

Laser Pyrolysis of Characterized Cyanurate Network Polymers

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Synopsis

A series of bisphenol A dicyanate network polymers with degree of crosslinking varied by addition of 4-cumylphenylcyanate were prepared and characterized by model compound study, infrared spectroscopy, DSC, TGA, and statistical analysis. Laser ablation energy measurements varied from 14 to 18 kJ/g and were found to linearly increase with degree of crosslinking. Comparative ablation energy analysis was made with other aromatic, nonaromatic, linear, and crosslinked polymers.

INTRODUCTION

Interest in the effect and mechanism of high energy laser radiation on polymeric materials has expanded considerably in recent years. Applications include the manufacturing of lithographic plates and integrated circuits, the study of flammability and combustion of materials, and the pyrolysis of coal. Of special interest are polymeric materials suitable as matrix binders for use in the fabrication of fiber-reinforced composites. These resins tend to be crosslinked network polymers which exhibit a relatively high thermal stability. Typical resins include thermally cured epoxies, polyimides, and phenolics. Pyrolysis of polymers by laser radiation involves massive breakage of chemical bonds and vaporization of the generated fragments. Previous work from this laboratory has indicated for a broad cross section of polymers that polymer systems with high degrees of crosslinking and aromatic character exhibit the highest ablation energies.¹ The purpose of this work is to investigate the laser ablation energy dependence on the molecular structure of a polymeric system using a characterized polymer with a known degree of crosslinking and aromatic character.

The system selected for study is the network polymer derived from the thermal trimerization of an aromatic dicyanate to a polycyanurate (Fig. 1). Quantitative conversions have been reported for this reaction in polymer-forming systems.² It is of interest that the network junction is an aromatic cyanurate structure with an appreciable resonance stabilization energy (30 kcal/mol as compared with 36 kcal/mol for benzene).³ This feature appeared particularly attractive for enhancing the laser ablation energy dependence on degree of crosslinking.

The specific system selected is that based on the dicyanate of bisphenol A, BPAOCN, with variable quantities of the cyanate of cumylphenol, CPOCN,

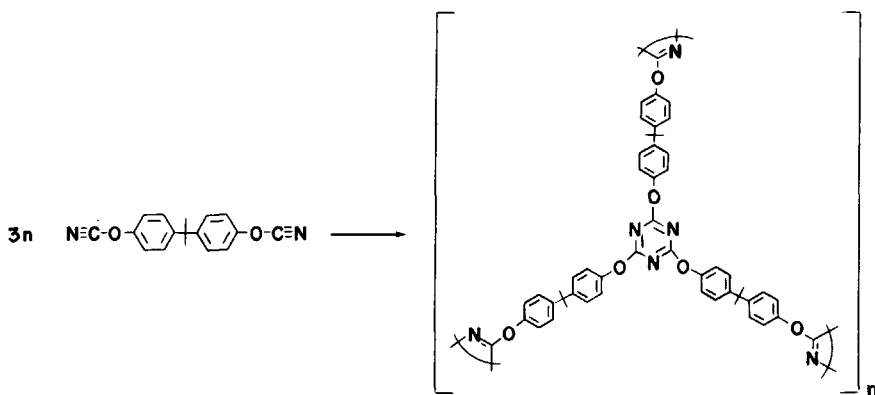


Fig. 1. Polycyclotrimerization of the bisphenol A dicyanate monomer to the cyanurate network structure.

added to vary the degree of crosslinking. Further considerations for this selection are as follows: BPAOCN has a facile synthesis, the polymerization has been previously studied,² it is of commercial importance,⁴ and it has been evaluated as a laminating resin in graphite-fiber composites.⁵ The polycyanurate synthesis, degree of crosslinking characterization, and dependence of laser ablation energy on degree of crosslinking and aromatic character are presented.

EXPERIMENTAL

Material Synthesis and Characterization

All reagents and solvents were reagent grade quality, purchased commercially, and used without further purification unless otherwise noted. Spectroscopic, chromatographic, and thermal analysis data were obtained with the following instruments: infrared, Perkin-Elmer 267; ¹H-NMR, Varian EM390 (90 MHz); mass spectroscopy, Hewlett-Packard 5982A coupled to Ribermag SADR GC/MS data system; gas chromatography, Varian GC Model 3700 (20% DC550 silicone on Gas-Chrom P-A/W DMCS 45/60, 4 ft × 0.25 in. stainless-steel column); thermal analysis, DuPont 1090 thermal analyzer, 910 DSC, and 951 TGA. Elemental analyses were performed by Schwartzkopf Microanalytical Laboratory. Melting points are uncorrected.

2,2-Bis(4-Cyanatophenyl)propane (BPAOCN). To a three-neck 2-L flask fitted with a 100-mL dropping funnel, overhead stirrer, and thermometer were added 750 mL acetone and 90.0 g (0.395 mol) bisphenol A (freshly recrystallized from 1,2-dichloroethane and vacuum-dried). A 50.8-g (0.826-mol) quantity of cyanogen chloride (Matheson) was measured gravimetrically by transfer through a gas dispersion tube to a 300-mL Erlenmeyer flask containing 150 mL acetone at -78°C . After cooling the 2-L reaction flask to -20°C with a dry ice bath, the cyanogen chloride/acetone solution was added and 83.4 g (0.826 mol) triethylamine (freshly distilled) was placed in the dropping funnel. The reaction flask was maintained at -15 – -20°C by raising and lowering the ice bath, and the triethylamine was added dropwise over a 1 h period. Stirring was continued for 1.5 h while the mixture warmed to room tempera-

ture. The product was isolated by slowly pouring the reaction mixture into 4 L of stirred ice water, filtering, and washing until neutral filtrate was obtained. After vacuum drying, the crude product was recrystallized from cyclohexane. Yield 99.2 g (90.3%); mp 82–83°C (lit.⁶ 80°C); NMR (CDCl₃) δ 1.65 (s, 3H), δ 7.2 (s, 4H).

