*Macromolecules* 1981, *14*, 1693-1697

# Conformational Energies of Deuterated Stereoregular Poly(methyl methacrylate)

**J. M. O'Reilly,* D. M. Teegarden, and R. A. Mosher**

*Xerox Webster Research Center, Webster, New York 14580.* *Received January 16, 1981*

ABSTRACT: Conformational energies of syndiotactic, atactic, and isotactic PMMA-$d_8$ have been calculated from the temperature dependence of infrared absorbance and compared with previous results on PMMA-$h_8$ polymers. The results are in fair agreement with the model proposed for PMMA-$h_8$, in which changes in both backbone and side-chain conformations contribute to measured conformational energies. A consistently higher (600 cal/mol) side-chain conformational energy, $\Delta H_{sc}$, is observed for PMMA-$d_8$ over PMMA-$h_8$ at temperatures below $T_g$. Conformational energies reported here are discussed relative to rotational isomeric state calculations and chain dimensions to be measured by SANS. Comparisons with Gibbs–DiMarzio theory and specific heat calculations are made.

## Introduction

Previous work has demonstrated the effects of stereoregularity on the conformational energy[1] and other physical properties, such as glass transition temperature and unperturbed dimensions, of poly(methyl methacrylate). Deuteration has been historically applied to polymers to elucidate the infrared spectra through the shift in vibrational frequencies with the increase in reduced mass. Deuteration of polymers also provides the contrast in neutron scattering required to study the radius of gyration and second virial coefficient of solutions of hydrogenous and deuterated polymers in the solid state. Deuterated isotactic, atactic, and syndiotactic poly(methyl methacrylate) samples were prepared for neutron scattering measurements of unperturbed dimensions as a function of temperature.[2] These polymers were used for FT IR measurements of conformational energies of stereoregular poly(methyl methacrylate) to substantiate the previous measurements on hydrogenous polymers. We assume, as is the usual case, that the replacement of hydrogen atoms by deuterium atoms does not affect the physical properties of the chain except by increasing the mass of the hydrogen atoms. It is recognized that there are some small differences between hydrogenous and deuterated polymers, such as melting point and perhaps glass transition temperatures.

## Experimental Section

All solvents were thoroughly dried, distilled, degassed, and stored over an efficient drying agent. Inhibited methyl methacrylate-$d_8$ was passed through a short column of basic alumina under argon and twice distilled from $CaH_2$. Purified monomer, which gave an acceptable GLC trace and refractive index ($n_D{}^{20}$ = 1.4132), was used immediately.

**Syndiotactic PMMA-$d_8$.** The initiator, ethyl(pentamethyleneimino)magnesium, was prepared according to the procedure of Joh and Kotake.[3] In a typical preparation, a solution of 0.003 mol of initiator in 100 mL of toluene was transferred via a double-tipped needle under argon into a carefully dried, argon-filled crown-capped bottle, which was then cooled in a dry ice–methanol bath. Then 0.11 mol of monomer was added to the stirring toluene solution (from a syringe). At the end of the reaction, which was virtually complete in 3–5 min, the product was precipitated in 2 L of methanol containing 2 mL of HCl, filtered, washed, and dried. The crude product was then stirred with 1 L of 10% aqueous HCl, washed thoroughly with water, dried, dissolved in benzene, and freeze-dried; yield 80%.

**Isotactic PMMA-$d_8$.**[4] Sufficient $LiAlH_4$ was added to anhydrous ethyl ether to make a 0.003 M solution. With a syringe technique, 150 mL of the clear solution was transferred to an argon-filled crown-capped bottle and the solution cooled to dry ice–methanol temperature. From a syringe 0.15 mol of monomer was added and the reaction mixture was stirred at −78 °C for 22 h. The product was precipitated and purified as before; yield 50%.

**Atactic PMMA-$d_8$.** Atactic polymer was prepared by free radical polymerization and was obtained from Dr. Leslie Stanford, E. I. du Pont and Co.

