Comparison Between the Glass Transition Temperatures of the Two PMMA Tacticities: A Molecular Dynamics Simulation Point of View

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Abstract: The difference in the glass transition temperatures, T_g, of the iso- and syndiotactic forms of PMMA has been investigated through molecular dynamics simulations of short duration (110 ps) using an accurate force field, *pcff*. To correlate with the Gibbs-DiMarzio theory, which specifies that conformational energy is a primary factor in determining T_g, an energetic analysis has been carried out. It is found that syndiotactic PMMA possesses lower intramolecular energy where the governing contribution is brought by the angle bending term; whereas the isotactic PMMA exhibits lower intermolecular energy. Such a behavior suggests that the chain packing greatly determines the difference in the T_g.

INTRODUCTION

In determining mechanical properties of a polymer material, the glass transition temperature, T_g, is of particular interest since it splits apart two domains of different mechanical behavior. In the glassy state, below T_g, molecular motions are largely restricted to vibrations and short-range rotational motions, large scale configurational fluctuations being slow. In the rubbery region, above T_g, the polymer chains present long-range rubber elasticity. Therefore the T_g of a polymer governs its use. However the phenomenon of the glass transition in polymers is not yet fully understood from a molecular point of view. Its knowledge is as relevant for universities as for industries. Three main models are currently used to describe such a transition: the "free-volume" (Ref. 1), the kinetic (Ref. 2) and the thermodynamics theories (Ref. 3). Other theories exist, such as the concept of a cooperatively rearranging region (Ref. 4), but they are derived from the main models cited previously. Nowadays computer simulation offers a real approach to the

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microscopic understanding. Specifically, molecular dynamics can be used to show how bulk properties are related to intermolecular forces. In this context, the glass transitions of the two polymethylmethacrylate, PMMA, tacticities are investigated using molecular simulations. The energy behavior is then inspected connecting our results with the Gibbs-DiMarzio thermodynamic theory (Ref. 3). Gibbs and DiMarzio promulgates that conformational energy is a principal factor in determining T_g.

The difference in T_g of the two PMMA stereoisomers has been attributed by MacKnight and Karasz to a conformational energy difference (Ref. 5). Such an effect was expected in view of the Gibbs-DiMarzio theory. On the other hand, intermolecular interactions, i.e. packing and arrangement of the side groups, have been mentioned by O'Reilly and Mosher to be important factors in the determination of T_g (Ref. 6). In order to investigate the difference in T_g and the energy contribution, molecular dynamics simulations are carried out through a simulated dilatometric experiment.

SIMULATION PART

SIMULATION FRAMEWORK

For convenience, i-PMMA and s-PMMA will be used to denote the iso- and syndiotactic forms of PMMA, respectively. From an experimental point of view, the dilatometric technique is currently employed to determine T_g: the specific volume is reported for different temperatures as the system is cooled; the intersection between the two lines joining the data of the glassy and melt regions gives the glass transition temperature; actually the slope of this line furnishes the thermal expansion coefficient in the considered region. Atomistic molecular dynamics gives the opportunity to explore this kind of time dependent properties, but these simulations are limited by current computing resources to times of order nanoseconds. Simulation cooling rates are much higher (of order 10^{12} $K.s^{-1}$) than what could be achieved in even the fastest quenching experiments, and hence molecular dynamics simulations will not access the same spectrum of conformational fluctuations. This can generate ergodicity problems, since simulations cannot run long enough to sample fully all the phase space. However the process can be done as mentioned by Clarke and Brown (Ref. 7) or Rigby and Roe (Ref. 8).

