Conformational Energies of Stereoregular Poly(methyl methacrylate) by Fourier Transform Infrared Spectroscopy

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ABSTRACT: Conformational energies have been determined by Fourier transform infrared (FT IR) spectroscopy for isotactic, atactic, and syndiotactic PMMA's and the results have been compared with rotational isomeric state (RIS) calculations. Results for syndiotactic PMMA by FT IR (2000 cal/mol) are in good agreement with RIS calculations (1900 cal/mol), but FT IR results for isotactic PMMA indicate a lower conformational energy (700 cal/mol). Conformational energies for the side chain vary from 700 to 900 cal/mol with tacticity. Conformational contributions to the specific heat change at the glass temperature are calculated and compared with experimental results and previous analyses. The constancy of $\Delta H/RT_g$ predicted by the Gibbs–DiMarzio theory is found not to hold. $\Delta H/RT_g$ varies from 1.2 to 2.6 with tacticity. Other factors, such as the conformation and packing of side chains, must influence the glass transition process.

Introduction

Stereoregular PMMA (isotactic and syndiotactic) polymers have been shown to have widely varying physical properties, i.e., glass transition temperature[1] (T_g), chain dimensions in Θ solvents[2] ($\langle R_0{}^2\rangle$), specific heat (C_p) and entropy,[3] and viscoelastic properties[4] (J_e). These polymers provide a unique example where changes in physical properties might be interpreted in terms of differences in molecular characteristics without interference due to other complicating factors. An important molecular characteristic, which has been identified as contributing to certain physical properties, is the conformational energy ($\Delta H = H_{tg} - H_{tt}$). Infrared spectroscopy is the time-honored method of measuring energy differences between conformational isomers[5] and has been applied to polymers.[6] The unperturbed dimensions of isotactic and syndiotactic PMMA's have been analyzed[2] in terms of the molecular geometries and the populations of conformational states which are determined by the energies. Measurements of conformational energies of stereoregular polymers by infrared spectroscopy permit a direct experimental comparison with energies derived from rotational isomeric state calculations. These measurements are the first such test of theory and experiment for polymers.

In addition, the differences in glass temperature between isotactic (T_g = 45 °C) and syndiotactic (T_g = 115 °C) polymers has been attributed by MacKnight and Karasz[7] to the conformational energy difference between the stereoisomers. This thesis can be tested by the direct comparison of reduced energies ($\Delta H/RT$ and ϵ/RT) for the stereoisomers by identifying the conformational energy (ΔH) with the flex energy, ϵ. The successful description of the dimensions and glass temperature of stereoregular polymers with their conformational energies would be a significant achievement for polymer theory and would forecast the analysis of other more complex physical properties, such as viscoelastic or relaxation properties. Progress is reported in this direction but critical questions remain.

Table I
Molecular Characterization Data for PMMA

	$[\eta]$, dL g^{-1}	M_w/M_n (GPC)	% isotactic	% heterotactic	% syndiotactic
isotactic	0.89		92	5	3
atactic	0.44	2.5		40	60
syndiotactic	0.47			23	77
atactic (ideal)[10]			22	48	30

Table II
Vibrational Assignments for PMMA (cm^{-1})

isotactic	syndiotactic	
2995		ν_a(C—H)
2948		ν_s(C—H)
1750		ν(C=O)
	1485	$\delta_a(\alpha\text{-CH}_3)$
1465	1450	$\delta(\text{CH}_2)$, $\delta_a(\text{CH}_3\text{—O})$
	1438	$\delta_s(\text{CH}_3\text{—O})$
	1388	$\delta_s(\alpha\text{CH}_3)$
	1270	$\delta_s(\alpha\text{CH}_3)$
1260		ν_a(C—C—O)
1252		coupled with ν(C—O)
	1240	
1190	1190	skeletal
1150	1150	
996	988	$\gamma_r(\text{CH}_3\text{—O})$
950	967	$\gamma_r(\alpha\text{-CH}_3)$
759	749	$\gamma(\text{CH}_3)$ + skeletal

Experimental Section

The infrared spectra were recorded on a Digilab FTS 15-B, using a resolution of 1 cm^{-1} with 256 scans. Polymer films (2–6 μm) were cast onto KBr windows and mounted in a Beckman RIIC temperature cell. Temperature was monitored with a chromel-alumel thermocouple and controlled to ±0.5 °C during interferogram collection. Maximum absorbance was adjusted to 0.6–1.0 by dip coating the sample except in some cases where the carbonyl band absorbance at 1760 cm^{-1} reached 1.4. Several thicknesses on some samples were run to check the effect of thickness and to investigate the weaker bands. There was no dependence of ΔH on film thickness within the experimental uncertainty. The samples of stereoregular polymer were obtained from previous work[3] or were synthesized by methods described in the literature for isotactic[8] and syndiotactic[9] polymers. A sample of nearly ideal atactic PMMA was included in the study through the generosity of Dr. D. J. Plazek.[10] Triad distribution by proton NMR analysis and molecular weight characterization by intrinsic viscosity and GPC are given in Table I.