**Characterization.** Intrinsic viscosities, molecular weight data, and tacticities are given in Table I. Viscosity data were obtained at 25.0 °C in chloroform. Molecular weight results were calculated from gel permeation chromatography data by means of a universal calibration method. Tacticities are expressed as triads on the basis of NMR spectra (proton spectra (400 MHz) of residual hydrogens in the perdeuterio polymers as well as deuterium spectra (61.42 MHz)) obtained on a Bruker WH-400 Fourier transform spectrometer. Spectra were obtained with nitrobenzene ($d_5$ or $h_5$) as solvent at 100–110 °C. Infrared spectra were recorded on a Digilab FTS 15B by methods previously described.[1]

## Results and Discussion

Previous work[5] has assigned the changes in carbon–hydrogen vibrational frequencies upon deuteration in the Raman and infrared spectra. The complex band series, 1000–1350 cm$^{-1}$, attributed to C–O stretching and skeletal vibrations, are sensitive to backbone and side-chain conformations. The four bands in the region 1000–1350 cm$^{-1}$ and the carbonyl stretching frequency at 1750 cm$^{-1}$ are the most sensitive to temperature. The analysis of the temperature dependence of these bands yielded conformational energies[1] for a series of stereoregular poly(methyl methacrylates). The most temperature-dependent bands were assigned to coupled vibrations among atoms on the backbone and side group which involve the C–O stretching vibration. Upon deuteration, these bands shift to different frequencies (usually lower) and may involve changes in the coupling of the different vibrations.

The changes in intensity of certain absorption bands with stereoregularity for the deuterated poly(methyl methacrylate) are illustrated in Figure 1. Differences with stereoregularity are comparable for the hydrogenous and deuterated polymers. The changes in absorbance with temperature for the syndotactic PMMA-$d_8$ are shown in Figure 2. As in the case of the hydrogenous polymers, these four major bands, plus the carbonyl band, show a strong temperature dependence. The temperature dependence and the isosbestic points are attributed to a conformational equilibria between low-energy trans–trans states and high-energy trans–gauche states. Application of the analysis described previously[1] using the van't Hoff equation yields the conformational energies listed in Table II. A van't Hoff plot for syndiotactic PMMA is shown in Figure 3. The bands at 1287/1260 and 1195/1182 cm$^{-1}$ are attributed to the backbone vibrations and the energies

---

* To whom correspondence should be addressed at Eastman Kodak Co. Research Laboratories, Rochester, N.Y. 14650.

0024-9297/81/2214-1693$01.25/0 © 1981 American Chemical Society

Table I
Characterization Data for PMMA-$d_8$

| | [$\eta$], dL/g | $M_w \times 10^{-3}$ | MWD | % tacticity, triads: isotactic | heterotactic | syndiotactic |
|---|---|---|---|---|---|---|
| isotactic | 0.43 | 115 | 2.8 | >98 | | |
| atactic | 0.46 | 124 | 2.8 | 6 | 36 | 58 |
| syndiotactic | 0.54 | 152 | 2.0 | 2 | 22 | 76 |

Table II
Conformational Energies for Syndiotactic PMMA-$d_8$ (cal/mol)

| | $T > T_g$ | $T < T_g$ |
|---|---|---|
| 1750/1725 | 1247 ± 60 | 270 ± 100 |
| 1287/1260 | 2568 ± 114 | 1471 ± 6 |
| 1195/1182 | 2033 ± 82 | 1444 ± 5 |
| 1115/1104 | 1119 ± 100 | 1428 ± 100 |
| 1091/1079 | 1330 ± 223 | 995 ± 60 |