From a molecular dynamics point of view, the choice of a force field greatly determines the accuracy to experimental value of the calculated property. The use of a reduced force field has the advantage to lower the Central Processing Unit (CPU) time of a simulation, and to

concentrate the study on the understanding of the phenomena accountable for the property. This force field has to possess at least a connectivity function, a flexibility part and an intermolecular potential, i.e., long-range van der Waals interactions (usually Lennard-Jones potential), plus electrostatic nonbonded potentials (Ref. 7). This study is focused on the use of an accurate force field, *pcff* from MSI, which has been especially built up to work with a great number of polymers (Ref. 9). Due to the presence of numerous cross-terms in its analytic expression, the vibrational motions of polymers are adequately expressed. Recently it has been chosen to investigate the infrared absorption spectra of PMMA from a combination of classical molecular simulation and Kramers-Kronig relations (Ref. 10). The calculated vibrations and the intensities have shown a very good agreement with experiment. Therefore, *pcff* seems to be the appropriate force field to determine the T_g of the two PMMA tacticities.

The first aim of the use of *pcff* is to approach experimental values considering the rapid cooling rate employed in a simulation. Once the difference in T_g is correctly represented, an energetic analysis could take place. The specifically important problem encountered with the use of an accurate force field is the CPU duration of an integration time step. As the temperature decreases, interactions between monomers make the chain motions restricted, and the large scale configurational fluctuations appear slower. The long relaxation times cannot afford accumulating equilibrium data in a relatively short simulation. It is the reason why specifically the molecular dynamics time is of nanosecond order. Due to the long CPU time, such a long simulation is hardly achieved with a "good" force field. Furthermore the simulation time scale motions of chain segments are highly localized (quasi-ergodic hypothesis) (Ref. 11). Nevertheless each specific volume data point of the dilatometric experiment has been obtained through a relatively short molecular dynamics (110 ps) while considering an accurate force field. The studies were carried out with a polymer chain length of 100 monomers for both stereoisomers. Eqs 1 and 2 represent respectively the variations of the T_g with the polymer molecular weight for the iso- and syndiotactic forms of PMMA, according to the Fox and Flory equation (Ref. 12).

$$T_{g_{isotactic}} = 49.6 - \frac{4.34 \cdot 10^4}{M} \tag{1}$$

$$T_{g_{syndiotactic}} = 123.3 - \frac{9.38 \cdot 10^4}{M} \tag{2}$$

where M is the molecular weight of the polymer;

T_gs are in Celsius degrees.

According to Eqs 1 and 2 the expected T_g values for iso- and syndiotactic PMMA are respectively 45.3 and 114.0 °C, which correspond to differences of 4.3 and 9.3 °C with $T_g(M_\infty)$. It can then be argued that local dynamics of the simulated chains are representative of the high molecular weight sample.

SIMULATION METHODOLOGY

The initial chain configuration is generated according to the propagation procedure implemented in MSI's *Amorphous_Cell*® program. This program is based on a combination of Theodorou and Suter's procedure (Ref. 13) and Meirovitch's scanning method (Ref. 14). The chain backbone is grown step by step looking for long range excluded volume. In the Theodorou and Suter's model, the Rotational Isomeric States (RIS) conditional probability (Ref. 15), which is the probability to find the next bond of the backbone chain in a specific state, is modified to take into account the long range potential term. In the scanning method, all the possible continuations of the chain are theoretically looked at. In practice the lookahead is restricted to four bonds. It has to be noted that the temperature is directly incorporated into the RIS model through the statistical weight. Once the "parent" polymer chain is built, it is embedded in a cubic cell whose volume is determined by the density and the molecular weight of the polymer. The experimental density of 1.115 $g.cm^{-3}$ found at the T_g (Ref. 16), was chosen for the first configuration volume cell in spite of the fact that the dilatometric experiment begins at a higher temperature. Periodic boundary conditions are imposed on the system and, in order not to duplicate interactions, the minimum image convention is applied (Ref. 17). A molecular dynamics simulation in the NVT ensemble, i.e. constant number of particles, volume and temperature, is then performed on the cell in order to relax the system. The integration step is 0.001 ps using the Verlet-leap frog algorithm. The temperature is controlled with a Nose-Hoover thermostat bath (Ref. 18). To approach experimental features, the NPT ensemble, i.e. constant number of particles, pressure and temperature, is chosen to perform simulations. The simulation in the NPT ensemble has been carried out using the pressure control algorithm of Parrinello-Rahman (Ref. 19). A first 10 ps molecular dynamics simulation is accomplished in order to bring the system to the desired temperature. A 100 ps molecular dynamics simulation then takes place. A chain configuration is saved every 0.1 ps. The final density is saved. The system is then cooled to a 20 K lower temperature. Another series of relaxation and molecular dynamics are then performed. This process is carried out until the system has reached the final temperature.

