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Backbone and Ester Group Conformations of Stereoregular Poly(methyl methacrylate)s in the Stereocomplex

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Introduction

Although the stereocomplex of isotactic and syndiotactic poly(methyl methacrylate) (i-PMMA and s-PMMA) has been studied over decades,[1] its structure and the driving force of complexation are yet a matter of controversy. Challa et al.,[2,3] on the basis of X-ray diffraction studies, proposed a model in which the sterecomplex is built of double-stranded helixes of the complementary chains having backbone conformations close to all-trans (in the staggered approximation). In their opinion, the stereocomplex results from a good sterical fit between the two chains, stabilizing each other's conformation by weak, van der Waals forces. An alternative model of Schneider et al.,[4,5] which emerged from IR and NMR studies, resembles that of Challa et al. in the backbone conformation but for the driving force assumes relatively strong, dipolar interactions of ester groups. Besides, the two models differ greatly in the ester group conformation. In the first model, the s-ester groups alternate in cis and trans positions and the i-ester groups are in the trans state,[3] whereas in the second model, the cis−trans alternation is characteristic of the i-ester groups and the s-ester groups are in the cis state.[5] Neither model has received a sufficient experimental evidence because no solid data on the backbone and ester group conformations of stereocomplexed chains have been obtained so far.

Recently,[6] we performed a rigorous analysis of the temperature dependence of IR intensities for C−O stretching bands of PMMA, in the region 1100−1300 cm^{-1}, and found that each band represents single conformational state of the ester group or the backbone. Here, we employ the established conformational assignment for a FTIR spectroscopic evaluation of the backbone and ester group conformations of i-PMMA and s-PMMA in the stereocomplex.

Experimental Section

Samples of stereoregular PMMA with the following molecular weight characteristics and triad tacticities were used. i-PMMA: $M_w = 2.08 \times 10^5$, $M_w/M_n = 3.37$, i/h/s = 91/6/3%. s-PMMA: $M_w = 1.99 \times 10^5$, $M_w/M_n = 4.24$, i/h/s = 4/21/75%. Further details can be found in ref 6. Each polymer was dissolved in benzene at a concentration of 2% (w/v), and the solutions were mixed under continuous stirring in a 1/1 ratio. The i-PMMA/s-PMMA blend film with a thickness of 9 μm 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 about 20 h. Single-component films of i-PMMA and s-PMMA, 8 μm in thickness, were prepared in a similar way.[6]

Wide-angle X-ray diffraction (WAXD) was measured on a Rigaku automated diffractometer using Cu Kα radiation, with a scan speed of 4°/min. 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 spectra were analyzed by second derivatization in the 1050−1300 cm^{-1} region for their component compositions and peak frequencies using the Omnic 3.1a software. Lorentzian[7] curve-fitting was then performed, using the Origin 6.0 (Microcal) software, as described elsvere.[6] In each case, the quality of the fit was evidenced by the fact that the discrepancies between component frequencies obtained by second derivatization and the Lorentzian curve-fitting were below 3 cm^{-1} and for the majority of component bands amounted to less than 1 cm^{-1}. Besides, if we varied the starting positions of component bands by ±2 cm^{-1} relative to the positions obtained by second derivatization, the quantitative results of the curve-fitting (including the integrated intensities) were practically not affected, suggesting that the unique fit was obtained.

Results and Discussion

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[1] 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[8] of the blend film prepared from the 1/1 mixture was confirmed by WAXD measurements (Figure 1). 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 consisting of four major peaks at 7.9°, 11.8°, 15.7°, and 19.5° 2θ. The shape of the curve and the location of the peaks were identical to those reported by Challa et al. on solid stereocomplexes of PMMA.[9] Hereafter, the blend film under consideration will be referred to as the stereocomplex film.

The FTIR spectra of the single-component and stereocomplex films, in the 1050−1300 cm^{-1} region, with the fitted component bands are shown in Figure 2. The C−O stretching bands[10] are designated as ν_1 to ν_5 inclusive, and their spectral positions and conformational assignments are summarized in Table 1. In what follows, the integrated band areas (normalized by the area of the internal reference band at 2997 cm^{-1})[11] are considered in the order ν_1, ν_2; ν_3, ν_4; and ν_5.

