

Dynamics of Poly(cyclohexene carbonate) as a Function of Molar Mass

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Carbon dioxide, the main greenhouse gas, offers exciting possibilities for polymer synthesis due to its low cost and natural abundance.¹⁻² Stereoregular poly(cyclohexene carbonate) (PCHC) homopolymers were prepared via copolymerization of cyclohexene oxide and carbon dioxide (CO₂) using (*R,R*)-(salcy)-CoCl and bis(triphenylphosphine)iminium chloride as a catalyst.³ The homopolymers had molar masses in the range of 4800 g·mol⁻¹ to 33000 g·mol⁻¹. PCHC is viewed as rigid and biodegradable, an alternative bio-based polymer to polystyrene. 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 CO₂-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, τ_{NM} , and of the zero-shear viscosity, η_o , on molar mass, M , have respective dependencies as $\tau_{NM}/\tau_{SM} \sim M^{3.2}$ and $\eta_o \sim M^{1.4}$ revealing an intermediate behavior between Rouse and entangled chains.

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