FLAMMABILITY STUDIES OF NEW CYANATE ESTER RESINS

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ABSTRACT

We have synthesized several new cyanate ester functionalized polystyrene polymers and copolymers. Poly(4-cyanatostyrene), PCS, poly(4-cyanatostyrene) "polymer grade", PCS-PG, poly(4-cyanatostyrene) "novalak grade", PCS-NG, poly(4-cyanatostyrene-co-methylmethacrylate), PCS-MMA, and poly(4-cyanatostyrene-co-1,3-butadiene), PCS-BD, were all prepared via cyanation of the corresponding 4-hydroxystyrene polymer or copolymer, using cyanogen bromide and triethylamine. The synthesis gives good yields of these polymers. Differential scanning calorimetry, DSC, of these polymers shows that they cure completely under standard, non-catalyzed, thermal cure conditions. Flammability tests, performed using the Microscale Combustion Calorimeter, show significant differences in flammability of the cured polymers, depending on polymer structure.

KEY WORDS: Cyanate ester, Flammability, Toughening, Synthesis

1. INTRODUCTION

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 products during incineration. Halogen based fire retardants also tend to increase the yield of carbon monoxide and soot during combustion. Some phosphorus based fire retardants also tend to increase the yield of carbon monoxide and soot during combustion (by as much as five to ten times). Hydrates, which decompose by an endothermic process to produce water, such as aluminum trihydrate (ATH), must be used at such high loading (mass fraction of 40 % - 70 %) that the physical properties of the base polymers are 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 50 kW/m^2 at 75 kW/m^2 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 ulta-fire-safe materials. We are in the process of investigating the relationship between polymer structure and polymer flammability.

We have synthesized a series of cyanate ester polymers which when cured yield triazine crosslink sites. Cyanate ester polymers were chosen because of the greater thermal stability of the triazine moiety, as compared to the aliphatic crosslinks that were examined in previous polymer structure - flammability studies (2, 3). The first three polymer structures in this series, poly(4-cyanatostyrene), PCS, (poly(4-cyanatostyrene) "polymer grade", PCS-PG, and poly(4-cyanatostyrene) "novalak grade", PCS-NG, shown in Figure 1, allows us to study the effect of the degree of branching, and hence the effect of crosslink density, on the flammability of this type of polymer. The random copolymers , poly(4-cyanatostyrene-co-1,3-butadiene), PCS-BD, and poly(4-cyanatostyrene-co-methylmethacrylate), PCS-MMA, shown in Figure 1, allow us to examine the effect of incorporation of butadiene and methylmethacrylate units into the PCS polymer. In addition to the effect these changes may have on flammability we envision changes in the mechanical properties too. Specifically these resins may be useful as toughening agents for more "brittle" commercial cyanate ester resins. However, since the primary goal of this work is to design next generation ulta-fire-safe materials for aircraft interior applications, any candidate toughening agent must not substantially increase the flammability when combined with the commercial resin.

2. EXPERIMENTAL

2.1 Synthesis. The following preparation (4) of the homopolymer, poly(4-cyanatostyrene), PCS, prepared from the commercially available poly (4-hydroxystyrene) (5), represents a typical procedure for synthesis of the series of cyanate ester polymers and random copolymers; (poly(4-cyanatostyrene) "polymer grade", PCS-PG, , poly(4-cyanatostyrene) "novalak grade", PCS-NG, poly(4-cyanatostyrene-co-1,3-butadiene), PCS-BD, and poly(4-cyanatostyrene-co-methylmethacrylate), PCS-MMA, shown in Figure 1 (except the commercial Primaset PT30 resin).