2-Phenyl-2-(4-Cyanatophenyl)propane (CPOCN). To a three-neck 250-mL flask fitted with a dropping funnel, overhead stirrer, and thermometer were added 125 mL acetone, 20.0 g (94.3 mol) cumylphenol, and 10.5 g (99.0 mol) cyanogen bromide (dried by distillation through a calcium chloride column). The flask was cooled to -10°C and 10.0 g (99.0 mmol) triethylamine (freshly distilled) were added dropwise over 35 min while temperature was maintained at -5–-10°C. The mixture was stirred for 1.5 h while warming to room temperature. The product was isolated by slowly pouring into 550 mL stirred ice water, separating an oily phase, followed by two 50 mL methylene chloride extractions of the aqueous phase. The combined extracts and oily residue were dried over sodium sulfate, treated with charcoal, filtered through Celite, and concentrated under vacuum. The crude product was purified by vacuum distillation (< 1 mm/140°C) to yield a colorless oil. Yield 13.8 g (61.8%); no detectable impurities by GC; IR (neat) 3070, 2980, 2885, 2280, 2250, 1610, 1510, 1453, 1373, 1202, 1178, 1021, 840, 780, 707 cm⁻¹; NMR (CDCl₃) δ 1.62 (s, 2H), δ 7.2 (m, 3H); *m/e* 237 (P).

Tris(4-Cumylphenoxy)-1,3,5-Triazine. To a 3.5-mL vial was added 0.5 g CPOCN and a trace of aluminum chloride. The mixture was heated with stirring for 5 min at 100°C. The crude product was recrystallized from benzene. Yield 0.42 g (84%); mp 163–164°C; IR (see Fig. 3); NMR (CDCl₃) δ 1.63 (s, 2H), δ 7.0–7.3 (m, 3H).

ANAL. Calcd for C₄₈H₄₆N₃O₃: C, 80.98%; H, 6.37%; N, 5.90%. Found: C, 80.93%; H, 6.46%; N, 6.06%.

Polymerization Procedure

BPAOCN and the mixtures of BPAOCN–CPOCN were weighed (5 g total quantity) into 10-mL vials, fused while stirring to ensure homogeneity, and poured as a melt into aluminum pans (1-in. diameter, 0.25 in. height), yielding two samples each weighing 2–2.5 g. Five uncured samples with BPAOCN content ranging from 100 to 62.4 mol % were prepared. Each sample was placed in an aluminum container (1.5-in. diameter, 0.5-in. height) with a tight fitting cap and the seam was wrapped with two turns of Teflon tape. This prevented evaporation of the CPOCN monomer during cure. The samples were cured at 180°C for 35 h in a nitrogen atmosphere followed by a postcure 225°C heat treatment for 1 h also under nitrogen. The cured samples were transparent with a yellow coloration.

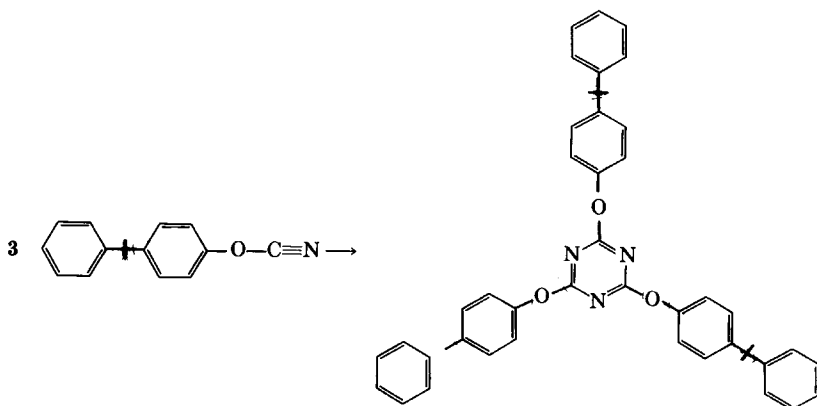
For infrared, DSC, and TGA characterization, the samples were pulverized using a Wig-L-Bug amalgamator. The capsule was cooled in dry ice immediately before pulverizing. Infrared spectra were obtained from pressed KBr pellets. DSC and TGA thermograms were obtained from the powdered samples in nitrogen atmospheres at heating rates of 10°C/min. Polycyanurate solvent swelling experiments were attempted by immersion of 50–100 mg solid samples in chloroform and benzene. Swelling and particle breakup were observed, but reproducible gravimetric measurements of swelling were not successful, possibly due to loss of small particles.

Laser Ablation Measurements

The laser used in these experiments was a Coherent Radiation Laboratory Model 42 CW CO₂ system with an internal water-cooled shutter, thus allowing the laser to remain on between consecutive irradiations. The system was operated between 20 and 40 W at an on-target irradiance ranging between 150 and 300 W/cm². Laser power was measured before and after each target exposure by a 100 W calorimeter power meter also manufactured by Coherent. The incident beam has a nearly circular cross section and a Gaussian energy distribution. A low speed air flow was swept across the target surface during irradiation to reduce absorption of the incident beam by escaping degradation products. The time of irradiation was determined using a small thermocouple, barely exposed to the edge of the beam, coupled to a high-speed strip chart recorder. A temperature increase in the thermocouple indicated that the shutter was open and the target was exposed to laser radiation. Irradiation times ranged from 1 to 10 s and were accurate to within 0.05 s. Fresh clean surfaces of polycyanurate were irradiated and weight loss was determined gravimetrically. Growth of a char nodule was observed on the irradiated sample surface, especially those with high BPAOCN concentration. Weight loss measured at various irradiation times and extrapolated to zero irradiation time was used to calculate ablation energy, thus minimizing the effect of char buildup.

RESULTS AND DISCUSSION

Monomer and Model Compound Syntheses. The BPAOCN and CPOCN monomers were prepared by the reaction of bisphenol A and cumylphenol with cyanogen chloride or cyanogen bromide in the presence of triethylamine in acetone solution.⁶ The characterization data for BPAOCN is consistent with that in the literature. Analytical data for CPOCN is presented in the experimental section. The model cyanurate compound, 2,4,6-tris(4-cumylphenoxy)-1,3,5-triazine, was synthesized in quantitative yield by the aluminum chloride catalyzed trimerization^{6,7} of CPOCN, and is consistent with the structural characterization data presented in the Experimental section.



