Cooperativity in Backbone to Side-Chain Conformational Rearrangements in Stereoregular PMMA

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Received December 27, 1996; Revised Manuscript Received December 12, 1997

ABSTRACT: The infrared multiple absorption bands in the 1300−1100 cm^{-1} range, attributed to the ν_a(C−C−O) vibration of PMMA, and the carbonyl shift of the solid-state NMR spectra, have been analyzed in terms of conformational restrictions. The $A\nu_2/A\nu_1$ infrared ratio, calculated from the absorbances of ν_1 (at 1260−1275 cm^{-1}) and ν_2 (at 1240 cm^{-1}), is found to give the ratio of the backbone conformational energy relative to the overall energy of the chain segment. From this ratio, it is suggested that there are cooperative motions between the backbone and the side chain in i-PMMA, but not in s-PMMA.

Introduction

According to the rotational isomeric state (RIS) calculations of Vacatello and Flory[1] and Sundararajan,[2] there are conformational differences between isotactic and syndiotactic poly(methyl methacrylate) (i-PMMA and s-PMMA, respectively). The most stable conformation is trans−trans (tt) in the two cases, but the racemic tt state of s-PMMA is imposed by the backbone whereas the meso tt state of i-PMMA is stabilized by side-group interactions. Moreover, the conformation of the backbone and side chain of amorphous i-PMMA seems to be less restricted to specific rotational angles than the conformation of the syndiotactic isomer.[1,2]

In this article, a series of stereoregular PMMAs is investigated by infrared (IR) and solid-state nuclear magnetic resonance (NMR) spectroscopies. IR spectroscopy can be used to study the conformation of PMMA since the 1300−1000 cm^{-1} absorption range is known to be conformation sensitive.[3−5] Absorption peaks ν_1 (1270 cm^{-1}) and ν_2 (1240 cm^{-1}) have been used in the literature to calculate the van't Hoff conformational energies (ΔE) of different stereoisomers.[6,7] Here, the relationship between the $A\nu_2/A\nu_1$ ratio and local backbone and side-chain conformational energies is discussed as a function of PMMA tacticity.

Experimental Section

The PMMAs used in this study are listed in Table 1. The stereoregular samples were prepared by anionic polymerization under anhydrous conditions in a toluene/tetrahydrofuran cosolvent mixture using (α-methylstyryl)lithium as initiator. The atactic sample was provided by Aldrich Chemicals. The tacticity of all samples was determined by ^{1}H NMR spectroscopy, using a Varian XL-200 instrument. Molecular weights were determined by size exclusion chomatography using a Waters chromatograph. A Mettler DSC-30 apparatus was used for T_g measurements at a heating rate of 20 K/min. The midpoint temperature of the C_p jump was taken as T_g. Finally, i-PMMA was found by DSC to be slightly crystalline but was studied in that state.

FT-IR spectra were recorded in transmission with a Bomem MB-102 apparatus at 2 cm^{-1} resolution. In the analysis of the spectra, peak heights were used (not peak areas). The uncertainty on the $A\nu_2/A\nu_1$ ratio is estimated at ±0.04. Bulk samples were dispersed in KBr pellets or cast from solvent on KBr, and solutions were prepared in a liquid cell in CDCl$_3$. Temperature-dependent measurements were made with a SPECAC heating cell.

Table 1. Characteristics of the PMMAs Used

PMMA	tacticity (%)[a] i:h:s	racemic diad content (%)	n_s[b]	$10^{-3}M_n$	M_w/ M_n	T_g (K)
i-PMMA1	85:15:0	7	1	8	5.6	322
i-PMMA2	63:24:13	25	2	97	3	348
i-PMMA3	46:33:21	37	2.3	40	3	355
a-PMMA	7:39:54	74	4.3	102	2.5	378
s-PMMA1	5:26:69	82	6.2	66	1.4	400
s-PMMA2	0:18:82	91	10	106	1.1	406

[a] Tacticity calculated from the α-methyl peak in ^{1}H liquid-state NMR. (i = isotactic triad, h = heterotactic triad, s = syndiotactic triad). [b] n_s is the average syndiotactic sequence length.

