Confirmation of Polybenzoxazole Structure in Thermally Rearranged Polymers by Cross-Polarization/Magic Angle Spinning Solid State ^{13}C NMR

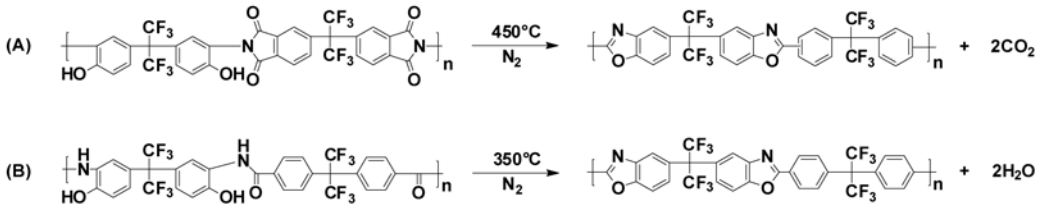
Z.P. Smith (U. of Texas, Austin); S. Wi (NHMFL); B.D. Freeman (U. of Texas, Austin)

Introduction

Thermally rearranged (TR) polymers are formed from the solid-state thermal reaction of poly(*hydroxy*-imide)s (PHI). TR polymers are insoluble and the goal of this work is to determine the structure of TR polymers through solid-state NMR spectroscopy. The chemical structure of TR polymers, which was originally proposed to be a polybenzoxazole (PBO), has recently come under debate.[1-3] An insoluble TR polymer (APAF-6FDA PBO) system was characterized by cross-polarization ^{13}C-NMR spectroscopy under the magic-angle spinning (MAS) condition.

Experimental

The chemical structures of the polymers are shown in Scheme 1. Scheme 1 (A) shows the reaction of a PHI to form a TR polymer with proposed PBO structure (i.e., APAF-6FDA PBO). Scheme 1 (B) shows the reaction of a poly(*hydroxy*-amide) to form a partially soluble PBO (i.e., APAF-6fCl PBO).



Scheme 1. (A) Reaction of APAF-6FDA, a PHI, to form an insoluble TR polymer with the proposed PBO structure shown and (B) reaction of APAF-6fCl, a poly(*hydroxy*-amide), to form a partially soluble PBO. Both PBO structures have identical chemical structure except for the oxazole-aromatic linkage, which is only a *para* configuration for the APAF-6fCl PBO and is either *meta* or *para* configuration for APAF-6FDA.

Results and Discussion

The ^{13}C NMR spectra are shown in Figure 1 below. The bottom spectra is the solution NMR spectra for the partially soluble APAF-6fCl PBO and the middle spectra is the CP/MAS spectra for the solid sample. These spectra confirm identical structure between the partially soluble portion and the insoluble portion of the PBO. The top spectra is the CP/MAS spectra for the TR polymer shown in Scheme 1A. Interestingly, this spectra has the exact same peaks and nearly identical peak intensities as the partially soluble PBO, the only difference being peak m, which is influence by the *para*/*meta* isomer effect shown in Scheme 1. These spectra confirm the chemical structure of TR polymers to be PBOs.

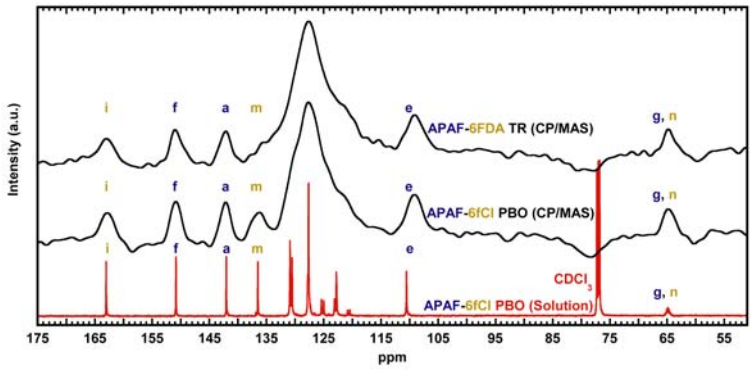


Figure 1. Comparison of solution-state ^{13}NMR and solid-state CP/MAS ^{13}C NMR of the APAF-6fCl PBO and the APAF-6FDA TR polymer.

Conclusions

The chemical structure of TR polymers is confirmed to be PBOs through the NMR work performed in this report. In addition, the soluble and insoluble fraction of the APAF-6fCl sample are identical in chemical structure.

Acknowledgements

The authors are grateful for support from the Department of Energy Office of Basic Energy Sciences through contracts DE-FG02-02ER15362, and for support from the Department of Energy Office of Basic Energy Sciences Graduate Fellowship Program through contract DE-AC05-06OR23100.

References

[1] Hodgkin, J.H., *et al.*, European Polymer Journal, **45**, 3081-3092 (2009).
[2] Hodgkin, J.H., *et al.*, European Polymer Journal, **47**, 394-400 (2011).
[3] Kostina, J., *et al.*, Industrial & Engineering Chemistry Research, **52**, 10476-10583 (2013).