Bands ν_1 and ν_2. These bands are assigned to the trans and cis conformation of ester group, respectively. In the individual films, the trans conformation strongly dominates in i-PMMA (the estimated trans fraction is 0.9), whereas in s-PMMA the cis form is preferred (the cis fraction is 0.65).[6] The ν_1 band of i-PMMA (ν_1^{iso} = 1265 cm^{-1}) is downshifted relative to that of s-PMMA (ν_1^{syndio} = 1273 cm^{-1}). The ν_1^{iso} peak shifts further to 1257 cm^{-1} on complexation, while the position of ν_1^{syndio} does not change (Table 1). The normalized intensities of ν_1^{iso} and ν_1^{syndio} bands are represented graphically in Figure 3a. The band intensities in the stereocomplex film were multiplied by 2 to account for 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 conform-

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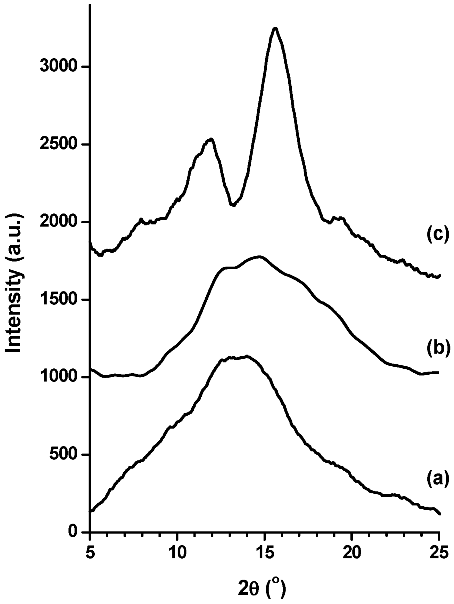

Figure 1. WAXD patterns observed with the films of (a) i-PMMA, (b) s-PMMA, and (c) 1/1 i-PMMA/s-PMMA stereocomplex.

ers for the s-ester groups. Unlike the ν_1^{syndio} band, the ν_1^{iso} band lowers its intensity (by ~30%). This change could be indicative of reduction in the trans content of i-ester groups, provided that the absorptivity of the band is not affected by complexation. However, as noticed above, the ν_1^{iso} band shifts by as much as 8 cm^{-1} upon complexation. The factor responsible for the band shift could also affect the absorptivity. We will clarify this issue after the following analysis of the band ν_2.

The position of ν_2 band is nearly the same for i-PMMA (1239 cm^{-1}) and s-PMMA (1242 cm^{-1}). In the spectrum of stereocomplex film in this range, both second derivation and Fourier self-deconvolution (not shown) reveal a singlet centered at 1240 cm^{-1}. Apparently, the individual ν_2 bands retain their positions on complexation and, thus, result in the single band composed of two unresolved components. In that case, it is reasonable to assume 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 cis content. The normalized intensities of ν_2 band for the single-component and stereocomplex films are compared in Figure 3a. 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 cis content on complexation. The marked increase in the trans content for the s-ester group, established in the above analysis of ν_1 band, must result in a proportionally high decrease in the syndiotactic cis content and, thus, cause a decrease in the intensity of the s-component of ν_2 band. So, first, we check whether this mechanism alone is sufficient to explain the reduced intensity of ν_2 band in the stereocomplex. From the temperature dependence of the intensity ratio of ν_1 and ν_2 bands,[6] 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 3a yield a value of 2.2 for the normalized intensity of ν_2 band in the stereocomplex film, under the 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.