RESULTS AND DISCUSSION

In Fig. 1 the specific volume is plotted versus the temperature for the pure i-PMMA and s-PMMA. For clarity the standard deviations are not shown on the graphs: they range from 0.009 to 0.023 as the temperature is increased.

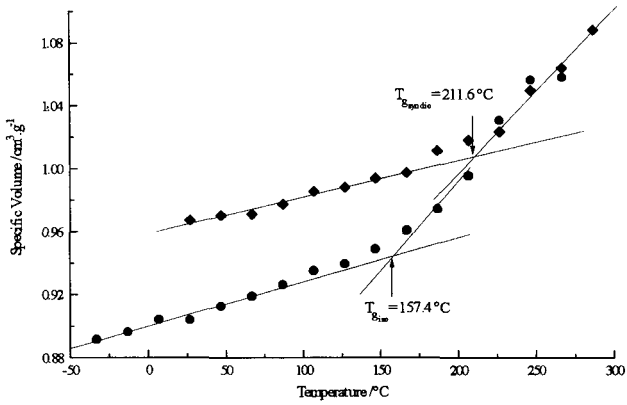

Fig. 1. The specific volumes of i-PMMA (•) and s-PMMA (◆) are plotted versus temperature. T_g is determined by the intersection of the regression fit lines (——).

As can be seen in Fig. 1, the specific volume varies differently according to the tacticity, therefore two T_gs are extracted. Thus simulated dilatometry furnishes for i-PMMA a T_g of 157.4 °C and for s-PMMA a T_g of 211.6 °C. The high values of T_gs, in contrast to the expected ones (45.3 and 114 °C), are not really surprising since the cooling rate is extremely rapid. The experimental specific volume is 0.84 $cm^3.g^{-1}$ at 25 °C, and has to be compared to the simulated value of 0.90 $cm^3.g^{-1}$ found at the same temperature. A longer molecular dynamics simulation duration can therefore amend this problem. It has to be noted that besides this "classical" dilatometric study, another procedure has been pursued. It takes advantage of the Theodorou and Suter's model and the Meirovitch's scanning method to generate a new configuration at each temperature step of the dilatometric experiment. With the same simulation duration it gives a better agreement with expected values. It will be largely explained in a subsequent paper (Ref. 20).

However this study shows an excellent accuracy of the differences in T_gs between iso- and syndiotactic PMMA: the simulated difference is 54.3 °C, while it has to be 68.7 °C according to the Fox and Flory equations (Eqs 1 and 2). Despite the low molecular dynamics duration, 110 ps, the result is found really satisfactory. Such a result clearly indicates the accuracy of the *pcff* force field, and the rightness of the procedure (chain propagation, relaxation, molecular dynamics). Moreover the volumetric thermal expansion coefficients of the glassy and rubbery states are respectively found equal to $3 \cdot 10^{-4}$ K^{-1} and $11 \cdot 10^{-4}$ K^{-1} for i-PMMA and, $2.4 \cdot 10^{-4}$ K^{-1} and $10 \cdot 10^{-4}$ K^{-1} for s-PMMA. In the glassy regions the coefficients satisfactorily fit the experimental data ($2.7 \cdot 10^{-4}$ K^{-1}) while in the rubbery region, they are higher than the experimental value ($5.7 \cdot 10^{-4}$ K^{-1}). Such a difference has been already mentioned by Fan and al (Ref. 21).

Since difference in T_g has been observed from molecular dynamics simulations, investigations on the microscopic behavior of the two stereoisomers can be carried on. This study is particularly focussed on their energetic behavior. The plot of the total potential energy of the PMMA tacticities versus temperature is shown in Fig. 2. Further inquiries will be presented in subsequent papers. It has to be pointed out that methyl group rotations in PMMA have been analyzed by Nicholson and Davies (Ref. 22), and their method can be applied to our study.