For the solid-state ^{13}C NMR studies, PMMA powder was packed in a 7 mm zirconium spinner, spun at 4 kHz in CP/MAS/DD conditions, and run on a Bruker 300 MHz spectrometer. The pulse sequence was made of a $\pi/2$ pulse of 4 ms and a contact time of 2 ms, with decoupling during FID acquisition and recycling time. Frequency adjustments were made with an adamantane standard.

Results and Discussion

Figure 1 shows the four high-intensity absorption bands in the 1300−1100 cm^{-1} range, assigned to the ν_a(C−C−O) vibration coupled to the ν(C−O) vibration. These bands are generally seen in polymethacrylates, but they overlap with an increase of the length of the side chain[5] due to their fewer conformational restrictions; this gives rise to two or three broad absorption bands in this region of the infrared spectrum.

Figure 1 also shows that the 1300−1100 cm^{-1} absorption area is sensitive to the tacticity of PMMA. For example, ν_1 is shifted from 1260 for i-PMMA to 1271 cm^{-1} for s-PMMA and, similarly, ν_4 is shifted from 1153 to 1164 cm^{-1}; however, ν_2 and ν_3 remain stable whatever the isomer considered. A lower ν_1 frequency at 1260 cm^{-1} (partially merged with the ν_2 peak) for the i-PMMA can be interpreted by weaker conformational restrictions originating from shorter syndiotactic sequences: the conformational flexibility of the isotactic backbone[6] and the weak restrictions on both the side-chain and

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S0024-9297(96)01913-4 CCC: $15.00

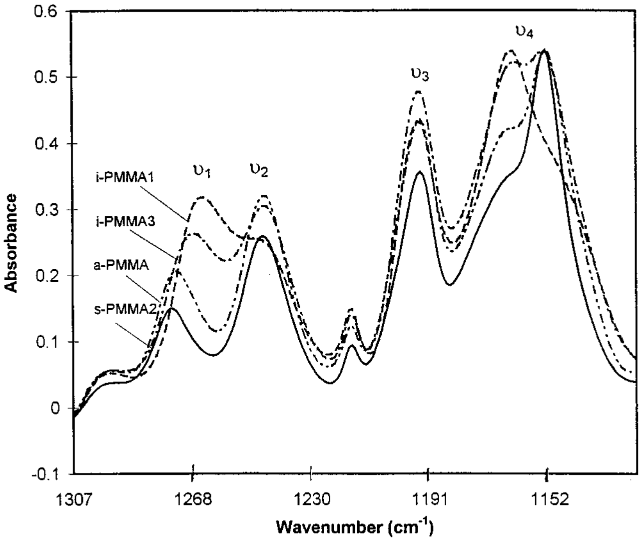

Figure 1. Infrared absorbance of PMMAs with different syndiotactic ratios. The solid curve represents s-PMMA2, the dash–dot–dotted curve represents a-PMMA, the dash–dotted curve represents i-PMMA3, and the dashed curve represents i-PMMA1. The spectra were taken in a $CDCl_3$ solution (5% w/w in $CDCl_3$) and at room temperature.

