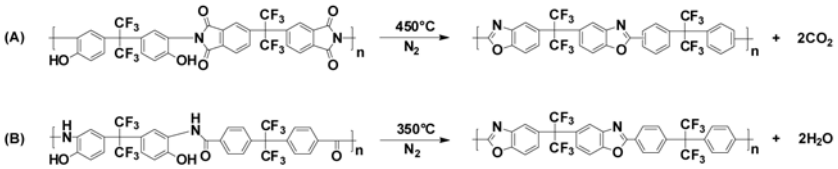
Confirmation of Polybenzoxazole Structure in Thermally Rearranged Polymers by Cross-Polarization/Magic Angle Spinning Solid State ^{13}C NMR

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

Introduction

Thermally rearranged (TR) polymers are formed from the solid-state thermal reaction of poly(*hydroxy*-imide)s (PHI). The chemical structure of TR polymers, which was originally proposed to be a polybenzoxazole (PBO), has recently come under debate.[1-3] Solid-state NMR spectroscopy was utilized for characterizing insoluble TR polymers to determine their structures and dynamics.



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.

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).

Results and Discussion

The solid-state ^{13}C NMR spectra of insoluble APAF-6FDA PBO and partially soluble APAF-6fCl PBO are shown in Figure 1 with the solution-state ^{13}C NMR spectrum for the partially soluble APAF-6fCl PBO. These spectra confirm identical structure between the partially soluble portion and the insoluble portion of the PBO. The only difference observed is the peak marked by m, which is influenced by the *para*/*meta* isomer effect shown in Scheme 1. ^{1}H T_1-rho relaxation data were acquired based on the ^{1}H-^{13}C cross-polarization magic-angle spinning (CPMAS) spectroscopy for identifying network-structured chain structures. The solid-state NMR data confirm that oxazole functionality is formed in these TR polymers. Furthermore, NMR data are compared to the gas permeation results that are provided for the precursor polymers and their corresponding TR polymer. The differences in the NMR data and transport properties for these polymers result from differences in the isomeric nature of oxazole-aromatic linkages and the resulting differences in free volume and free volume distribution, polymer rigidity, and crosslinking. This work was published in a recent scientific journal: Polymer 55, 6649-6657 (2014).

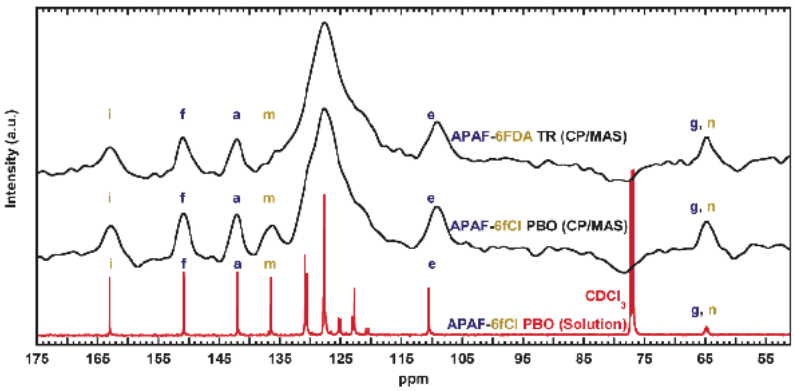


Figure 1. Comparison of solution-state ^{13}NMR and solid-state CP/MAS ^{13}C NMR obtained at 600 MHz at NHMFL of the APAF-6fCl PBO and the APAF-6FDA TR polymer.

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 fractions of the APAF-6fCl sample are identical in chemical structure.

Acknowledgements

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References

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[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).