Syntheses and Properties of Poly(*B*-vinylborazine) and Poly(styrene-*co*-*B*-vinylborazine) Copolymers

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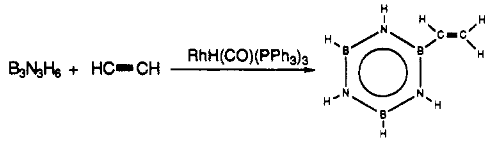
ABSTRACT: *B*-Vinylborazine has been found to readily polymerize in solution using free-radical initiation with AIBN to yield soluble poly(*B*-vinylborazine) homopolymers. Molecular weight characterization using size exclusion chromatography/low angle laser light scattering (SEC/LALLS) suggests that poly(*B*-vinylborazine) has a heterogeneous chain structure consisting of linear and, possibly, branched polymer chains. AIBN initiation has also been employed to produce a range of new hybrid organic/inorganic poly(styrene-*co*-*B*-vinylborazine) (SVB) copolymers with controlled compositions and molecular weights. Random copolymerization of styrene and *B*-vinylborazine monomers was confirmed by relative reactivity ratios and excimer fluorescence measurements. SEC/LALLS in conjunction with ultraviolet absorption detection (SEC/LALLS/UV) suggests that the copolymerization conditions that promote copolymer compositional heterogeneity may also produce a fraction of branched copolymer molecules due to dehydropolymerization reactions of the *B*-vinylborazine monomer.

Introduction

We have previously reported[3,4] the metal-catalyzed synthesis of *B*- vinylborazine (eq 1), a compound that may be considered the inorganic analogue of styrene. Furthermore, we also demonstrated[4] (eq 2) that *B*-vinylborazine can be readily thermally polymerized to give the new polystyrene-type inorganic polymer poly(*B*-vinylborazine).



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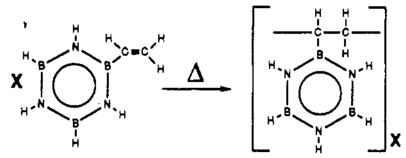

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In our original studies we found that insoluble polymeric materials result from thermally induced polymerizations of pure liquid *B*-vinylborazine and only when polymerizations were carried out in the presence of added borazine could soluble polymers be obtained.[4] We have now examined alternative methods and conditions for inducing *B*-vinylborazine polymerizations and report here our studies demonstrating that soluble poly(*B*-vinylborazine) homopolymers and a range of new poly(styrene-*co*-*B*-vinylborazine) copolymers with controllable compositions and molecular weights can be readily obtained by using free-radical initiation with AIBN.

Experimental Section

Materials. *B*-Vinylborazine was prepared as described previously.[3,4] Styrene was purchased from Aldrich, and the inhibitor was removed by successive washings with 15% NaOH aqueous solution. The styrene was then distilled, dried over white Drierite, and kept at dry ice temperature until use. The 2,2′-azobis(isobutyronitrile) (AIBN) was recrystallized from methanol and stored in a refrigerator until used. Benzene and glyme (ethylene glycol dimethyl ether) were freshly distilled from sodium benzophenone. Anhydrous grade pentane (H_2O <0.005%) was purchased from Aldrich and used as received.

Solution Homopolymerization of *B*-Vinylborazine. In a typical reaction, a 50-mL round-bottom flask equipped with a high-vacuum Teflon stopcock and stirbar was charged with 0.018 g of AIBN (0.11 mmol). The flask was attached to a vacuum line, and 0.732 g (7.02 mmol) of *B*-vinylborazine and 1 mL of benzene were vacuum distilled into the flask. The mixture was next subjected to three freeze-pump-thaw cycles to remove any traces of oxygen. The flask was sealed and then heated with stirring at 80 °C in an oil bath for 20 h. The flask was then opened in a drybag under nitrogen and the reaction mixture dropped into 30 mL of pentane, which produced a white precipitate. The precipitate was collected and then redissolved in benzene. This operation was repeated two more times, to yield 0.18 g of polymer. The polymer was dried in vacuo at room temperature for 24 h prior to spectroscopic measurements and elemental analyses. Dried poly(*B*-vinylborazine) was found to be moisture sensitive and had to be handled under a dry atmosphere to prevent the formation of insoluble materials. Under anhydrous conditions, the polymer was fully soluble in the organic solvents that were used for spectroscopic and chromatographic analyses. Anal. Calcd $[(CH_2CH)B_3N_3H_5]_n$, C, 22.4; B, 30.8; N, 39.3; H, 7.47. Found: C, 23.63; B, 28.44; N, 37.82; H, 6.60. ^{1}H NMR (THF-d_8) showed broad peaks in the ranges 4.2-6.6 ppm, arising from the N-H and B-H protons, and 2.1-0.5 ppm, attributed to the backbone C-H groups. The ^{11}B NMR spectrum of the polymer was too broad to allow definitive assignment. IR data are given in Figure 1a.