Poly (4-hydroxystyrene) (dried) was dissolved in acetone (anhydrous, mass fraction 2 % in acetone solution), cooled to - 5° C, under N_2, and was charged with cyanogen bromide (1.05 eq.) in acetone (anhydrous) and triethylamine, TEA, (anhydrous, 1.0 eq.) in acetone (anhydrous). The reaction temperature was kept below 0° C during these additions. The reaction was allowed to stir for 60 minutes while warming to 10° C to 15˚ C. The reaction was then filtered, while cold, to remove the TEA:HBr salts. The filtered solution, containing the dissolved polymer, was precipitated into methyl alcohol (0˚ C, anhydrous, 1:10 filtrate to alcohol ratio, 1 X). The polymer was then washed with additional cold methanol. Solvent was removed in vacuo (24 h, 25˚ C, 0.1 mm Hg) over P_2O_5, to give a 75 % to 80 % yield of PCS.

3. CHARACTERIZATION

3.1 Solid state ^{13}C NMR Analysis. Figure 2 shows the solid state ^{13}C NMR analysis of poly(4-cyanatostyrene). The techniques of cross polarization (CP) and magic angle spinning (MAS) were used to obtain the spectrum shown in the middle of Figure 2. An interrupted decoupling experiment which allows observation of only the non-protonated carbons in the structure yielded the spectrum shown on the bottom of Figure 2. The difference spectrum shown in the top of the Figure was obtained by subtracting the bottom spectrum from the middle spectrum, and shows only the protonated carbons in the structure. The predicted ^{13}C NMR signals for poly(4-cyanatostyrene) are shown in Figure 3 (6,7). 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).

3.2 GPC and FTIR Analysis. GPC analysis (relative to polystyrene standard) (and ^{13}C NMR analysis) gave a Mn of ~3,300 g/mole for poly(4-cyanatostyrene). Mw by GPC was 6,200 g/mole for poly(4-cyanatostyrene). The other copolymers shown in Figure 1 were synthesized from 4-hydroxystyrene precursors of similar molecular weights. (Mn : 2,600 g/mole - 8,000 g/mole, polydispersity : 2-7, manufacturers data). FTIR showed the characteristic doublet cyanate ester stretch at 2200-2300 cm^{-1} and little or no phenol OH stretch following the cyanation reaction (see Figure 4, middle spectrum).

4. THERMAL CURE

4.1 Cure Schedule. All the cyanate ester polymers were successfully cured using the following non-catalyzed thermal cure schedule:

Initial-Cure:

1) 22 ° C to 100 ° C using a 5.5 ° C/minute heating rate, hold for 30 minutes.

2) 100 ° C to 177 ° C using a 1.0 ° C/minute heating rate, hold for 120 minutes.

Post-Cure:

1) 22 ° C to 100 ° C using a 5.5 ° C/minute heating rate, hold for 30 minutes.

2) 100 ° C to 150 ° C using a 8.0 ° C/minute heating rate, hold for 30 minutes.

3) 150 ° C to 200 ° C using a 5.5 ° C/minute heating rate, hold for 60 minutes.

4) 200 ° C to 250 ° C using a 3.0 ° C/minute heating rate, hold for 180 minutes.

4.2 FTIR and DSC Cure Monitoring. The loss of the characteristic doublet cyanate ester stretch at 2200-2300 cm^{-1} (8) (observed for all the PCS cyanate esters) can be seen by comparing the FTIR for poly(4-cyanatostyrene) before the initial-cure (middle spectra, Figure 4) and after the post-cure (top spectra, Figure 4). Further evidence for a complete (90 % to 95 %) cure can be seen from DSC analysis. Figure 5 and Figure 6

show, respectively, the DSC for poly(4-cyanatostyrene) before initial-cure and after post-cure. No cure exotherm is observable after the post-cure for any of the cyanate ester polymers. TGA analysis of the cured polymer (not shown) gives a peak mass loss rate at ~ 450° C, therefore, the peaks in Figure 6 (and in Figure 5) above 400° C are from the decomposition of the cured polymer.