Polycyanurate Cure. Reports that aromatic dicyanates in general² and BPAOCN in particular^{2b} will undergo a quantitative polycyclotrimerization uncomplicated by side reactions to yield a cyanurate network structure of exceptionally high degree of crosslinking exist in the literature, although a review^{2a} of this work does reserve the stipulation that side reactions are possible. The basis for these reports appears to be extrapolation from monofunctional model compound work. Intuitively in such a network forming system, it would be expected that, at high conversion, reactive functional groups and possibly dimer intermediates would become isolated and immobilized in the network matrix. Since a degree of crosslinking measurement is critical to the interpretation of the laser ablation energy measurement in this work, an analytical procedure to account for the fate of cyanate groups at high conversions and assessment of degree of crosslinking must be developed. Further, this analysis should treat networks where the mobile monofunctional CPOCN has been added in variable quantities to regulate the degree of crosslinking.

As an evaluation method for development of a cure procedure as well as an analytical tool for network structure and degree of crosslinking analysis, a model compound strategy was used. Initial experiments to determine a cure temperature and to verify the thermal conversion of cyanate to cyanurate were conducted by pressing thin films of CPOCN and BPAOCN between two polished NaCl discs. A reaction temperature of 180°C was selected as one where the monomers were not appreciable volatilized and the cure proceeds at a reasonable rate. The curing reaction was monitored using IR spectroscopy to compare spectra of the polymerization mixture and the cyanurate model compound. Spectra as a function of cure time for the CPOCN and BPAOCN films are presented in Figures 2(a) and 2(b), respectively. After 24 h cure at 180°C, the 2280 and 2240 cm^{-1} cyanate bands of CPOCN have effectively disappeared, and the spectrum matches that of the cyanurate model compound with the exception of a partially resolved weak absorption at 1640 cm^{-1} . The triazine bands of the model compound at 1380 and 1580 cm^{-1} , although slightly narrower, are very close in wavenumber and relative intensity to those of the CPOCN-cured sample. For the BPAOCN sample under the same cure conditions, a limiting conversion of the cyanate group after 24 h cure is observed, and a weak new band appears in the $\text{C}\equiv\text{N}$ region at 2220 cm^{-1} . The strong triazine bands are present but slightly shifted (ca. 10 cm^{-1}) and broader in comparison with those of the model compound spectrum. The 1640 cm^{-1} band is also present and more intense. Additional cure time (5 days) or a higher temperature results in little spectral change. An assignment for the 2220 and 1640 cm^{-1} bands has not been made at this time.

Cure temperature and reaction times may be reduced by addition of catalytic quantities of Lewis acids or bases.^{5,6} Aluminum chloride has been found to be particularly effective.^{6,7} The spectra of samples prepared from AlCl_3 -catalyzed CPOCN and BPAOCN cure experiments analogous to that of the thermal cure experiments are presented in Figures 3(a) and 3(b), respectively. The CPOCN cure is complete in less than 15 min as indicated by disappearance of the $\text{C}\equiv\text{N}$ absorption, and the spectrum is identical to that of the uncatalyzed thermally cured sample. The AlCl_3 -catalyzed BPAOCN sample also cured more rapidly than the uncatalyzed sample but again not to