Results and Discussion

The infrared spectra of PMMA[12-14] have been recorded and analyzed by several workers and many band assignments are available. No detailed normal-coordinate calculation has been made for the amorphous polymer but

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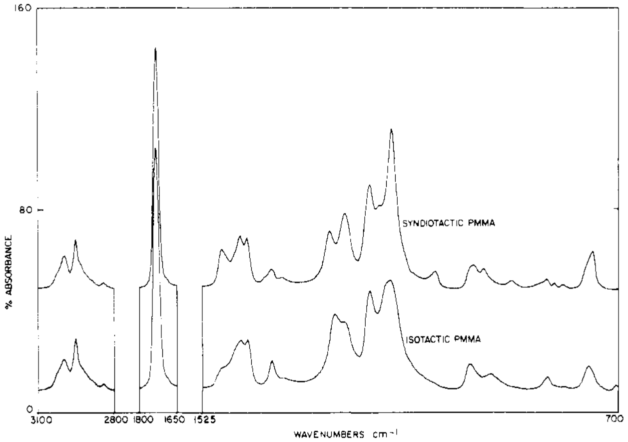

Figure 1. Infrared absorbance of syndiotactic and isotactic PMMA's (3100–700 cm^{-1}).

a preliminary analysis has been reported.[15] Bands which are sensitive to tacticity are illustrated in the absorbance spectrum shown in Figure 1. Nagai[12] has made assignments of stereoregular PMMA based upon deuterium substitution and group frequencies (Table II). Havriliak and Roman[13] analyzed the bands between 1050 and 1300 cm^{-1} by allowing for different conformational environments of the ester side group with temperature-dependent populations. More recently, Schneider and co-workers[14] have reanalyzed the C–H stretching and deformation vibrations in the infrared and Raman spectra of deuterated stereoregular PMMA's. They confirm Nagai's assignments but no new information about the interesting 1050–1300-cm^{-1} region was reported. Schmidt, Schneider, Dirlikov, and Mihailov[16] have measured changes in intensities of atactic PMMA and its deuterated analogues. Changes in intensities with temperature may be caused by intermolecular interactions, by changes in conformational populations, by complications of Fermi resonance, or by the dynamics of molecular groups. These authors attributed the temperature-dependent intensities of the asymmetric O–CH$_3$ vibration (1450 cm^{-1}) to mobility about the O–CH$_3$ bond.

With the advent of Fourier transform methods and the associated computer-assisted analysis, intensities of infrared bands can be measured with high precision, in most cases better than 0.005 absorbance. These methods are applied to the stereoregular forms of PMMA and interpreted in terms of conformational populations which are temperature dependent. It is important to remember that this is our initial premise. The analysis of the temperature dependence of polymer spectra is at an early stage and information on temperature-dependent processes other than conformational equilibria is not well documented even for simple molecules. The interpretation we will present after analysis of the temperature-dependent spectra is consistent with the experimental observations, but this interpretation does not preclude other interpretations based upon other assumptions or processes.

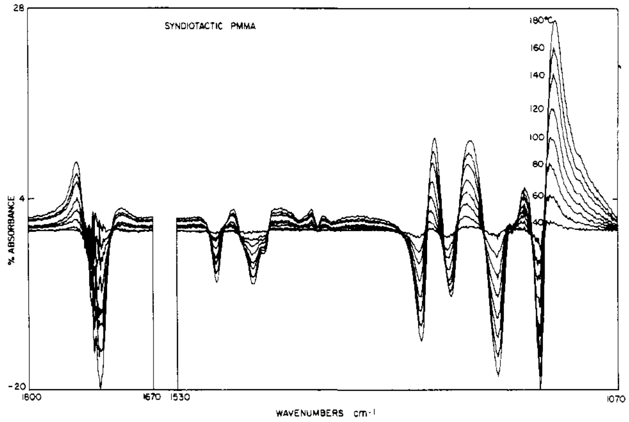

Figure 2. Difference spectra of syndiotactic PMMA at 20 °C intervals.

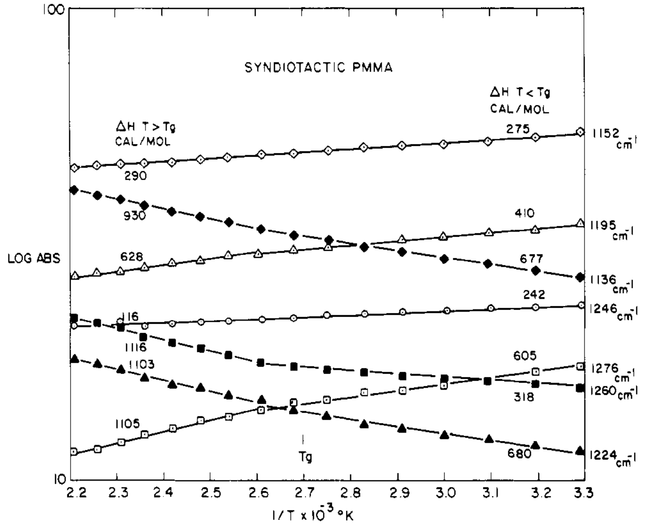

Figure 3. van't Hoff plot of log absorbance vs. reciprocal temperature for vibrational frequencies listed. Enthalpies calculated from slopes are indicated at temperature above T_g and below T_g.