5. FLAMMABILITY ANALYSIS

5.1 Microscale Combustion Calorimeter. Flammability data on the cyanate esters were obtained using the Microscale Combustion Calorimeter. This apparatus is a custom built system developed by Lyon and Walters, details of which are reported elsewhere, and in these proceeding (9, 10). This calorimeter couples a thermogravimetric analysis instrument with a gas-phase flow combustion system. The microscale calorimeter rapidly heats (>200 K/minute) a milligram size sample to 625° C, and hold that temperature for ~5 minutes, in the TGA under an inert atmosphere, and then burns the pyrolysis gases in excess oxygen at high temperature.

As Figure 7 shows, there are significant differences in the "micro-heat release rate" (μHRR) and char yield data for these materials (11). As expected the resins with the higher char yields have lower peak μHRRs. (Char yields obtained under standard type TGA conditions, 10° C/minute in N_2, are identical to those reported in Figure 7.) Figure 7 also shows that the PT30 resin has a lower peak μHRR than all of the PCS resins. This is most likely due to the greater thermal stability of the phenol-formaldehyde structure as compared to the styrenic-type structure of the PCS resins. Comparison of the results for PCS, PCS-PG and PCS-NG reveals that as the degree of branching increases, the peak μHRRs decrease and the char yields increase. The branched structures (PCS-PG, PCS-NG) yield a more highly crosslinked network, once the resins are completely cured. That is, the level of substitution of the aromatic structures in the cured resins is higher for the branched resins. The PCS is disubstituted, the PCS-PG is both disubstituted and trisubstituted, and the PCS-NG is trisubstituted and tetrasubstituted. This poly-substitution results in 42 % and 54 % lower peak μHRRs for PCS-PG and PCS-NG respectively. This behavior is consistent with the relationships, found by Van Krevelen, between the number of methylene brigdes in phenol - formaldehyde type polymers, and the char yield and flammability (measured by oxygen index) (12). The two PCS random copolymers have very different behavior. The PCS-BD has the same peak μHRR and char yield as the parent PCS, even though it has a higher equivalent weight, hence a lower the crosslink density. This indicates that the BD portion may be crosslinking during pyrolysis. The PCS-MMA resin has the highest peak μHRR. This is most likely due to the presence of the low thermal stability, methylmethacrylate, units in the backbone of the copolymer (13), and the higher equivalent weight (PCS-MMA : 245 g/eq) as compared to the other resins (PCS, PCS-PG, and PCS-NG : 145 g/eq.). In general, the higher the equivalent weight the lower the crosslink density in the cured resin.

6. CONCLUSIONS

We have synthesized several new cyanate ester functionalized polystyrene polymers, via cyanation of the corresponding 4-hydroxystyrene polymer or copolymer, using cyanogen bromide and triethylamine. DSC of the polymers shows that they cure completely under standard, non-catalyzed, thermal cure conditions. Flammability tests, performed using the Microscale Combustion Calorimeter, showed significant differences in flammability of the cured polymers, depending on polymer structure. The more

highly branched PCS polymers, PCS-NG and PCS-PG, exhibited lower flammability than the unbranched PCS. The PCS-BD showed similar behavior to PCS indicating that the BD portions may be crosslinking during pyrolysis. The PCS-MMA copolymer was the most flammable, presumably due to the low thermal stability of the MMA segments.