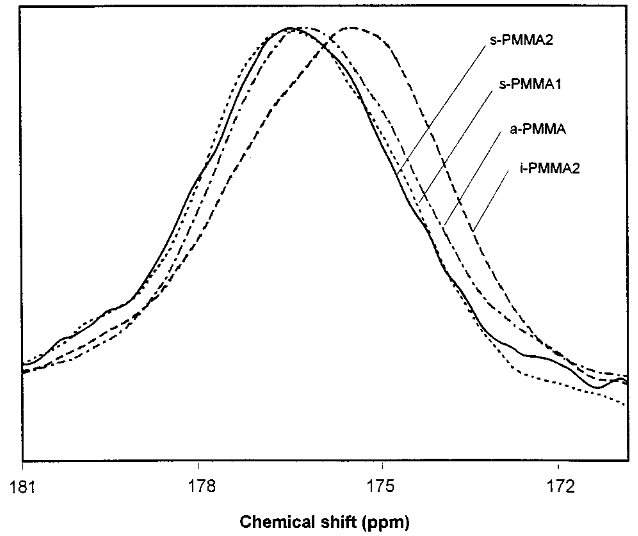

Figure 2. ^{13}C solid-state NMR spectra of PMMAs of different syndiotactic contents for the carbonyl carbon area. The solid curve represents s-PMMA2, the dotted curve represents s-PMMA1, the dash–dotted curve represents a-PMMA, and the dashed curve represents i-PMMA2. The spectra were taken at room temperature.

backbone conformations may allow us to keep an equal distance between attractive groups along the chain in a cooperative effect between the backbone and the side chains, as discussed later. Therefore, the meso tt state exhibits strong side-group interactions[2] that lead to a stabilization of that conformation, which accounts for a chain conformation governed by the packing and arrangements of the side groups.[6] In contrast, for the s-PMMA chain, the strong side-group interactions localized along tt and tg^- linkages are due to highly restricted backbone conformations.[1,2]

Solid-state ^{13}C NMR spectroscopy provides information about dipolar interactions in tactic PMMAs. For our purpose, the peak due to the carbonyl group is particularly useful. As shown in Figure 2, the chemical shift of the C=O peak increases from 176.4 to 178.2 ppm with an increase of syndiotacticity while the chemical shift of the 82% s-PMMA can be compared to the chemical shift of the prevailing racemic pentads of the atactic PMMA spectrum in $CDCl_3$ solution.[8] The differences in chemical shift shown in Figure 2 can be ascribed to variations in shielding since the electronic environment of the carbonyl carbon atom becomes poorer (downfield shift) as the syndiotacticity increases. A dipole steric interaction between ester groups may induce a delocalization of the electronic cloud toward the oxygen atom and a lower shielding of the carbon atom. Intramolecular side-group interactions between chain segments in the tt and tg states, which are the more frequent states in s-PMMA, are more favored than the interactions between chain segments in the tg state for i-PMMA on the basis of RIS calculations. This factor can explain the larger shielding of the carbonyl carbon atom in i-PMMA, for which the average level of interaction is likely to be low. This interpretation is consistent with the presence of more conformational restrictions in s-PMMA than in the isotactic isomer.

O'Reilly et al. have used the ν_1 and ν_2 IR absorption bands to calculate the difference in conformational energy (ΔE) between tt and tg states for the different stereoisomers of PMMA in a two-state scheme.[6,7] From ν_1, ΔE has then been found to be higher than that calculated from ν_2.[6,7] According to model II of O'Reilly and Mosher,[6] the ν_1 peak is associated with $\Delta E_{bb} + \Delta E_{sc}$, that is, the conformational energy of the whole chain segment, and the ν_2 peak with the backbone conformation, i.e., ΔE_{bb}. The higher ΔE_{bb} values found by O'Reilly et al. for s-PMMA as compared to a- or i-PMMA correlate with RIS results which show that the probability of finding a trans conformation increases with syndiotacticity. On the other hand, ΔE_{sc} increases on going from the a- to s-PMMA due to a restricted cis conformation. Moreover, the conformational energy ΔE_{sc} is lower for s-PMMA than ΔE_{bb} whereas side-chain and backbone conformational energies are believed to be equal for i-PMMA.[2]

Since the conformational energies ΔE_{bb} and ($\Delta E_{bb} + \Delta E_{sc}$) can be calculated from the absorbances of the ν_2 and ν_1 peaks, the absorbance ratio $A\nu_2/A\nu_1$ can then be correlated with the $\Delta E_{bb}/(\Delta E_{bb} + \Delta E_{sc})$ ratio and used as a semiquantitative measure of the latter. This ratio has already been assumed to be conformation sensitive,[4] but only the rotational state of the side group was taken into account. This interpretation is too restrictive and inconsistent with the high conformational energy of the backbone calculated for a- and s-PMMA. In this work, both the backbone and side-chain conformations are taken into account in the interpretation of the $A\nu_2/A\nu_1$ ratio. In other words, a high $A\nu_2/A\nu_1$ ratio indicates that the backbone conformation imposes the chain conformation while a low ratio is related to a local equilibrium between backbone and side-chain conformations.