In other experiments, *B*-vinylborazine polymerizations were carried out under different conversion conditions and with varying AIBN ratios to investigate the effects on molecular weight. Separate reactions of 0.36 and 0.37 g of *B*-vinylborazine with 0.043 and 0.0093 g of AIBN, respectively, were carried out in 1 mL of benzene solution at 80 °C for 3.5 h and the resulting polymeric products separated and purified as described above. SEC/LALLS analyses of the resulting polymers gave M_w = 4900 and 5300, respectively. Reactions of 0.38 and 0.35 g of *B*-vinylborazine with 0.0298 and 0.0105 g of AIBN, respectively, in benzene solutions (1 mL) for 20.5 h at 80 °C gave soluble polymers with M_w = 23 000 and 17 000.

Copolymerization of *B*-Vinylborazine and Styrene. All copolymerization reactions were carried out in a manner similar to that described above. Measured quantities of *B*-vinylborazine, styrene, and AIBN were transferred into the reaction flasks, and then in each case 1 mL of benzene solvent was vacuum distilled into the flask. After the mixture was heated at 80 °C

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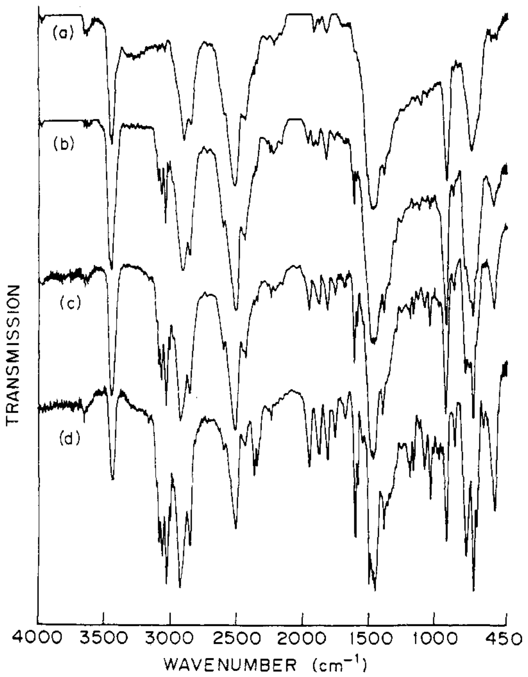


Figure 1. IR spectra for poly(*B*-vinylborazine) and SVB copolymers: (a) poly(*B*-vinylborazine); (b), SVB1; (c) SVB3; (d) SVB6.

Table I
Polymerization and Composition Data for Styrene/ *B*-Vinylborazine Copolymers

resin[a]	f_2[b]	f_1[c]	% conversion	F_1[d]
PVB	1.0	0.	24.7	0.
SVB1[g]	0.874	0.126	23.0	0.50[e]
SVB2[g]	0.781	0.219	23.5	0.68[f]
SVB3[g]	0.614	0.386	24.7	0.75[f]
SVB4[g]	0.600	0.400	21.5	0.77[f]
SVB5[g]	0.408	0.592	32.4	0.86[f]
SVB6[g]	0.213	0.787	30.0	0.94[f]
SVB7[h]	0.470	0.530	4.8	0.88[i]
SVB8[h]	0.470	0.530	23.9	0.85[i]
SVB9[h]	0.470	0.530	32.5	0.84[i]
PS	0.	1.0	57.9	1.0

[a] Abbreviations: PVB, poly(*B*-vinylborazine); SVB, styrene-*co*-*B*-vinylborazine copolymer; PS, polystyrene. [b] Weight fraction vinyl borazine in feed. [c] Weight fraction styrene in feed. [d] Weight fraction styrene in polymer. [e] Determined by proton NMR. [f] Determined by elemental analysis. [g] Set 1 copolymer. [h] Set 2 copolymer. [i] Estimated by relative excimer fluorescence using relative excimer fluorescence vs wt % styrene calibration curve generated from polymers PS, SVB6, SVB5, SVB4, SVB2.

for 16 h, the polymer product was isolated and purified as described above for the homopolymer. The products were dried in vacuo at room temperature for 24 h before all spectroscopic or physical measurements. A series of experiments were performed at similar AIBN concentrations, in which the styrene/*B*-vinylborazine ratios were varied, and the results of these reactions are summarized in Table I. Anal. Found: SVB2, C 70.78; B 8.94; N 12.00, H 6.16; SVB4, C 74.97, B 5.98, N 8.72, H 7.12; SVB5, C 79.46, B 4.52, N 5.29; SVB6, C 87.31, B 1.65, N 2.19, H 7.18; SVB1, C 45.70, B 20.38, N 25.51, H 7.40; SVB3, C 70.16, B 9.23, N 10.31, H, 7.40. IR spectra for selected examples are given in Figure 1. The ^{1}H NMR spectra of all samples showed two broad resonances at 6.5–7.6 ppm (aromatic C–H protons), two resonances between 0.5 and 3.0 ppm (saturated C–H protons), and several broad peaks in the region 4.1–6.5 ppm (borazine B–H and N–H protons). The ^{11}B NMR spectra of all samples were too broad to allow interpretation.

