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SHORT PAPER

Polyureidoborazines

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Polyureidoborazines were synthesized by the reaction of tri-isocyanato-trimethylborazine with linear aliphatic diamines. The insoluble oligomers were characterized by infrared spectroscopy and the effect of the number of methylene units on thermal transitions determined by differential scanning calorimetry (DSC). The oligomers were pyrolyzed in argon and ammonia–nitrogen atmospheres and the residues analyzed for boron, nitrogen and carbon.

Keywords: Polyureidoborazines, oligomers, preceramic precursors, pyrolysis, infrared spectra, differential scanning calorimetry

INTRODUCTION

We recently reported the synthesis of transition metal-containing polyamides and polyureas,[1] utilizing low-temperature interfacial and solution techniques. We have now attempted to extend the low-temperature solution method to the synthesis and characterization of boron-containing polyureas. These polymers are of increasing interest as potential precursors for B–N–C type ceramic materials.[2]

Synthesis of highly crosslinked polyureidoborazines have been reported but the products were not described in detail.[3] Polyborazines linked by diamido groups have been postulated from the reactions of hexamethylene di-isocyanate with *N*-trimethyl- and *N*-triphenyl-borazines. These polymer structures have not been well characterized.[4] Related polymers have been postulated from *B*-trialkylborazines and isocyanates but attempts to repeat these reactions have proved unsuccessful.[5] In all the above syntheses high-temperature reflux conditions were used. Other cyclolinear borazine polymers derived by transamination with diamines have been reported.[6]

EXPERIMENTAL

Materials and equipment

Chlorobenzene was dried over phosphorus pentoxide and distilled under argon. Benzene was dried over calcium hydride and freshly distilled before use, also under argon. All the reactions were conducted under argon in Schlenk ware. In all the syntheses, the apparatus was freshly assembled after removal from the hot oven and subjected to repeated evacuation and purging by argon. Argon gas was dried over concentrated sulfuric acid and phosphorus pentoxide, and residual oxygen removed by a BASF catalyst. Boron trichloride (BCl_3) (Matheson), silver cyanate (AgNCO) and amines (Aldrich Chem. Co.) were used as received.

Infrared spectra were recorded on a Perkin–Elmer 983 spectrometer interfaced with a data station. DSC scans were made on a Perkin–Elmer DSC-2 calorimeter interfaced with a thermal analysis data station. Polymers were pyrolyzed in a quartz combustion tube in a tube furnace (Lindberg Model 54252 interfaced with a Eurotherm model 810 microprocessor).

Monomer synthesis

Trichlorotrimethylborazine (TCTMB)

Trichlorotrimethylborazine (TCTMB, $(CH_3)_3B_3N_3Cl_3$) was synthesized by a slight modification of the original procedure of Brown and Laubengayer.[7] A 300 cm^3 three-neck round-bottom flask was fitted with a water-cooled reflux condenser on top of which was mounted a dry-ice acetone reflux head. Inlet and outlet tubes for argon were provided, and the outlet tube was connected to a mercury check valve. BCl_3 was introduced via a long needle which extended to the bottom of flask. Methylamine hydrochloride ($CH_3NH_2.HCl$) (16.1 g; 0.24 mol) and 200 cm^3 of dry distilled chlorobenzene were placed in the flask and stirred vigorously by a magnetic stirrer. A slow stream of BCl_3 gas was passed into this mixture. The

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reaction mixture was heated to 130°C and refluxed for 6 h with the continuous passage of BCl_3 gas. The flow of BCl_3 was discontinued and the reaction mixture left to stir overnight at 80°C. The flask was then cooled to 40°C and the contents filtered in a stream of argon. The solvent was removed by vacuum distillation and the remaining solid purified by vacuum sublimation (60°C, 0.05 Torr). Yield 8.5 g (47%); m.p. 155°C (Lit.[6] 156°C). The IR spectrum was similar to that reported earlier.[8,9]

Tri-isocyanato-trimethylborazine (TITMB)

This monomer $[(CH_3)_3B_3N_3(NCO)_3]$ was synthesized from trichlorotrimethylborazine by the procedure of Lappert and Pyszora.[3] Yield 95%; m.p. 74°C (lit.[3] 85°C).