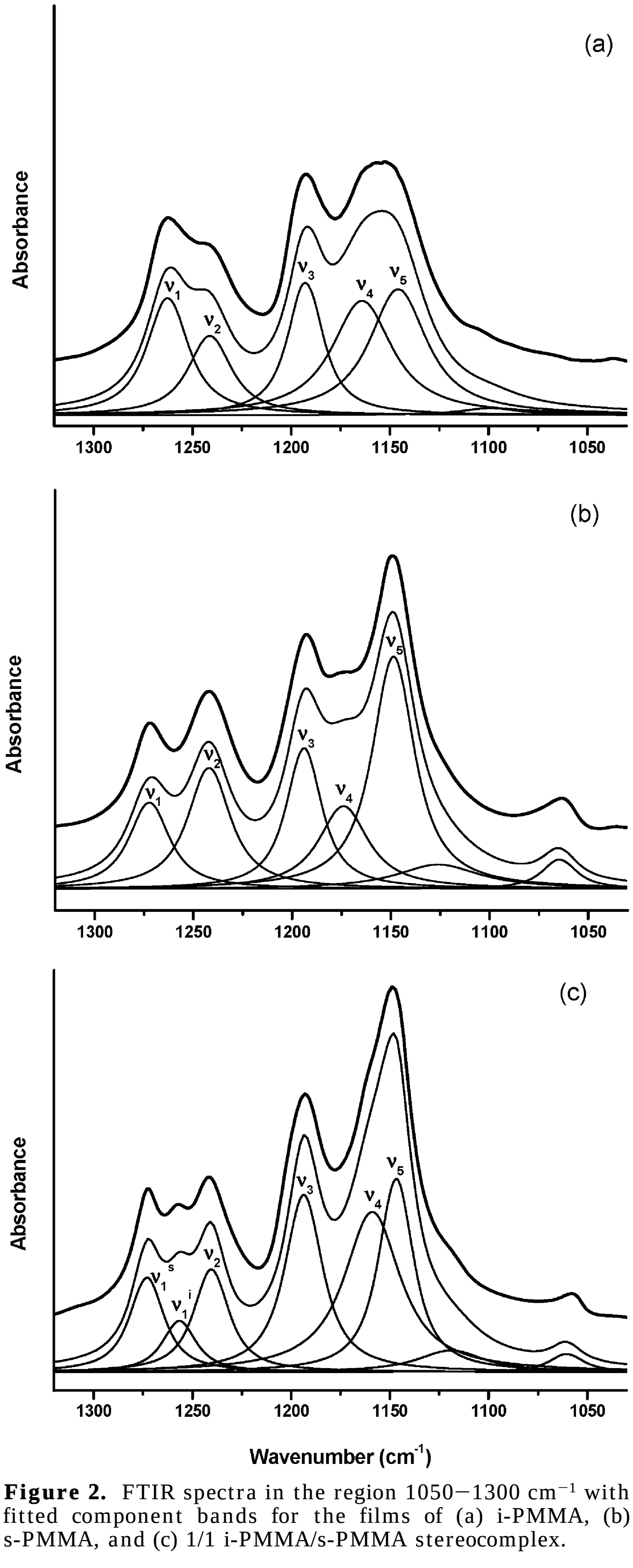

Figure 2. FTIR spectra in the region 1050−1300 cm^{-1} with fitted component bands for the films of (a) i-PMMA, (b) s-PMMA, and (c) 1/1 i-PMMA/s-PMMA stereocomplex.

Now, returning to the ν_1^{iso} band, we may conclude that its reduced intensity in the stereocomplex is due largely to a change in the absorptivity, which probably results

Table 1. Conformational Assignment of the Ester Bands in the Region 1100−1300 cm^{-1} for PMMA[6]

	frequency (cm^{-1})			conformational assignment	
band designation	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

