Molecular Modeling Used as a Probe of Interactions to Study the Polymeric Glass Transition

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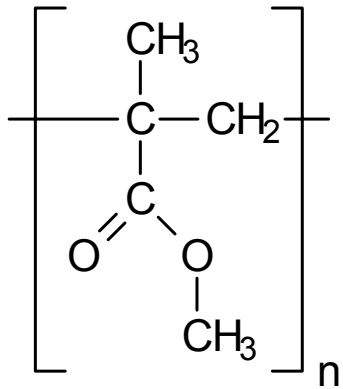
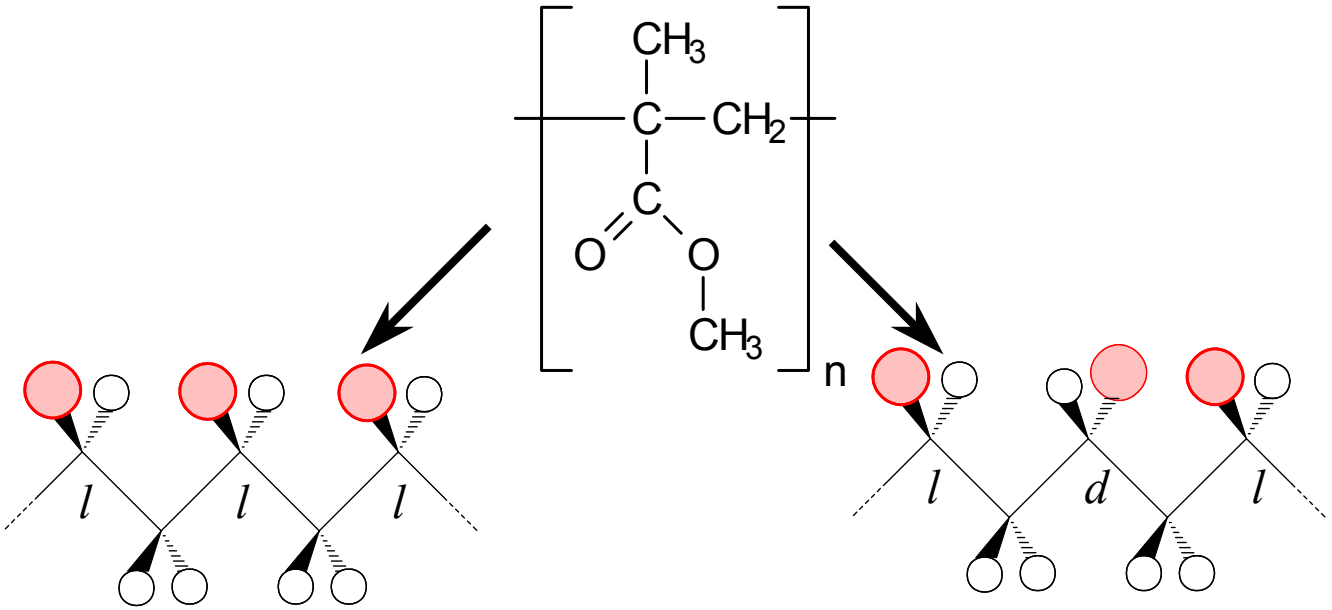


Tacticity



ISOTACTIC

SYNDIOTACTIC

Experimental $T_g = 45.3\ °C$

$T_g = 114\ °C$

Can we manage such a difference by the use of molecular modeling ?

If affirmative → better understanding of the difference → glass transition …

Simulation of the Amorphous Phase

✓ Design of a cubic box

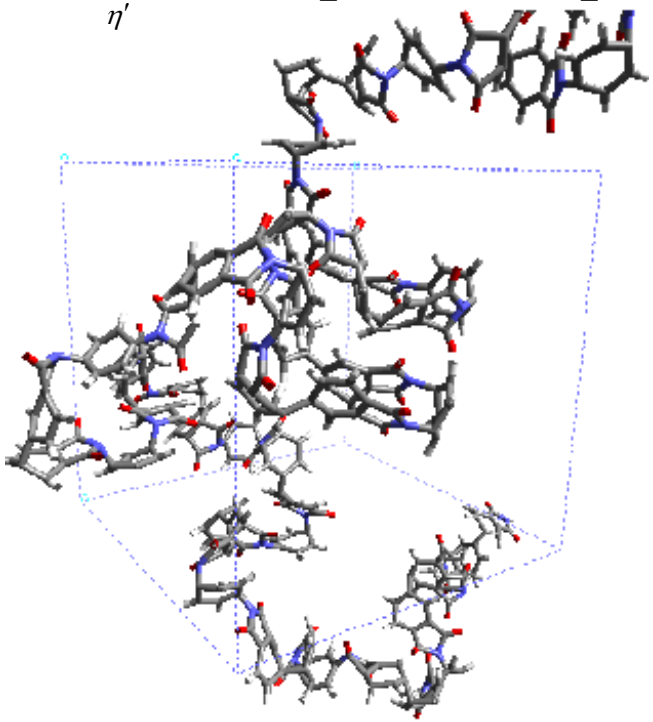
- From the knowledge of the density and the mass of the polymer
- All the space is filled by replica of this box

✓ Chain design

- A propagation procedure (MC) is begun to design 1 polymer configuration
- The chain backbone is grown step by step looking for long range excluded volume

RIS

$$q'_{\xi\eta;i} = q_{\xi\eta;i} \frac{\exp\left[-\Delta U^{LR}_{\eta;i} / RT\right]}{\sum_{\eta'} q_{\xi\eta';i} \exp\left[-\Delta U^{LR}_{\eta';i} / RT\right]}$$