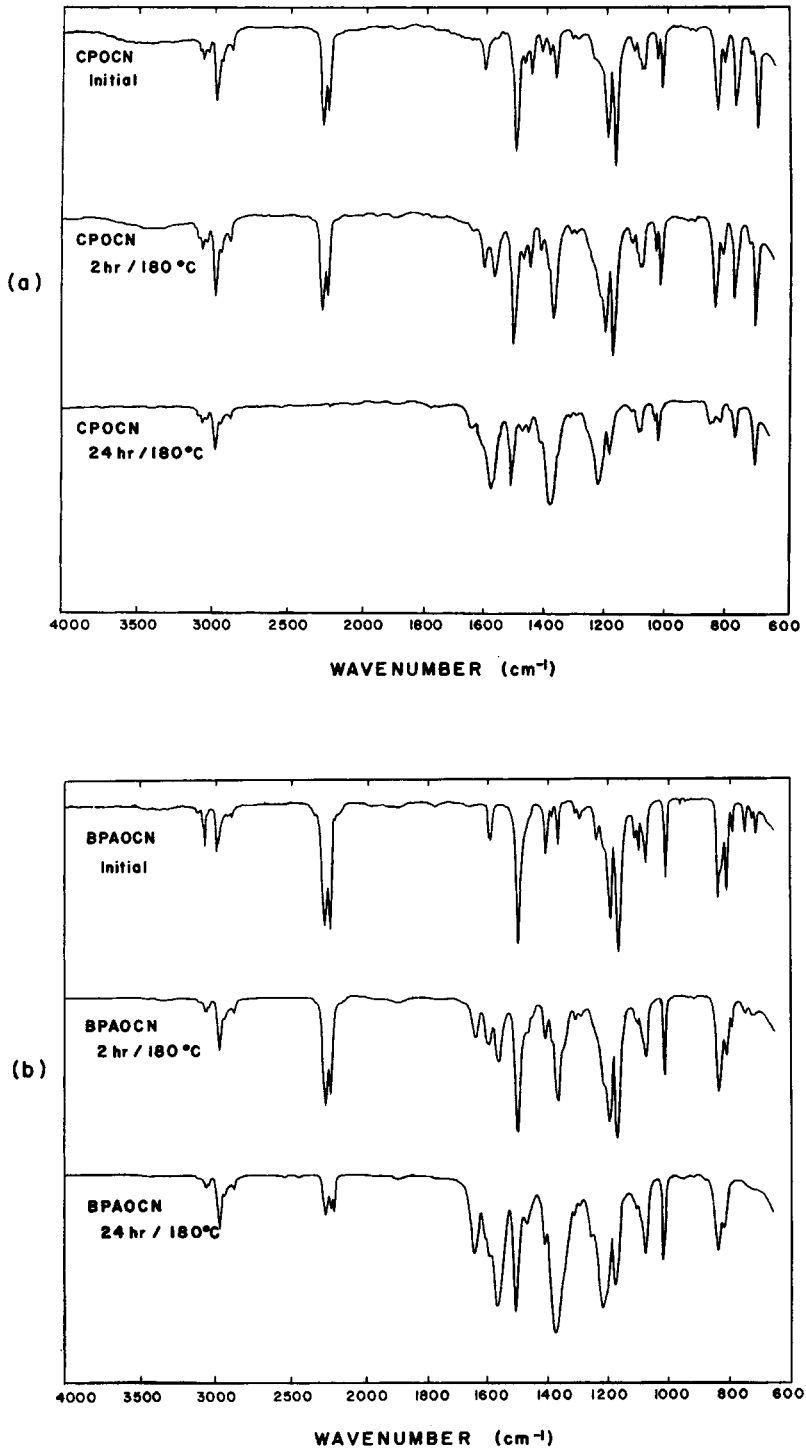


Fig. 2. Successive infrared spectra of (a) CPOCN and (b) BPAOCN monomers cured as thin films at 180°C for 2 and 24 h.

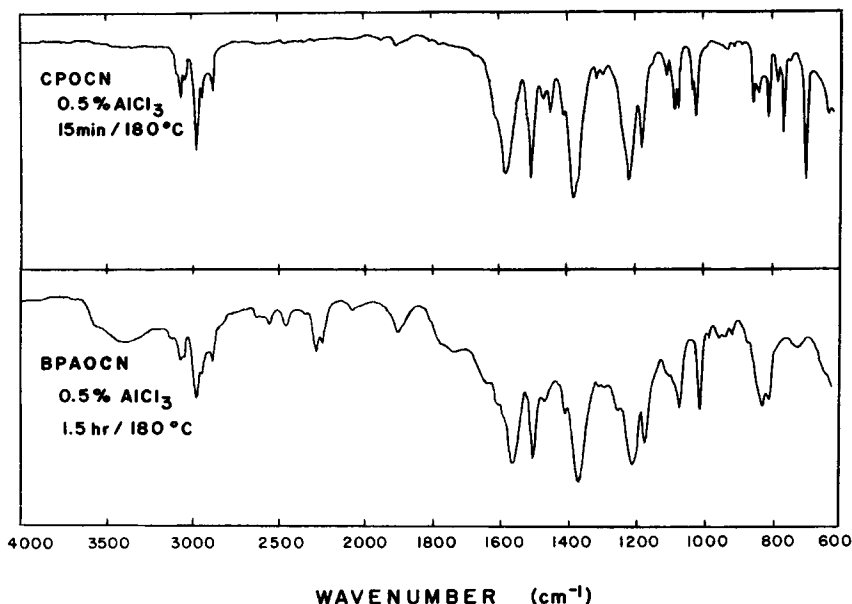


Fig. 3. Infrared spectra of CPOCN and BPAOCN monomers cured as thin films with an aluminum chloride catalyst.

complete conversion of the cyanate groups. The 2220 and 1640 cm^{-1} absorptions were not as intense, but an N—H or O—H absorption at 3400 cm^{-1} could be observed.

Samples for the laser ablation energy measurement were prepared by thermal cure since the effect of catalytic quantities of residual AlCl_3 would be unknown. Bulk samples were prepared in a nitrogen atmosphere by curing fused mixtures of BPAOCN and CPOCN ranging from 62 to 100 mol % BPAOCN at 180°C for 35 h followed by a post-cure thermal treatment at 225°C for 1 h. In appearance, the samples were a glassy solid with an amber yellow color.

Polycyanurate Network Characterization. The objective of the network characterization is to obtain a measure of the degree of crosslinking for correlation with the laser ablation energy measurement. The bulk samples were characterized by solvent swelling measurements, IR spectroscopy, DSC, and TGA. Of these techniques the IR spectroscopy is the most quantitatively useful with the others providing supporting evidence.

The IR spectra of five samples with initial BPAOCN content ranging from 62.4 to 100 mol % are presented in Figure 4. There is a good similarity with the BPAOCN thin-film cure spectrum of Figure 2(b) with the strong 1580 and 1380 cm^{-1} triazine bands present as well as the unreacted $\text{C}\equiv\text{N}$ absorptions. Relative to the 2980 cm^{-1} C—H band, there is a progressive increase in the intensity of the $\text{C}\equiv\text{N}$ band as the BPAOCN content increases. This would follow expectation since the ratio of OCN groups to CH_3 groups would correspondingly increase, and the higher OCN functional group mobility of the CPOCN monomer would facilitate a higher conversion of the total OCN groups. By measuring the number of unreacted OCN groups relative to the