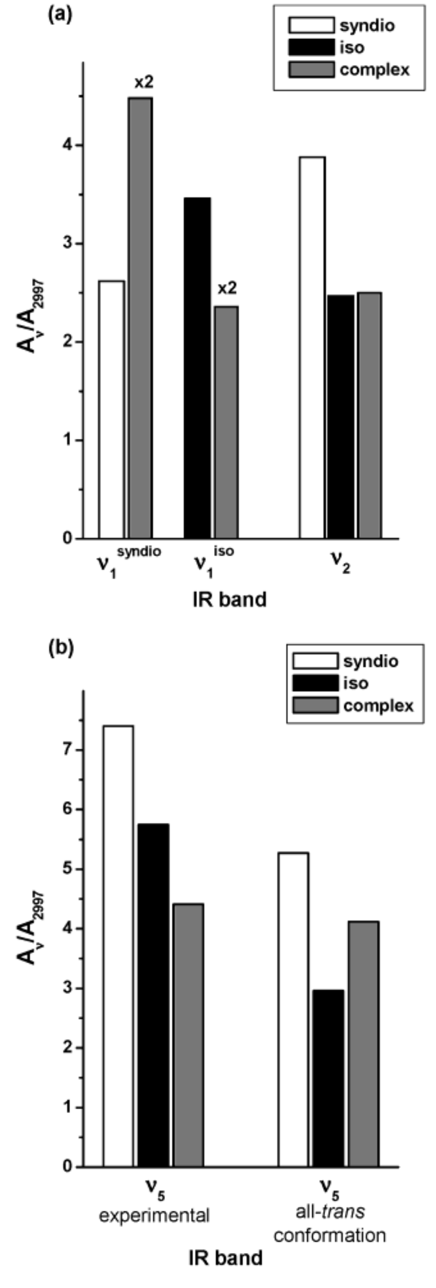

Figure 3. Comparison of the normalized intensities of the bands (a) ν_1, ν_2, and (b) ν_5 in the FTIR spectra of i-PMMA, s-PMMA and stereocomplex films. In part a, the intensity of ν_1^{iso} and ν_1^{syndio} bands in the stereocomplex film was multiplied by 2 to account for the 0.5 weight fraction of 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.

from a perturbation in the local bond environment for the i-ester groups residing in the trans state.

Bands ν_3 and ν_4. These bands are ascribed to the cis and trans conformation of methoxy group, respectively. The ν_3 band has practically the same frequency (1194 ± 1 cm^{-1}) in the spectra of all three films (Table 1). In contrast to the ν_3 band, positions of ν_4 peak in i-PMMA and s-PMMA differ by as much as 11 cm^{-1} ($\nu_4^{iso} = 1164$ cm^{-1} and $\nu_4^{syndio} = 1175$ cm^{-1}). Nevertheless, only a single band, shifted to 1158 cm^{-1}, could be resolved in this region for the stereocomplex film. Apparently, in the stereocomplex, the individual ν_4 bands come close, with a simultaneous large shift to lower wavenumbers, to give the seemingly single band. Likewise, the ν_1^{iso} band, the factor responsible for the band shift, could also affect the absorptivity. Therefore, though the normalized intensities of the ν_3 and ν_4 bands in the stereocomplex are by 30% (ν_3) and 50% (ν_4) higher than the corresponding arithmetic means for the single-component films (data not shown), interpretation of these differences remains a challenge.

Band ν_5. This band is positioned at 1147 and 1149 cm^{-1} in the spectrum of i-PMMA and s-PMMA, respectively. In the stereocomplex film, a single, narrow band at 1148 cm^{-1} is resolved in this region, indicating that the ν_5 bands of individual polymers retain their positions on complexation. As we have shown previously,[6] in both i-PMMA and s-PMMA, the band ν_5 consists of two elementary bands that coincide in the frequency (and, therefore, cannot be resolved experimentally) but differ in the absorptivity. 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 "*tt* band" is significantly lower than that of the "*tg* band". Hence, the overall intensity of ν_5 band decreases with increasing content of *tt* conformers. In the limiting case of all-trans backbone conformation, the normalized intensity of this band (A_{ν_5}/A_{2997}) is 2.96 for i-PMMA and 5.27 for s-PMMA.[6] The respective experimental values are higher than their all-trans limits (Figure 3b), indicating that *tt* states are diluted with *tg* states. The fraction of *tg* states can be estimated,[6] and the result is ~0.1, for both the i-PMMA and s-PMMA film.

In the stereocomplex film, A_{ν_5}/A_{2997} equals 4.41 (Figure 3b). This is by 30% lower than the arithmetic mean of A_{ν_5}/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_{ν_5}/A_{2997} for a hypothetical stereocomplex film consisting solely of all-trans chains, by averaging the known values of A_{ν_5}/A_{2997} for the all-trans i-PMMA and s-PMMA, and obtain $(2.96 + 5.27)/2 = 4.12$, which is by only 7% lower than the experimentally observed value. This result represents solid experimental evidence that the main-chain structure of both polymers in the stereocomplex approximates very closely the all-trans conformation.