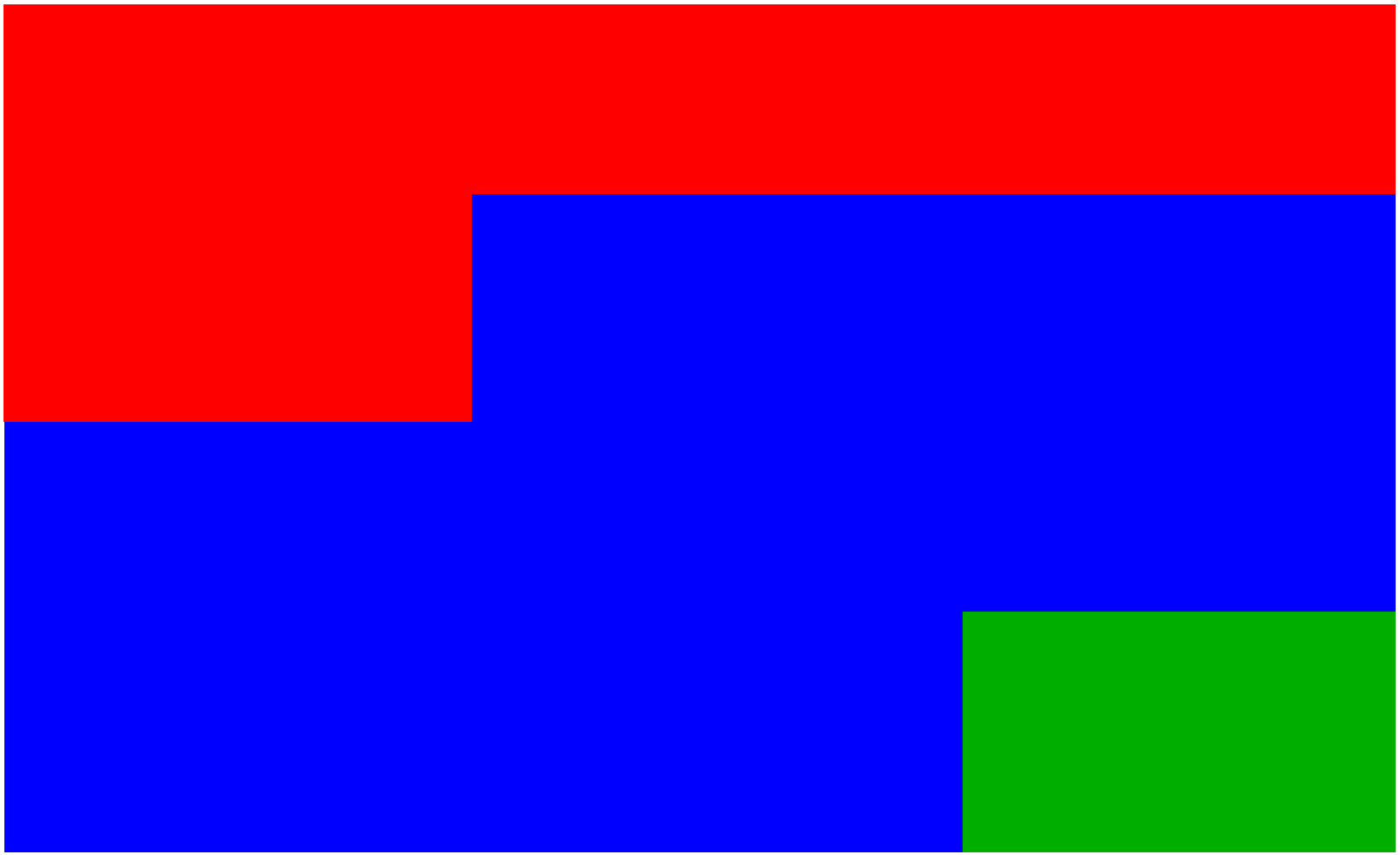
✓ Periodic Boundary Conditions

Each atom coming out from one face is automatically entering through the opposite face

✓ Relaxation Procedure

MD + minimization

pcff Force Field: schematic representation



connectivity + flexibility

cross terms

non-bonding terms

pcff Force Field: mathematical expression

$$V = \sum_b \left[K_2 (b-b_0)^2 + K_3 (b-b_0)^3 + K_4 (b-b_0)^4 \right] + \sum_\theta \left[H_2 (\theta-\theta_0)^2 + H_3 (\theta-\theta_0)^3 + H_4 (\theta-\theta_0)^4 \right]$$

$$+ \sum_\phi \left[V_1 \left[1-\cos\left(\phi-\phi_1^0\right) \right] + V_2 \left[1-\cos\left(2\phi-\phi_2^0\right) \right] + V_3 \left[1-\cos\left(3\phi-\phi_3^0\right) \right] \right] + \sum_\chi K_\chi \chi^2$$