In a separate set of experiments, 0.06 g (0.37 mmol) of AIBN, 1.55 g (14.9 mmol) of styrene, 1.38 g (13.2 mmol) of *B*-vinylborazine, and 5.7 mL of benzene were mixed in vacuo. The mixture was then separated under an inert atmosphere into three portions by pipet. Each sample was weighed (1.70, 2.03, and 2.08 g) and transferred to a reaction flask which was then evacuated. Three freeze–pump–thaw cycles were performed to remove any traces of oxygen. The flasks were then heated at 80 °C in an oil bath for 2, 21, and 33 h, respectively. Separation of the resulting polymeric products in the manner described above gave 0.03, 0.18, and 0.25 g of material, respectively, corresponding to 4.8%, 23.9%, and 32.5% conversions.

Physical Measurements and Instrumentation. Diffuse reflectance IR spectra were obtained on a Perkin-Elmer 7770 Fourier transform spectrophotometer equipped with the appropriate diffuse reflectance attachment. Elemental analyses were performed at Gailbraith Laboratories, Knoxville, TN.

Fluorescence emission spectra were obtained from an SLM Model 4800 spectrofluorometer using an excitation wavelength of 258 nm. Emission was monitored from 270 to 450 nm at 2-nm intervals with a 4-nm bandpass. Sample temperature was regulated at 20 °C. All fluorescence spectra were corrected for the THF Raman scattering at 282 nm. Electronic absorption spectra were obtained from a Hewlett-Packard Model 8450 diode array spectrophotometer. Polymer solutions were prepared in UV grade tetrahydrofuran at concentrations of approximately 0.1 mg/mL.

Size Exclusion Chromatography (SEC). A size exclusion chromatography/low angle laser light scattering/ultraviolet (SEC/LALLS/UV) detector system was used to characterize molecular weight averages and the compositional heterogeneity of the polymers. The SEC/LALLS/UV was a modular system assembled from a Model 590 pump (Millipore/Waters Inc.), a Model 712 WISP autosampler (Millipore/Waters), a Model KMX-6 low angle laser light scattering detector (LDC/Thermal Co.), a Model 490 multiwavelength ultraviolet detector (Millipore/Waters), and a Model 410 differential refractive index detector (Millipore/Waters). SEC/LALLS/UV chromatograms were acquired by a micro PDP 11/23+ computer (Digital Equipment Co.) and stored for subsequent calculations.

A four-column styrene–divinylbenzene column set (PL Laboratories Ltd.) with mean permeabilities of 10^6, 10^5, 10^4, and 10^3 Å were used. The SEC/LALLS/UV system was equilibrated with UV grade tetrahydrofuran (Burdick and Jackson Co). A nominal chromatographic flow rate of 1.0 mL/min was used. Actual flow rates were determined gravimetrically prior to sample injection onto the SEC/LALLS/UV system.

Since the polymers were found to be moisture sensitive, the polymer solutions for SEC/LALLS/UV analysis were prepared with anhydrous glyme. Glyme, instead of THF, was used since the polymer–glyme solutions were observed to have greater long-term stability. A nominal concentration of 10 mg/mL was used for each copolymer. The actual solution concentrations for the copolymers were determined gravimetrically to ensure the accuracy of SEC/LALLS molecular weight calculations. In the case of poly(*B*-vinylborazine), solutions for SEC/LALLS molecular weight characterization were prepared under a dry atmosphere by using freshly isolated polymers (still damp with the polymer precipitant, pentane) and anhydrous glyme. The solution concentration of the polymer was not determined gravimetrically but was measured indirectly from the polymer's DRI detector response. Quantitative determinations with the DRI were obtained by calibrating the DRI detector's response with polystyrene. Using the measured specific refractive indices (d*n*/d*c*) for polystyrene and poly(*B*-vinylborazine) in combination with DRI responses for the polymers, the concentration of poly(*B*-vinylborazine) injected onto the SEC/LALLS/UV system was determined. An injection volume of 100 μL was used for all copolymers, and an injection volume of 200 μL was used for poly(*B*-vinylborazine).