7. FUTURE WORK

We are continuing to evaluate the structure flammability relationships of these materials. With respect to utilization of this data to design a cyanate ester toughening agent that will not increase the flammability of the system, a structure which combines the advantages derived from a branched structure (PCS-PG or PCS-NG) with the toughening expected from a polybutadiene segment (PCS-BD) is envisioned (see Figure 8). This proposed PCS structure and some of the PCS polymers (e.g. PCS-MMA and PCS-BD) will be evaluated as toughening agents for commercial cyanate esters. In future studies larger, bench-scale, Cone Calorimeter tests will be used in addition to the Microscale Combustion Calorimeter to evaluate flammability.
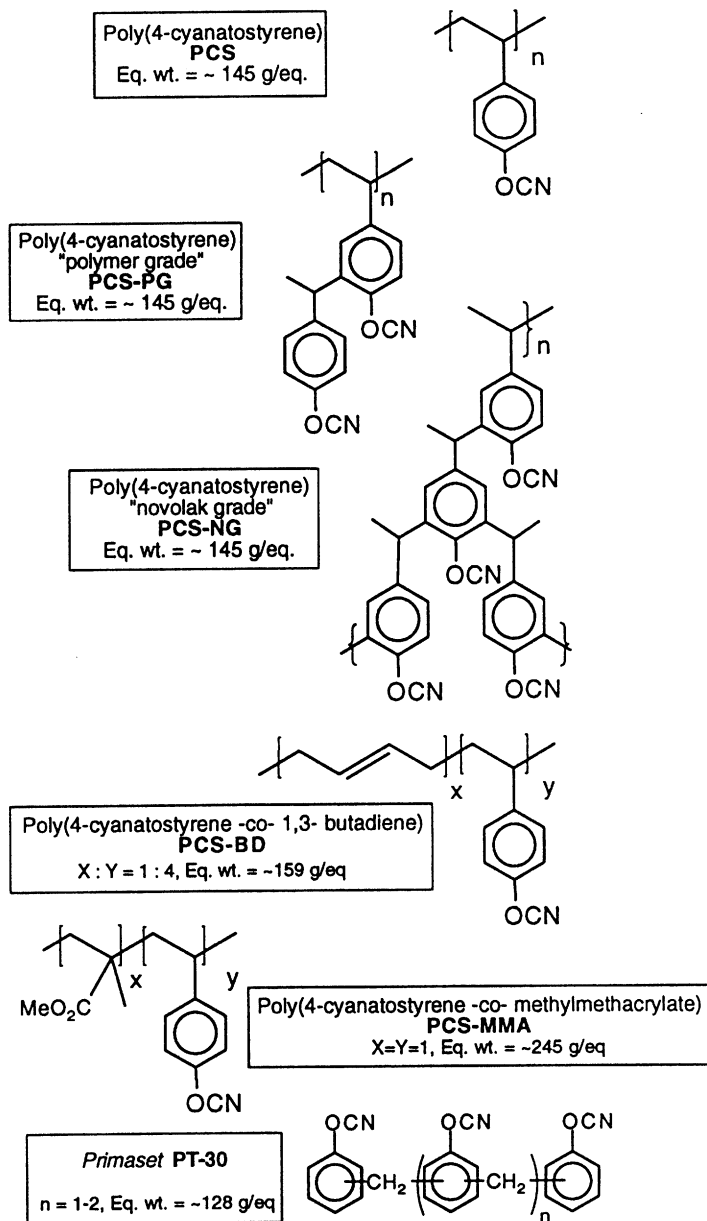
8. ACKNOWLEDGMENTS

Figure 1. New cyanate Ester resins prepared from the corresponding phenol precursor via cyanation reaction, and the commercial PT30 resin.
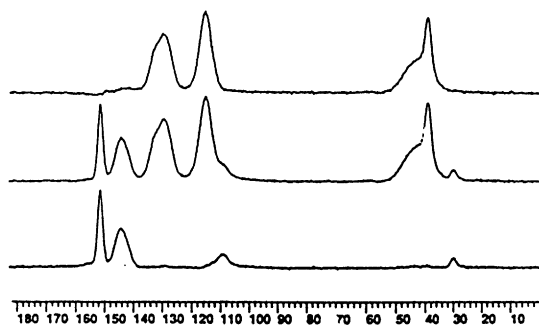
Figure 2. Solid State ^{13}C NMR analysis of Poly(4-cyanatostyrene).