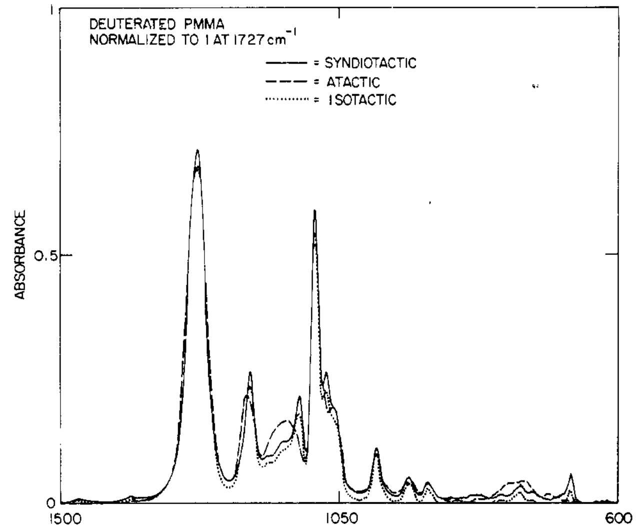

**Figure 1.** Absorbance spectra of syndiotactic, atactic, and isotactic PMMA-$d_8$.

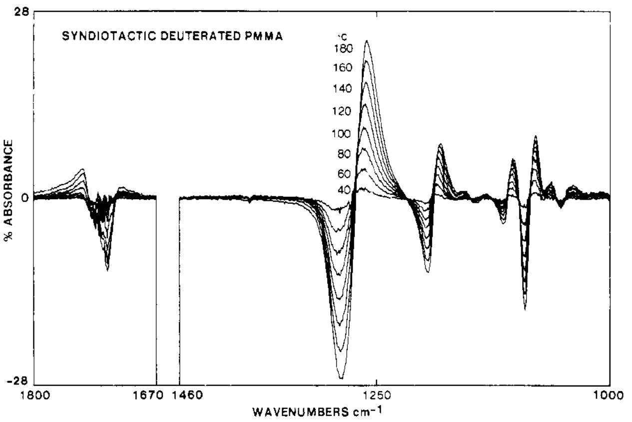

**Figure 2.** Differential absorbance spectra for syndiotactic PMMA-$d_8$ as a function of temperature. Difference spectra are absorbance at temperature indicated minus absorbance at 30 °C.

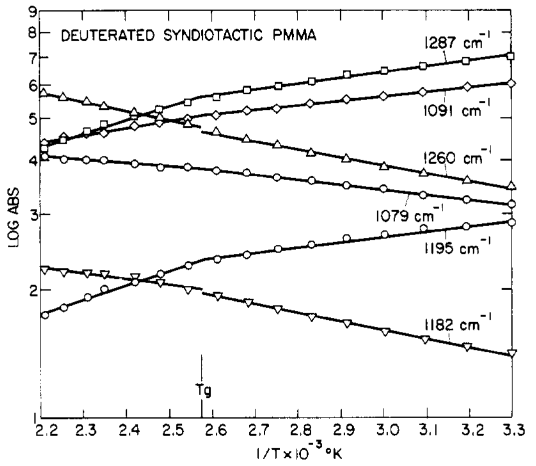

**Figure 3.** van't Hoff plot of log absorbance vs. reciprocal temperature for vibrational frequencies listed. Enthalpies calculated from slopes are indicated at temperatures above $T_g$ and below $T_g$.

are associated with changes in conformations of backbone, i.e., trans–trans to trans–gauche. These bands have the highest conformational energy for all of the stereoregular forms and, therefore, are all assigned to conformational energies of the backbone. For the hydrogenous polymers, only the highest frequency band (1276/1260 cm$^{-1}$) could be assigned to a backbone conformation. The reason both of the high-frequency band pairs of the deuterated polymers involve backbone conformations is not obvious. One reason may be that deuteration of the poly(methyl methacrylate) backbone leads to a mixing of carbon–deuterium stretching, carbon–oxygen stretching, and skeletal modes which is different from the case of the hydrogenous polymers. Normal mode calculations of Lipschitz and Gray[6] indicate that extensive mixing of vibrations is possible but more quantitative conclusions cannot be drawn at this time. The bands at 1750/1725, 1115/1104, and 1091/1079 cm$^{-1}$ are interpreted as involving the backbone and side-chain conformations, as was the case for the hydrogenous polymers. An average conformational energy 1232 ± 100 cal/mol is obtained for these bands. From these studies and other studies, the conformational energies are reproducible with ±200 cal/mol in all cases and ±100 cal/mol in favorable cases.

Below the glass transition temperature, the conformational energies should involve only changes in the side chain because the backbone conformation is frozen at $T_g$. The side-chain conformational energies are 500–800 cal/mol higher than those observed for the hydrogeneous polymers, PMMA-$h_8$, and the difference between the 995 and 1470 cal/mol energies, observed for different frequencies, is significant. The discussion of these large and unexpected energy differences will be deferred until later. Other conformational energies obtained below $T_g$ range from 995 to 1471 cal/mol. The carbonyl band at 1740 cm$^{-1}$ has a low energy, 270 cal/mol, below $T_g$, as in the case of the hydrogenous polymers.