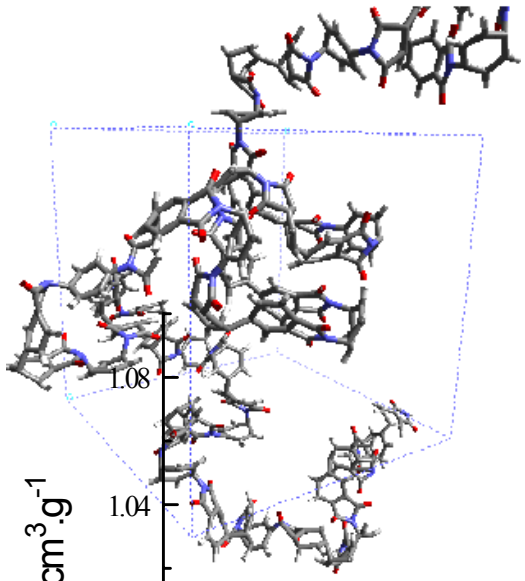
$$+ \sum_b \sum_{b'} F_{bb'} (b-b_0)(b'-b'_0) + \sum_\theta \sum_{\theta'} F_{\theta\theta'} (\theta-\theta_0)(\theta'-\theta'_0) + \sum_b \sum_\theta F_{b\theta} (b-b_0)(\theta-\theta_0)$$

$$+ \sum_b \sum_\phi (b-b_0)\left[V_1 \cos\phi + V_2 \cos 2\phi + V_3 \cos 3\phi \right] + \sum_{b'} \sum_\phi (b'-b'_0)\left[V_1 \cos\phi + V_2 \cos 2\phi + V_3 \cos 3\phi \right]$$

$$+ \sum_\theta \sum_\phi (\theta-\theta_0)\left[V_1 \cos\phi + V_2 \cos 2\phi + V_3 \cos 3\phi \right] + \sum_\phi \sum_\theta \sum_{\theta'} K_{\phi\theta\theta'} \cos\phi (\theta-\theta_0)(\theta'-\theta'_0)$$

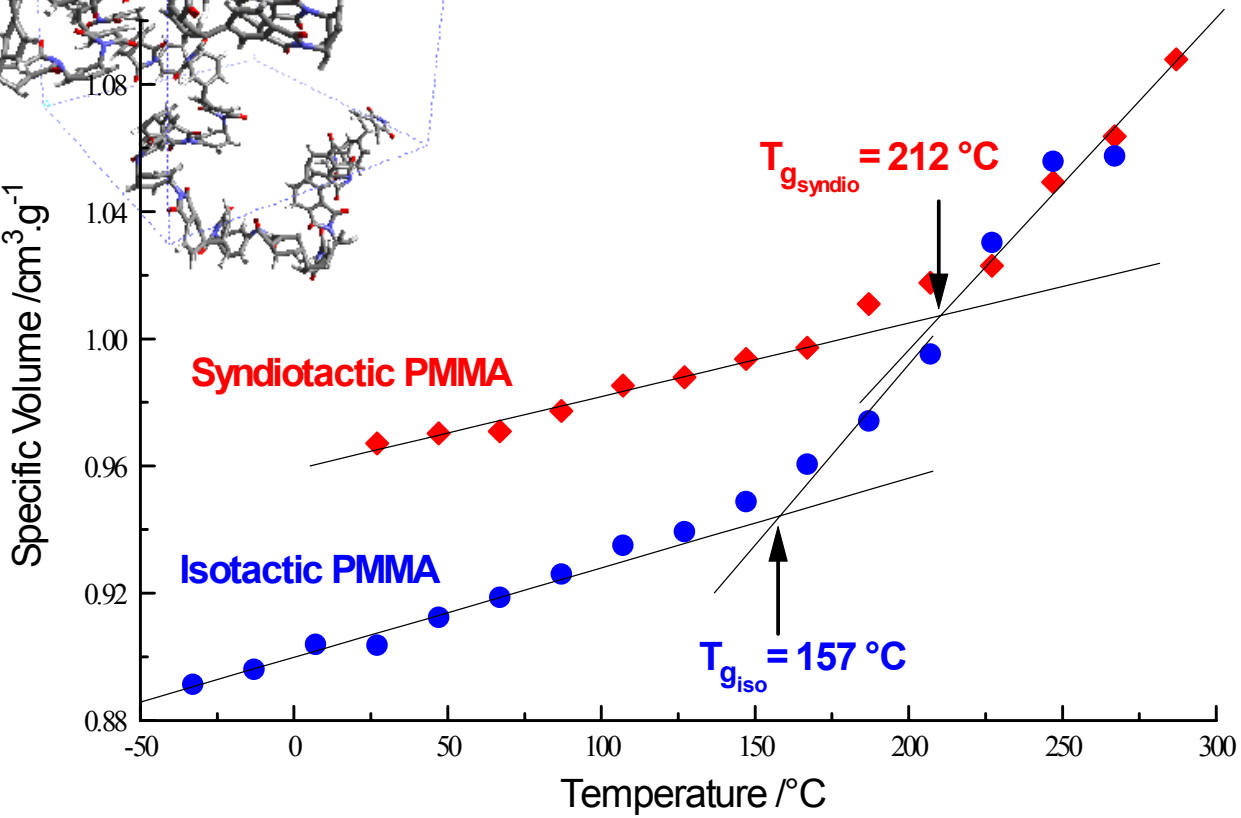
$$+ \sum_{i>j} \frac{q_i q_j}{\varepsilon r_{ij}} + \sum_{i>j} \left[\frac{A_{ij}}{r_{ij}^9} - \frac{B_{ij}}{r_{ij}^6} \right]$$

Dilatometric Simulation



NPT ensemble
Number of RU: 100
Simulation time: 110 ps by data
force field: *pcff*

12 hours
in SGI O2000 /
data



Simulated ΔT_g = 55 °C
Expected ΔT_g = 69 °C

Investigations to understand such a difference can be carried out

Energetic Analysis

✓ Principles

- The 2 PMMA configurations have the same force field parameters
- Changes in their molecular behavior will be directly linked to changes in their molecular characteristics

