1.56 kcal/mol for s-PMMA and i-PMMA, respectively) indicate that the assumption of infinite $(\Delta E_{t-c})^{methoxy}$ in the theoretical calculations is not a realistic approximation.

5. Relationship with T_g. The T_g of PMMA is highly dependent on the tacticity and varies from 50 to 60 °C for i-PMMA to 120−130 °C for s-PMMA. The physical origin of this behavior is not yet understood. The issue has gained a particular importance after O'Reilly's conclusion that the Gibbs−DiMarzio (GDM) theory of glass transition is not valid because it fails to predict the difference in T_g between i-PMMA and s-PMMA from their conformational (flex) energies.[20] Recently, other authors noticed an important role of intermolecular interactions,[9,52] and assumed that these, if considered as the second parameter (the hole energy) of GDM theory, may account for the large disparity in T_g.[52] However, the origin of these interactions and why their magnitude depends on the tacticity remains unclear.

The GDM theory requires the backbone conformational energy of s-PMMA to be higher than that of i-PMMA by a factor of 1.25 according to the T_g values,[20] provided that the GDM hole energy is equal for the two polymers. The experimental data reveal the difference by a factor of only 1.10 (Table 4). Is the GDM theory invalid[20] or there is a difference in the hole energy (i.e., in the energy of intermolecular interactions)? The answer can be found in the temperature dependence of the conformational dynamics of ester groups shown in Figure 6. The trans−cis isomerization of ester groups in i-PMMA does not show any signs of slowing down when the temperature decreases below T_g (55 °C). This indicates that the dynamics of ester groups is independent of the backbone dynamics. In other words, the ester groups do not contribute to vitrification and, thus, the T_g of i-PMMA is defined by the backbone conformational energy alone. A principally different situation is seen in s-PMMA. Here, the freezing of ester-group conformations starts at 120 °C, i.e., at the T_g of s-PMMA. Remember that in i-PMMA the ester-group isomerization freezes at 40 °C. Since the conformational flexibility of ester groups in s-PMMA is markedly higher than in its isotactic counterpart, the upward shift of the freezing temperature by 80 °C is remarkable. Certainly, some *strong* intermolecular interactions, either repulsive or attractive ones, must be responsible for this behavior. Repulsive interactions, however, must be ruled out, because there is no physical reasons that would cause the repulsion of the *flexible* ester groups of s-PMMA to be stronger than that of the *rigid* ester groups of i-PMMA; the flexible groups would easier optimize unfavorable contacts by conformational adjustments in comparison with the rigid groups. It appears, therefore, that the high-temperature freezing of ester groups in s-PMMA is due to a *strong intermolecular attraction*. There is only one source of strong intermolecular attraction in esters—carbonyl−carbonyl dipole interactions. Specifically, the attraction energy of an *antiparallel* dimer of carbonyl groups can be as high as −5 kcal/mol, i.e., comparable to medium-strength hydrogen bonds.[53] This prompts us to conclude that the high-temperature freezing of the ester groups in s-PMMA occurs due to their association by the carbonyl−carbonyl interactions. These coupled groups act as physical cross-links that prevent the main-chain rotational isomerizations and, thus, elevate the glass transition temperature relative to that expected from the backbone conformational energy alone. We may summarize using the GDM terminology that there is a large difference in the hole energy between i-PMMA and s-PMMA. That is, the hole energy of i-PMMA is due solely to weak, van der Waals interactions, and therefore, it has virtually no contribution to the glass transition. In s-PMMA, there are strong dipole−dipole interactions between carbonyls, which significantly increase the hole energy and, thus, elevate the glass transition temperature.

Finally, one has to answer the question why the postulated intermolecular association of carbonyls takes place in s-PMMA but does not take place in i-PMMA. The most likely reason is, again, the difference in the conformational flexibility of ester group between the two polymers. Because of the high conformational flexibility, a pair of the ester groups of s-PMMA can easily orient in the way that their carbonyls come into a molecular contact in the mutual antiparallel orientation and, eventually, associate into an intermolecular dimer. On the contrary, the conformationally rigid ester groups of i-PMMA lack this freedom of orientational mobility, and as a result, the carbonyl−carbonyl association is suppressed.

Conclusions

The detailed analysis of the temperature dependence of the integrated intensities of five (i.e., ν_1 to ν_5) IR bands associated with C−O stretching modes of PMMA, in the region 1050−1300 cm^{-1}, revealed that each band represents a single conformational state of the side group or the polymer backbone. Specifically, the bands ν_1 and ν_2 are due to the trans and cis conformation of

the ester group, and the bands ν_3 and ν_4 are due to the cis and trans state of the methoxy group, respectively. The band ν_5 consists of two superimposed bands differing in the absorptivity. The low absorptivity band is due to the trans−trans conformation, and the high absorptivity band is due to the trans−gauche conformation of polymer backbone. The unambiguous conformational assignment of IR bands enabled reliable IR spectroscopic determination of the difference in the energy of accessible conformational states for the backbone and for the ester group. The conformational energy results indicate a strong preference of trans−trans backbone conformation both for i-PMMA and s-PMMA; the preference is only slightly higher for s-PMMA. The two polymers differ markedly in the conformational characteristics of ester side 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. The marked difference in the conformational mobility of ester group appears to be 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.

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