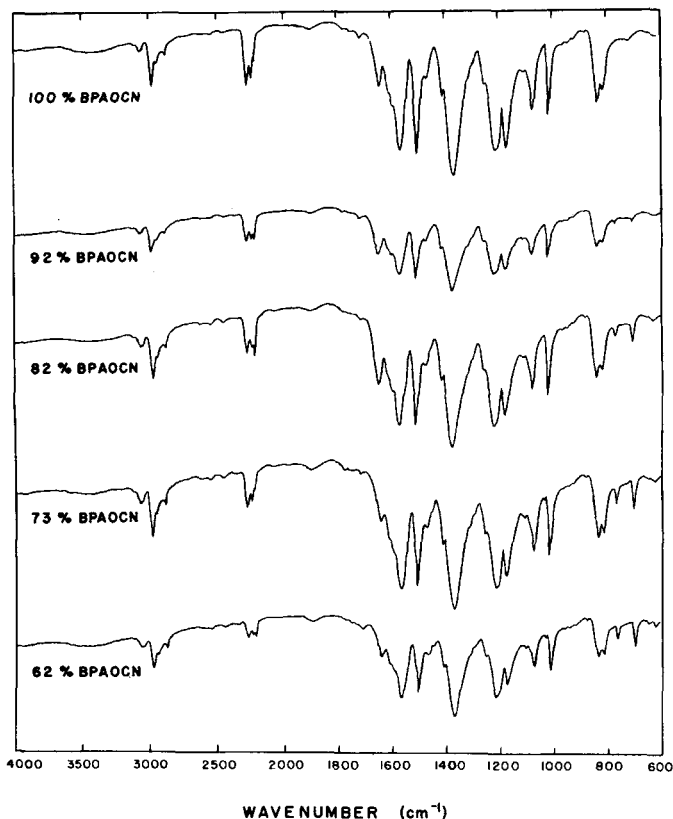


Fig. 4. Infrared spectra of cured bulk polymer samples (KBr pellet) with variable BPAOCN-CPOCN content prepared for laser ablation energy measurements.

CH_3 internal standard and using the BPAOCN : CPOCN composition data, it is possible to construct a network model upon which a calculation of degree of crosslinking may be made. Such a model is represented in Figure 5(a).

The following designations, assumptions, and definitions are made for calculation of the degree of crosslinking. Two types of cyanate functional groups are designated; type B (—) derived from BPAOCN and type C (—) derived from CPOCN. Each polymer linkage connects three monomers and has three functional possibilities; a branch point (or crosslink unit) if three type B groups are joined (\wedge), a linear segment if two type B and one type C groups are joined (\wedge), and a terminal point if 1 type B and 2 type C groups are joined (\wedge). The assumptions for the degree of crosslinking calculation are as follows:

- (1) Only triazine (cyanurate) products are formed.
- (2) Conversion is quantitative for type C cyanates (i.e., residual unreacted cyanate is type B).
- (3) Reactivity of type B and type C cyanate groups is equal (i.e., proportional to their number fraction).

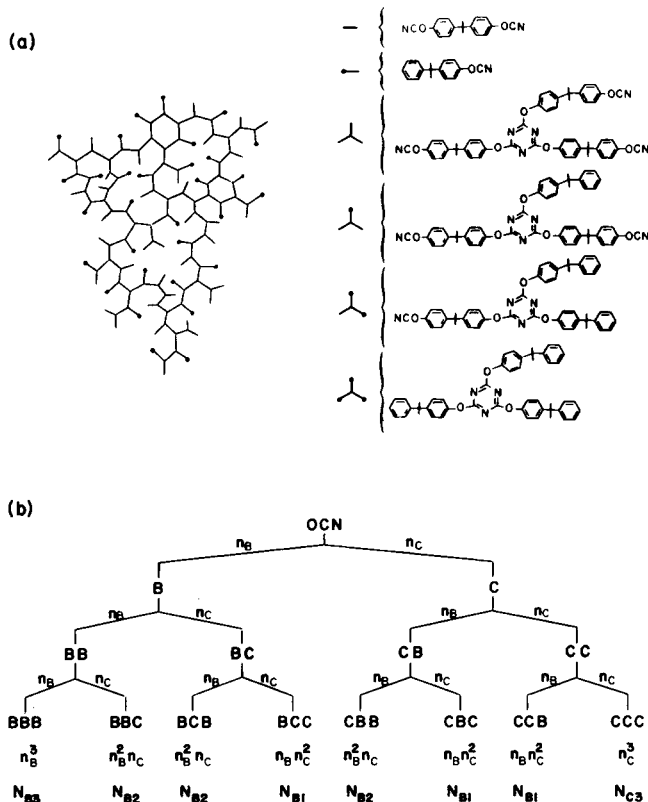


Fig. 5. (a) Structural representation of a BPAOCN-CPOCN cyanurate network polymer. (b) Statistical distribution of types of cyanurate polymer linkages based on number fractions of BPAOCN and CPOCN cyanate groups (e.g., a BBC cyanurate type linkage probability is proportional to $n_B^2 n_C$ and designated by N_{B2}).

(4) The molar absorbtivity of the 2980 cm^{-1} C—H stretching band used as an internal standard in the infrared spectra is equal for the BPAOCN and CPOCN monomers (but corrected for stoichiometry).

The degree of crosslinkng is defined as the number of branch points (i.e.,) type linkages) relative to the total number of linkages that may form (i.e., , ,) type linkages and 1/3 of the unreacted cyanate groups). The calculations are normalized to 1 mol of total monomers. The important quantities to be obtained are: (1) the number of unreacted type B groups, N_B , (2) the number of branch point linkages () , N_{B3} , (3) the number of linear-segment linkages () , N_{B2} , and (4) the number of terminal-point linkages () , N_{B1} , as well as the number of CPOCN trimmers () , N_{C3} . These quantities can then be converted to numbers of crosslinks and aromatic centers per mole of monomers or per unit volume.

Based on the network model of Figure 5(a), a statistical distribution of trimeric monomer linkages generated by the number fractions of type B cyanate groups, n_B , and type C cyanate groups, n_C , is presented in Figure

5(b). The relative quantities of each type of linkage is determined by the product over the probability for three successive additions of a type B or C cyanate group and can be interrelated as follows:

$$\frac{N_{B3}}{n_B^3} = \frac{N_{B2}}{3n_B^2 n_C} = \frac{N_{B1}}{3n_B n_C^2} \quad (1)$$

The coefficient 3 appears in the second and third expressions because the order of addition is not distinguishable, and there are three sequences of additions to generate N_{B2} and N_{B1} as opposed to one for N_{B3} . The number of unreacted type B groups, N_B , is related to the number of type B groups forming the N_{B3} , N_{B2} , and N_{B1} polymer linkages by the mass balance equation

$$N_B^0 = N_B + 3N_{B3} + 2N_{B2} + N_{B1} \quad (2)$$

where N_B^0 is the initial number of type B groups. Combining eqs. (1) and (2) yields an expression for N_{B3} :

$$N_{B3} = \left(1 - \frac{N_B}{N_B^0}\right) \frac{N_B^0}{3\left(1 + \frac{n_C}{n_B}\right)^2} \quad (3)$$

