# Dynamics of CO$_2$-based Poly(cyclohexene carbonate) as a Function of Molar Mass

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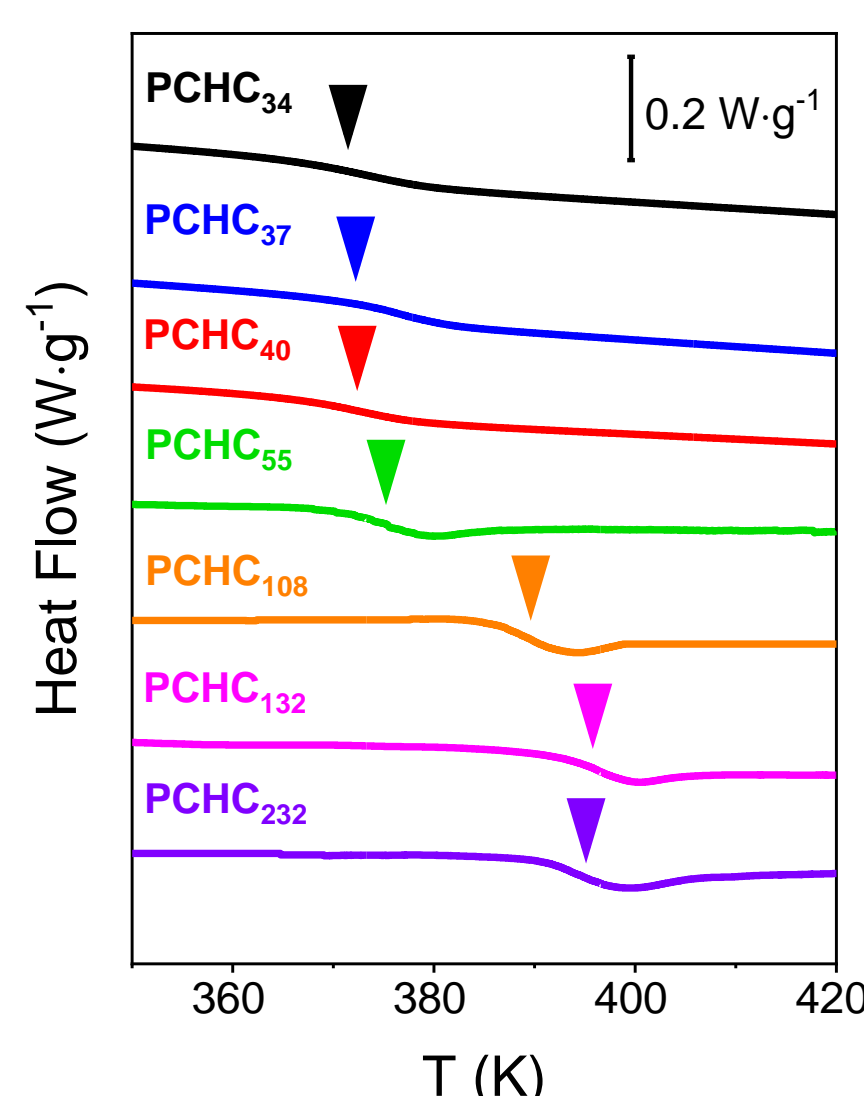
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Stereoregular poly(cyclohexene carbonate) (PCHC) homopolymers were prepared via copolymerization of cyclohexene oxide and carbon dioxide (CO$_2$) using (R,R)-(salcy)-CoCl and bis(triphenylphosphine)iminium chloride as a catalyst. The homopolymers had molar masses in the range of 4800 g·mol$^{-1}$ to 33000 g·mol$^{-1}$ and relatively narrow dispersity after careful fractionation, as required for the molecular dynamics investigation. We employed differential scanning calorimetry and dielectric spectroscopy, the latter as a function of temperature and pressure, for the thermal properties and the molecular dynamics, respectively. The segmental dynamics in the vicinity of the liquid-to-glass temperature was very complex. The dual segmental processes were inseparable by decreasing temperature or by increasing pressure. Based on DFT calculations of the dipole moment, they were ascribed to different stereo sequences of the PCHC backbone. The limiting glass temperature, $T_g$, for very high molar masses was ~ 125 °C. The high $T_g$ value obtained herein well justifies its application as a CO$_2$-based alternative for polystyrene in a variety of materials based on block copolymers. Moreover, fragility increased with increasing molar mass with values intermediate to poly(styrene) and poly(cyclohexyl methacrylate). The flexible cyclohexyl group in PCHC undergoing intra-molecular chair-to-chair conversion increases the packing ability and consequently decreases the fragility. PCHC is a brittle material, because it lacks entanglements even for the higher molar masses investigated herein, which is relevant for application as a polystyrene substitute. Within the investigated range of molar masses the dependence of the terminal relaxation times, $\tau_{NM}$, and of the zero-shear viscosity, $\eta_o$, on molar mass, $M$, have respective dependencies as $\tau_{NM}/\tau_s \sim M^{3.2}$ and $\eta_o \sim M^{1.4}$ revealing an intermediate behavior between Rouse and entangled chains.