As discussed[1] previously, the equilibrium constant can be determined from the absorptivity ratio, which is assumed to be independent of temperature. The independence of the absorptivity ratio as a function of temperature can be demonstrated by the linearity of the plot of the decreasing absorbance, $A_-(\nu)$, vs. increasing absorbance, $A_+(\nu)$ (Figure 4). The results for syndiotactic PMMA-$d_8$ are comparable to the results for PMMA-$h_8$. Values of the equilibrium constant, $K$, and the ratio of the absorptivities, $\alpha_-/\alpha_+$, are listed in Table III. These results for the absorptivity ratios $\alpha_-/\alpha_+$ range from 0.3 to 4.5,

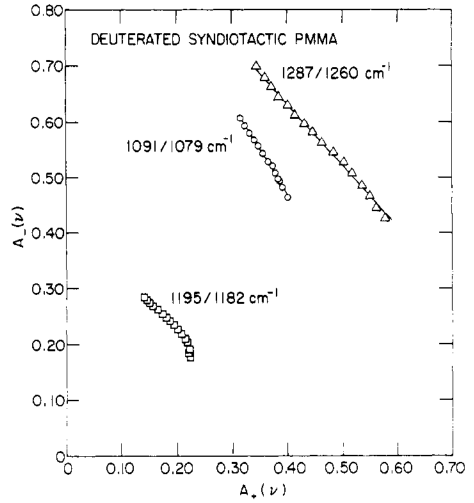

**Figure 4.** Absorbance of band of decreasing intensity (low-energy conformation) vs. absorbance of band of increasing intensity. Negative of slope equals ratio of absorptivities.

Table III
Equilibrium Constants ($K$) and Absorptivity Ratios ($\alpha_-/\alpha_+$)

| | isotactic | | atactic | | syndiotactic | |
|---|---|---|---|---|---|---|
| | $K$ | $\alpha_-/\alpha_+$ | $K$ | $\alpha_-/\alpha_+$ | $K$ | $\alpha_-/\alpha_+$ |
| 1750<br>1725 | 0.7 | 2.0 | 0.1 | 0.3 | 0.7 | 4.5 |
| 1287<br>1260 | 0.7 | 1.1 | 0.8 | 1.0 | 1.2 | 1.3 |
| 1195<br>1182 | 1.0 | 1.9 | 0.7 | 0.8 | 1.4 | 1.5 |
| 1091<br>1079 | 1.2 | 1.5 | 0.5 | 0.6 | 1.5 | 1.9 |

Table IV
Conformational Energies[a] for Atactic PMMA-$d_8$ (cal/mol)

| | $T > T_g$ | $T < T_g$ |
|---|---|---|
| 1750/1725 | 1175 | 200 |
| 1287/1260 | 2504 | 1359 |
| 1195/1182 | 2066 | 1389 |
| 1115/1104 | 1070 | 1010 |
| 1091/1079 | 1121 | 956 |

[a] Single run; estimated error ±100 cal/mol.

which agree with the values for the PMMA-$h_8$ polymers. Equilibrium constants from 0.1 to 1.5 are in the range observed for PMMA-$h_8$. A comparison of the individual values of $\alpha_-/\alpha_+$ and $K$ is consistent with the assignments of the energy levels to backbone or side-chain conformation but does not appear to offer any further information regarding the assignments.

The values of the conformational energies for atactic PMMA-$d_8$ are listed in Table IV. As expected from the high syndiotacticity from NMR measurements (Table I), the conformational energies of atactic PMMA-$d_8$ closely follow these values for the syndiotactic polymer and the remarks made above regarding syndiotactic PMMA apply. The conformational energies attributed to the backbone (1287/1260, 1195/1182 cm$^{-1}$) are higher than those for PMMA-$h_8$. The values for 1115/1104 cm$^{-1}$ are less reliable because of the partial overlap of the bands.

For isotactic PMMA-$d_8$, the difference spectra are similar to the difference spectra for syndiotactic PMMA-$d_8$ and are displayed in Figure 5. Calculated values of the conformational energies are listed in Table V. The results for isotactic PMMA-$d_8$ parallel the results for the other stereoregular polymers but the energies are systematically lower. Isotactic PMMA has a lower $T_g$ (45 °C), which precluded measurements below $T_g$. Conformational energies of the backbone are 1620 ± 100 cal/mol and significantly less than the other tactic PMMA-$d_8$. Yet, these values are significantly higher than the value for PMMA-$h_8$, 680 ± 30 cal/mol. The energies attributed to backbone and side-chain conformations (573–882 cal/mol) are slightly higher than the results for isotactic PMMA-$h_8$.