⇒ Energy differences

✓ Total Energy

$E(Iso)-E(Syndio)=10\ kcal.mol^{-1}$

⇒ 3 splits will be performed

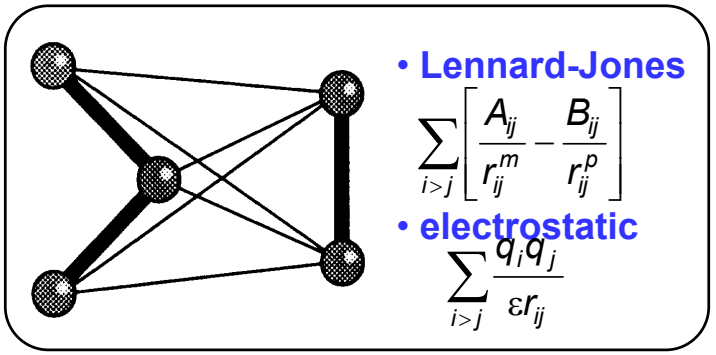
1. Inter and intramolecular contributions
2. Inside the intramolecular part
3. Molecular contribution

Splits in the Energy Contributions

1) Total energy

Intermolecular & Intramolecular

-35 (±8)



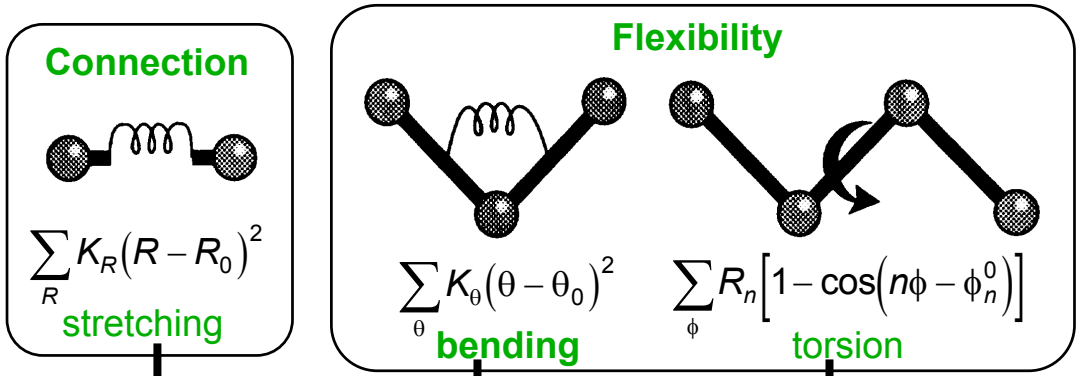
- **Lennard-Jones**

$$\sum_{i>j}\left[\frac{A_{ij}}{r_{ij}^{m}}-\frac{B_{ij}}{r_{ij}^{p}}\right]$$

- **electrostatic**

$$\sum_{i>j}\frac{q_i q_j}{\varepsilon r_{ij}}$$

45 (±8)



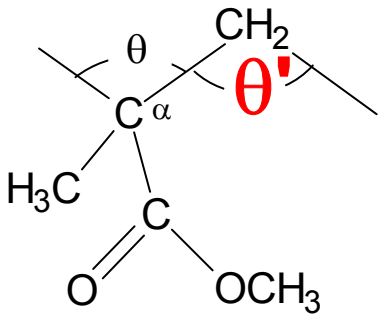
2) Intramolecular Energy

15 (±7)

75 (±10)

15 (±5)