## Motivation

Carbon dioxide, the main greenhouse gas, offers exciting possibilities for polymer synthesis due to its low cost and natural abundance.[1] Through the copolymerization of carbon dioxide with epoxides, Poly(cyclohexene carbonate) (PCHC), an aliphatic polycarbonate based on CO$_2$ and cyclohexene oxide, was used in several works to demonstrate the efficiency and selectivity of different catalyst systems.[2-5] Because of its rather high glass temperature ($T_g$) (reported values are in the range from 115 °C to 120 °C),[6,7] PCHC is viewed as rigid and biodegradable, CO$_2$-based alternative for polystyrene in block copolymers. Although PCHC plays an important role in polycarbonate chemistry (as a high $T_g$ polymer), its physical properties are largely unexplored. For this purpose, we synthesized a series of PCHC homopolymers with molar masses in the range from 4800 g·mol$^{-1}$ to 33000 g·mol$^{-1}$ and with relatively narrow dispersities. We employed density functional theory calculations of the dipole moments of the different conformers, while the thermal properties, the molecular dynamics and the viscoelastic properties were investigated by differential scanning calorimetry, dielectric spectroscopy (as a function of temperature and pressure) and rheology.[8]
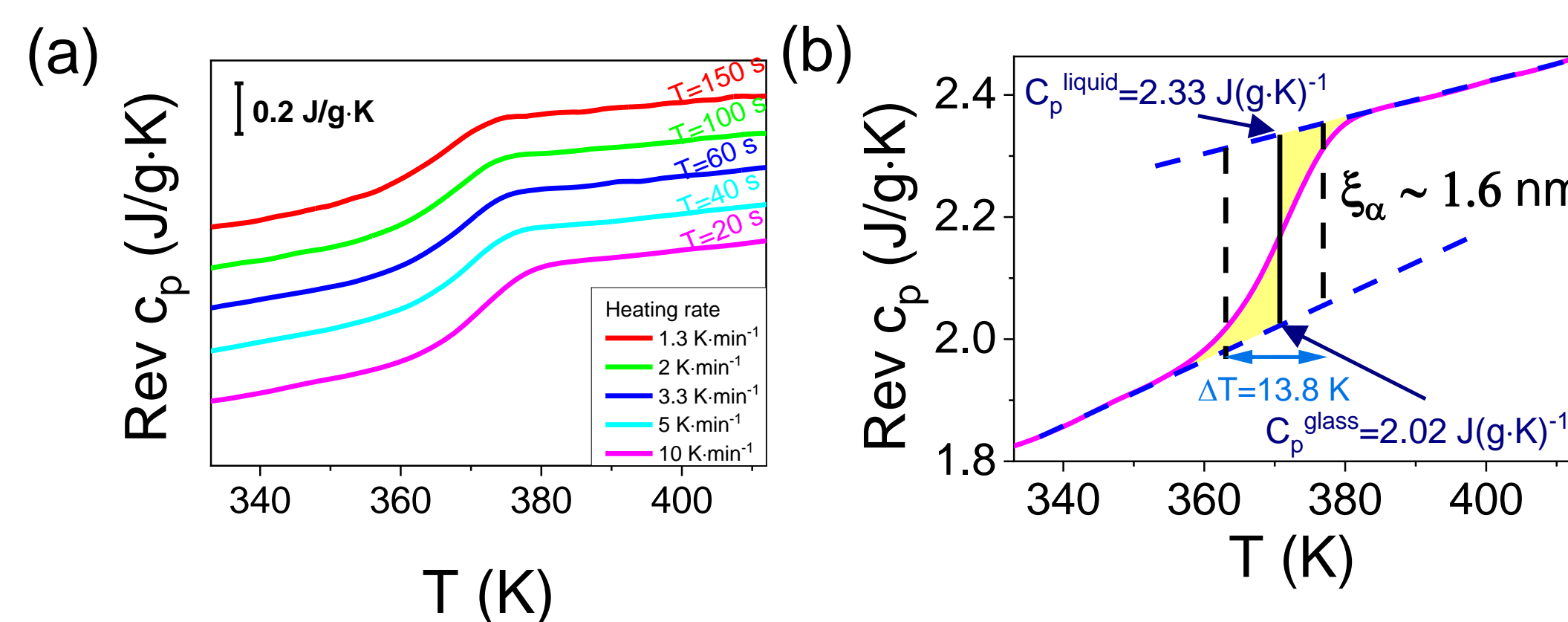
## Thermodynamic Properties



High $T_g$ polymer!

**Figure 2.** DSC traces of the different molar masses of PCHC obtained during heating at a rate of 10 K·min$^{-1}$. Vertical arrows indicate the respective glass temperatures. Curves are shifted vertically for clarity.

**Figure 3.** (a) Temperature dependence of the reversing heat capacity for PCHC$_{34}$, obtained from TM-DSC at different periods of modulation as indicated. Data are shifted vertically for clarity. (b) Temperature dependence of the reversing heat capacity for PCHC$_{34}$ for an oscillation period of $T = 20$ s and the characteristic length related with the glass temperature, $\xi_\alpha$.

## Computational Methods

DFT-ω-B97X-D/aug-cc-pVDZ
syndiotactic trans-poly(cyclohexene carbonate)

0.7 D

isotactic trans-poly(cyclohexene carbonate)

3.8 D

**Syndiotactic trans-PCHC dimer**
- **low value of dipole moment** because it is highly symmetric
- the existing electric dipoles cancel each other