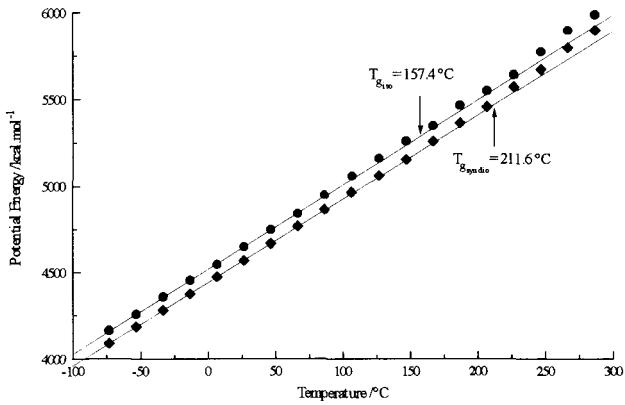

Fig. 2. The total potential energies of i-PMMA (•) and s-PMMA (◆) are plotted versus temperature. Regression fit lines (——) are plotted for low temperature data. The T_gs obtained from Fig. 1 are also indicated.

The s-PMMA potential energy is always found lower than the i-PMMA one. According to Sundararajan's RIS calculations on PMMA, such a behavior is not expected (Ref. 23). An

energetic analysis has to be examined thoroughly. Furthermore the difference in energy between the two forms is very important, 80 kcal.mol^{-1} for temperatures above the isotactic T_g. A first explanation lies in the *pcff* potential which includes numerous terms (Ref. 9). A second explanation lies in the fact that simulation duration is short, creating an important standard-deviation of the energy, order of 20 kcal.mol^{-1}. Nevertheless a heat capacity can be deduced from the slope drawn in Fig. 2, at the lower temperatures. The experimental heat capacity at constant pressure, C_p, ranges from 0.585 to 2.05 kJ.kg^{-1}.K^{-1} at temperatures below T_g, whereas calculated heat capacity at constant volume, C_v, is found order of 2 kJ.kg^{-1}.K^{-1}. Since, in a first approximation, the product of the pressure and the volume, PV, is negligible, C_p can be compared to the heat capacity at constant volume, C_v. Such a result is in accordance with the accuracy of the force field used for PMMA. The difference in the slope, i.e. the difference in the heat capacity, is too ill-defined to give a single value of T_g. The T_gs obtained from the simulated dilatometric experiment are elsewhere indicated on the graph.

Since difference in T_gs between the two stereoisomers is obtained, the difference in energy is significant, and the studies of the energetic behavior can be carried out thoroughly. The total potential energy is thus split into intra- and intermolecular terms. The intramolecular contribution to the total potential energy contains connectivity (bond term), flexibility (angle and torsion terms) and cross terms, and is plotted versus the temperature in Fig. 3.

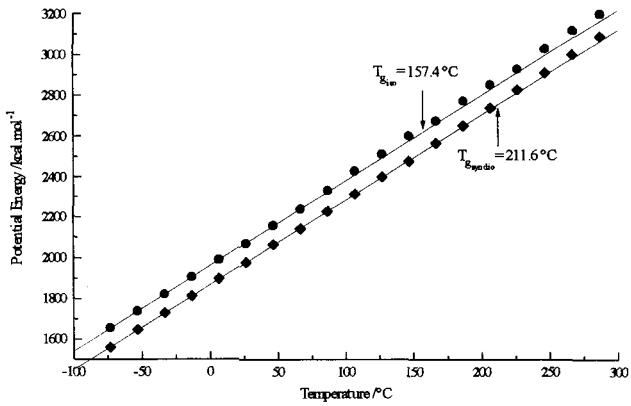

Fig. 3. The intramolecular potential energies of i-PMMA (•) and s-PMMA (◆) are plotted versus temperature. Regression fit lines (——) are plotted for low temperature data. The T_gs obtained from Fig. 1 are also indicated.