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.
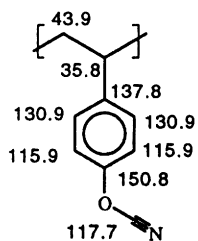

Figure 3. Calculated (solution) ^{13}C NMR chemical shifts for poly(4-cyanatostyrene).
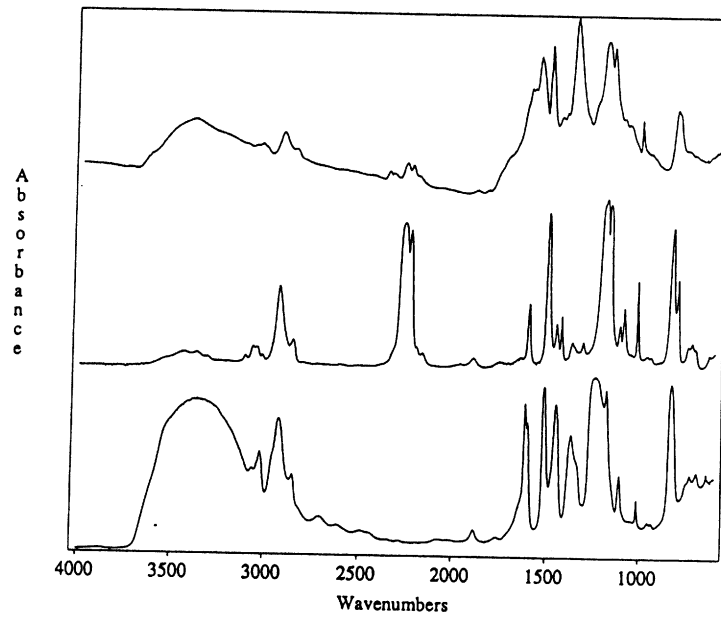
Figure 4. FTIR spectra of poly(4-hydroxystyrene) (bottom), poly(4-cyanatostyrene), PCS, (middle), post-cured PCS (top).
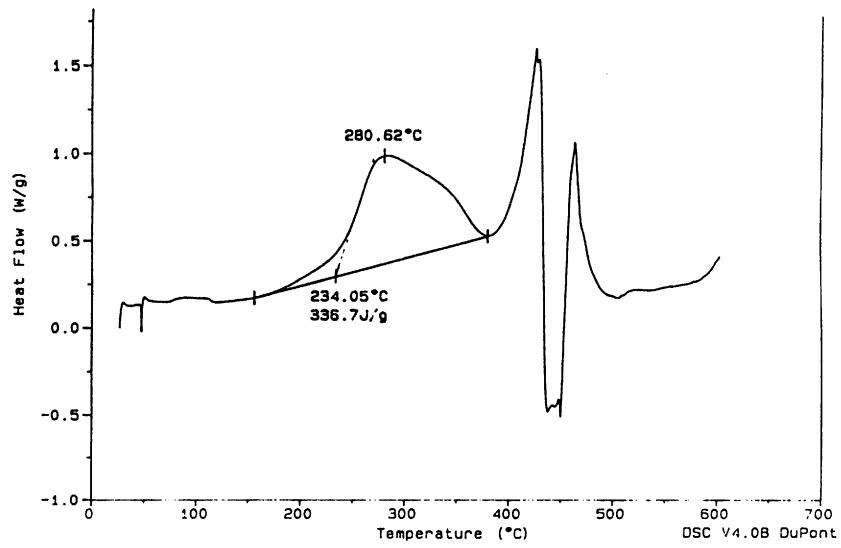

