

Elucidation of Chemical Reaction Pathways and Structure of Polyacrylonitrile Stabilized under Air and Inert Atmosphere  
by Solid State NMR

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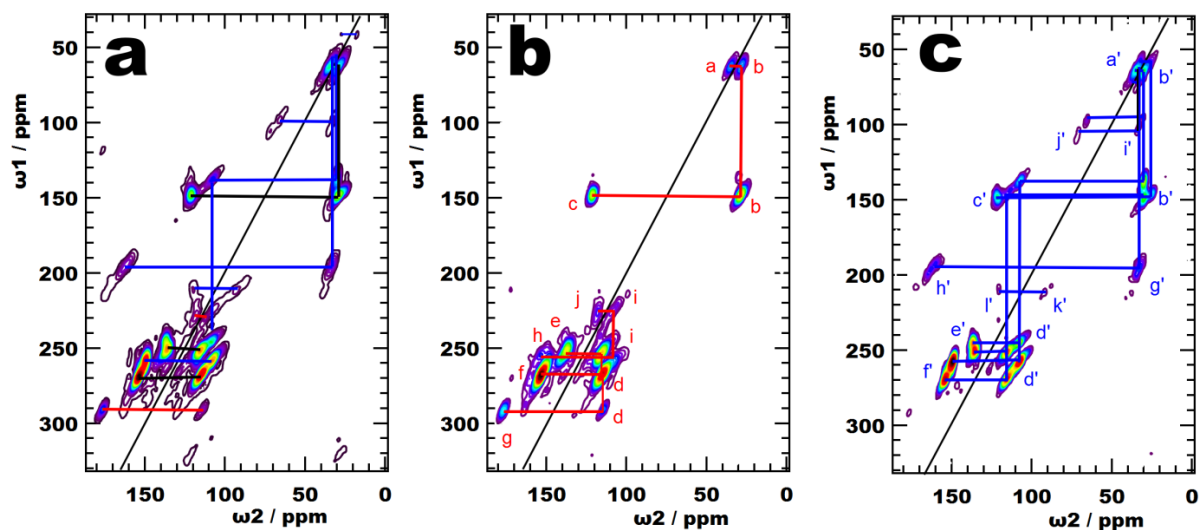
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Carbon fibers with diameter of 10-20  $\mu\text{m}$  is an evolution material due to a very small gravity, excellent mechanical property, high temperature tolerance, chemical resistance, *etc.* Nowadays, 90 % of carbon fibers in the market is made of *atactic*-Poly(acrylonitrile) (*aPAN*) based copolymers. Carbon fiber process requires several steps in heat-treatments of *aPAN* precursor fibers at different temperatures and times, under different atmospheres. Among them, heat-treatment at the lowest temperatures of 200 – 300  $^{\circ}\text{C}$  under air, so called, stabilization process is the most important one to set the structure. Stabilization conditions significantly affect mechanical strength of the final carbon fibers. Thereby, stabilized structures and chemical reaction mechanisms of *aPAN* have been extensively studied in the past decades. However, stabilized structure and reaction mechanisms of *aPAN* are very complex and thus have been debatable matter in literatures. Recently, Liu *et al.*<sup>1, 2</sup> reported that two dimensional (2D) correlation solid-state (ss) NMR techniques combined with  $^{13}\text{C}$  isotope labeling have significantly improved spectral resolutions of the  $^{13}\text{C}$  signals of *aPAN* powders heat-treated under air and vacuum (inert gas). Based on through bond correlation NMR, Liu *et al.* proposed that fully stabilized structure of *aPAN* powder is consisting of four major subgroups. These structures commonly include heterocyclic six-membered rings and polyene structure including unsaturated carbon-carbon bonds, intermolecular cross-linkings, oxidized carbons which are “thermally stable” structure. Under vacuum, 7- 8 subgroups were observed and six-membered pyridine as a major structure in addition to saturated six-membered rings including piperidine, which arises from initial reaction of cyclization. Absence of oxygen leaves significant amounts of saturated carbon-carbon bonds in the six membered rings as well as the linear alkyl chains. These saturated bonds are exposed to chain scission and thus may not survive at further high temperature process.

In the cases of fibers/films, oxygen diffusion is limited and thus chemical reactions show the depth dependences, depending on oxygen concentrations. Auger Electron Spectroscopy (AES) and Electron Energy Loss Spectroscopy (EELS), Near-edge X-ray absorption fine structure (NEXAFS), Synchrotron IR imaging were applied to investigate depth profiles of elements and functional groups of *aPAN* fibers. As results, it was indicated that concentration of  $\text{C}\equiv\text{N}$  group in the core is lower than that at the surface. It was suggested that chemical reactions are more significant in the core than those at the surface. However, the structural change from  $\text{C}\equiv\text{N}$  to  $\text{C}=\text{N}$  group is induced by cyclization process, which does not involve oxygen. Thereby, a higher concentration of the  $\text{C}=\text{N}$  group in the core than that at the surface is not sufficient to understand the stabilized structure. A novel approach, which can elucidate spatially heterogeneous chemical structures of *aPAN* fiber/films heat-treated under air, is definitively necessary.

In this work, thickness effect on spatially heterogeneous chemical reactions of  $^{13}\text{C}$  labeled *atactic*-Poly(acrylonitrile) (*aPAN*) films with thickness of 5 – 30  $\mu\text{m}$  heat-treated under air was for the first time investigated by ssNMR and  $^{13}\text{C}$  isotope labeling. It was found that both  $^{13}\text{C}$  direct polarization magic angle spinning (DPMAS) NMR spectra and  $^1\text{H}$  spin-lattice relaxation time ( $T_{1\text{H}}$ ) of the *aPAN* films heat-treated under air show thickness dependences. Tunable  $T_{1\text{H}}$  filtered  $^{13}\text{C}$  –  $^{13}\text{C}$  INADEQUATE NMR selectively revealed detailed chemical structures of

either *a*PAN stabilized well in the presence of oxygen or *a*PAN stabilized poorly under less oxygen in the film (as shown in Figure 1). A simple  $^{13}\text{C}$  line-shape analysis was proposed to estimate fractions of the well stabilized region in the whole films. This technique will be useful for detailed analysis of industrial fibers.



**Figure 1.**  $^{13}\text{C}$ – $^{13}\text{C}$  INADEQUATE spectra of  $^{13}\text{C}$  labeled *a*PAN films with a thickness of 20  $\mu\text{m}$  heat treated under air (a) without and with  $^1\text{H}$   $T_1$  filters of (b) 350 and (c) 165 ms, measured at 25  $^\circ\text{C}$ . (b) The spectrum in (b) and (c) corresponds to the spectra for the chemical structure of *a*PAN stabilized well under air and poorly under less oxygen in the 20  $\mu\text{m}$ .

This two years project significantly enhanced our understanding basic chemical reactions of industrially important materials. This program has supported two PhD students and two master students. Based on thie achievement, we will propose a new grant to a federal agency. Thank you very much for supporting us.

## References

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