Fig. 3 exhibits the same behavior as the total potential energy (Fig. 2), i.e., the syndiotactic intramolecular energy is lower than the isotactic one. The difference of energy is lower but still high. A slight variation of the difference between the two stereoisomer intramolecular energies is seen. Further investigations have been undertaken in order to determine the major contribution to the difference in intramolecular energy. The torsional energy difference is too small to put forward: as mentioned by Sundararajan, low simulation duration cannot allow to see energy difference between the different isomeric states, *tt* and *tg* (Ref. 23). However since different T_gs are observed according to the PMMA tacticity, another energy contribution has to be found. The predominant intramolecular contribution is brought by the angle bending energy term, E_θ, expressed in the *pcff* force field by Eq. 3. The difference between the i-PMMA E_θ and s-PMMA E_θ is shown in Fig. 4.

$$E_\theta = K_2(\theta - \theta_0)^2 + K_3(\theta - \theta_0)^3 + K_4(\theta - \theta_0)^4 \qquad (3)$$

where θ_0 is the equilibrated angle bending value.

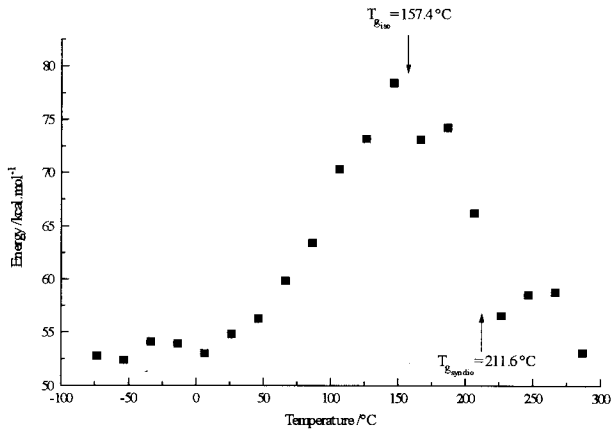

Fig. 4. The angle bending energy difference between i-PMMA and s-PMMA is plotted versus temperature. The T_gs obtained from Fig. 1 are also indicated.

Further inquiries have shown that three angles are mainly accountable for the variation of E_θ: the two backbone angles plus the angle between the two pendent groups at the chiral carbon. Decreasing the temperature, vibrational motions are more restricted for the syndiotactic chains than for the isotactic ones, explaining the increase in variation of E_θ. As a matter of fact, the onset temperature can be matched to the syndiotactic T_g. Due to the high fluctuations in this

temperature region, the onset temperature is superior to the previous syndiotactic T_g found by dilatometric study. The increase of the E_θ variation decreasing the temperature indicates that the syndiotactic chains are restricted to short-range rotational motions, while the isotactic chains still exhibit long-range rubber elasticity. The decrease of the E_θ variation then suggests that both polymer chains are in the same state, i.e., the glassy state. As a consequence, the uphill temperature corresponds to the i-PMMA T_g which fits perfectly well with the previous one. Additional investigations have to be done to consider this as a new method to determine T_g from a molecular point of view: a longer simulation duration or more data in the high temperature region can solve such a problem and then determine with a better accuracy the T_gs. However the variation in E_θ cannot in itself explain the observed difference in T_g.

In the Gibbs-DiMarzio model, the variations in entropy of the two tacticities are equal at T_g $\left(\Delta S_{iso}(T_g) = \Delta S_{syndio}(T_g)\right)$, the $\Delta H/RT$ ratio, where ΔH is the variation of enthalpy, R the molar gas constant and T the absolute temperature, has then to be a constant. O'Reilly and Mosher have presented the first lack of constancy of this ratio (Ref. 6). As a matter of fact intramolecular energy is not the only factor to explain the difference in T_g, intermolecular interactions between chain segments have to be taken into account. The intermolecular contribution (Lennard-Jones and electrostatic potentials), i.e. nonbonded potential, for the two tacticities is then plotted versus the temperature (Fig. 5).