**Isotactic isomer**
- does not have a highly symmetric structure
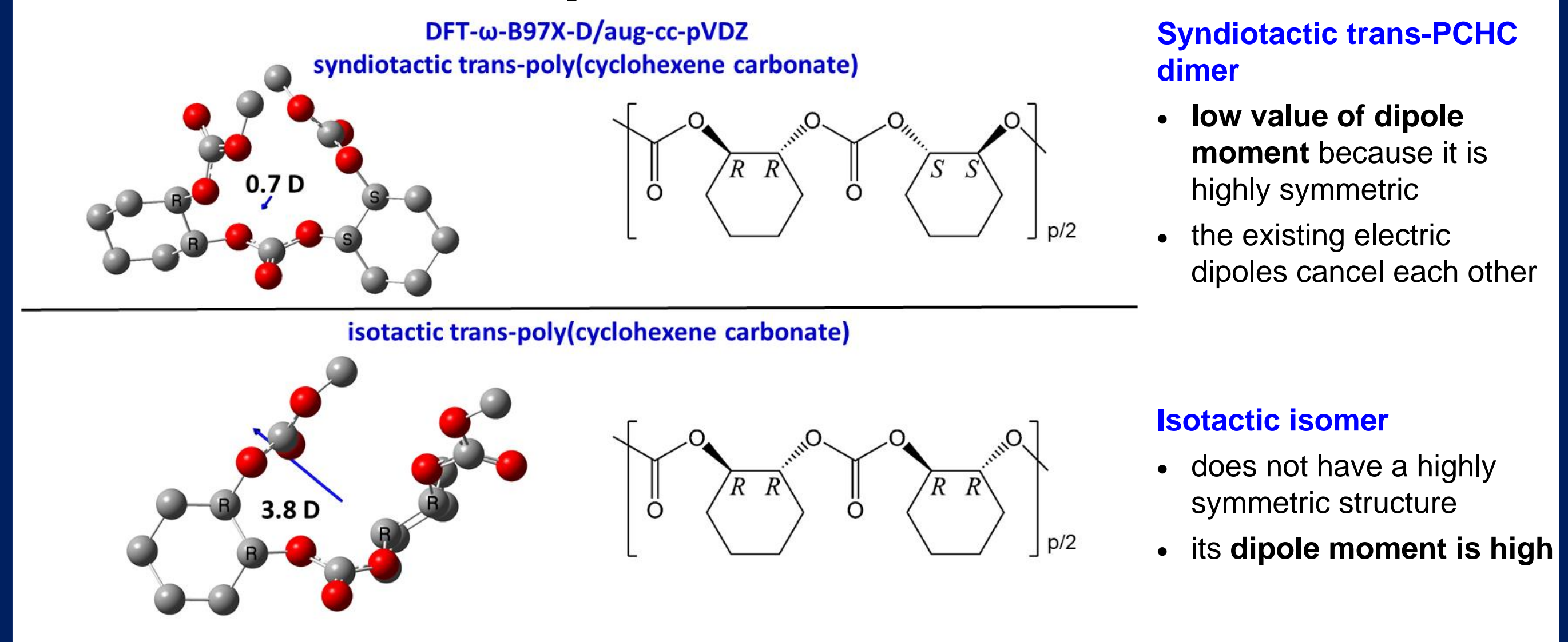- its **dipole moment is high**

**Figure 1.** Minimized structures and dipole moments of syndiotactic (top) and isotactic (bottom) trans-poly(cyclohexene carbonate). The vectors indicate the direction of the dipole moment. $p$ is the degree of polymerization.

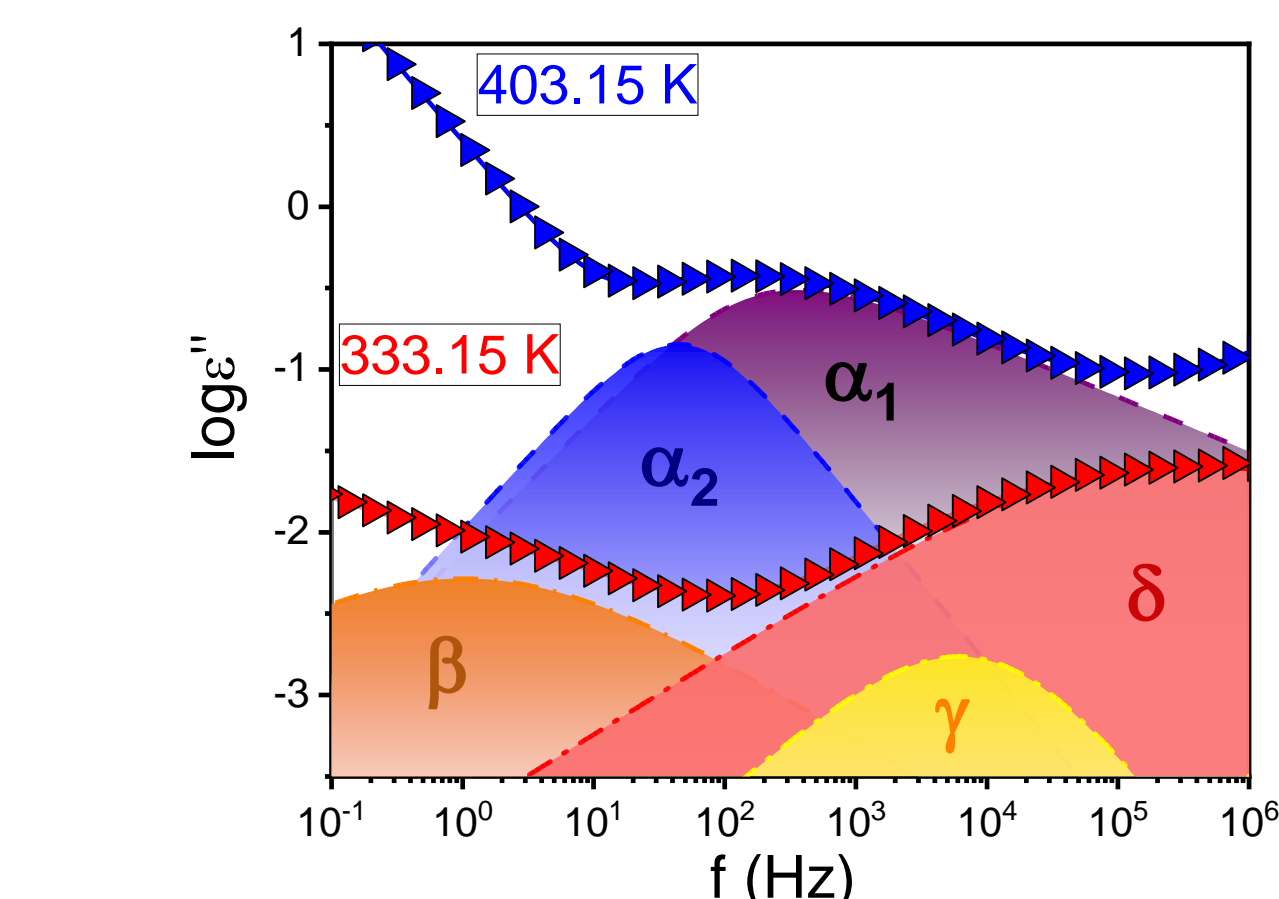## Molecular dynamics as a function of temperature and pressure



