

# SYNTHESIS OF NEW CYANATE ESTER RESINS FOR POLYMER FLAMMABILITY STUDIES

Jeffrey W. Gilman, James E. Brown, and Kimberly D. Oliver

Materials Fire Research Group, Building and Fire Research Laboratory,  
National Institute of Standards and Technology, Gaithersburg, Maryland 20899

## Abstract

We have synthesized several new cyanate ester substituted polystyrene polymers and copolymers. The synthesis and thermal analysis of these polymers is part of an ongoing effort in our lab to investigate the relationships between polymer structure, degradation behavior and flammability.

## Background

Current approaches to fire retarding polymeric materials are limited by a number of issues. In terms of additives approaches; halogen based fire retardants produce corrosive combustion products and some are alleged to produce toxic doxins and dibenzofurans during the burning. Halogen based fire retardants are also tend to increase the yield of carbon monoxide and smoke during combustion. Phosphorus based fire retardants also increase the amount of carbon monoxide and smoke during combustion (by five to ten times as much). Hydrates, which decompose by an endothermic process to produce water, must be used at such high loadings that (40-70% wt) the physical properties of the base polymers are excessively compromised.

All of these types of additives are already in use in the fire retarded materials used in commercial aircraft cabin components (glass fiber-reinforced phenolic composites, polyurethane foam, etc.). These components, however, do not meet the new goal set forth of 15 minutes for the time available for escape from a post-crash aircraft cabin fire. This goal enumerates an order-of-magnitude improvement in aircraft materials fire performance and translates to a requirement for the development of new fire-safe materials with heat release rates less than 40-50 kW/m<sup>2</sup> at 75 kW/m<sup>2</sup> heat flux using the standard Cone Calorimeter materials flammability test ASTM E-1354(1).

To be successful at reaching this quite challenging goal we must discover the relationships between polymer structure, degradation behavior and flammability and then use this information to design next generation fire-safe materials. We are in the process of investigating the relationship between crosslink density and polymer flammability. We have designed and synthesized a series of cyanate ester polymers which when cured contain a specific but variable number of triazine crosslink sites which have exceptional thermal stability.

## Synthesis

The poly(4-cyanatostyrene-styrene) copolymers were prepared via the synthetic route shown in Scheme 1 (2). Different monomer ratios of the 4-acetoxystyrene and styrene were used in the initial polymerization to prepare

copolymers with varying degrees of cyanate ester functionality in the final copolymers. The homopolymer, poly(4-cyanatostyrene) was prepared from the commercially available poly(4-hydroxystyrene) which was generously donated to us by Hoechst Celanese Corporation.

Poly(4-acetoxystyrene-co-styrene) copolymers, with general structure 1, were prepared as follows: the monomers, 4-acetoxystyrene (inhibitor free, Aldrich 98%) and styrene (inhibitor free, Aldrich 98%) were combined in the desired relative amounts and freeze-thaw-degassed three times in vacuo to remove O<sub>2</sub>. Benzoyl peroxide was added and the sealed container heated at 68 °C for 24-48 hours. The polymers were isolated by dissolving in acetone and precipitation into hexanes. The polymers were characterized by GPC, FTIR and <sup>13</sup>C NMR. The data was consistent with their structures and that published in the literature (3).

Poly(4-hydroxystyrene-co-styrene) copolymers, with general structure 2, were prepared by dissolving the crude poly(4-acetoxystyrene-co-styrene), 1, in dioxane. To this solution was added hydrazine hydrate (2%) and water (1%) (4). The reaction was stirred for three days at ambient temperature. The reaction was diluted with dioxane and precipitated into hexanes (1x). The residue was dissolved in acetone, re-precipitated into hexanes (1x) and water (1x) and dried in vacuo (24h) to give a quantitative yield.

The following preparation (5) of the homopolymer, poly(4-cyanatostyrene), prepared from the commercially available poly(4-hydroxystyrene), represents a typical procedure for synthesis of the poly(4-cyanatostyrene-co-styrene) copolymers. Poly(4-hydroxystyrene) was dissolved in acetone (2% soln.) cooled to -5 °C and charged with cyanogen bromide (1.5 eq.) in acetone and triethylamine (1.7 eq.) in acetone. The reaction temperature is kept below 0 °C during these additions. The reaction was allowed to stir for 40 minutes at 0 °C and then was allowed to warm to room temperature over 30 minutes. The reaction mixture was poured over ice water and the polymer collected by filtration followed by washing with cyclohexane. It is critical that the reaction go to completion, i.e., that all the phenol be cyanated, or the residual phenol can catalyze cure reactions and prematurely crosslink the polymer. In addition we found that if the final cyclohexane wash was omitted the polymer would slowly become insoluble sitting at ambient temperature. Typical yields were ~75-85%.