Polymerization

The general procedure for the synthesis of the various polyureidoborazines is illustrated by the following example.

Tri-isocyanato-trimethylborazine (0.62 g; 0.0025 mol) was dissolved in a Schlenk flask in 40 em^3 benzene. The contents of the flask were vigorously stirred and 0.29 g (0.0025 mol) hexamethylenediamine in 60 cm^3 benzene added to the flask. Immediately a white solid precipitated out. Stirring was continued for 1 h. The solution was then filtrered and vacuum dried. Yield 0.85 g (93%). IR (KBr) (cm^{-1}): —NH, 3348; CH, 2935; NCO, 2302, 2169; C=O, 1650; B—N, (ring) 1481, 1392; C—H 1145. Analysis: Calcd for $B_3C_{12}H_{25}N_8O_3$: C, 39.80; H, 6.90; N, 30.94; B, 9.10; O, 13.26%. Found: C, 37.70; N, 28.53; H, 7.44; B, 7.77; O, 18.56%.

RESULTS AND DISCUSSION

Monomers

The monomer tri-isocyanto-trimethylborazine (TITMB) was synthesized from trichloro-trimethylborazine (TCTMB) according to the method reported in the literature.[3,9] The intermediate TCTMB was synthesized via a modification of the procedure of Brown and Laubengayer.[7] Methylamine hydrochloride and excess of BCl_3 were refluxed in chlorobenzene for 6 h and then maintained for 16 h at 80°C. The reaction mixture was filtered warm, vacuum-dried and subsequently sublimed under reduced pressure. A slight increase in yield (12%) of pure TCTMB was achieved. The pure TCTMB was then reacted with silver cyanate to obtain TITMB. The above synthesis is given in Scheme 1. The IR spectrum of TITMB was similar to that reported previously.

Polyureidoborazines

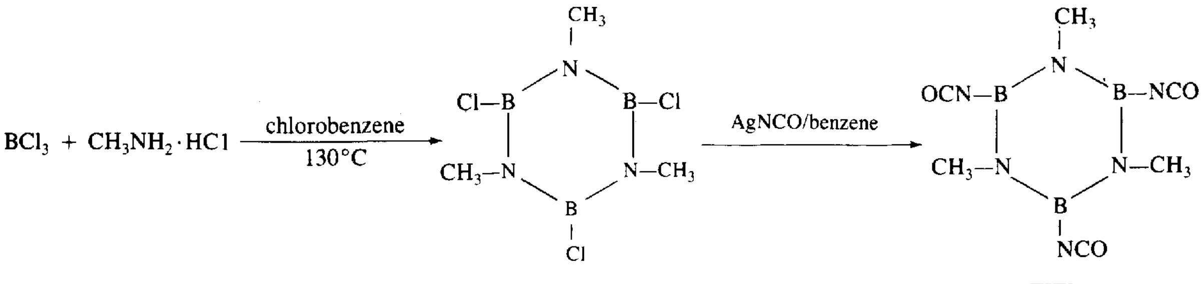
Polyureidoborazines (PUBs) were synthesized by reacting various aliphatic diamines with TITMB. In general, the monomer TITMB was dissolved in benzene and reacted with the diamine at ambient temperature. Reaction appeared to be immediate as evidenced by the solution turning cloudy followed by the formation of a white precipitate. The concentrations of the reactants were also varied to determine the effects on polymer formation. Polymerization conditions are summarized in Table 1. The synthesis of PUB molecules is shown in Scheme 2.