From our results, the $A\nu_2/A\nu_1$ ratio is shown to increase linearly with the amount of racemic diad, as shown in Figure 3, not only for the bulk samples but also for the polymers in THF and $CDCl_3$ solutions. As discussed above, this increase of the $A\nu_2/A\nu_1$ ratio can be interpreted as an increase of the backbone conformational energy relative to the overall chain energy upon an increase of the syndiotacticity. In s-PMMA, the backbone is more likely to impose the local conformation of the chain. The predominance of the backbone conformation in the establishment of the overall chain

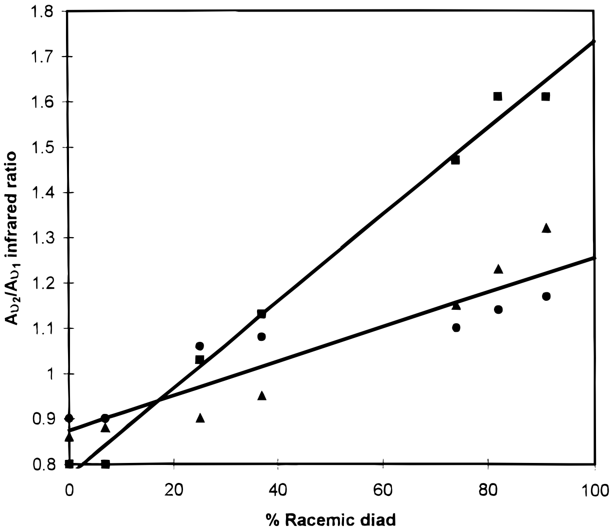

Figure 3. IR $A\nu_2/A\nu_1$ ratio as a function of the percentage of racemic diads for spectra taken in the bulk (●), in CDCl$_3$ solution (■), or in THF solution (▲). Examples of original spectra are given in Figure 1.

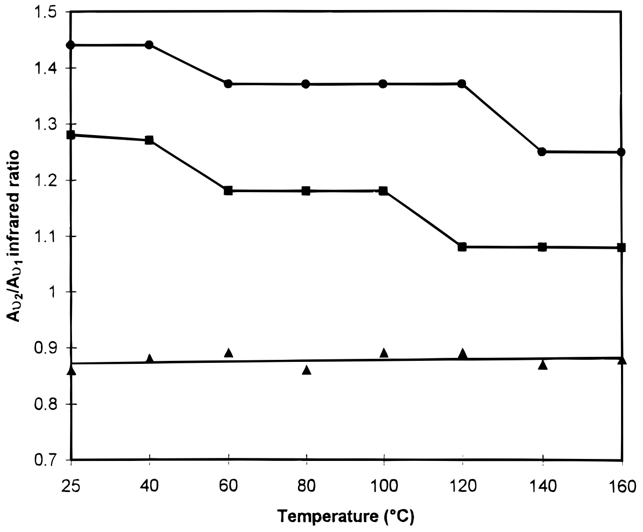

Figure 4. IR $A\nu_2/A\nu_1$ ratio of a-PMMA (■), i-PMMA2 (▲), and s-PMMA2 (●) as a function of temperature. The spectra were taken on films cast from solution on a KBr pellet. For the definition of ν_2 and ν_1, see Figure 1.

conformation of s-PMMA has already been pointed out from RIS calculations,[2] but also from the high backbone conformational energy ΔE_{bb} measured for that isomer.[6]