Bandwidths. A previous IR study of PMMA stereocomplex[5] revealed narrowing of several IR bands upon

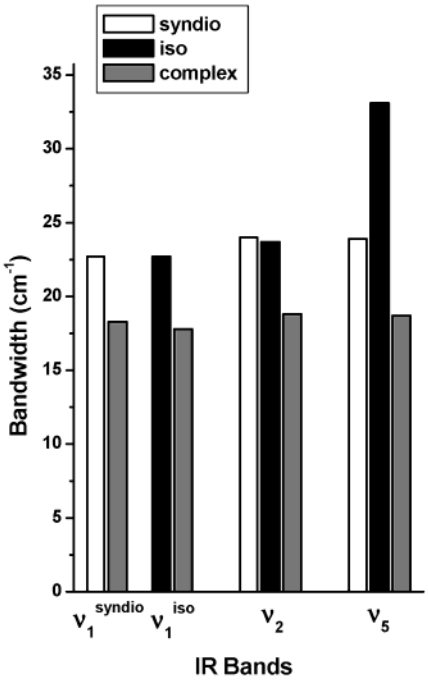

Figure 4. Half-height width for the ν_1, ν_2, and ν_5 bands in the films of i-PMMA, s-PMMA, and 1/1 i-PMMA/s-PMMA stereocomplex.

Table 2. 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	stereocomplex
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)

complexation, which was ascribed to restricted skeletal and ester group mobility. 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 4). 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,[6] 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 for 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.[6] 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.[12] 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 for 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. But then, one has to explain why such ordering does not occur in s-PMMA. The explanation can be found in a theoretical work of Vacatello and Flory,[13] which shows that there is no variation in the torsion angles of *tt* states in s-PMMA, whereas in i-PMMA there can be *tt* sequences with the torsion angles deviating from those of the lowest energy *tt* state. This feature may explain also why the width of ν_5 band in the amorphous s-PMMA film is significantly lower than in the amorphous i-PMMA film.

Conclusions

This FTIR study revealed significant changes in the conformational characteristics of i-PMMA and s-PMMA chains, occurring on complexation (Table 2). Both polymers take on all-trans backbone conformations. This observation is an experimental proof of the previously postulated main-chain structure of stereocomplexed chains.[3,5] Besides, new important details are disclosed. Namely, complexation causes a significant increase in the regularity of torsion angles for backbone 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 between i- and s-ester groups may play an important role in the stabilization of stereocomplex.

References and Notes

(1) For reviews, see: (a) Spevacek, J.; Schneider, B. *Adv. Colloid Interface Sci.* **1987**, *27*, 81. (b) Nijenhuis, K. T. *Adv. Polym. Sci.* **1997**, *130*, 1.
(2) Bosscher, F.; ten Brinke, G.; Challa, G. *Macromolecules* **1982**, *15*, 1442.
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(6) Tretinnikov, O. N.; Ohta, K. *Macromolecules* **2002**, *35*, 7343.
(7) Gaussian fitting, unlike Lorentzian, produced unreasonably high band-to-band variations in the bandwidth, indicating that the ester peaks are better approximated by Lorentzian lines.
(8) Stereocomplexation does not take place in the vicinity of the film surfaces, because i-PMMA/s-PMMA blends segregate at the surfaces, favoring the syndiotactic form. See: Tretinnikov, O. N.; Ohta, K. *Langmuir* **1998**, *14*, 915.
(9) Vorenkamp, E. J.; Bosscher, F.; Challa, G. *Polymer* **1979**, *20*, 59.
(10) While the ν_1−ν_4 bands represent “pure” stretching modes of the ester moiety, the band ν_5 is essentially mixed with C−C stretches of the backbone.[6]
(11) The absorptivity of the 2997 cm^{-1} band is independent of tacticity and conformation.[6]
(12) Stuart, B.; George, W. O.; McIntyre, P. S. *Modern Infrared Spectroscopy*, 1st ed.; John Wiley & Sons: New York, 1996.
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