The polymers were insoluble in most organic solvents, making their structural and molecular weight determinations difficult. However, on the basis of

Table 1 Polymerization conditions of tri-isocyanato-borazines and diamines

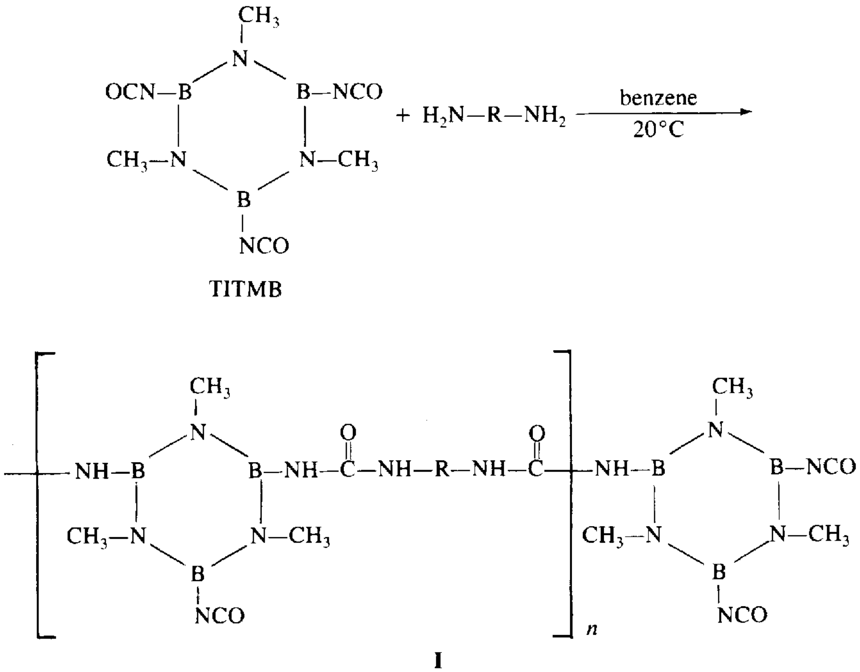
			Vol. of benzene used in polymerization (cm^3)			
Sample no	M_1	M_2	0.0025 mol M_1 in benzene	0.0025 mol M_2 in benzene	Yield (%)	Thermal transitions[a] (°C)
1	Tri-isocyanato-trimethylborazine	Ethylenediamine	40	60	90	244, 331
2	Tri-isocyanato-trimethylborazine	Butylenediamine	40	60	95	230, 245
3	Tri-isocyanato-trimethylborazine	Hexamethylenediamine	40	60	94	203, 227
4	Tri-isocyanato-trimethylborazine	Hexamethylenediamine	250	5	92	186, 228
5	Tri-isocyanato-trimethylborazine	Octamethylenediamine	40	60	92	160, 226
6	Tri-isocyanato-trimethylborazine	Ethylenediamine	40	0.0038 mol in 60 cm^3	100	—

[a] Determined by DSC: heating rate 20°C min^{-1} in nitrogen.



TCTMB TITMB

Scheme 1



TITMB

I
PUB

$R = -(CH_2)_x-$
$x = 2,4,6,8$

Scheme 2

infrared spectroscopy studies and thermal analysis we have deduced that the above reactions do result in higher-molecular-weight materials. Elemental analysis in conjunction with IR spectroscopy data show reasonable evidence that the repeat unit in the PUBs have the structure **I** shown in Scheme 2.