## Characterization

GPC analysis and <sup>13</sup>C NMR analysis both gave a *M<sub>n</sub>* of ~3.3K. *M<sub>w</sub>* by GPC was 6.2K. FTIR showed the

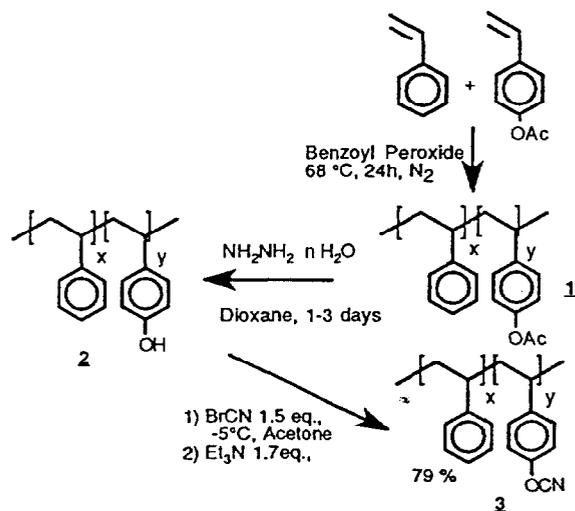
characteristic doublet cyanate ester stretch at 2200-2300  $\text{cm}^{-1}$  (6) and no phenol OH stretch. The solid state  $^{13}\text{C}$  NMR analysis of poly(4-cyanatostyrene) is shown in Fig. 1. The techniques of cross polarization (CP) and magic angle spinning (MAS) were used to obtain the spectrum shown in the middle of Fig. 1. An interrupted decoupling experiment which allows observation of only the non-protonated carbons in the structure yielded the spectrum shown on the bottom of Fig. 1. The difference spectrum obtained by subtracting the bottom spectrum from the middle spectrum shows only protonated carbons in the structure and is shown in the top of Fig. 1. The predicted  $^{13}\text{C}$  NMR signals for poly(4-cyanatostyrene) are shown in Fig. 2 (7,8). The combination of these data allows the following assignments: 30 ppm (t-butyl end group from initiator used by Hoechst Celanese), 39 ppm (methine carbon), 44 ppm (methylene carbon), 110 ppm (cyanate ester carbon), 114 ppm (3,3' aromatic carbons), 130 ppm (2,2' aromatic carbons), 144 ppm (1 position aromatic carbon) and 150 ppm (4 position, OCN substituted, aromatic carbon).

### Thermal Analysis

DSC and TGA thermal analysis of poly(4-cyanatostyrene) is shown in Fig. 3 and Fig. 4. respectively. The substitution of cyanate ester functionality on to PS has radically changed the decomposition behavior of the polymer. In the DSC we see a series of overlapping exothermic cure reactions occurring between 200 and 400  $^{\circ}\text{C}$ . These cure reactions must be crosslinking the polymer and must be responsible for the very high residue yield of ~55%. We are continuing our investigation of these polymers with the goal of understanding the relationships between polymer structure, degradation behavior and polymer flammability.

### Acknowledgements

The authors thank Mr. Michael Smith for DSC analysis. The authors are grateful for partial support of this work by the Federal Aviation Administration under Interagency Agreement DTFA003-92-Z-0018, and for discussions with Dr. Richard E. Lyon (FAA) and Dr. Sagel Das (Lonsa Ltd).



Scheme 1. Synthesis of Poly(4-cyanatostyrene-co-styrene)

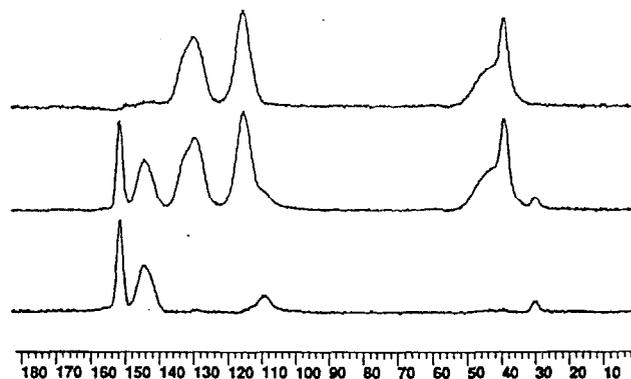


Fig. 1. Solid State  $^{13}\text{C}$  NMR analysis of Poly(4-cyanatostyrene).