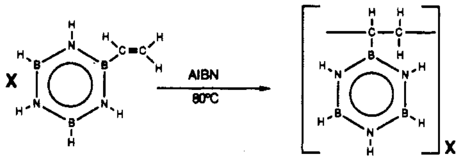
SEC/LALLS Molecular Weight Determination. SEC/LALLS molecular weight averages were determined by using the program MOLWT3 (LDC/Thermal) with the DRI detector serving as the polymer mass detector. Prior to molecular weight calculations, the delay time between the detectors of the SEC/LALLS/UV system was determined by measuring the time differences between the LALLS, UV, and DRI chromatographic peak maxima for a 96 400 molecular weight polystyrene standard (M_w/M_n = 1.05). The raw responses from the DRI and UV detectors were offset by the measured delays (18.2 s for LALLS to DRI and 7.8 s for the LALLS to UV). In the case of UV chromatograms, there was no time delay for UV chromatograms obtained at different wavelengths (230 and 259 nm in the present study) since the UV detector monitored multiple wavelengths simultaneously. Molecular weight calculations performed by MOLWTS have been previously described.[5]

Specific refractive index increments (dn/dc) for the polymers in THF at 25 °C were determined by using a KMX-16 laser differential refractometer (LDC/Thermal).

Results and Discussion

Homopolymerization of *B*-Vinylborazine. In contrast to the results observed from the thermally induced polymerization of *B*-vinylborazine in the liquid phase,[4] it was found that the solution polymerization of *B*-vinylborazine using the free-radical initiator AIBN proceeds smoothly to give soluble homopolymers. For example, when the polymerization of *B*-vinylborazine was carried out in benzene solution for 20 h at 80 °C in the presence of 1.6 mol % of AIBN, a white polymeric solid was obtained at 24.7% conversion that could be totally dissolved in solvents such as benzene or ethers. In a separate experiment, no significant polymerization of *B*-vinylborazine was observed in benzene solution at 80 °C in the absence of AIBN initiator.

Elemental analyses confirmed the proposed composition, and the spectroscopic data further support a polystyrene-type structure, as indicated in eq 3. Thus, the IR spectrum in Figure 1a shows absorptions characteristic of the B–H (2600–2500 cm^{-1}), N–H (3400 cm^{-1}), and B–N (1400 cm^{-1}) units of borazine as well as the C–H (3000–2900 cm^{-1}) absorptions of the polyethylene backbone. The absence of an olefin stretching absorption at 1620 cm^{-1} also supports a saturated carbon structure. The ^{1}H NMR spectrum shows only broad resonances but in the ranges expected for B–H, N–H, and C–H protons. Molecular weight studies of this sample using size exclusion chromatography/low angle laser light scattering (SEC/LALLS) gave M_w = 18 000 and M_n = 10 700.



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Vinyl derivatives of alkylated borazines have been known for some time,[6-10] including *B*-vinylpentamethylborazine, *B*-trivinyl-*N*-triphenylborazine, and, more recently, *B*-vinyl-*B*-R$_2$-*N*-R$_3$-borazine (R = Me or Ph). However, attempts to polymerize the alkylated compounds have been unsuccessful. For example, it has been reported that neither *B*-trivinyl-*N*-triphenylborazine[8] nor *B*-vinyl-*B*-R$_2$-*N*-R$_3$-borazine (R = Me or Ph) derivatives[9] will undergo polymerization with AIBN.[11] These reports contrast sharply with the facile AIBN-initiated polymerization reactions reported herein for the parent *B*-vinylborazine and suggest the steric interactions of the ring substituents in the alkylated derivatives inhibit polymerization.

M_w values for two poly(*B*-vinylborazine) polymers prepared under identical conditions, but with AIBN concentrations of 0.128 M and 0.046 M, were 23 000 and 17 000, respectively. This decrease in molecular weight with a decrease in initiator concentration is, in fact, opposite to what is normally observed in free-radical polymerizations. However, these polymers exhibited high molecular fractions that skewed their SEC/LALLS molecular weight determinations. Therefore, the dependence of molecular weight on initiator level could not be established. When the poly(*B*-vinylborazine) polymerizations were carried out to low conversions, the high molecular weight mode was not generated and measured SEC/LALLS molecular weights were representative of the bulk of the polymer mass. Thus, M_w values for two low-conversion homopolymers, prepared with AIBN concentrations of 0.188 M and 0.040 M, were 4900 and 5300, respectively. The observed increase in molecular weight with decreased initiator concentration is consistent with a free-radical polymerization of the *B*-vinylborazine, but the magnitude of the change was significantly less than the [initiator]$^{-1/2}$ dependence expected for chain length as a function of initiator concentration.[12]