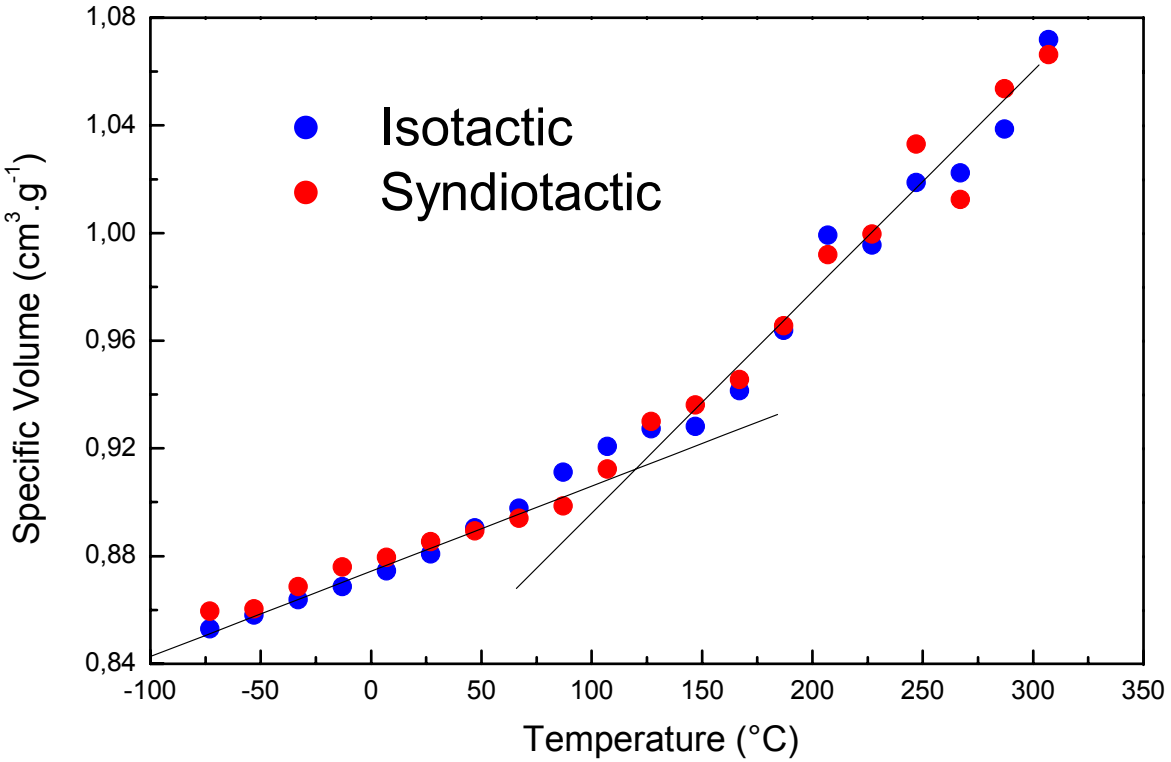
3) Bending Energy

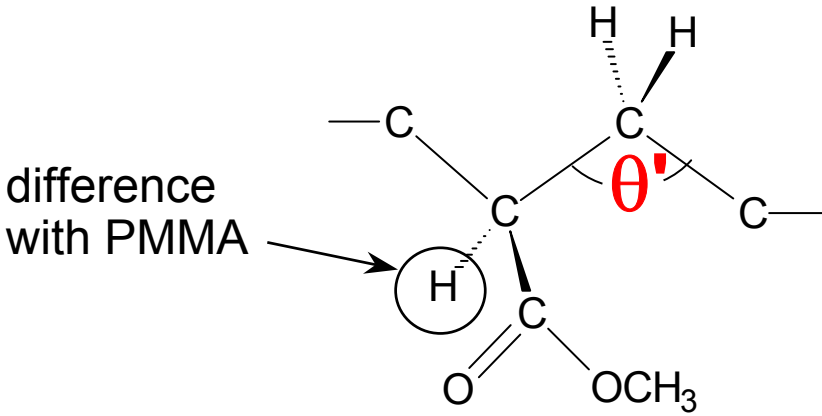


Syndiotactic: 126.7° (±0.1)

Isotactic: 127.8° (±0.1)

T_g Determination of PMA





$$T_g\left(PMA\right) < T_g\left(I-PMMA\right) < T_g\left(S-PMMA\right)$$

No differences In T_gs between the 2 PMA configurations, in agreement with experimental data

Energetic Analysis
- Comparisons to PMA data -

✓ **Intermolecular energy differences**

$$E_{inter}(S-PMMA) > E_{inter}(I-PMMA) >> E_{inter}(PMA)$$
$$350\ kcal.mol^{-1} \qquad 258\ kcal.mol^{-1} \qquad 78\ kcal.mol^{-1}$$

✓ **Intramolecular energy differences**

In the bending term associated with the intra-diad angle, θ'

$$\theta'(I-PMMA) > \theta'(S-PMMA) >> \theta'(PMA)$$
$$127.8° \qquad 126.7° \qquad 118.0°$$

✓ **Conclusions**

- Results are in agreement with the Free Volume Theory

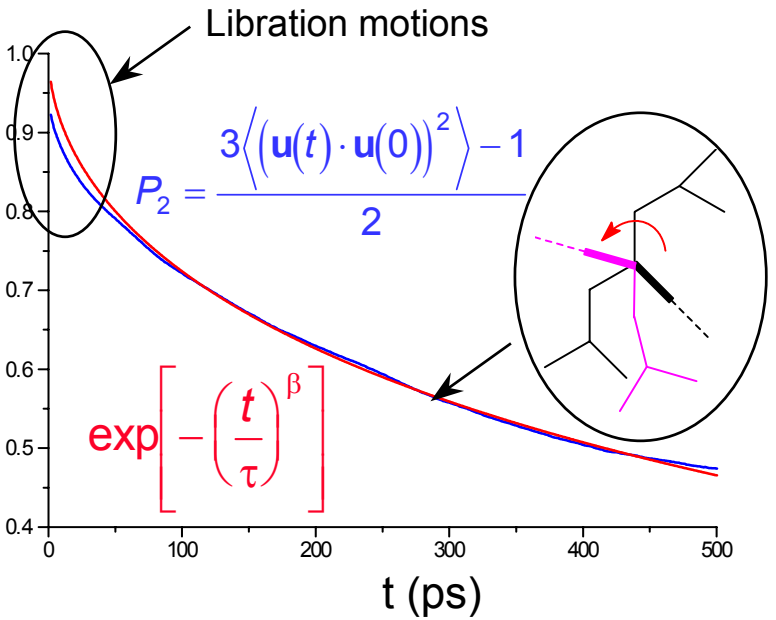
  Higher interactions between neighboring polymer chains segments will give a higher T_g