**Figure 4.** Dielectric loss curves of PCHC$_{34}$ are shown at two temperatures as indicated. At 430.15 K, the shadowed gray and blue areas correspond to simulations of the $\alpha_1$ and $\alpha_2$ processes. At 333.15 K, the shadowed orange, yellow and red areas are simulations of the HN function for the three processes in the glassy state (β, γ, and δ).
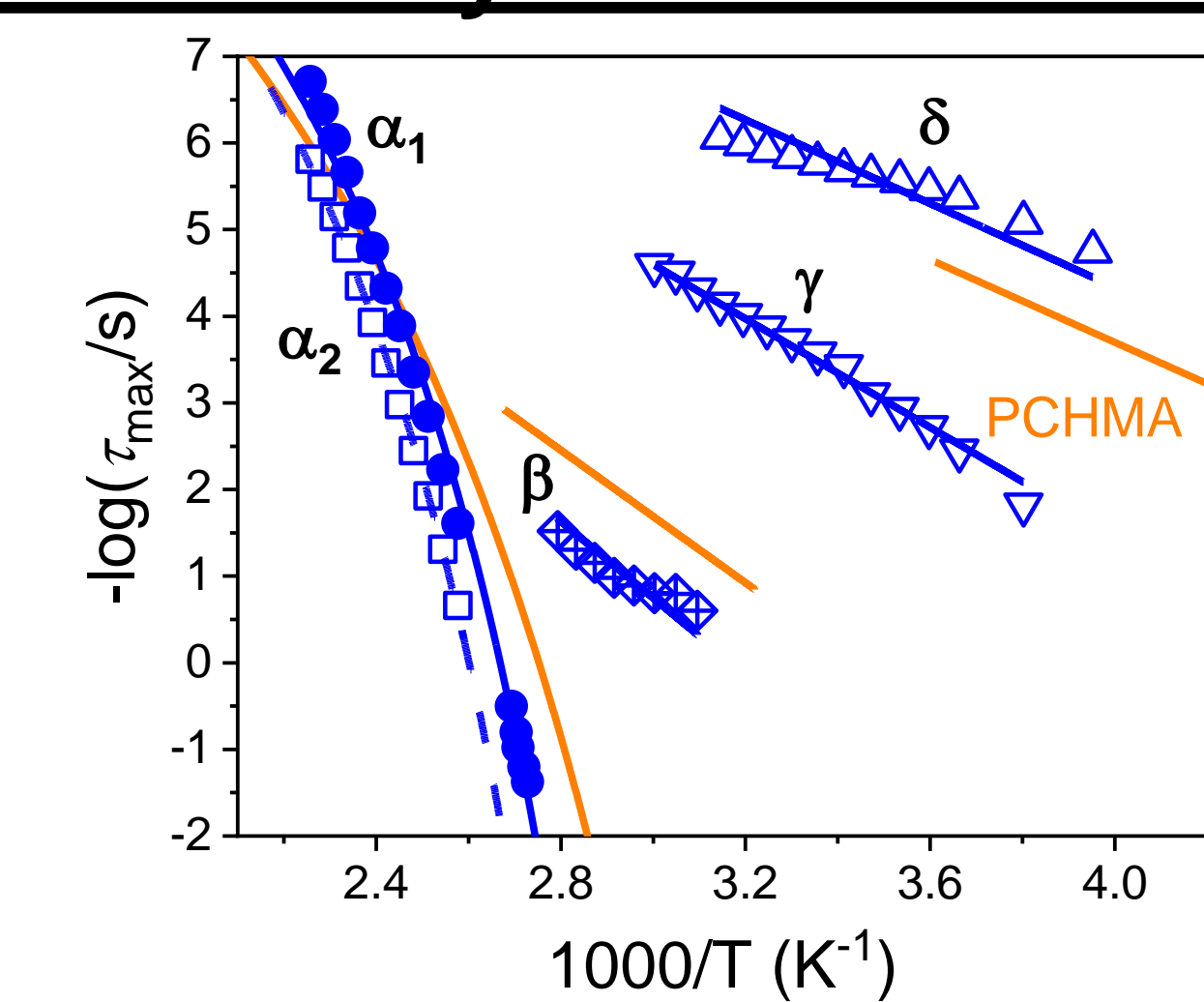
**Figure 5.** Activation plot of the relaxation times for the different processes of PCHC$_{34}$. Starting from higher temperatures: (squares) $\alpha_2$ process, (circles) $\alpha_1$ segmental process, (crossed rhombi) β process, (down triangle) γ process and (up triangle) δ process. TM-DSC data are also shown. The lines represent fits to the VFT and Arrhenius equations. The relaxation processes of PCHMA are plotted with orange lines.[9,10]
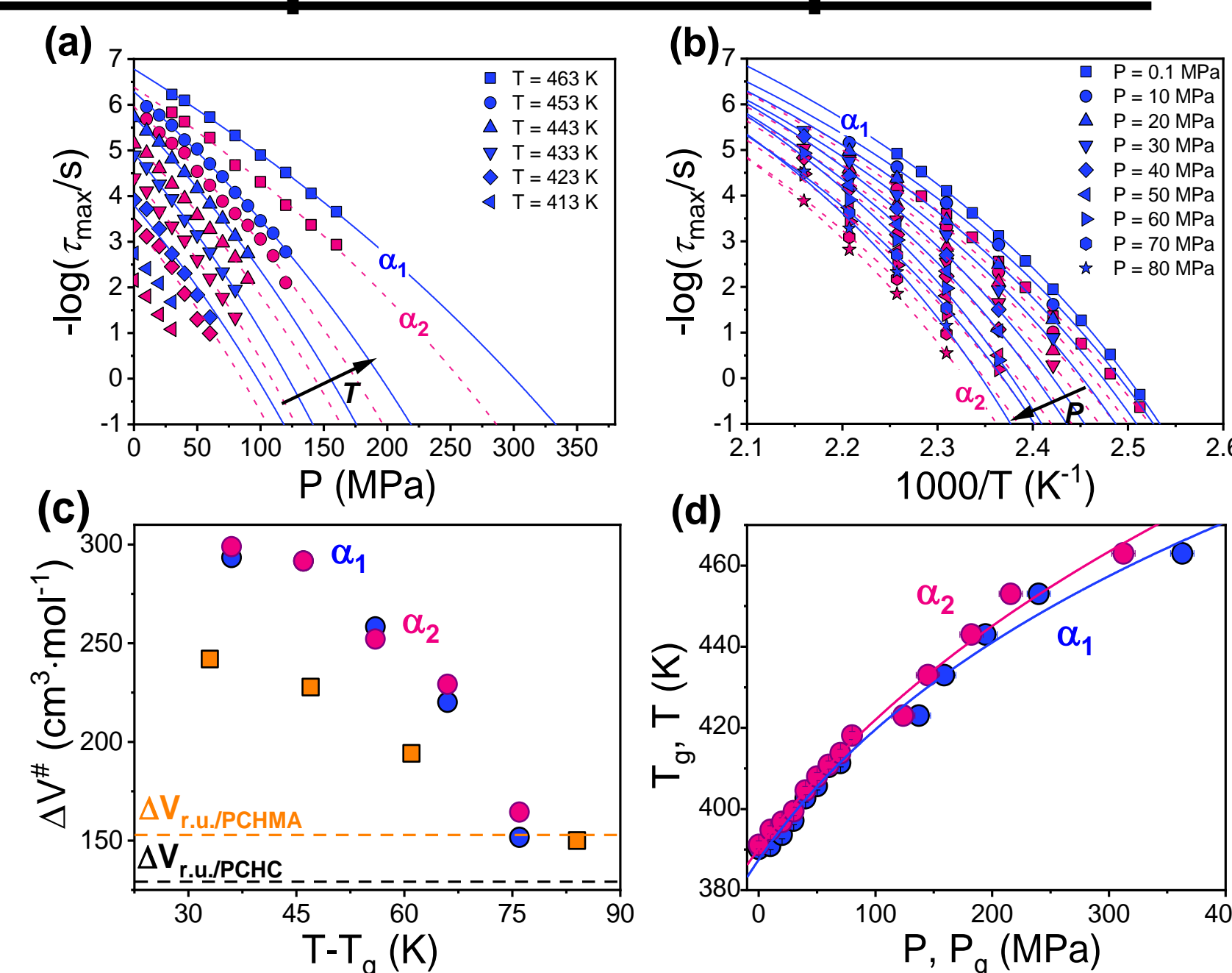
**Glassy State:**
- **δ-process** (the most intense process) is associated with the chair-to-chair conformational motion of the cyclohexane ring
- **γ-process** reflects a more local motion of the cyclohexene group
- **β-process** is associated with the partial rotation of the carboxyl group