Analysis of Spectra

The difference spectra were plotted in Figure 2 as the absorbance at temperature T minus the absorbance at starting temperature (30 °C). No corrections were applied to the data. Changes in apparent absorbance due to changes in sample thickness are estimated to be less than 1–2% over the temperature range 30–180 °C. Only small changes (<1%) in some bands, such as ν(C–H) at 2930 and 2995 cm^{-1}, support this estimate. The samples showed little change in absorbance after each thermal cycle, which suggests that changes in absorbance from other causes are not significant. From the differential absorbances (Figure 2) and the peak absorbances at these frequencies, tables of absorbances as a function of temperature were prepared. These data were analyzed by using the van't Hoff equation and plotted as shown in Figure 3. For these measurements, we obtained more consistent results by using peak heights rather than integrated intensities. In the future, an analysis of the band shapes as a function of temperature is planned when the computer program is available.

We use the convention of assigning an energy defined by the equation

$$h_{\pm} = -R\ \partial \ln A_{\pm}(\nu)/\partial(1/T) \tag{1}$$

The bands which increase in intensity, $A_+(\nu)$, or decrease in intensity, $A_-(\nu)$, yield the energies h_+ and h_-, respectively. The van't Hoff energy is defined as

$$\Delta H = h_+ - h_- \tag{2}$$

$$= -R\ \partial[\ln \{A_+(\nu)/A_-(\nu)\}]/\partial(1/T) \tag{3}$$

$$= -R\ \partial \ln K/\partial(1/T) \tag{4}$$

The equilibrium constant is defined by

$$K = [A_+(\nu)/\alpha_+]/[A_-(\nu)/\alpha_-] \tag{5}$$

where $A_{\pm}(\nu)$ and $\alpha_{\pm}$ are the peak absorbances and extinction coefficients of the increasing and decreasing bands, respectively.

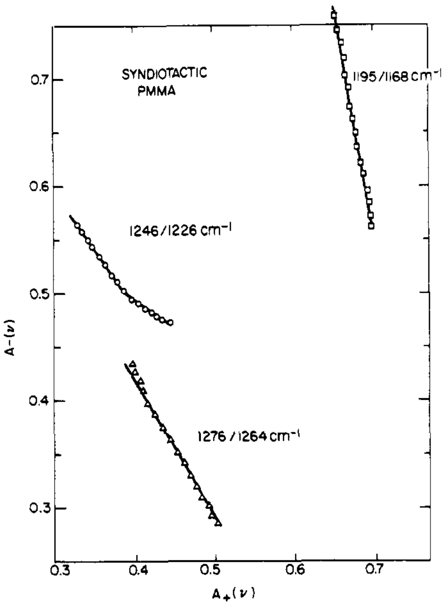

Figure 4. Absorbance of band of decreasing intensity vs. absorbance of band of increasing intensity. The slope is equal to the ratio of extinction coefficients. Syndiotactic PMMA 1276/1264-, 1246/1226-, and 1195/1168-cm^{-1} bands.

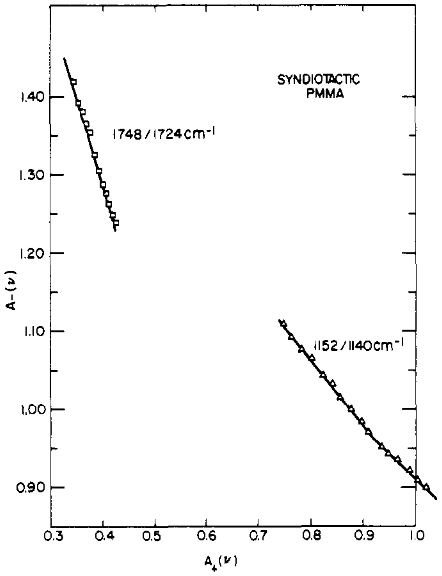

Figure 5. Absorbance of band of decreasing intensity vs. absorbance of band of increasing intensity. The slope is equal to the ratio of extinction coefficients. Syndiotactic PMMA 1748/1724- and 1152/1140-cm^{-1} bands.

Table III
Conformational Energies for Syndiotactic PMMA (cal/mol)

frequency, cm^{-1}	sample/run				ΔH_{av}
	1/1	1/2	2/1	2/2	
		A. $T > T_g$			
1748	795	842	601		1227 ± 115
1724	363	384	395		
1276	1061	1105	1054	1073	2000 ± 222
1264	1169	1116	535	888	
1246	55	116	264	266	1124 ± 170
1226	1213	1102	664	816	
1195	643	628	742	979	1008 ± 136
1168	338	368	150	185	
1152	402	290	450	449	1261 ± 138
1140	999	929	676	848	
		B. $T < T_g$			
1748		75	310		354 ± 160
1724		119	203		
1276	710	605	604	520	950 ± 129
1264	365	318	380	298	
1246	310	241	337	286	880 ± 118
1226	698	680	482	487	
1195	395	410	457	519	604 ± 45
1168	190	187	116	143	
1152	326	273	337	287	950 ± 108
1140	750	677	524	625	

Many of the bands show a change in temperature dependence (conformational energy) at the glass transition temperature, so the energies were calculated for temperatures above and below T_g. In some cases, the energy was found to be the same above and below T_g. The causes and significance of this observation will be discussed later. All energies were calculated by linear regression analysis. The regression coefficient was between 0.98 and 0.99 except where the energies approach the experimental uncertainty (i.e., ±200 cal/mol).