The quantity N_B/N_B^0 is experimentally obtained from the cured polymer 2280 cm^{-1} cyanate infrared absorption compared with that of the unreacted monomer,

$$\frac{N_B}{N_B^0} = \left(\frac{A_{\text{OCN}}^P}{X_B A_{\text{CH}}^P}\right) \left/ \left(\frac{A_{\text{OCN}}^M}{A_{\text{CH}}^M}\right)\right. \quad (4)$$

where A_{OCN}^P , A_{CH}^P , A_{OCN}^M , and A_{CH}^M are the respective polymer and monomer infrared absorbances of the 2280 cm^{-1} cyanate band and the 2980 cm^{-1} CH internal reference band, and X_B is the mole fraction of BPAOCN in samples prepared from varying compositions of BPAOCN and CPOCN.

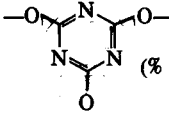
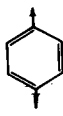
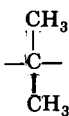
Values of $A_{\text{OCN}}^P/A_{\text{CH}}^P$, N_B^0 , n_B , N_B , N_{B3} , N_{B2} , N_{B1} , and N_{C3} for the five experimental samples are presented in Table I. The quantity N_{C3} is calculated

TABLE I
BPAOCN-CPOCN Polymer Composition, Cyanate IR Absorbance,
and Statistical Distribution of Cyanurate Polymer Linkages

Sample X_B	$\frac{A_{\text{OCN}}^P}{A_{\text{CH}}^P}$	N_B^0	n_B	N_B	N_{B3}	N_{B2}	N_{B1}	N_{C3}
1.00	0.99	2.00	1.00	0.61	0.463	0.000	0.000	0.000
0.92	0.86	1.84	0.96	0.52	0.404	0.052	0.002	0.000
0.82	0.70	1.64	0.90	0.432	0.325	0.108	0.012	0.001
0.73	0.62	1.45	0.84	0.363	0.257	0.146	0.027	0.002
0.62	0.49	1.25	0.75	0.301	0.178	0.177	0.059	0.008
BPAOCN ^a	3.26 ^a							

^aUnreacted monomer.

TABLE II
Substructure Compositions of Polycyanurate Samples per Mole
of Repeat Units

Sample X_B	Total triazine  (% Yield)	Benzene 	2,2-Propane 	Cyanate —OCN	Degrees of crosslinking $\frac{N_{B3}}{\frac{1}{3}(N_B^0 + N_C^0)}$
1.000	0.463 (69.5)	2	1	0.610	0.695
0.921	0.459 (71.6)	2	1	0.525	0.631
0.819	0.446 (73.5)	2	1	0.432	0.536
0.726	0.432 (75.1)	2	1	0.363	0.447
0.624	0.421 (77.9)	2	1	0.301	0.329

analogous to N_{B3} [i.e., eq. (3) with subscripts B and C interchanged]. These data show that the percent of unreacted cyanate groups ($N_B/N_B^0 \times 100$) decreases from 30% for the 100% BPAOCN sample to 24% for the 62.4% BPAOCN sample. The addition of monofunctional CPOCN appears to reduce the number of unreacted cyanate groups that are immobilized by the polycyanurate network formation. The addition of CPOCN also reduces the percentage of branch-point polymer linkages ($N_{B3}/\sum N_{Bn} \times 100$) from 100 to 42% while the total number of triazine structures undergoes very little change (see Table II). The % yield of triazine structures increases because less total triazine is possible with increasing CPOCN content. Using the BPAOCN-CPOCN polymer composition, cyanate conversion and statistical distribution of cyanurate linkages, we can calculate the triazine, benzene, 2,2-propane, and cyanate substructure concentrations and the degree of crosslinking of the network structure. The results are presented in Table II. Both the aromatic (triazine and benzene) and aliphatic (2,2-propane) characters remain remarkably constant while the cyanate group concentration and the degree of crosslinking decrease substantially with increasing CPOCN composition.

The validity of the four assumptions upon which the calculation is based should be questioned. The first assumption of a unique conversion of cyanate to cyanurate is tenuous. The $C\equiv N$ absorption at 2220 cm^{-1} , which is of unknown origin, would certainly appear to be derived from a side reaction of the OCN group. Also, the 1640 cm^{-1} absorption, while unassigned, is in the azomethine $C=N$ stretching region⁸ and could correlate with a polyimine structure. Since the corresponding structural change and molar absorbitivity relative to the OCN absorption are unknown, these apparent side reactions are not taken into account in the calculation. The second assumption, that all of the CPOCN cyanate groups react, appears to be valid. The IR cure experiment of Figure 2(a) indicates a complete conversion. The third assumption of equal BPAOCN and CPOCN functional group reactivity would appear to be valid on the basis of structural similarity. However, DSC thermograms display a higher trimerization exotherm temperature for cure of BPAOCN than for CPOCN (see Fig. 5). It has been reported that BPAOCN is less reactive than other cyanate monomers based on DSC observations.⁵ Since the

BPAOCN cyanate groups are present in significant excess ($N_B > N_C$), the assumption may hold for moderate differences in reactivity. The fourth assumption, that the 2980 cm^{-1} C—H absorption may be used as an internal standard for relative measurement of OCN functional group, has been used previously^{2b,9} and should not be too critical to this work since assumption 2 appears to have validity.