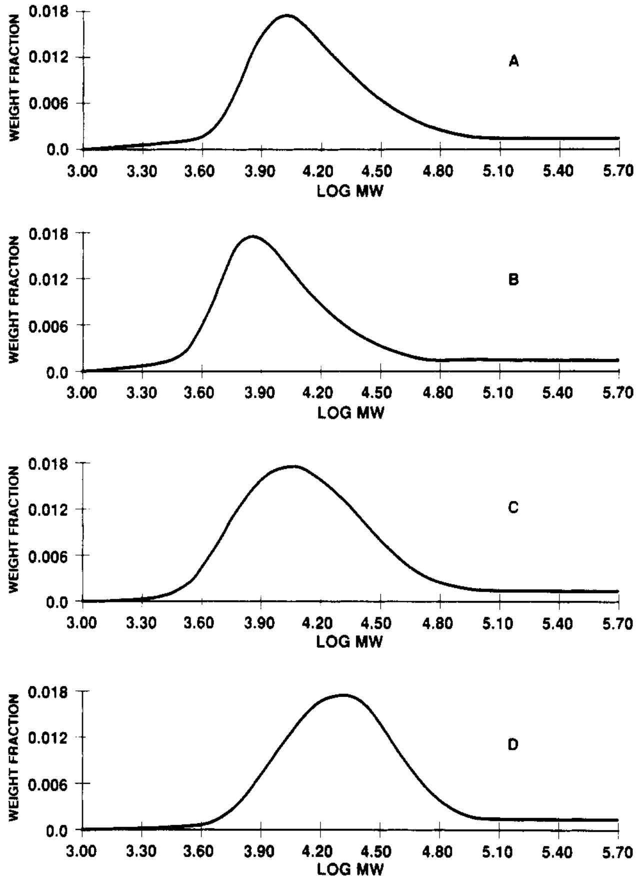
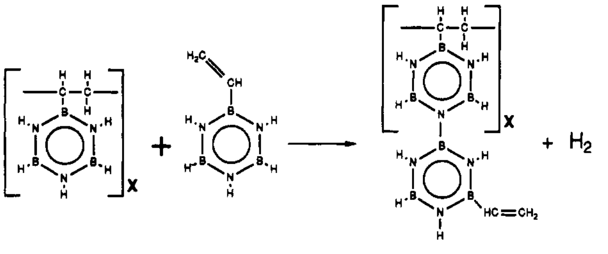


Figure 2. Molecular weight distribution for SVB copolymers and corresponding homopolymers of each comonomer. (A) Poly(*B*-vinylborazine); (B) SVB2 (68% styrene, 32% *B*-vinylborazine); (C) SVB6 (94% styrene, 6% *B*-vinylborazine); (D) polystyrene.

The difficulty in preparing linear high molecular weight poly(*B*-vinylborazine) suggests the presence of strong chain termination and/or retarding reactions during polymerizations. A possible retarding reaction is chain transfer to an unreacted *B*-vinylborazine monomer or to the polymer. The involvement of *B*-vinylborazine in chain-transfer reactions is also a possible reason for the presence of the high molecular weight mode observed in poly(*B*-vinylborazine) samples prepared at higher conversions (approximately 25%). Under such conditions, intermolecular chain transfer to polymer might be expected, leading to the formation of higher molecular weight branched molecules.

As mentioned above, the molecular weight distributions of the poly(*B*-vinylborazine) resins obtained at higher conversion conditions, as shown in the example in Figure 2A, are skewed toward the highest molecular weights. This skewing is the product of intense LALLS detector response from the earliest eluting molecules in the size exclusion chromatogram. From the DRI detector response it was estimated that the amount of polymer corresponding to this fraction was no greater than 15–20% of the total polymer mass. The chemical nature of the higher molecular weight polymer fraction could not be directly obtained from the SEC/LALLS data. But its strong LALLS detector response suggested lightly cross-linked or branched polymer chains. This interpretation is supported by the results of previous SEC/LALLS studies of long-chain branched polymers produced by free-radical polymerization.[13,14] In such cases intense LALLS detector response from long-chain branched polymers is typically found in the high molecular weight region of the size exclusion chromatogram.

Chain branching in poly(*B*-vinylborazine) may have resulted from the chain-transfer reaction discussed above or, alternatively, by a cross-linking dehydrocoupling reaction, such as has been observed in the related polymer, poly(borazylene). In poly(borazylene), chain branching is believed to result from the thermally promoted dehydropolymerization of borazine at more than two ring positions.[15] If dehydropolymerization also occurs in poly(*B*-vinylborazine), *B*-vinylborazine groups, joined to the polymer chain through B–N bonds to the pendant borazine rings, could serve as branching and/or cross-linking points in the polymer. The growth of branched chains could then proceed through free-radical vinyl polymerization or further dehydropolymerization of the borazine rings.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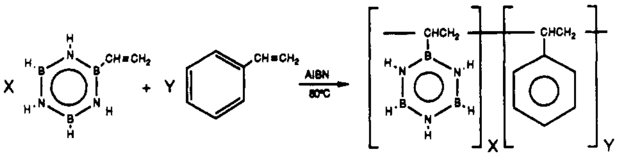
The fact that M_w increased with increased AIBN level when the polymerization was carried out to higher conversions could be consistent with either a strong chain transfer to polymer or a dehydrocoupling reaction. However, the highest conversions studied did not exceed 35%, and under such conditions chain transfer to the monomer should be predominant. Therefore, the borazine ring dehydrocoupling reaction, rather than the chain transfer to the polymer, is the more probable source of the higher molecular weight chain branched components. The likelihood of dehydrocoupling is further supported by the expected termination of the free-radical polymerization during high-conversion (16–20 h) polymerizations due to the depletion of the initiator [AIBN $t_{1/2}$ 78 °C (benzene solvent) ≈ 2.5 h].[16a]