- Due to a greater aperture of θ', the isotactic chains should be more mobile

→ **Study of the local dynamics**

Local Dynamics Analysis
- Principles -

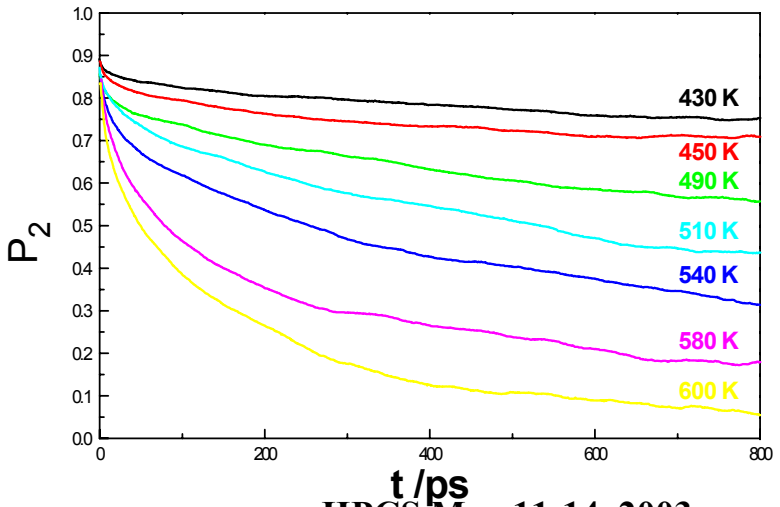
- ✓ **Computation of the orientation function P_2**
  - From MD, acquisition of the bond autocorrelation function $\langle(\mathbf{u}(t)\cdot\mathbf{u}(0))\rangle$
  - Computation of the 2nd Legendre polynomial term with respect to time, $P_2(t)$



- ✓ **Computation of the correlation time, τ_c**
  - Fit of $P_2(t)$ with a stretching exponential, KWW

$$\tau_c = \int_0^\infty P_2(t)dt \quad \Rightarrow \quad \tau_c = \frac{\tau}{\beta}\Gamma\left(\frac{1}{\beta}\right)$$

- ✓ **Procedure is carried out at different temperatures**

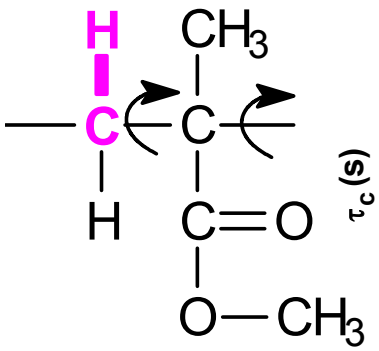


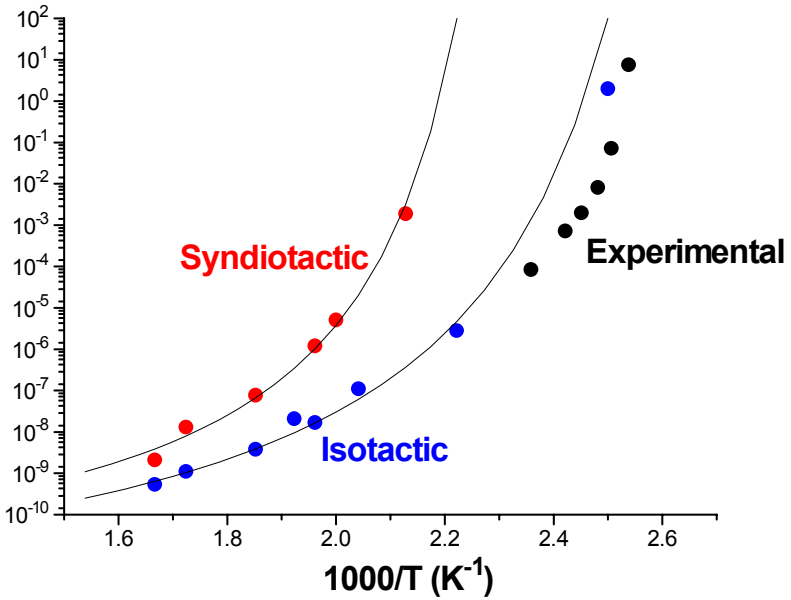
- ✓ **Fit with a VFT equation** (or WLF)

