



Probing the Mechanism of Glass Transition in Precisely Designed Polymers by Variable Temperature Solid State MAS NMR

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Introduction

In polymer chemistry, the occurrence of a glass transition from the amorphous phase is quite ubiquitous, and has been long known but despite extensive investigations, the molecular mechanism(s) underlying this cooperative phenomenon still remains unclear. Detailed understanding of this phenomenon is deemed important from both the fundamental significance of resolving this long-standing issue, and because the ability to control the glass transition temperature is a basic parameter for many applications. As expected, NMR has been widely used in polymer studies, including probing the glass transition but, the results have not been clear cut, likely because the polymer is not precisely engineered. Hence the structural and dynamical parameters are an averaging of different microstructural ensembles and thus hard to delineate. Here, we report on a collaborative study to probe the mechanism of the glass transition in a precision polymer (HP4PCP) by solid-state MAS NMR.

Experimental

High-resolution solid-state ^{13}C CPMAS NMR spectra were acquired on a Bruker Avance 600 MHz NMR spectrometer using a 4mm Bruker HFX triple-resonance CPMAS probe.

Results and Discussion

Figure 1 (a) presents the skeleton of the newly designed polymer.^[1] This polymer is well entangled (number average molar mass = 51.5 kDa and molar mass between entanglements $M_e = 3.6$ kDa)^[2] and has a moderate dispersity ($\mathcal{D} = 1.68$) as determined by size exclusion chromatography. Fig 1(b) shows the differential scanning calorimetry (DSC) measurements pinpointing the glass transition temperature (T_g) around 291 ± 3 K. Figure 2 (a) shows the ^{13}C CPMAS spectra of the polymer at 278.5 K, where the resonances are assigned based on the ^1H - ^{13}C dipolar-dephased spectrum (purple). Without directly attached ^1H , the C_4 signal intensity attenuates slightly, while other carbons diphase more, depending on their ^1H - ^{13}C dipolar couplings. In the backbone, the signal intensities for C_5 , C_6 , and C_7 decrease by 30%, 13%, and 16%, respectively, in the dipolar-dephased spectrum owing to their different number of covalently bonded protons. But, the phenyl group ($\text{C}_{1,2,3}$), where a single proton is bonded to each carbon site decreases only by 46%, compared to that for C_5 , implying that the phenyl group is undergoing a fast motion. This is consistent with the CODEX (centerband-only detection of exchange)^[3] measurements. The plot of normalized pure-exchange ^{13}C CODEX intensities vs. temperature, as shown in Figure 2 (b), indicates that the phenyl group undergoes a millisecond time scale motion even below T_g , while interestingly, the backbone carbons, especially for C_6 site, begins to experience a millisecond time scale motion at ~ 292 K, which coincides with the glass transition of the polymer. In other words, the polymer's backbone motion appears to be a major factor for the glass transition.

Acknowledgements

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References

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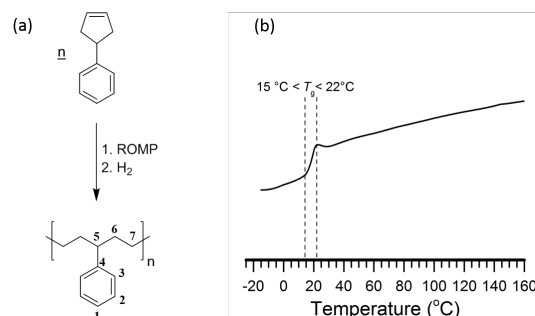


Figure 1 (a) Synthesis of precision polymer (HP4PCP) with seven distinct carbons. (b) Differential scanning calorimetry of HP4PCP showing a glass transition temperature (T_g) of $18 \pm 3^\circ\text{C}$

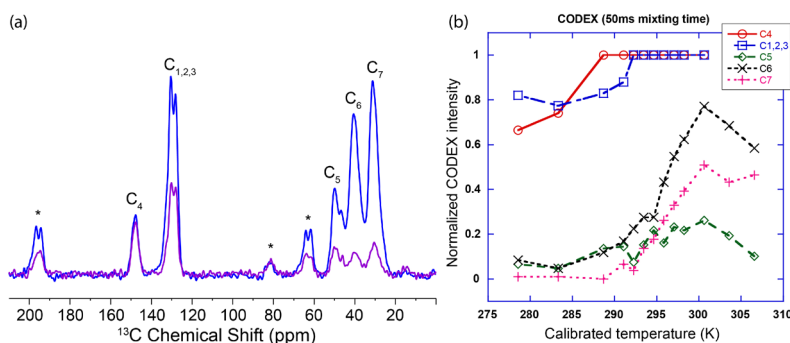


Figure 2 (a) Spin-echoed ^{13}C spectra with (blue) and without (purple) ^1H decoupling during the echo time. (b) Normalized pure-exchange CODEX intensities as a function of temperature.