Infrared spectra

IR spectra for polyureidoborazines (PUBs) are summarized in Table 2. In all the PUBs we prepared, B—N ring vibrations were present at 1400–1450 cm^{-1} with the strong NCO absorption at 2300 cm^{-1} and also possibly at 2170 cm^{-1}. PUBs synthesized by reacting equimolar amounts of TITMB and diamine showed these two possible NCO absorptions compared with a single absorption at 2310 cm^{-1} for the NCO group in the monomer TITMB. In the synthesis of polymer **6**, where the ratio of monomer TITMB to the diamine was 1:1.5, no peak was observed at 2300 or 2170 cm^{-1} for the NCO absorption. In the latter case all the NCO groups in TITMB are expected to react with an equivalent number of amino groups forming a highly crosslinked polymer. In the case of polymers

Table 2 Infrared spectra of polyureidoborazines

No. of methylene groups	NH	CH	NCO	CO(amide)	B—N(ring)	C—N
2	3395	2948	2300, 2163	1650	1480, 1400	1090
4	3399	2941	2300, 2163	1660	1481, 1398	1151
6	3348	2935	2302, 2169	1650	1481, 1392	1145
8	3349	2959	2301, 1269	1650	1450, 1400	1214

1–5 where the ratio of TITMB to diamine was 1:1, the NCO absorption was observed and appears at two frequencies. This may be ascribed to the presence of two types of NCO group, one attached to every borazine ring in the repeat unit and the other due to NCO end-groups.

As mentioned above, due to the insolubility of the polymers in organic solvents, we have attempted to determine the structure of these polymers and their degree of polymerization by using IR spectroscopy techniques. To provide a basis for structure **I** we deduced that there is approximately one NCO group in the repeat unit thereby limiting extensive chain branching. For this purpose the extinction coefficient ϵ of the monomer TITMB was determined. The net absorbance for the NCO peak was measured for peak maxima at 2298 cm^{-1} at varying concentrations. The samples were obtained by finely mixing and grinding TITMB in KBr using a Wig-L-Bug and obtaining a pressed pellet. From a plot of absorbance versus concentration, ϵ was determined to be 506 mm^{-1} $mmol^{-1}$ dm^3. Assuming that the NCO absorption in the polymer approximates to those in TITMB, the extinction coefficient ϵ' for the polymer is one-third of ϵ, i.e. 160 mm^{-1} $mmol^{-1}$ dm^3. From ϵ' and infrared absorptions for polymer NCO peaks at 2298 cm^{-1} it was assessed that the number of NCO groups per repeat unit is 0.6. This value can be considered to approximate unity if scattering losses in the polymer as well as losses in reflection are accounted for.

On the basis of the above, the area under the NCO peaks in the polymers was compared with the corresponding area in TITMB. The $\overline{DP}$ calculated ranged between 3 and 5.

Differential Scanning Calorimetry (DSC)

Endothermic melting transitions were observed at 155°C and 74°C for TCTMB and TITMB respectively. The DSC thermograms for the PUBs are depicted in Fig. 1 and the transition temperatures summarized in Table 1. The observed transitions for the PUBs are significantly higher than those of the monomer TITMB which is indicative of a reaction between the monomer and the diamines resulting in a higher-molecular-weight material. A distinctive trend in the thermal transitions of the polymers with respect to the number of methylene units in the backbone is also evident. In the case of the PUB synthesized from ethylenediamine a transition was observed at 244°C with possible ensuing degradation (endothermic peak at 331°C). In oligomers obtained from 1,4-diaminobutane, 1,6-diaminohexane and 1,8-diamino-octane, two endothermic transitions were observed, at 160–230°C and 226–245°C. The separation of the two transitions in the hexamethylene and octamethylene polymers is indicative of a possible narrow 'processing window' for the melt spinning of these polymers into 'green fibers'.[2]

Pyrolysis

The PUBs were pyrolyzed from ambient temperature to 900°C in an ammonia stream and then from 900 to 1200°C in a nitrogen stream. The char yield was approximately 80%. The residue from polymer **1** was white while the remainder were brownish beige. All the residues gave broad IR bands centered at 1400 cm^{-1}, indicative of B–N bonds. No carbonyl or NCO absorptions were observed. These results are reasonable since boron nitride $(BN)_n$ is reportedly synthesized by heating the condensation product of orthoboric acid and urea in a stream of ammonia to 1650°C.[10] However, when the pyrolyses were conducted in argon, a black residue was left, indicative of a significant amount of carbon in the char. The weight loss was approximately 70%. Initial characterization by X-ray powder diffraction techniques on the former residues indicate the presence of a graphite phase, a small amount of $(BN)_n$ and other complex B–N–C phases.