Since the polymer prepared in this study was fully soluble, extensive cross-linking reactions did not occur. Thus, the presence of lightly cross-linked or branched chains would seem to best account for both the polymer's solubility and the high molecular weight fraction apparent in its LALLS chromatogram.

Copolymerization of *B*-Vinylborazine and Styrene. The discovery that soluble poly(*B*-vinylborazine) homopolymers could be readily formed in solution at 80 °C with the aid of AIBN initiation has opened the way to controlled copolymerization reactions. Given the close structural relationship of the *B*-vinylborazine and styrene, our initial studies focused on copolymers derived from these monomers and have resulted in the production of a range of new organic/inorganic hybrid poly(styrene-*co*-*B*-vinylborazine) copolymers.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In all cases, ether (glyme, THF) soluble copolymers were obtained as white solid products. As can be seen in Figure 1, the IR data are consistent with their styrene-*co*-*B*-vinylborazine formulations, showing absorptions characteristic of the borazinyl, phenyl, and polymer backbone fragments. As expected, the relative intensities of these absorptions change with the copolymer composition. For example, as shown in Figure 1b–d, with increasing styrene content, the aromatic C–H absorptions between 3100 and 3000 cm^{-1} grow, while the borazine B–H (2500 cm^{-1}) and N–H (3400 cm^{-1}) absorptions decrease. Likewise, the ^{1}H NMR spectra of the copolymers show the broad resonances expected for these fragments with relative intensities characteristic of their relative styrene/*B*-vinylborazine compositions.

Two sets of styrene-*co*-*B*-vinylborazine (SVB) copolymers were prepared in this study. The first set (SVB1–SVB6 in Table I) employed variable monomer feed ratios and approximately constant percent conversion in the copolymerization. In set 2 (SVB7, SVB8, SVB9) the percent conversion was varied while the monomer feed ratio was held constant. Monomer feed and percent conversion data for both sets of copolymers and the corresponding homopolymers of each comonomer are summarized in Table I. On the basis of the high styrene incorporation for all monomer feed compositions, styrene was more reactive than *B*-vinylborazine in the polymerization. This qualitative observation was quantitatively confirmed by the determination of monomer reactivity ratios (r_1, r_2) using the copolymer equation[16b]

$$F_1 = \frac{r_1 f_1^{\,2} + f_1 f_2}{r_1 f_1^{\,2} + 2 f_1 f_2 + r_2 f_2^{\,2}}$$

where F_1 and F_2 are the mole fractions of styrene (monomer 1) and *B*-vinylborazine (monomer 2) in the polymers, f_1 and f_2 are the mole fractions of styrene and *B*-vinylborazine in the monomer feed, and r_1 (styrene) and r_2 (*B*-vinylborazine) are the relative reactivity ratios. The above equation was rearranged to give a linearized form which was graphically solved by linear regression analysis for r_1 (slope) and r_2 (y intercept):

$$\frac{f_1(1 - 2F_1)}{(1 - f_1)F_1} = r_2 + \frac{f_1^{\,2}(F_1 - 1)}{(1 - f_1)^2 F_1} r_1$$

Ideally, calculations of r_1 and r_2 should employ copolymers prepared at low conversion.[16b] However, the use of the higher conversion copolymers listed in Table I was justified by the small average composition differences between resins prepared with identical monomer feed but different conversions (see resins SVB7–SVB9). Graphical solution using the data in Table I yielded $r_1 = 4.02$ and $r_2 = 0.078$. These values indicate that the SVB copolymers are characterized by isolated *B*-vinylborazine units separated by styrene sequences of random length.