**Above $T_g$:**
**$\alpha_1$ segmental process**
- syndiotactic units have a low dipole moment ($\mu \sim 0.7$ D/dimer unit)

**$\alpha_2$ segmental process**
- some isotactic units have higher dipole moment ($\mu \sim 3.8$ D/dimer unit)

**VFT pressure**
$$\tau = \tau_o \exp\left(\frac{D_P P_o}{P_o - P}\right)$$

**Activation Volume**
$$\Delta V^\# = 2.303 RT \left(\frac{\partial \log \tau}{\partial P}\right)_T$$

- at $T > T_g$ the activation volumes are very high
- as $T \uparrow$ they approach the repeat unit volume ($\Delta V_{r.u./PCHC} = 129$ cm$^3$·mol$^{-1}$)

$\alpha_1$ and $\alpha_2$ processes have undistinguishable $\Delta V^\#$ values they both reflect segmental relaxation of different stereoregular repeat units!

$$T_g(P) = T_g(0)\left(1 + \frac{v}{\mu}P\right)^{1/v}$$

$\alpha_1$: $dT_g/dP|_{P\to 0} = 418$ K·GPa$^{-1}$
$\alpha_2$: $dT_g/dP|_{P\to 0} = 389$ K·GPa$^{-1}$

these values are characteristic of polymers having a rigid backbone!

**Figure 6.** (a) Pressure dependence of the $\alpha_1$ (blue symbols) and $\alpha_2$ (pink symbols) processes at temperatures from 413 K to 463 K. (b) Temperature dependence of the same segmental processes under "isobaric" conditions. Pressure increases along the arrow. (c) Apparent activation volume of PCHC at 0.1 MPa as a function of temperature. Blue and pink symbols represent the $\alpha_1$ and $\alpha_2$ segmental processes, respectively. The corresponding volume for PCHMA is also included (orange symbols). The horizontal dashed lines give the corresponding repeat unit volumes. (d) Pressure dependence of $T_g$ (circles) and temperature dependence of $P_g$ (squares) for the $\alpha_1$ segmental process (green) and the $\alpha_2$ segmental process (pink). Data are obtained from the "isothermal" and "isobaric" representations at $\tau = 100$ s.