An attempt was made to correlate the degree of crosslinking results from the IR measurement with chloroform solvent swelling data. Immersed polycyanurate samples were found to swell and fragment into smaller pieces of gel. Accurate gravimetric measurements of solvent uptake could not be made. Visually, the swelled particles from the samples with the higher percentages of CPOCN appeared to be more highly expanded. These observations suggest that all of the polycyanurate samples are incompletely crosslinked (50–70%), which is consistent with the infrared result. Theoretically, a critical conversion for gel formation of a polycyclotrimerization of 50% has been calculated.⁹

DSC characterization of the BPAOCN and CPOCN monomers, cyanurate model compound, and polycyanurate bulk samples was obtained with the objective of correlating thermal transitions with the degree of crosslinking. Thermograms are presented in Figure 6. The BPAOCN monomer exhibits a sharp melting point endotherm at 81°C , a broad trimerization exotherm at 280°C , and a decomposition exotherm maximum at 425°C . These values compare very well with those in the literature.⁵ The CPOCN monomer displays partially superimposed endotherm and exotherm maxima at 180 and 230°C , respectively. The endotherm may indicate an evaporation of the CPOCN, and the exotherm would correspond to the trimerization which is close in temperature to that of other monofunctional cyanates reported in the literature.⁵ The cyanurate model compound displays a sharp melting endotherm at 164°C and a decomposition at 430°C . The thermograms of the bulk polymer samples with BPAOCN content ranging from 62 to 100% display a broad exotherm which regularly increases in temperature maxima and intensity with increasing BPAOCN content. The temperature at which this exotherm occurs is intermediate between the CPOCN and BPAOCN trimerization exotherms, and the intensity parallels the residual unreacted OCN functional group content as determined by IR spectroscopy. All of the samples exhibit a decomposition exotherm at $430\text{--}440^\circ\text{C}$, which is in good agreement with the TGA data (see Fig. 7). A well-defined glass transition temperature which might correlate with the degree of crosslinking determined by IR spectroscopy is not observed. In interpreting such T_g data, it should be recalled that a branch in the network terminated by a compact and highly polar OCN functional group would affect the T_g differently than a branch terminated by a bulky and nonpolar cumylphenoxy group. The DSC data indicates that the reaction of cyanate groups may be advanced to a higher degree of conversion with a higher curing temperature.

The TGA data were obtained with the objective of correlating thermal stability with degree of crosslinking. TGA thermograms of the cyanurate model compound and polycyanurate bulk samples in a nitrogen atmosphere are presented in Figure 7. The cyanurate model compound displays an onset of weight loss at 375°C which increases to 10% at 430°C followed by a rapid weight loss to a 7% char residue at 700°C . All of the polycyanurate samples

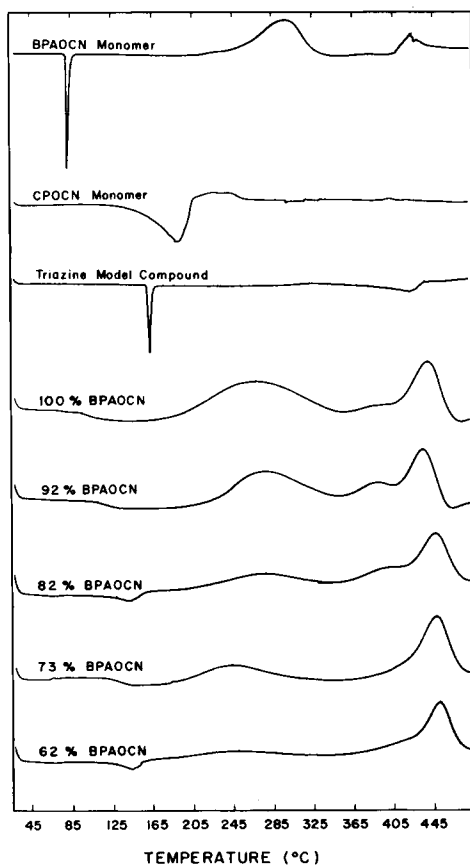


Fig. 6. DSC thermograms of BPAOCN and CPOCN monomers, CPOCN triazine model compound, and variable content (BPAOCN-CPOCN) cured polymers (heating rate 10°C/min, nitrogen atmosphere).

exhibit a weight loss onset at approximately 200°C which gradually increases to 10% at 420°C followed by a rapid weight loss to a residue which ranges from 37 to 41% at 700°C as the BPAOCN content increases from 62 to 100%. The rapid weight loss at 420–430°C corresponds well with the DSC decomposition exotherm at 430–440°C. The initial gradual weight loss up to 10% between 200 and 420°C does not parallel that of the model compound and suggests the presence of structures which decompose at lower temperatures or volatile side reaction products or impurities (i.e. water, solvent). The char residue at 700°C is much greater than that of the model compound. While the polymer sample char yield is small in relative variation from the 62 to 100% BPAOCN sample, its order does correlate with the degree of crosslinking as determined by IR spectroscopy or with that which might ultimately be obtained by higher cyanate conversion.

Laser Ablation Energy Measurements. Ablation energy is the amount of energy (J) required to remove 1 g of material. The measurement was made by irradiating a fresh, clean polymer surface with the continuous wave carbon dioxide laser and subsequent determination of the mass loss. The ablation

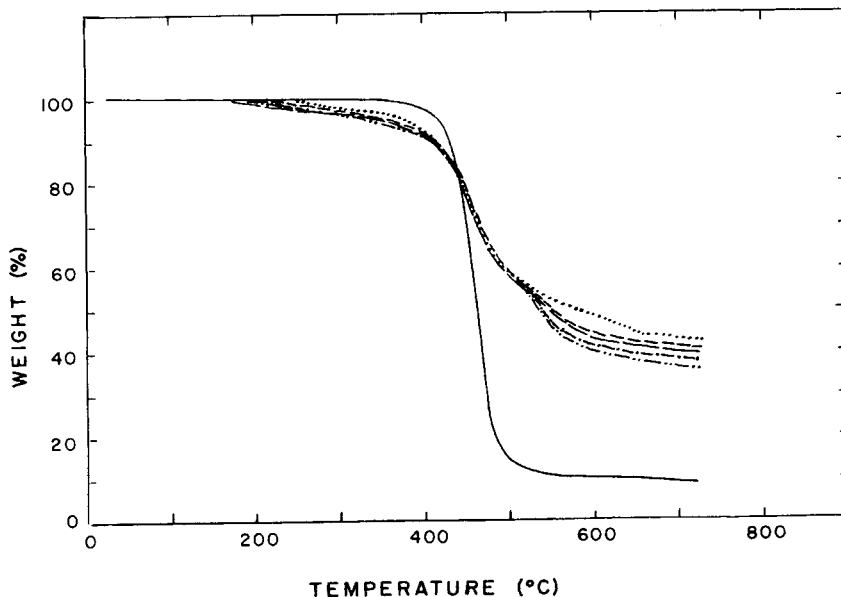


Fig. 7. TGA thermograms of CPOCN triazine model compound and variable content (BPAOCN-CPOCN) cured polymers (heating rate $10^{\circ}\text{C}/\text{min}$, nitrogen atmosphere). BPAOCN (90): (\cdots) 100; ($---$) 92; ($---$) 82; ($---$) 73; ($---$) 62; ($---$) triazine model compound.