The characteristics of SVB copolymers determined from reactivity ratios were further substantiated by excimer emission spectroscopy. Excimer formation in styrenic polymers is a well-known phenomenon.[17–21] In dilute solution, the primary mechanism of excimer formation is through intramolecular interactions of nearest-neighbor aromatic rings. The relative ratio of excimer to monomer styrene emission has been used in a quantitative manner

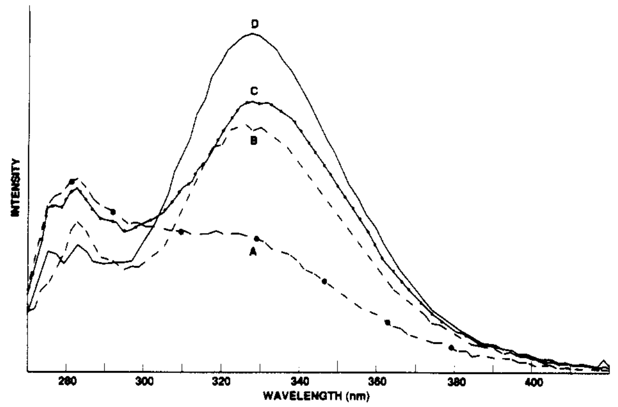

Figure 3. Fluorescence emission spectra for SVB copolymers. (A) SVB2 (68% styrene, 32% *B*-vinylborazine); (B) SVB4 (77% styrene, 23% *B*-vinylborazine); (C) SVB5 (86% styrene, 14% *B*-vinylborazine); (D) SVB6 (94% styrene, 6% *B*-vinylborazine).

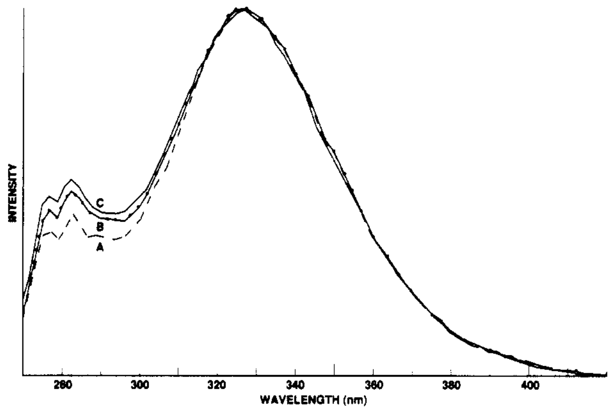

Figure 4. Fluorescence emission spectra for SVB copolymers. (A) SVB7 (88% styrene, 12% *B*-vinylborazine, 4.8% conversion); (B) SVB8 (85% styrene, 15% *B*-vinylborazine, 23.9% conversion); (C) SVB9 (84% styrene, 16% *B*-vinylborazine, 32.5% conversion).

to analyze styrenic copolymer sequence distributions.[22,23] For example, the normalized excimer to monomer emission intensity ratio has been shown to be directly related to the fraction of adjacent phenyl rings along the polymer backbone in poly(acrylonitrile-*co*-styrene) copolymers.[22]

For SVB copolymers, ultraviolet absorption and fluorescence spectra indicated that the borazine ring does not contribute to the copolymer's UV absorption at 260 nm or to its fluorescence emission at 330 nm. Therefore, the excimer emission specifically measures the styrene component and can be used as an indicator of the arrangement of styrene monomers along the polymer chain.

Fluorescence spectra for a set of SVB copolymers prepared with various styrene feed ratios are shown in Figure 3. It is clear that the relative intensities of the monomer and excimer emission vary with feed composition used in the copolymerization. However, even for copolymers prepared with very low styrene in the feed, the relative intensity of the excimer emission indicates that there exists a significant number of adjacent styrene units. These results are consistent with relative reactivity ratios which point out the greater reactivity of styrene in the polymerization. In Figure 4 the effect of conversion on the excimer emission spectra is shown. The relative amount of excimer emission increases as a function of decreasing percent conversion. This result would be expected if styrene was the more reactive monomer, thereby producing longer styrene sequence lengths early in the polymerization.

Excimer to monomer emission ratios obtained from the spectra in Figure 3 were normalized for average styrene composition [(I330/I284)$_n$], and these values are listed in Table II. Previous investigations[23] have shown (I330/I284)$_n$ to be proportional to styrene mean sequence length, and in the present study (I330/I284)$_n$ increased with increasing average styrene content in the copolymers. This trend is indicative of random copolymerization for which longer average sequence lengths are expected with increasing styrene content.

Table II
Fluorescence Intensity Ratios and Compositions for Styrene/*B*-Vinylborazine Copolymers

monomer feed[a]	styrene[b]	% conversion	I330/I284	(I330/I284)$_n$[c]
0.22	0.68	23.5	0.696	1.0
0.40	0.77	21.5	1.33	1.7
0.59	0.86	32.4	1.97	2.3
0.79	0.94	30.0	2.70	2.9
1.00	1.00	57.9	3.23	3.2

[a] Weight fraction styrene in feed. [b] Weight fraction styrene in polymer. [c] Intensity ratio, normalized for weight fraction styrene in polymer.