An additional test[10] of the assumption that the extinction coefficient is independent of temperature can be applied by plotting $A_-(\nu)$ vs. $A_+(\nu)$. If a linear curve is obtained, then the extinction coefficients are independent of temperature or have the same temperature dependence. Such a result is obtained for the bands as shown in Figures 4 and 5. From the slope of the curves, the ratio of extinction coefficient α_+/α_- can be obtained. Knowing α_+/α_- permits the calculation of ΔF, the free energy change, and the entropy change from the equations

$$\Delta F = -RT \ln K \qquad (6)$$

$$\Delta S = [\Delta H - \Delta F]/T \qquad (7)$$

The uncertainty in ΔH and ΔF is such that a detailed discussion of ΔS is unwarranted at this time. However, this method of estimating ΔS and the degeneracy of conformational states deserves further attention. Table III lists the van't Hoff enthalpies for syndiotactic PMMA which we will refer to as conformational energies. We are assuming that the major and dominant cause of the temperature dependence of intensities is the conformational equilibria between trans–trans (tt) and trans–gauche (tg) states. The well-defined isosbestic points are clear evidence of an equilibrium process, which we assign to a conformational equilibrium. Note, also, that any shifts in peak position are small, less than 1–2 cm^{-1} over the entire temperature range. Changes in intensity due to changes in band frequencies or line widths with temperature are not larger than 10% and contribute to the fundamental uncertainties in the conformational energy. We will adopt the convention[2] that the lowest energy conformation of PMMA is tt and measured by $A_-(\nu)$ and the high-energy conformation is tg and measured by $A_+(\nu)$. The ΔH's are listed at several frequencies for two separate samples and two runs on each sample. The error limits reported are the mean deviation.

The conformational energies (van't Hoff enthalpies) are largest (2000 cal/mol) for the 1276/1264-cm^{-1} bands and range from 1080 to 1283 cal/mol for the 1195/1168- and 1152/1140-cm^{-1} bands. The carbonyl band yields a ΔH of 1127 cal/mol.

Below T_g the ΔH's range from 605 to 950 cal/mol. The experimental uncertainties are between ±100 and ±200 cal/mol. These errors are larger than would be expected for an error in absorbance $\delta A = 0.005$, $\delta A/A \sim 1$–5%, and temperature $\delta T/T = 0.2\%$. Typical errors expected for

Table IV
Conformational Energies for Atactic PMMA (cal/mol)

band frequency, cm^{-1}	$T > T_g$	$T < T_g$
1750/1725	970 ± 85	300 ± 10
1276/1262	1426 ± 14	800 ± 50
1243/1226	920 ± 70	630 ± 30
1195/1168	840 ± 40	450 ± 10
1153/1140	893 ± 70	710 ± 50

Table V
Conformational Energies for Atactic (Ideal) PMMA (cal/mol)

band frequency, cm^{-1}	$T > T_g$	$T < T_g$
1751/1725	1145 ± 125	200 ± 100
1273/1258	2360 ± 15	870 ± 60
1243/1226	1220 ± 10	890 ± 60
1197/1170	band overlap	band overlap
1151/1134	1060 ± 170	790 ± 6

Table VI
Conformational Energies for Isotactic PMMA (cal/mol)

band frequency, cm^{-1}	$\Delta H\ (T > T_g)$
1747/1724	680
1270/1254	720 ± 20
1242/1226	( ) (350)
1197/1174	( ) (350)
1165/1132	( ) (535)

ΔH would be ±1–5% or ±50 cal/mol. Reasons for the larger uncertainties are not apparent but may be due to changes in line shape with temperature.

The difference spectra and the derived conformational energies for the atactic polymer are similar to the results for the syndiotactic polymer. Conformational energies are listed in Table IV. Most of the energies are lower for the atactic polymer. The deformation frequencies $\delta(C-CH_3)$ at 1489, 1450, 997, and 969 cm^{-1} show a temperature dependence for the atactic polymer which is quite low (300 ± 100 cal/mol). There is very little evidence for an increase in absorbance due to the population of high-energy (gauche) states at these frequencies. Therefore, the temperature dependence associated with these bands may be due to intermolecular or dynamic effects. Results on ideal atactic PMMA were similar to the results on atactic PMMA and are tabulated in Table V. The conformational energies above T_g for the ideal sample are all higher than the corresponding values for the atactic. This result is surprising because of the expected trend with syndiotactic and heterotactic dyads, syndiotactic > atactic > ideal atactic > isotactic.

Difference spectra in isotactic PMMA are shown in Figure 6 and conformational energies are listed in Table VI. The weak temperature dependence of the important bands at 1242, 1174, and 1165 cm^{-1} prevents the calculation of a conformational energy difference for the band pairs. It is possible that there is some band overlap in this region which leads to cancellation of positive and negative changes in band intensities. Even with the loss of information in this region, the conformational energies of isotactic PMMA are significantly lower than for the atactic and syndiotactic polymers. Allowing for a maximum energy of 200 ± 200 cal/mol for the energy of the indeterminate bands (1242, 1174, and 1165 cm^{-1}), the derived conformational energies for all the bands would range between 550 and 750 cal/mol. Measurements could not be extended below the glass temperature because the cryogenic facilities were not set up.