## Viscoelastic Properties



∠ 3.2 ± 0.2

∠ 1.4 ± 0.1

**Figure 9.** (a) Master curves of the storage (filled symbols) and loss (open symbols) shear moduli for PCHC$_{40}$ (red), PCHC$_{55}$ (green), PCHC$_{132}$ (blue) and PCHC$_{232}$ (purple) all at the same reference temperature of 423 K. The data are shifted horizontally with respect to the PCHC$_{132}$ data so as to coincide at the glass temperature. Lines with slopes of 1 and 2 are shown. The inset gives the shift factors fitted to the WLF equation with the shown parameters. (b) Complex viscosity as a function of angular frequency for the same PCHC homopolymers at the same reference temperature (423 K).

**Figure 10.** Double logarithmic plot of the chain dynamics normalized to the corresponding segmental dynamics (red squares) and of the zero-shear viscosity (blue circles) as a function of molar mass at the same reference temperature, $T_{ref} = 423$ K. Lines with slopes of 1 and 2 are shown with dashed lines.

The molar mass dependence of the terminal relaxation times follows the scaling $\tau_{NM}/\tau_s \sim M^{3.2}$. At the same time, the zero-shear viscosity scales as $\eta_o \sim M^{1.4}$ revealing an **intermediate behavior between Rouse and entangled chains**.
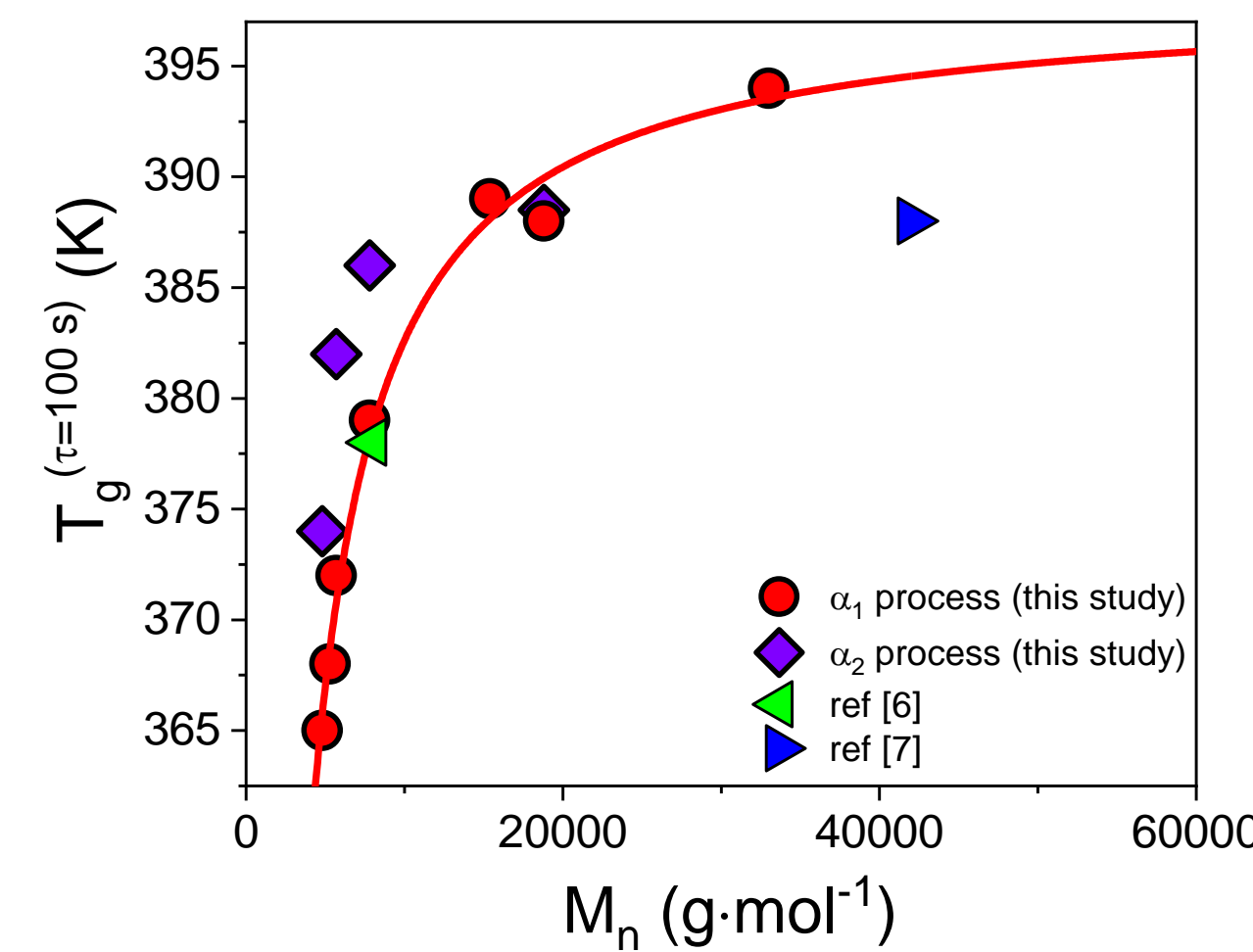


**Figure 7.** Molar mass dependence of the glass temperature of PCHC homopolymers. Data are obtained from DS (the glass temperature is operationally defined as the temperature where the dielectric loss maximum of the segmental processes is at 100 s). Additional literature data are included for comparison.[6,7]