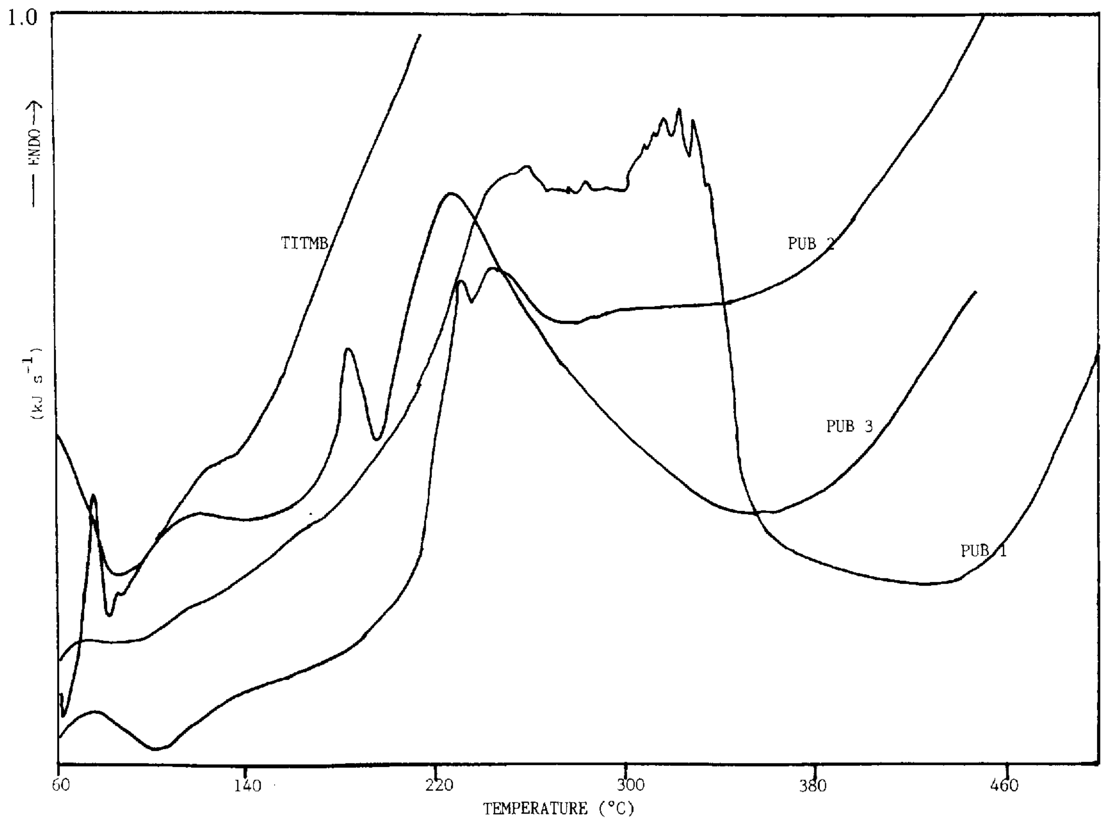


Figure 1 DSC thermograms of polyureidoborazines. Heating rate 20°C min^{-1} in nitrogen.

CONCLUSION

Extensive thermal and rheological characterizations of the polyureidoborazines are planned. This is necessary to ascertain the melt processability of these materials into 'green fibers' and their subsequent pyrolysis into ceramics. The latter are of fundamental importance in the development of ceramic and metal matrix composites. Attempts to blend titanium-containing monomers or polymers with meltable boron-containing polymers are being developed as a route to Ti—B—N—C ceramics, particularly in fiber form. These results will be reported subsequently.

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