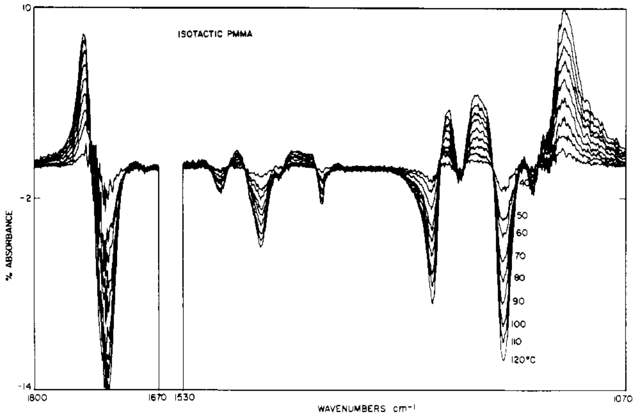

Figure 6. Difference spectra of isotactic PMMA at 10 °C intervals. Absorbance spectrum at temperature T minus spectrum at 30 °C.

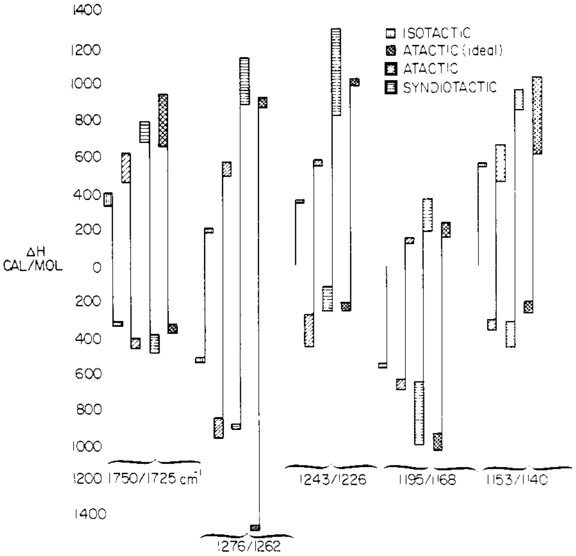

Figure 7. Conformational energies of isotactic, syndiotactic, atactic, and atactic (ideal) PMMA's from indicated vibrational bands.

In order to interpret the conformational energies as a function of tacticity, a graph of the energies is presented in Figure 7. Since a range of energies is measured, it is necessary to consider conformational energy states of the chain backbone (trans and gauche) (ΔH_{bb}) and the side group (two orientations denoted as up and down) (ΔH_{sc}). Therefore, four conformational energy levels are needed to describe the system. The problem at hand is to describe the observed energies with the two energy differences (ΔH_{bb} and ΔH_{sc}). There are two ways of assigning the observed energies to the conformational states of backbone and side chain. It is important to remember in this discussion that a measurable temperature dependence results from the two states (i.e., trans and gauche) having resolvable (larger than a few cm^{-1}) vibrational frequencies whose intensity changes with temperature. If there is no difference in the vibrational frequencies for the conformers, then no temperature dependence will be observed. There would also be no temperature dependence in the fortuitous case where the energy difference between conformers is small (50–100 cal/mol). The conformational energy derived from the 1276/1264-cm^{-1} band pair is the highest and

Table VII
Conformational Energies for PMMA (cal/mol)

model I	model II	syndiotactic	atactic	ideal	isotactic
ΔH_{bb}	$\Delta H_{bb} + \Delta H_{sc}$	2000 ± 222	1430 ± 15	2360 ± 15	680 ± 30
$\Delta H_{bb} - \Delta H_{sc}$	ΔH_{bb}	1164 ± 80	905 ± 70	1140 ± 80	685 ± 75
ΔH_{sc}	ΔH_{sc}	835 ± 100	650 ± 110	850 ± 60	not measd

is most probably associated with changes in conformation of the backbone (trans–gauche). The four sets of bands at 1748/1724, 1246/1226, 1195/1168, and 1152/1140 cm^{-1} give an average value of 1164 ± 80, 905 ± 65, and 685 ± 75 cal/mol for the syndiotactic, atactic, and isotactic polymers, respectively. Below the glass transition temperature, the conformational energies derived for the four bands from 1276 to 1136 cm^{-1} are 845 ± 100 and 650 ± 110 cal/mol for the syndiotactic and atactic polymers. No values were measured for the isotactic polymer below T_g because of the closeness of T_g to room temperature. Since the backbone conformations are presumed to be frozen in at temperatures below T_g, we assume that conformational energies derived at temperatures below T_g refer to changes in conformation of the side group. Therefore, the intermediate values of the energies (1246–1140 cm^{-1}) must be associated with changes in both backbone and side group. Then the states involved are trans–up ↔ gauche–down (model I) and the conformational energies are $\Delta H_{bb} - \Delta H_{sc}$. A summary of these values is given in Table VII.