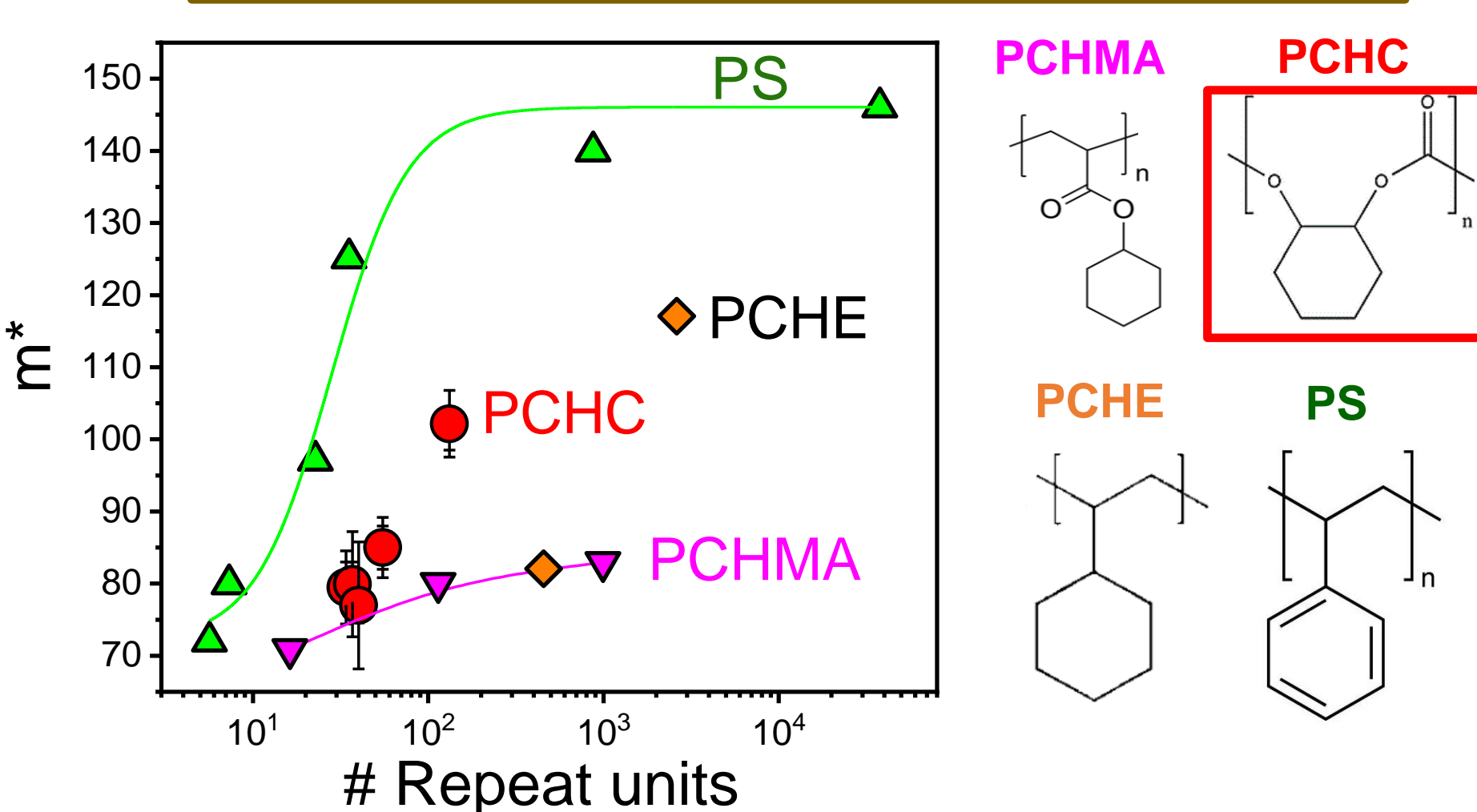the process that couples to the specific heat and freezes at $T_g$ is $\alpha_1$

**Figure 8.** Fragility or steepness index as a function of the number of repeat units. The data refer to some structurally similar polymers: (spheres): PCHC, (up triangles): PS, (down triangles): PCHMA, and (rhombi): PCHE.[11]