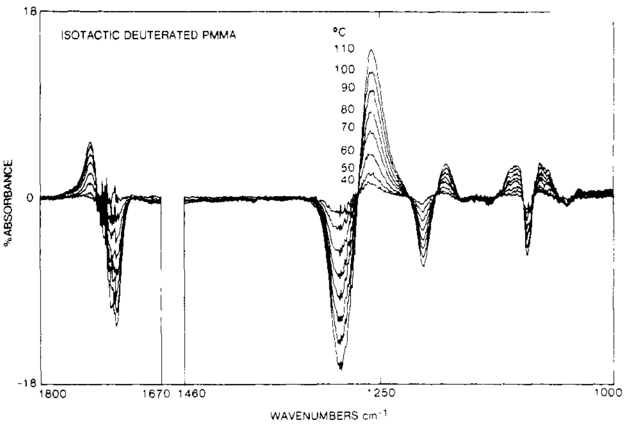

**Figure 5.** Differential absorbance spectra for isotactic PMMA-$d_8$ as a function of temperature. Difference spectra are absorbance at temperature indicated minus absorbance at 30 °C.

Table V
Conformational Energies for Isotactic PMMA-$d_8$ (cal/mol)

| | $T > T_g$ | | $T > T_g$ |
|---|---|---|---|
| 1746/1718 | 882 ± 27 | 1134/1106 | 866 ± 100 |
| 1294/1260 | 1687 ± 77 | 1092/1079 | 573 ± 46 |
| 1203/1178 | 1554 ± 106 | | |

Table VI
Conformational Energies of Stereoregular PMMA (cal/mol)

| model I | model II | syndiotactic | atactic | isotactic |
|---|---|---|---|---|
| $\Delta H_{bb}$ | $\Delta H_{bb}$ + $\Delta H_{sc}$ | 2300 ± 270<br>(2090 ± 30) | 2285 ± 220<br>(1430 ± 14) | 1610 ± 90<br>(680 ± 30) |
| $\Delta H_{bb}$ − $\Delta H_{sc}$ | $\Delta H_{bb}$ | 1232 ± 110<br>(1164 ± 80) | 1121 ± 100<br>(905 ± 70) | 750 ± 120<br>(685 ± 75) |
| $\Delta H_{sc}$ | $\Delta H_{sc}$ | 1335 ± 200<br>(835 ± 100) | 1233 ± 100<br>(650 ± 110) | a<br>a |

[a] Not measured.

The results for syndiotactic, atactic, and isotactic PMMA-$d_8$ are summarized in Table VI using the assignments previously developed for the stereoregular PMMA-$h_8$. Model I assumes that only the backbone conformations contribute to the changes in absorbance while model II assumes that both changes in backbone and side-chain conformation contribute to absorbance changes. Model I applied to PMMA-$d_8$ assumes that the 1290/1260- and 1200/1180-cm$^{-1}$ bands involve changes in backbone conformation $\Delta H_{bb}$(trans–gauche) alone, with no change in side-chain (up–down) conformation. These changes would involve trans-down ↔ gauche-down and trans-up ↔ gauche-up transitions. Vibrational frequencies which involve changes in both backbone and side-chain conformation are represented as trans-up ↔ gauche-down and are described by the energy $\Delta H_{bb} - \Delta H_{sc}$. These energies are obtained from bands such as 1750/1725, 1115/1104, and 1091/1079 cm$^{-1}$ for syndiotactic PMMA-$d_8$. Side-chain conformational energies, $\Delta H_{sc}$, are derived at temperatures below $T_g$, where the backbone conformations are frozen.