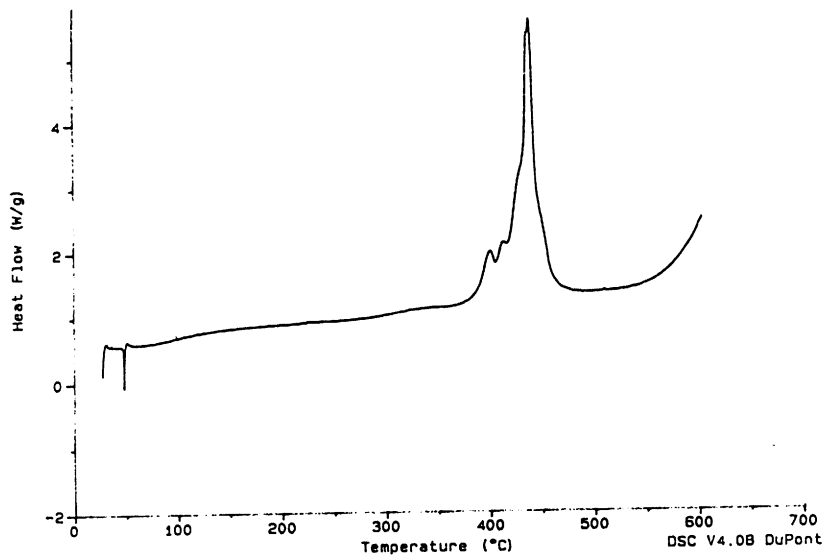Figure 5. DSC of poly(4-cyanatostyrene), PCS, showing exotherm from 200 °C to 380 °C.

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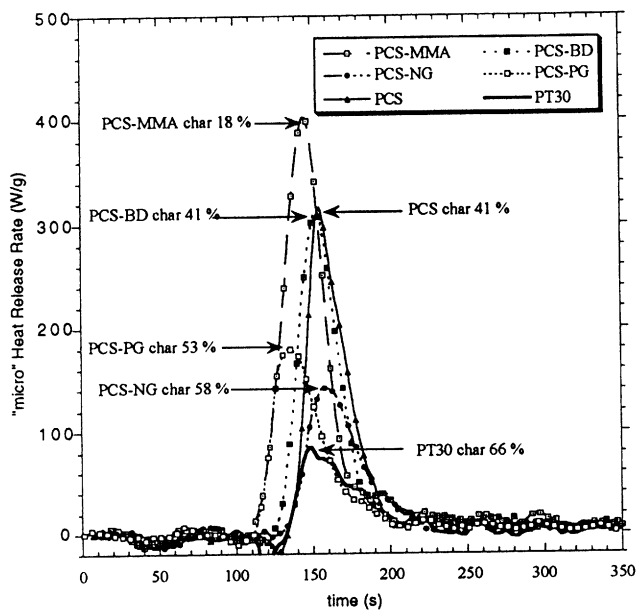Figure 6. DSC of post-cured poly(4-cyanatostyrene), PCS, showing no residual cure exotherm.

Figure 7. Flammability data (μ-HRR) on the cyanate esters, obtained using the Microscale Combustion Calorimeter.
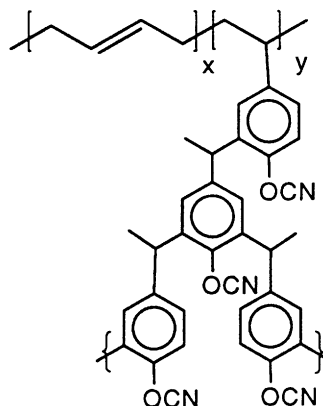
Figure 8. Proposed PCS copolymer structure which combines the advantages derived from a branched structure (PCS-PG or PCS-NG) with the toughening expected from a polybutadiene segment (PCS-BD).

8. REFERENCES

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5. 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.

6. Carbon NMR chemical shift were predicted using the 13-C NMR module contained in Chemintosh a molecular drawing software package from SoftShell Inc.

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11. Due to the uncertainty in the time of the peak µHRR (± 20 %) the differences observed for these data are not significant. Typical uncertainty, calculated using standard methods, in the value of the peak µHRR is ± 5 % (i.e., ± 1 standard deviation), uncertainty in the char yield is ± 1 %, see reference 10.

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