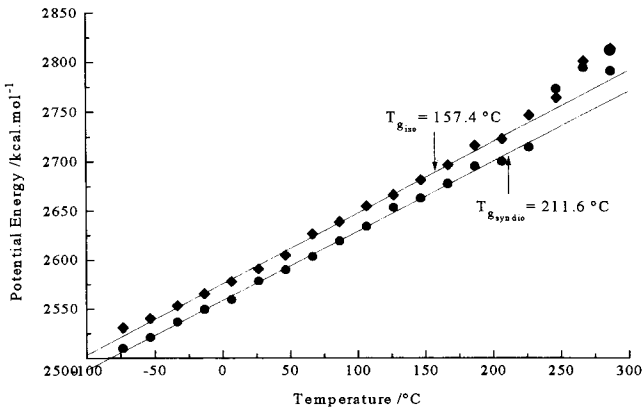

Fig. 5. The intermolecular potential energies of i-PMMA (•) and s-PMMA (◆) are plotted versus temperature. Regression fit lines (——) are plotted for low temperature data. The T_gs obtained from Fig. 1 are also indicated.

Contrary to the intramolecular energy behavior, the isotactic form possesses a lower intermolecular energy than the syndiotactic form all along the simulated dilatometric experiment (Fig. 5). A lower intermolecular energy of i-PMMA indicates that isotactic chains tend to pack together. The tendency of the isotactic chains to pack together can be regarded through the difference in the Lennard-Jones potential: since the potential is lower for i-PMMA the distance between two adjacent chains has to be lower, such a behavior is revealed by a pair distribution function. An increase of molecular packing denotes a higher density and therefore a lower specific volume. Actually such a behavior is in accordance with density measurements from both simulation and experiments (Ref. 24): a lower specific volume, i.e. a higher density, is obtained for the isotactic polymer at temperatures below T_g (Fig. 1). Moreover, a higher molecular packing between isotactic chains is related to a restrained conformational behavior of these chains. The decrease in chain flexibility usually produces an increase in T_g but, since difference in T_g is due to backbone angle vibrational motions, i.e. a difference in E_θ, the T_g of i-PMMA occurs at a temperature below that of s-PMMA. As a consequence, the intermolecular interactions between i-PMMA chains can explain the increase of i-PMMA T_g at interfaces (Ref. 25).

EXPERIMENTAL PART

The molecular simulation was performed using a Silicon Graphics Indigo 2 XZ.
The simulation results were obtained using software programs from Molecular Simulation Inc. of San Diego. Physical properties of polymers were carried out with *Synthia*®. Molecular mechanics and dynamics simulations were performed with the *Discover_3*® program. The amorphous polymer modeling was conducted with the *Amorphous_Cell*® program.

CONCLUSION

Despite the low molecular dynamics simulation duration (110 ps) compared to the long relaxation times expected, the use of the accurate force field, *pcff*, allows investigating the energetic behavior of the two PMMA stereoisomer chains versus the temperature. The unexpected lower intramolecular potential energy is found for the syndiotactic form which possesses the higher T_g. Moreover the major contribution to intramolecular energy is brought by the angle bending energy which reveals the angle vibrational motions. The plot of this potential versus the temperature brings to the determination of the T_g from a computational point of view.

However a lower intermolecular potential energy is found for i-PMMA. Such a behavior denotes an increase in the packing of the isotactic chains in relation to syndiotactic chains. As a consequence, the i-PMMA density is higher than the s-PMMA one. Since angle vibrational motions are primary factor in distinguishing between the two T_gs, the i-PMMA chains give rise to a departure from equilibrium density, i.e. specific volume, at a lower temperature. Therefore results presented in this paper are not contrary to the Gibbs-DiMarzio model which specifies that the conformational energy is a primary factor in determining the T_g of a specific polymer. Molecular simulation explains the difference in T_gs by intermolecular interactions. However further studies have to be accomplished to correlate these results with other T_g models including cooperativity problems between chain unit motions (Ref. 26).

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