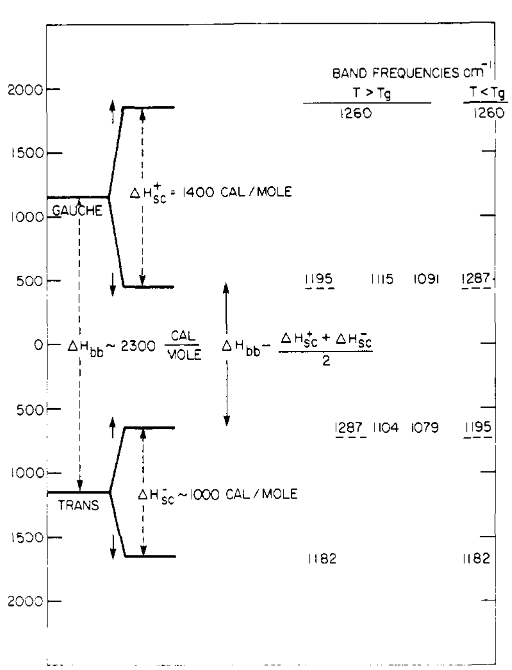

**Figure 6.** Conformational energy diagram showing backbone conformational energy $\Delta H_{bb}$ and side-chain conformational energies $\Delta H_{sc}{}^{g}$ (upper state) and $\Delta H_{sc}{}^{t}$ (lower state).

The results for syndiotactic and atactic PMMA-$d_8$ show sufficient differences to warrant refinement of models I and II, which described all the measured conformational energies of PMMA-$h_8$ in terms of $\Delta H_{bb}$ and $\Delta H_{sc}$. Differences in conformational energies measured below $T_g$, which could be attributed to conformational states of the side chains for syndiotactic and atactic polymers, are 1450 ± 50 and 995 cal/mol and 1370 ± 50 and 960 cal/mol, respectively. The differences of 455 ± 50 and 410 ± 50 could be assigned to a difference in side-chain conformational energy between the trans and gauche states of the backbone. An energy diagram illustrating such differences is shown in Figure 6. A consequence of a model with different side-chain energies dependent upon backbone conformation is that the conformational energies derived at temperatures above $T_g$ should reflect the differences in side-chain energy. The backbone conformational energies would be $\Delta H_{bb} \pm (\Delta H_{sc}{}^{g} - \Delta H_{sc}{}^{t})$ or 2500 and 2100 cal/mol. The conformational energies which involve both a change in backbone and side-chain conformation would lead to energies of $\Delta H_{bb} \pm (\Delta H_{sc}{}^{g} + \Delta H_{sc}{}^{t})/2$. The high and low conformational energies cannot be uniquely identified from these data and the designation of the high energy ($\Delta H_{sc}{}^{g}$) with the high-energy conformation of the backbone is arbitrary. For syndiotactic PMMA, the best values of $\Delta H_{bb}$, $\Delta H_{sc}{}^{g}$, and $\Delta H_{sc}{}^{t}$ are 2300, 1460, and 1000 cal/mol, respectively. For atactic PMMA, the best values of $\Delta H_{bb}$, $\Delta H_{sc}{}^{g}$, and $\Delta H_{sc}{}^{t}$ are 2285, 1375, and 960 cal/mol, respectively. Although this explanation appears plausible initially, further scrutiny reveals some deficiencies. For example, the 1195-cm$^{-1}$ band would measure the population trans-up state ($T < T_g$) and the gauche-down state for $T > T_g$. Also, the 1287-cm$^{-1}$ band would measure the population of the trans-up state and the gauche-down state. Therefore, the conformational energy differences for 1287/1260 cm$^{-1}$ (2568 ± 118 cal/mol) and 1195/1182 cm$^{-1}$ (2033 ± 82 cal/mol) are not simply due to differences in the conformational energies of the side group. Since these energy differences are outside the experimental uncertainty (±200 cal/mol) and are observed for the syndiotactic and atactic polymers, we ascribe the differences to additional backbone conformations. Since the trans–trans (tt) and trans–gauche (t$\bar{g}$) states have been considered already, additional gauche states, tg and gg, must be considered. Recent calculations of Sundararajan[7] would support this conjecture. The differences in conformational energy observed at temperatures below $T_g$ still suggest that there are measurable differences in the conformational energies of the side group. These differences in side-chain conformation, as well as at least three backbone conformations (two energy differences), must be considered to account for the energies measured for syndiotactic and atactic PMMA-$d_8$ above and below $T_g$.