An alternative explanation of observed results is that the higher energy derived from the 1276/1260-cm^{-1} bands involves both changes in backbone and changes in side group (trans–down ↔ gauche–up) (model II); i.e., $\Delta H = \Delta H_{bb} + \Delta H_{sc}$. The conformational energies derived from the measurements below T_g still yield ΔH_{sc}. The other bands (1244–1136 cm^{-1}) would involve changes in backbone alone (i.e., trans–down ↔ gauche–down and trans–up ↔ gauche–up). This assignment is equally consistent with the experimental results. The results of model I are more consistent with our interpretation of other data favoring the larger ΔH_{bb}. There are some shortcomings in these explanations. The carbonyl band shows only a weak dependence at temperatures below T_g but would be expected to show a well-defined ΔH_{sc}. Similarly, model II would assign the temperature dependence of the carbonyl band above T_g to the differences in energy of backbone conformations. Although there may be some mixing of the vibrational states, these changes appear to be too large to be due to such a cause. We have chosen to interpret these results in terms of a minimum number of backbone and side-chain conformations necessary to describe the temperature dependence of intensities above and below T_g. Additional conformations of the backbone are possible and should be considered when they can be identified by normal-coordinate calculations, rotational isomeric state calculations, or, as required, by additional temperature-dependent bands.

The values of the equilibrium constant defined by eq 5 and calculated from the data are listed in Table VIIIA. The ratios of α_-/α_+ range from 0.3 to 5.0 (Table VIIIB) and are in the range expected from other studies. Because of the relatively large errors associated with K, only qualitative statements about the observed trends are in order. Equilibrium constants from 0.3 to 1.0 are reasonable for the bands at 1750/1725, 1244/1224, and 1151/1136 cm^{-1}, with a tendency favoring the high-energy state as the tacticity changes from syndiotactic to isotactic. Larger values of K are calculated from the bands at 1276/1260 and 1195/1167 cm^{-1}, which indicates that entropic factors are favoring the high-energy state in spite of the enthalpy differences.

Table VIII

A. Equilibrium Constants (K)

frequency, cm^{-1}	isotactic	atactic	syndiotactic	atactic (ideal)
1750/1725	1.0	0.8	0.6	0.1
1276/1260	3.4	1.5	1.1	1.3
1244/1224		0.6	0.3	2.2
1195/1157		4.5	3.1	
1151/1136		0.6	0.4	1.6

B. Extinction Coefficient Ratios (α_-/α_+)

frequency, cm^{-1}	isotactic	atactic	syndiotactic	atactic (ideal)
1750/1725	1.8	2.5	2.0	0.5
1276/1260	2.2	1.2	0.8	1.0
1244/1224		0.8	0.4	3.4
1195/1167		4.3	2.6	
1151/1136		0.7	0.5	2.4

Table IX
Comparison of Conformational Energies (cal/mol)

	RIS calculations	FT IR
isotactic	1330 (550–2200)	720 ± 200
atactic		1430 ± 200
syndiotactic	1930 (1700–2300)	2000 ± 200

Comparison with Other Results

Rotational Isomeric State Calculations. Sundararajan and Flory[2] have calculated energy differences between conformations of pure isotactic and syndiotactic PMMA. Their results and the results of this study are listed in Table IX. For the syndiotactic polymer, the results agree within the theoretical and experimental uncertainties. One must bear in mind that the experimental results are for polymers of defined but not 100% syndiotacticity or isotacticity. The theoretical calculations refer to the pure, tactic polymer and can be extended to polymers of specific tacticity. Although the tacticity is high, the results for the isotactic polymer are less satisfactory. The spectroscopic results for isotactic polymer are based on a minimum number of bands but are consistent with the overall interpretation. Rotational isomeric state calculations for the isotactic polymer are more sensitive[17] to the parameter σ, which accounts for the distance dependence (range) of the conformation-dependent polymer–solvent interaction. The range of values of the calculated conformational energy differences encompasses our experimental result but more work is necessary to reduce the margin of error to within the experimental uncertainty.

Direct spectroscopic measurements of side-group conformational energies have shown them to be comparable to energy differences in backbone conformations. In the rotational isomeric state calculations, the side chain was in a particular conformation. It is expected[18] that varying the side-chain conformation will have a significant effect on the calculated conformational energy of the backbone. The results for the atactic polymer are intermediate between those for the isotactic and syndiotactic polymers.