energy measurement was limited to materials that did not exhibit extensive melting or spattering to ensure that the principle mechanism for mass removal was volatilization and not discrete mass removal by physical means. Ablation energies at several irradiances and irradiation times were measured for each target material and plotted against irradiation time. The accepted ablation energy was taken to be the value obtained when extrapolated to zero irradiation time. This technique was used to minimize the effect of char buildup, thus ensuring that the measured value for the ablation energy most nearly corresponded to that of a fresh clean polymer surface rather than one which had begun to carbonize. Such a procedure is especially important in the case of polymers with extensive crosslinking and aromatic character.

Multiple ablation energy measurements were made on the characterized cyanurate polymers, and the average values as a function of BPAOCN content are presented in Table III. For the purpose of comparison, ablation energies of other polymers measured by the same technique from previous work¹ are entered in the lower part of Table III. These polymers may be classified as linear or crosslinked and aromatic or nonaromatic. The linear and nonaromatic polymers have ablation energies of 3–4 kJ/g. The polymers with aromatic chain structures have ablation energies greater than 13 kJ/g. The crosslinked phthalocyanine polymer ablation energy is substantially greater than 13 kJ/g. The cyanurate polymers have ablation energies greater than 13 kJ/g and increase with BPAOCN content or degree of crosslinking. Within the BPAOCN content range studied, the dependence on the degree of crosslinking is approximately linear (see Fig. 8).

An ablation process involves an accumulation of energy leading to the random but energy-dependent scission of chemical bonds and the production of

TABLE III
Laser Ablation Energy of Cyanurate and Other Polymers¹

Polymer	Ablation energy (kJ/g)
Polycyanurate (62% BPAOCN)	14.2
(73% BPAOCN)	15.6
(82% BPAOCN)	16.1
(92% BPAOCN)	16.6
(100% BPAOCN)	17.8
Poly(α -methylstyrene)	2.4
Polytetrafluoroethylene	3.8
Polystyrene	3.9
Poly(methyl methacrylate)	3.5
Poly(ethyl methacrylate)	3.4
Polybutadiene	3.4
Epoxy(bisphenol-A-polyamide)	4.3
Polycarbonate	13.3
Polyimide	13.3
Poly(phthalocyanine-C-10)	37.0

molecular fragments sufficiently small to escape from the sample at its elevated surface temperature. Linear polymers with nonaromatic chain structures have very similar ablation energies despite different pendent groups. The value for poly(α -methyl styrene) is anomalously low due to its low ceiling temperature of 61°C. The aromatic chain polymers (polycarbonate and poly-

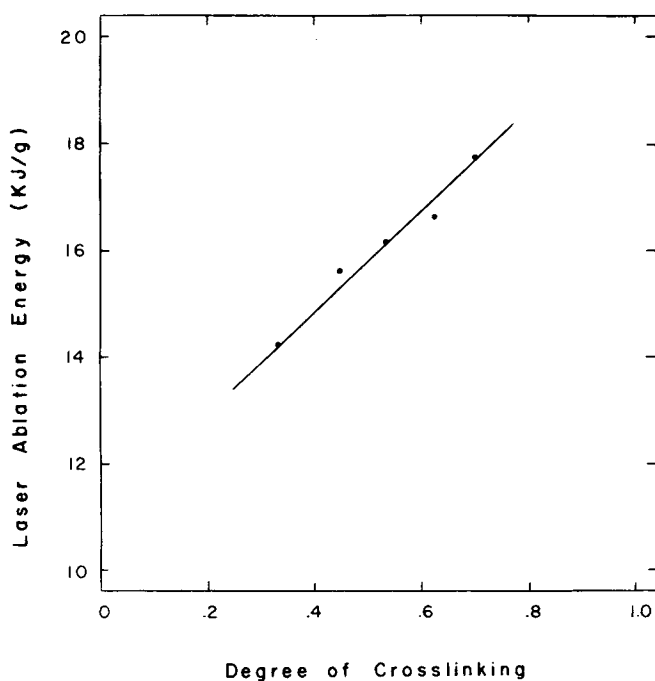


Fig. 8. Dependence of laser ablation energy on degree of crosslinking of BPAOCN-CPOCN polymers.

imide) require more energy for chain scission. Crosslinked polymers require more chain scissions to produce volatile molecule fragments.

The polycyanurate repeat unit consists of triazine and benzene aromatic elements and 2,2-propane nonaromatic elements, all of which remain approximately constant as the degree of crosslinking changes (see Table II). From the 14–18 kJ/g range of ablation energies, it would appear that the cyanurate polymer has a more aromatic than aliphatic character. If a speculative extrapolation of the data in Figure 8 is made to zero degree of crosslinking, an ablation energy of 11 kJ/g for a “linear” cyanurate polymer is obtained which would still indicate an aromatic character. Extrapolating to the other extreme of maximum degree of crosslinking (i.e., 1.0) yields an ablation energy of 21 kJ/g. This value is still substantially lower than the 37 kJ/g for the phthalocyanine network polymer and would indicate that more energy is required for scissions of phthalocyanine polymer bonds and/or for generation of volatile molecular fragments. It appears that large variations in the degree of crosslinking of cyanurate polymers cause significant but not drastic changes in laser ablation energy.

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