PCHC exhibits an increasing fragility with increasing molar mass

relation of polymer fragility to molecular structure[11,12]
- polymers with rigid backbones and bulky side groups have poorly packed chains that hence show higher fragilities
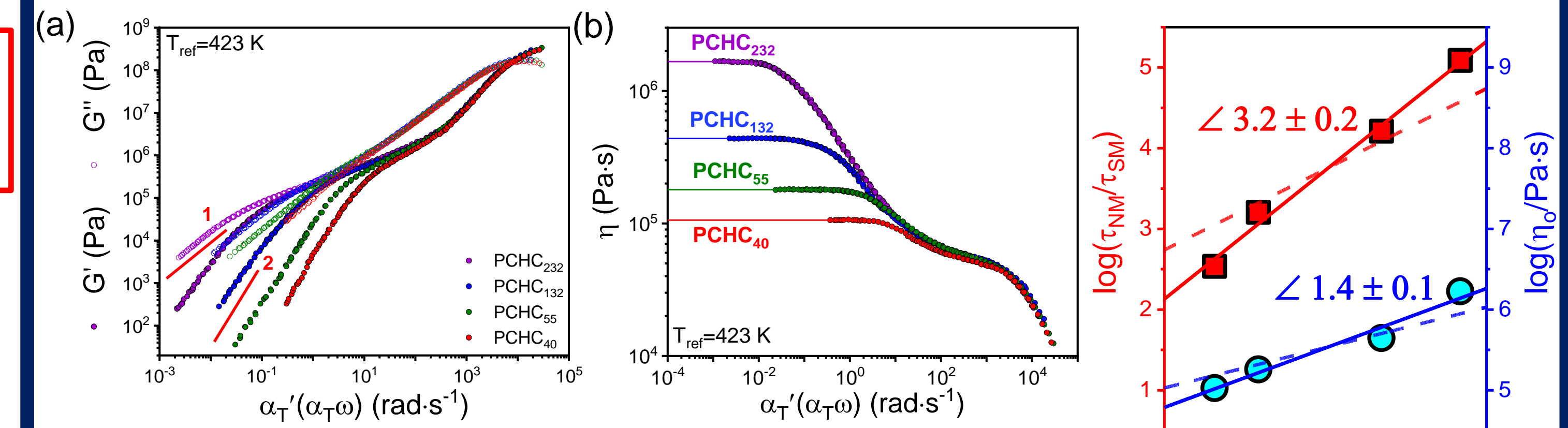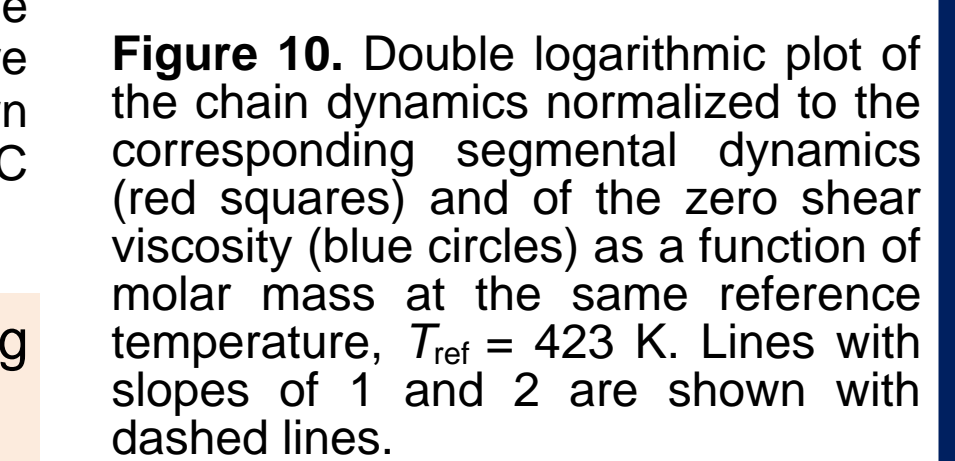- polymers with flexible chains pack better and exhibit lower fragilities

## Conclusions

A series of stereoregular poly(cyclohexene carbonate) homopolymers with molar masses in the range from 4800 g·mol$^{-1}$ to 33000 g·mol$^{-1}$ and with relatively narrow dispersities were synthesized via copolymerization of cyclohexene oxide and carbon dioxide using (R,R)-(salcy)-CoCl and bis(triphenylphosphine)iminium chloride as a catalyst. The main results are:

- The **dual segmental processes** were **inseparable by decreasing temperature or by increasing pressure.**
- Based on DFT calculations of the dipole moment, they were ascribed to **different stereo sequences** of the PCHC backbone.
- From the two processes it is only the faster one ($\alpha_1$ process) that **couples to the heat capacity.**
- The **predicted glass temperature** in the limit of very high molar masses is ~ 398 K. The high $T_g$ value justifies its **application as a CO$_2$-based alternative for polystyrene** in block copolymers.
- **Fragility increased with increasing molar mass**, an expectation born from rigid and bulky polymers. The flexible cyclohexyl group in PCHC increases the packing ability and consequently decreases the fragility.
- The molar mass dependence of the terminal relaxation times and the zero-shear viscosity with respective dependencies as $\tau_{NM}/\tau_s \sim M^{3.2}$ and $\eta_o \sim M^{1.4}$ reveal an intermediate behavior between Rouse and entangled chains.

Overall the data are suggesting that $M_e$ is well-above 16000 g·mol$^{-1}$, which plays a key role when aiming at the application of PCHC as a more sustainable replacement for polystyrene. Although PCHC is a high $T_g$ material, the lack of entanglements makes it brittle, at least for molar masses in the range of the present investigation. Efforts in CO$_2$ synthesis of PCHC should be directed at even higher molar masses, in excess of 50000 g·mol$^{-1}$.

## References

[1] Cohen, C. T.; Thomas, C. M.; Peretti, K. L.; Lobkovsky, E. B.; Coates, G. W. *Dalton Trans.* **2006**, 237–249.
[2] Hsu, T.-J.; Tan, C.-S. *Polymer* **2001**, *42*, 5143–5150.
[3] Kember, M. R.; Williams, C. K. *J. Am. Chem. Soc.* **2012**, *134*, 15676–15679.
[4] Wu, G.; Jiang, S.; Lu, X.; Ren, W.; Yan, S. Chin. *J. Polym. Sci.* **2012**, 30, 487–492.
[5] Zhang, D.; Zhang, H.; Hadjichristidis, N.; Gnanou, Y.; Feng, X. *Macromolecules* **2016**, *49*, 2484–2492.
[6] Thorat, S. D.; Phillips, P. J.; Semenov, V.; Gakh, A. *J. Appl. Polym. Sci.* **2003**, 89, 1163–1176.
[7] Koning, C.; Wildeson, J.; Parton, R.; Plum, B.; Steeman, P.; Darensbourg, D. *Polymer* **2001**, *42*, 3995–4004.
[8] Spyridakou, M.; Gardiner, C.; Papamokos, G.; Frey, H.; Floudas, G. . *ACS Appl. Polym. Mater.* **2022**, 4,3833-3843.
[9] Floudas, G.; Fytas, G.; Fischer, E.W. *Macromolecules* **1991**, 24, 1955-1961.
[10] Roland, C. M.; Casalini, R. *Macromolecules* 2007, 40, 3631-3639.
[11] Kunal, K.; Robertson, C.G.; Pawlus, S.; Hahn, S.F.; Sokolov, A.P. *Macromolecules* **2008**, 41, 7232-7238.
[12] Dudowicz, J.; Freed, K.F.; Douglas, J.F. *J. Phys. Chem. B* **2005**, 109, 21350-21356.