One qualification which must be made about this comparison is that the spectroscopic results are for bulk polymer and the solution properties are derived under Θ conditions. It has been demonstrated repeatedly[19] that dimensions in the bulk are equivalent to dimensions in Θ

Table X[a]

	syndio-tactic	atactic	isotactic
$\Delta C_p(T_g)$, J/(g K)	0.30	0.30	0.40
$\Delta C_{p\,\mathrm{hole}}$, J/(g K)	0.19	0.19	0.25
$(\Delta C_p - \Delta C_{p\,\mathrm{hole}})/R$ (per backbone bond)	1.14	1.14	1.50
$\Delta C_{p\,\mathrm{conf}}/R$			
backbone (calcd)	0.76	0.65	0.29
side chain (calcd)	0.22	0.18	0.23
total (calcd)	0.98	0.83	0.52

[a] $\Delta C_{p\,\mathrm{conf}} = (x)^2 f(1-f)$; $x = (\Delta H/RT)$; $f_{\mathrm{bb}} = 2e^{-x}/(1 + 2e^{-x})$; $f_{\mathrm{sc}} = e^{-x}/(1 + e^{-x})$.

conditions. The comparison[20] of observed and calculated ^{13}C NMR chemical shifts and the solution property determination of statistical weight parameters also show agreement. We would prefer to demonstrate the equivalence of conformational energies derived from methods sensitive to short-range interactions (spectroscopy) with energies derived from long-range properties (dimensions from SANS (small-angle neutron scattering)) for polymers in the bulk. Such an investigation is in progress.[21] The agreement between spectroscopic measurements and rotational isomeric state calculations is sufficiently appealing to warrant more detailed calculations and experiments.

Specific Heat Calculations. The change in specific heat at the glass transition[22–25] can be broken down into a volume (hole)-dependent term, a conformational term, and perhaps other terms.[26] The magnitude of the terms has been the subject of several papers. We have suggested that a method of assessing these terms is through the direct measurements of conformational energies. The measured values of conformational energies are used to calculate $\Delta C_{p\,\mathrm{conf}}$ for isotactic, atactic, and syndiotactic PMMA's and are displayed in Table X along with $\Delta C_{p\,\mathrm{hole}}$ and $\Delta C_p(T_g)$. Additional contributions to ΔC_p can be assessed by the difference $\Delta C_p - \Delta C_{p\,\mathrm{hole}} - \Delta C_{p\,\mathrm{conf}}$, which is the observed ΔC_p minus the calculated volume contribution and the conformational contribution calculated from the spectroscopically measured energies. From the results in Table X, the additional contributions to the change in specific heat for the syndiotactic polymer are negligible, less than 20%, which is the uncertainty in the calculations. For the atactic polymer, the difference is more significant, $\Delta C_p/R = 0.31$ or 30%, and additional contributions may be present; but the uncertainty is comparable with the experimental uncertainty. In the case of the isotactic polymer, the deficit in the calculated ΔC_p is experimentally well established. $\Delta C_v/R$ could be uncertain by 0.3. The conformational energy cannot be significantly larger than 700 cal/mol and, therefore, the maximum $C_{p\,\mathrm{conf}}$ is $0.3R$. Thus, these results support the thesis that there are additional contributions to ΔC_p. One problem which is often ignored in these calculations is the experimental uncertainty in ΔC_p (±0.01 J/(g K)) and in ΔC_v (±20%) (±0.04 J/(g K)), which lead to uncertainties in the $\Delta C_{p\,\mathrm{conf}}$ of ±0.05 J/(g K). The uncertainty of the conformational energies by FT IR and any other method is 10–20%, which leads to uncertainties in the calculated ΔC_p of 20–40% because of the dependence on $(\Delta H/RT)$.[2] Interpretation of differences $\Delta C_p - \Delta C_{p\,\mathrm{hole}} - \Delta C_{p\,\mathrm{conf}} < 0.02R/\mathrm{mol}$ is unwarranted by the experimental data.

The inclusion of contributions of the side-chain conformations to the specific heat is not totally consistent with the spectroscopic results because the side-chain populations are not frozen out at T_g. Conformational equilibration of the side chain below T_g is inferred from the continuous variation of absorbance with temperature. The results of model II would lead to values of $\Delta C_{p\,\mathrm{conf}}/R = 0.48$ and 0.34 for syndiotactic and atactic PMMA's, respectively, and the values for isotactic PMMA would not change. Because of the agreement with the RIS calculations, we favor model I. On the basis of specific heat data[3] and observations on vibrational spectra, we do not think that there are large contributions to entropy and specific heat from anharmonic effects or changes in vibrational frequencies at the glass temperature. The origin of these other contributions to ΔC_p remains unclear. In these results, the influence of chain conformation and holes (free volume) on the thermodynamic properties, entropy, enthalpy, and specific heat may involve, in addition to linear terms, cross terms due to interactions of volume and conformation-dependent properties.

Glass Transition and Conformational Energy. The stereoregular PMMA polymers represent a significant test of the idea promulgated by Gibbs and DiMarzio[27] that conformational energies are a primary factor in determining the glass temperature of a polymer. MacKnight and Karasz[17] applied these concepts to explain the differences in T_g with stereoregularity in polymers which contain double substituted carbon atoms in the backbone. If the intermolecular interactions between chain segments do not depend on tacticity, then the glass temperature differences should correlate directly with differences in conformational energies. More explicitly stated in the Gibbs–DiMarzio formalism, if $\Delta S_{\mathrm{iso}}(T_g) = \Delta S_{\mathrm{syn}}(T_g) = \Delta S_{\mathrm{atactic}}(T_g)$ and the hole configurational entropy is not dependent on tacticity, then ΔS is only a function of $(\Delta H/RT)$. Then

$$(\Delta H/RT_g)_{\mathrm{isotactic}} = (\Delta H/RT_g)_{\mathrm{atactic}} = (\Delta H/RT_g)_{\mathrm{syndiotactic}} = \mathrm{constant}$$