Differences are observed in Figure 3 between the samples analyzed in CDCl$_3$ and those analyzed in THF and in the bulk; these differences are particularly important at high racemic diad contents. For example, for the s-PMMA having a racemic diad content of 91%, the $A\nu_2/A\nu_1$ ratio is equal to 1.60 in CDCl$_3$ as compared to 1.20 in THF and in the bulk. This difference, between CDCl$_3$ and THF solutions, can be ascribed to the nature of the interactions[9,10] occurring between s-PMMA and the solvent. The acid–base interactions between CDCl$_3$ and the PMMA carbonyl groups reduce the intramolecular interactions between side groups and, therefore, the conformational energy of the side chain. Consequently, the energy level of the backbone increases relative to that of the overall segment. In contrast, in THF, the intramolecular interactions are less perturbed by the solvent and the energy level of the backbone remains constant, as compared to the bulk. For i-PMMA, the $A\nu_2/A\nu_1$ ratio remains constant in the different solvents (within experimental uncertainty). This behavior may result from the cooperativity between the backbone and the side chains, allowing the backbone to maintain constant its energy level by means of conformational rearrangements.

The interdependence between the backbone and side-chain conformations is assumed to allow a local compensation of the energy gained or lost by one or the other. This compensation can be total if $\Delta E_{bb} = \Delta E_{sc}$, or partial if $\Delta E_{bb} \neq \Delta E_{sc}$. If the local compensation is partial, the gain in energy must be compensated by conformational changes in the remainder of the chain. For the PMMA stereoisomers, the difference in energy between the backbone and the side chain decreases with an increase in isotacticity.[6] Therefore, i-PMMA is likely to compensate local changes in conformation by cooperative motions between the backbone and the side chain. This local compensation occurs less easily in s-PMMA since ΔE_{bb} and ΔE_{sc} are more different. This interpretation is consistent with Sundararajan's RIS results. Indeed, suppressing the side-group interactions, i.e., increasing the side-chain conformational energy, will result in an increase in the tt state population, i.e., increasing the backbone conformational energy, for s-PMMA, while it will result in an increase in the tg state population, i.e., a decrease in the backbone conformational energy, for i-PMMA. Therefore, it can be concluded that there is likely cooperativity in the isotactic isomer.

Figure 4 shows the $A\nu_2/A\nu_1$ ratio as a function of temperature for a-, s-PMMA, and i-PMMA. For a- and s-PMMA, two transitions are seen at about 40 and 110 or 130 °C whereas, for i-PMMA, the curve is flat. The higher transition temperature can be ascribed to the T_g. The decrease of the $A\nu_2/A\nu_1$ ratio, for s-PMMA, at the glass transition can be related to a decrease of the backbone conformational energy relative to the chain segment conformational energy. Above the glass transition, high-energy conformations (tg) of the backbone are known to be more favored and may originate from a weaker control of the segment conformation by the backbone, leading to a decrease of the IR ratio. In contrast, for i-PMMA, the stable $A\nu_2/A\nu_1$ ratio at T_g can be ascribed to a compensation of the conformational energies that may occur between the backbone and the side chain. In other words, a conformational transition of the backbone may be energetically compensated by a side-chain rotation and vice versa.

The decrease of the $A\nu_2/A\nu_1$ ratio in the s-PMMA curve at about 40 °C (Figure 4) can be ascribed to the β relaxation, which was first observed by dielectric spectroscopy measurements[11] (i-PMMA exhibits a poorly defined transition). If side-chain reorientations are at the origin of this relaxation[12] for the mainly syndiotactic PMMA, the conformational changes induced in the side chains at the β relaxation cannot be compensated locally by equivalent energy changes of the other part of the segment. There is, therefore, a decrease of the backbone energy level relative to that of the overall chain.

Conclusion

The $A\nu_2/A\nu_1$ IR ratio of PMMA can be related to the relative conformational energy of the polymer backbone with respect to the overall energy of the chain segment. The influence of the PMMA tacticity on the chain conformation can be monitored by this ratio. For mainly syndiotactic PMMA, this ratio varies with the state of the polymer (which changes with temperature or solvent) whereas it remains constant for i-PMMA due to cooperative conformational rearrangements that maintain the same energy of its chain backbone.

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MA961913+