$$\tau(T) = A\exp\left(\frac{B}{T - T_o}\right)$$

Local Dynamics of the Backbone

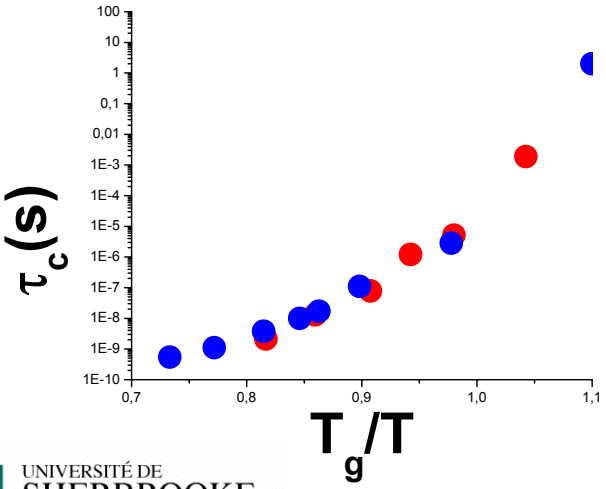
✓ Fit





B ($kJ.mol^{-1}$)
11.9
12.8

✓ Results



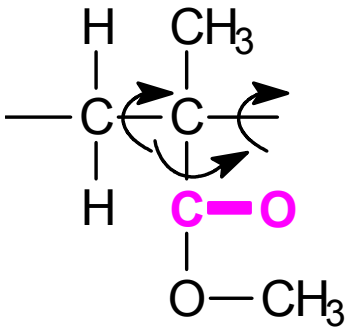
Behavior of the 2 isomers

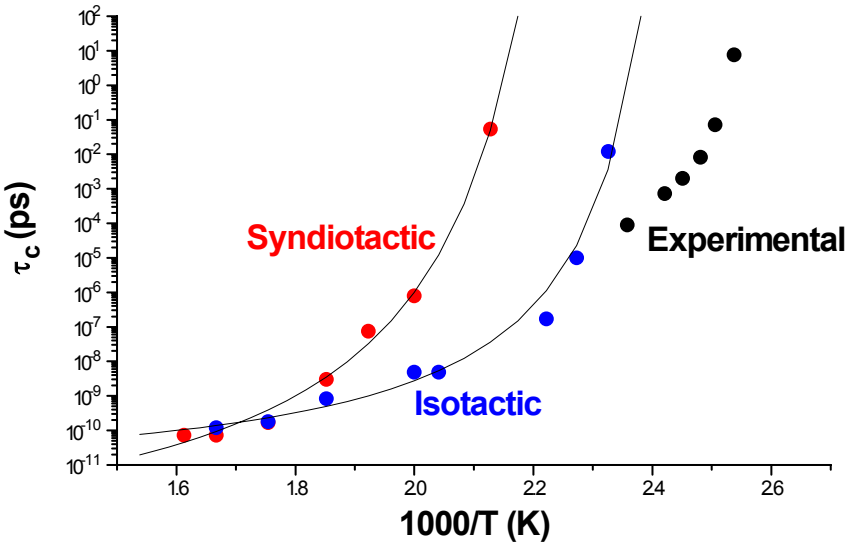
- at $T+T_g$: **Comparable**
- at T: **Different**

Study of the relaxation of the side chain

Local Dynamics of the Side-Chain

✓ Fit





B (kJ.mol^{-1})
11.5
5

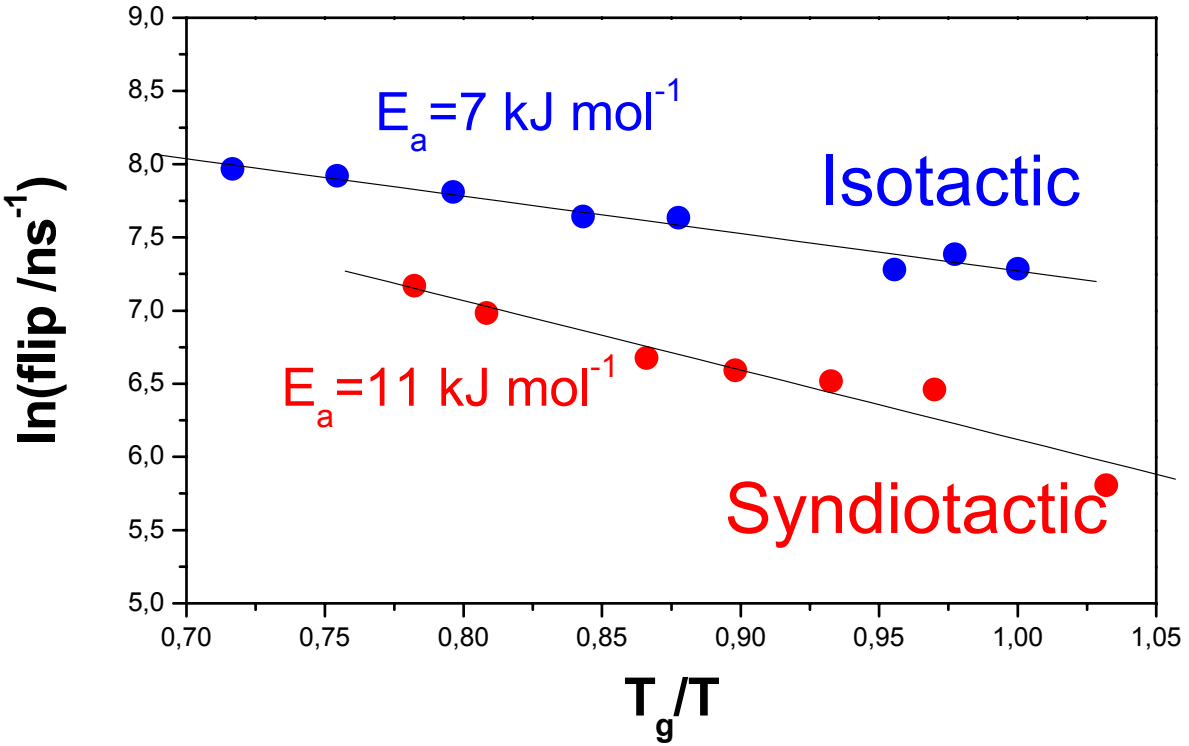
✓ Results

- Non-Arrhenian behavior, but such a relaxation corresponds to the β mode
- BUT, the simulation takes into account 3 motions:
  - » librational modes
  - » due to the side-chain (what we are interested in)
  - » due to the backbone

Mobility of the side-chain

✓ Number of transitions of the side-chain

Computation of the number of transitions between the UP and DOWN states of C=O



The behavior is Arrhenian like !

Compilation of the Results

✓ Correlation times

- **Backbone**
  - » Behavior of τ_c(C-H) is in agreement with published results:
    correlation times of iso PMMA are found inferior to the syndio PMMA ones
  - » The backbones of the 2 configurations present the same behavior at T + T_g, therefore the difference in T_gs could not be explained
- **Side-Chain**
  - » The side-chains of Iso-PMMA show a greater mobility than the syndio ones
  - » Behind this difference there lies a possible explanation of the difference in T_gs

✓ Comparison with experimental data

- From NMR experiments: compared with PEMA, PMMA showed that the greatest mobility of the side-chains induces a decrease of the lowest correlation time of the backbone

- Consequently, a higher side-chain rotation of iso PMMA generates a greater mobility of the backbone, and a greater mobility of the backbone explains a lower T_g