For model I, $\Delta H/RT_g = 2.6$, 1.9, and 1.1 for syndiotactic, atactic, and isotactic polymers. Clearly $\Delta H/RT$ is not constant. Reduced energies derived from model II are lower and also not constant. Independent estimates[28] of $(\Delta H/RT_g)$ are in the range 1.8–2.3. Syndiotactic and atactic polymers are within this range. Isotactic polymer, which has the lower T_g, has an even lower conformational energy. As far as we can assess, this is the clearest case of the lack of constancy of $\Delta H/RT$. The only explanation is that some of the assumptions are not valid. The density of the polymers in the liquid state above T_g is different by 0.5%, so there may be differences in the intermolecular and configuration-dependent properties. In the case of the isotactic polymer, the side-chain conformations differ as much in energy as do the backbone conformations. Therefore, the packing and arrangement of the side groups may be an important factor in the determination of T_g. The entropy of a polymer liquid must consist of a hole configuration term, a conformation term including backbone and side chain, and a term which accounts for the interdependence of the volume and conformational terms. It is not unexpected that simple theoretical models do not describe the complicated behavior of real, well-defined polymers. Yet it is important to demonstrate the inadequacy of these models in order that better theoretical treatments be developed which will approximate the behavior of real chain molecules.

Conclusions

These experimental results on the temperature dependence of infrared absorbances have been analyzed to yield conformational energies for stereoregular PMMA. Derived values of conformational energies have been interpreted in terms of a backbone conformational energy, ΔH_{bb}, and a side-chain conformational energy, ΔH_{sc}. These energies,

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ΔH_{bb} and ΔH_{sc}, depend upon the tacticity of the polymer. Conformational energies derived from spectroscopic measurements are compared with energies derived from rotational isomeric state calculations and from changes in specific heat at the glass temperature. Reasonable agreement is obtained when all the uncertainties are considered. Improvements in analysis and experiments will provide further tests of these concepts. The predictions of the Gibbs–DiMarzio theory are not supported by the observation that $\Delta H/RT_g$ is not constant (1.1–2.6 for isotactic and syndiotactic PMMA's). Side-chain conformations are identified as an important factor in the glass temperature behavior of isotactic PMMA. The utility and value of precise spectroscopic measurements in testing and extending polymer theory have been demonstrated.

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Conformational Properties of Poly(3,3-dimethylthietane)

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ABSTRACT: A sample of poly(3,3-dimethylthietane) (PDS) was obtained by cationic polymerization of 3,3-dimethylthietane, using acetyl hexafluoroantimonate as initiator. A fraction having $M_n = 8200$ was isolated and purified; dipole moment measurements carried out in benzene solutions in the temperature range 30–60 °C yielded values of $\langle \mu^2 \rangle / xm^2 = 0.616$–$0.627$ and a temperature coefficient $\mathrm{d} \ln \langle \mu^2 \rangle / \mathrm{d}T = 0.6 \times 10^{-3}\ \mathrm{K}^{-1}$ at 30 °C. The rotational isomeric state model was used to compute theoretical values of these quantities by utilizing calculated values of conformational energies. Agreement between theory and experiment is achieved if extra stabilization energies associated with gauche conformations about skeletal C–C bonds are postulated. Comparisons between several conformational properties of PDS, PDO [poly(3,3-dimethyloxetane)], and PTS [poly(trimethylene sulfide)] are presented.

Introduction

Conformational analysis of poly(3,3-dimethyloxetane) (PDO) has been reported in a previous paper.[1] It was found that this polymer is similar to poly(trimethylene oxide) (PTO) in molecular dimensions and flexibility but that the polymers differ vastly in their dipole moments. Rotational isomeric state computations carried out by utilizing calculated conformational energies gave a good account of the PDO dipole moments and their temperature coefficient without the need of postulating noticeable extra stabilization energies associated with the gauche conformations about the C–C bonds.

A similar treatment can be applied to poly(3,3-dimethylthietane) (PDS), the sulfur analogue of PDO. PDS differs considerably from PDO in its structural features; thus the C–S bond length is ca. 30% longer than the C–O bond length,[2-4] the CSC bond angle is about 10° smaller than the COC bond angle,[2-4] and the van der Waals radius of the S atom is about 20% larger than that of the O atom.[5] It should be interesting to investigate whether these differences manifest themselves in the conformational characteristics.

Another important purpose of the present investigation was to compare the configuration-dependent properties of PDS, mainly its dipole moments, with those of poly(trimethylene sulfide) (PTS). It has been suggested from spectroscopic studies on various simple alkyl sulfides that the bond sequence CS–CC is quite flexible, in contrast with the rigidity assigned to the CO–CC moiety of polyoxide chains.[6,7] For example, whereas gauche conformations about the former bonds seem to be slightly more stable than the trans conformations, these conformations about the latter bonds have an energy 0.9 kcal mol^{-1} higher than the corresponding trans states.[8-10] Moreover, recent calculations on the conformational energies of gauche states about SC–CC bonds in PTS indicate that these states have a slightly higher energy than the trans states.[11,12] It should therefore be interesting to investigate the influence of the

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