Top spectrum: difference spectrum (Middle-Bottom) shows only protonated carbons in the structure, Middle spectrum: normal CP/MAS spectrum, Bottom spectrum: interrupted decoupling spectrum shows only non-protonated carbons in the structure.

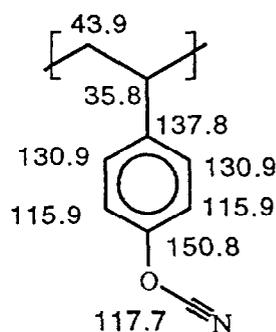


Fig. 2. Showing calculated  $^{13}\text{C}$  NMR chemical shifts for poly(4-cyanatostyrene).

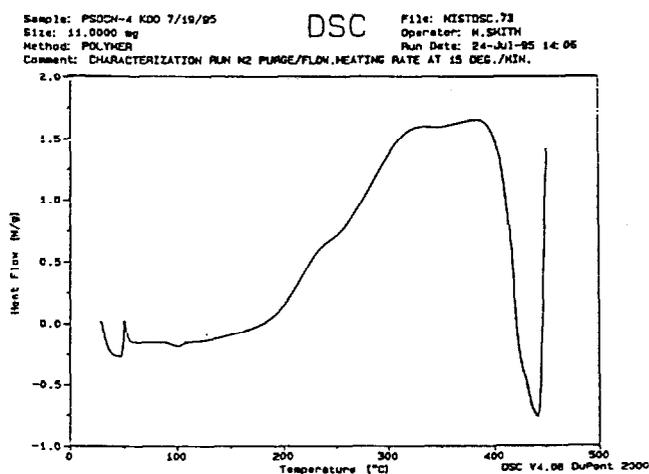


Fig. 3. DSC of Poly(4-cyanatostyrene).

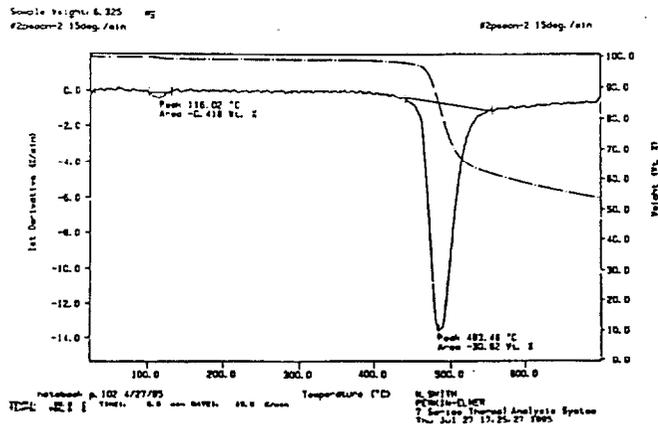


Fig. 4. TGA of Poly(4-cyanatostyrene).

## References

1. R. E. Lyon, Advanced Fire-Safe Aircraft Materials Research Program, DOT/FAA/CT-94/60, draft, June 1994.
2. Certain commercial equipment, instruments, materials, services or companies are identified in this paper in order to specify adequately the experimental procedure. This in no way implies endorsement or recommendation by NIST.
3. C. J. T. Landry, D. M. Teegarden, *Macromolecules*, 1991, 24, 4310.
4. K. J. Zhu, S. F. Chen, T. Ho, E. M. Pearce, and T. K. Kwei, *Macromolecules*, 1990, 23, 150.
5. In *Chemistry and Technology of Cyanate Ester Resins*, Chapter 2., pg 22, A. W. Snow, Ed. I. Hamerton, 1994, Chapman & Hall.
6. In *Chemistry and Technology of Cyanate Ester Resins*, Chapter 2., pg 8, A. W. Snow, Ed. I. Hamerton, 1994, Chapman & Hall.
7. Carbon NMR chemical shift were predicted using the <sup>13</sup>C NMR module contained in Chemintosh a molecular drawing software package from Softshell Inc.
8. In *Chemistry and Technology of Cyanate Ester Resins*, Chapter 2., pg 21, 49, A. W. Snow, Ed. I. Hamerton, 1994, Chapman & Hall.