The conformational energy results for stereoregular PMMA-$d_8$ are tabulated in Table VI, with results for PMMA-$h_8$ shown in parentheses. These results will be summarized in terms of model I, which considers only two backbone states and two side-chain conformational states which can be described by three measured energy differences. The most consistent and reproducible results have been obtained for the syndiotactic polymers for the conformational energies measured above $T_g$, i.e., backbone energies ($\Delta H_{bb}$) and backbone energy – side-chain energy ($\Delta H_{bb} - \Delta H_{sc}$). Atactic PMMA polymers give consistent results except for the 1276/1262-cm$^{-1}$ band of PMMA-$h_8$, which gives a lower $\Delta H_{bb}$ (1430 ± 14 cal/mol) compared to $\Delta H_{bb}$ = 2285 ± 220 cal/mol for PMMA-$d_8$. The energy of the band at 1262 cm$^{-1}$ appears suspect but careful inspection of the data reveals no reason for the discrepancy. Conformational energies derived for the isotactic polymers are limited because of the lack of data below $T_g$ and some apparent overlap of bands in the $h_8$ sample. Isotactic PMMA-$d_8$ yielded conformational energies which are almost twice the value for $\Delta H_{bb}$ for PMMA-$h_8$. Once again the low energy associated with the temperature dependence of the 1254-cm$^{-1}$ band (shifted from 1262 cm$^{-1}$ by tacticity) is suspect, but the reproducibility of the data is good. The energy associated with $\Delta H_{bb} - \Delta H_{sc}$ is equal to 750 ± 120 cal/mol for PMMA-$d_8$, which agrees with 685 ± 75 cal/mol for PMMA-$h_8$. A reproducible and perplexing result is the 500–600 cal/mol increase upon deuteration in the value of $\Delta H_{sc}$. This result is unexpected and such an effect of deuteration on conformational energy has not been reported previously. Deuteration has a measurable effect on the barrier heights in dimethyl ether as measured by microwave spectroscopy.[8] There are no direct studies of deuteration upon energy levels of small molecules which parallel our studies. One rationalization of our results could be that the potential energy curves are modified in shape and position so that the average energy is significantly different in the fully deuterated polymer.

Model II offers a partial resolution of the inconsistencies. The large effect of deuteration upon $\Delta H_{sc}$ remains. Assigning the intermediate energies to $\Delta H_{bb}$ allows the differences observed in the high energies to reflect the differences in the $\Delta H_{sc}$ with deuteration. We have previously discounted model II because it leads to low values of $\Delta H/RT_g$ and the associated change in $C_p$.

## Conclusions

Conformational energy results on stereoregular PMMA-$h_8$ were discussed with reference to chain dimensions, changes in specific heat at $T_g$, and the Gibbs–DiMarzio theory of the glass transition. No data on dimensions and specific heat are currently available for stereoregular PMMA-$d_8$ for comparison but some conclusions are possible. The values of $\Delta H_{bb}$ for stereoregular PMMA-$d_8$ lead to almost constant values of the reduced energy $\Delta H_{bb}/RT_g$, 2.95, 3.00, and 2.50 for syndiotactic, atactic, and isotactic PMMA-$d_8$, respectively, when the flex energy ($\epsilon$) of the Gibbs–DiMarzio model is identified with the conformational energy of the backbone. Since there are two bands which lead to the values of $\Delta H_{bb}$ for isotactic PMMA-$d_8$, more weight can be given to this result than to the $\Delta H_{bb}$ measured from a single band in PMMA-$h_8$. The higher value of $\Delta H_{bb}/RT_g$ is in better agreement with theory. However, the low values of $\Delta H_{bb}$ for isotactic PMMA-$h_8$ have been reproduced on several runs on the sample and on samples prepared by different polymerization techniques. All samples give low values of conformational energies and no persuasive explanation is now available. The results for the stereoregular PMMA-$d_8$ would be strong evidence supporting the Gibbs–DiMarzio theory if the uncertainty in the conformational energy of the isotactic PMMA-$h_8$ could be eliminated.