→ **T_g (i-PMMA) < T_g (s-PMMA)**

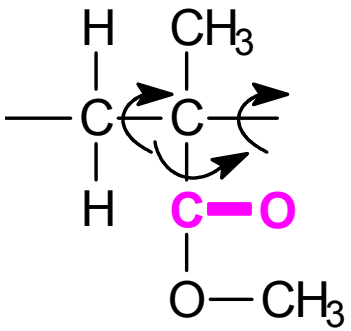
Cooperativity …

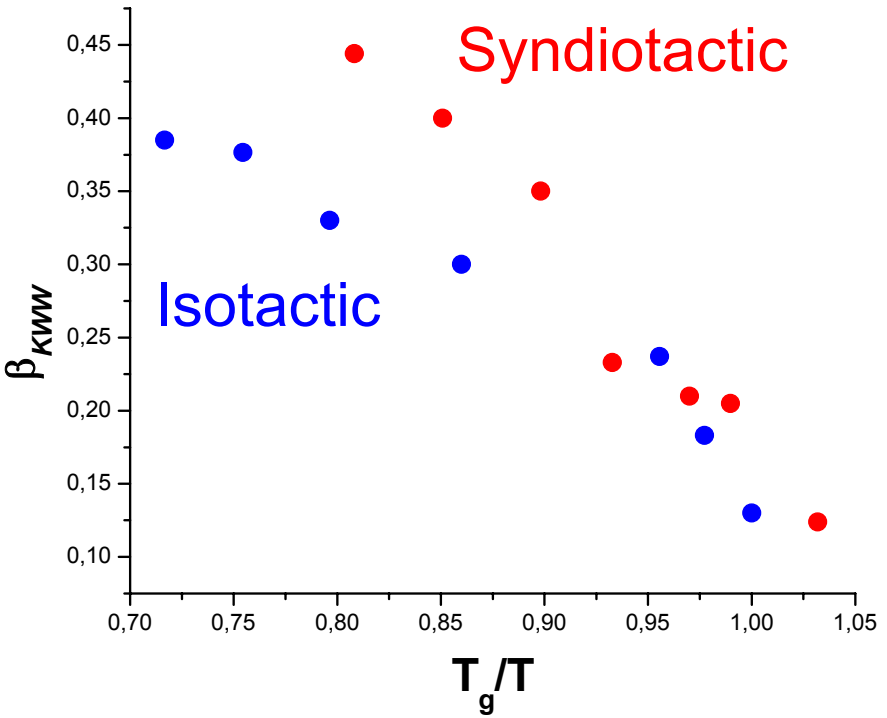
✓ Cooperativity observed by molecular simulation

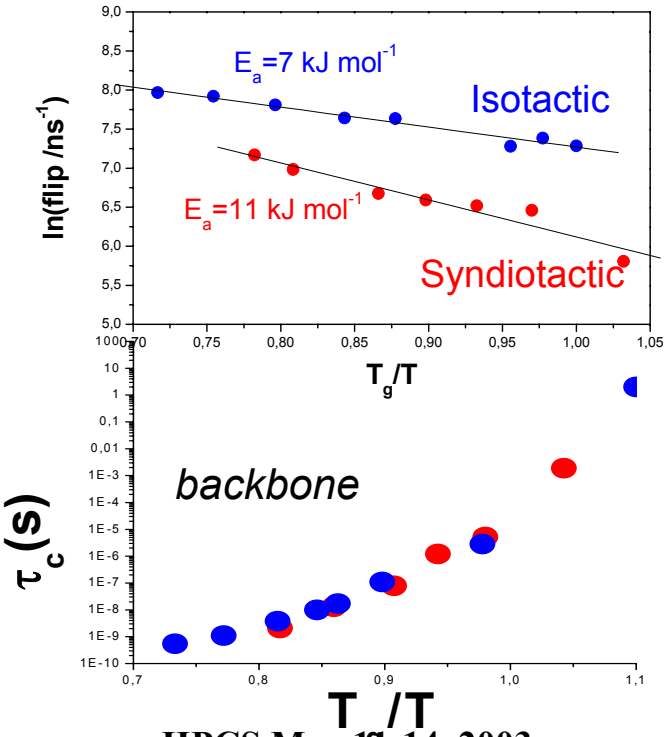
The stretching function: $$\exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right]$$

According to the Coupling Model: $\beta = n - 1$ where n is the coupling parameter, it actually corresponds to a measure of the cooperativity

Consequently, the coupling between the side-chain and the backbone can be directly observed:







Conclusions

- ✓ The substitution of H by CH_3 causes energetic variations
  - Augmentation of intermolecular interactions
  - Differenciation in the non-bonding interactions between the 2 stereomers
  - Aperture of the intra-diad angle to lessen side-chain interaction
  - Aperture of the intra-diad angle more important for the isotactic configuration

- ✓ The important mobility of the isotactic side-chain induces a greater mobility of the backbone, comparatively to the syndiotactic one: This cooperativity between the side-chain and the backbone was observed using molecular simulation

→ Such a behavior tends to lower the T_g of the isotactic configuration

- ✓ **The comparison of simulated data to experimental results are in agreement with the free volume concept to explain the difference in T_g between the two stereomers**

Questions

- ✓ **Is the local scale cooperativity observed here consistent with the CRR (Coupling Rearranging Region) theory ?**
- ✓ **Can the size or the shape of the CRR be affected by the PMMA tacticity ?**
- ✓ **The tacticity dependent size or anisotropic shape of the CRR may be a crucial point revealed by chain confinement:** $T_g\left(\text{tacticity and film thickness}\right)$
- ✓ **Further investigations will be performed on this topic in light of our molecular dynamics results.**

Acknowledgement

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DL_POLY

Réseau québécois de calcul de haute performance