Specific heat results are not available at this time but warrant detailed investigation based upon backbone and side-chain conformational energies. One would not expect differences in the specific heat of PMMA-$h_8$ and -$d_8$ if the molar heat capacities are compared. The specific heat (cal/(g °C)) would be approximately 8% lower for PMMA-$d_8$, owing to the higher molecular weight. In order to evaluate the conformational contribution to the specific heat, the density, expansivity, and compressibility of PMMA-$d_8$ would be needed. If there were only small differences in these thermodynamic properties, then $\Delta C_p$(PMMA-$d_8$) should differ from $\Delta C_p$(PMMA-$h_8$) by less than 10%. An investigation of these expected effects upon the specific heat of PMMA-$d_8$ is planned for the future.

Studies of the dimensions of stereoregular PMMA-$d_8$ by small-angle neutron scattering (SANS) are in progress to evaluate the radius of gyration and the temperature coefficient of the radius of gyration. Because of the differences which have been observed in the temperature dependence of the infrared absorbances of stereoregular PMMA, we are alerted to look for small differences between hydrogenous and deuterated PMMA.

## Summary

Conformational energies for stereoregular PMMA-$d_8$ derived from temperature-dependent infrared absorbance measurements are interpreted in terms of different conformational states of the polymer backbone and side chain. The results are in fair agreement with the results for stereoregular PMMA-$h_8$, but significant differences remain. Backbone conformational energies for syndiotactic PMMA-$d_8$ (2033–2568 cal/mol) agree with the value (2090 cal/mol) for PMMA-$h_8$. The differences (2033–2568 cal/mol) could reflect additional conformations (gg) of the backbone. Backbone conformational energies are significantly higher for atactic and isotactic PMMA-$d_8$ than for the equivalent hydrogenous polymers. No satisfactory explanation of this result is available but the mixing of the vibrational states may change upon deuteration and lead to a sampling of different conformational states.

The temperature dependence of certain bands above $T_g$ is attributed to energy differences between backbone conformations ($\Delta H_{bb}$) and side-chain conformations ($\Delta H_{sc}$). These bands yield energy differences ($\Delta H_{bb} - \Delta H_{sc}$) which agree within experimental error for PMMA-$d_8$ and -$h_8$. At temperatures below $T_g$, the conformational energies of side chain ($\Delta H_{sc}$) can be measured because the backbone conformations are frozen. $\Delta H_{sc}$ is greater (600 cal/mol) for syndiotactic and atactic PMMA-$d_8$ than for the hydrogenous polymers.

In spite of some anomalies, the overall results are self-consistent. In order to test quantitatively the correctness of the models and the results, a comparison with independent theoretical calculations and measurements is necessary. Detailed normal coordinate calculations of isotactic and syndiotactic PMMA dyads for different conformations would provide a basis for interpreting the spectral changes with temperature and tacticity. Independent measurements of conformational energies via SANS techniques and comparisons with the rotational isomeric state calculations can provide, in principle, the most direct test of these concepts. Such measurements are in progress. Comparisons of experimental conformational energies with the predictions of the Gibbs–DiMarzio theory and with specific heat measurements provide support for the validity of the analysis.

**Acknowledgment.** We are grateful to Dr. A. Leslie Stanford and E. I. du Pont and Co. for samples of atactic PMMA-$d_8$ and methyl methacrylate monomer ($d_8$). We also thank Dr. Samuel Kaplan for obtaining NMR spectra. The advice and encouragement of Dr. Thomas Smith during the course of this work are gratefully acknowledged. This material is based in part upon support received by D.M.T. from the National Science Foundation under Grant No. SPI-7916618.

## References and Notes

(1) O'Reilly, J. M.; Mosher, R. A. *Macromolecules* **1981**, *14*, 602.
(2) O'Reilly, J. M.; Teegarden, D. M.; Wignall, G. Oak Ridge National Center for Small Angle Scattering Research, Proposal no. 35.
(3) Joh, Y.; Kotake, Y. *Macromolecules* **1970**, *3*, 337.
(4) Tsuruta, T.; Makimoto, T.; Nakayama, Y. *Makromol. Chem.* **1966**, *90*, 12.
(5) Schneider, B.; Stokr, J.; Schmidt, P.; Mihailov, M.; Dirlokov, S.; Peva, N. *Polymer* **1979**, *20*, 705.
(6) Lipschitz, I.; Gray, J. M. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1979**, *20*, 503, 516.
(7) Sundararajan, P., private communication.
(8) Groner, P.; Durig, J. R. *J. Chem. Phys.* **1977**, *66*, 1856.