Table III
Molecular Weight Averages and Composition Data for Styrene/*B*-Vinylborazine Copolymers

resin	wt % styrene	d*n*/d*c*, mL/g	M_n	M_w	M_z
PVB1	0	0.116[b]	10 700	18 000	33 500
SVB2[d]	68[a]	0.164[b]	6 700	11 000	27 000
SVB4[d]	77[a]	0.171[b]	10 400	17 000	50 900
SVB5[d]	86[a]	0.177[b]	11 700	18 700	35 200
SVB6[d]	94[a]	0.183[b]	10 600	14 000	19 300
SVB7[e]	88[f]	0.179[b]	7 000	8 600	10 900
SVB8[e]	85[f]	0.176[b]	9 200	17 900	48 600
SVB9[e]	84[f]	0.176[b]	10 500	19 700	58 000
PS	100	0.189[c]	15 400	23 400	35 200

[a] Composition determined by elemental analysis. [b] Determined from data in Figure 5. [c] Determined by laser differential refractometry. [d] Set 1 copolymer. [e] Set 2 copolymer. [f] Determined by relative excimer fluorescence.

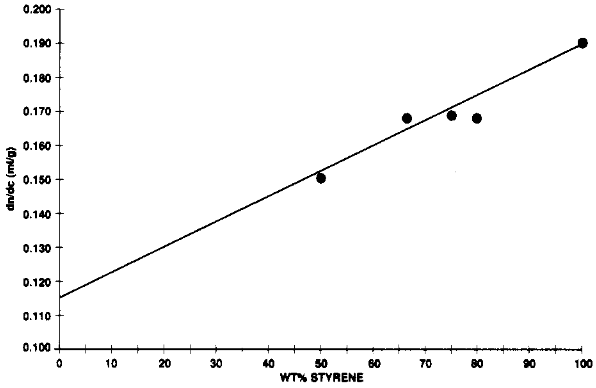

Figure 5. Specific refractive index increment (d*n*/d*c*) dependence on copolymer composition.

Copolymer Molecular Weight and Composition Distributions. Molecular weight averages determined for the polymers in Table I are summarized in Table III. The specific refractive index increment (d*n*/d*c*) used in the SEC/LALLS molecular weight determinations was obtained from the relationship between d*n*/d*c* and composition (weight percent styrene) shown in Figure 5. A set consisting of four SVB copolymers and polystyrene was used to generate the linear relationship between d*n*/d*c* and composition.

Since a constant d*n*/d*c* was used for a given copolymer, the copolymer's composition was implicitly assumed to be constant as a function of chain length (i.e., no compositional heterogeneity). This assumption was tested by overlaying normalized UV chromatograms obtained at

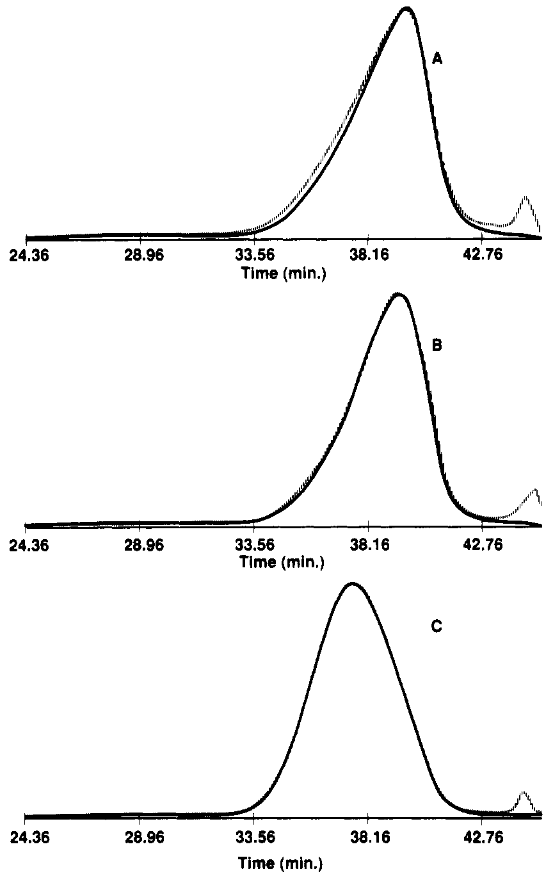

Figure 6. Overlay of normalized ultraviolet chromatograms for SVB copolymers and polystyrene. (Solid line) 259 nm; (hatched line) 230 nm. (A) SVB2 (68% styrene, 32% *B*-vinylborazine); (B) SVB4 (77% styrene, 23% *B*-vinylborazine); (C) polystyrene.

259 and 230 nm and searching for poor overlap which would indicate compositional heterogeneity. The overlap of the normalized UV chromatograms represented a particularly good test for compositional heterogeneity because the 259-nm chromatogram was selective for the styrene comonomer due to the very weak UV absorbance of poly(*B*-vinylborazine) at 259 nm.

The use of SEC/LALLS methods for the characterization of compositional heterogeneity in polymers has been previously demonstrated for copolymers[24,25] and functionalized polymers.[26] This approach provides quantitative compositional heterogeneity data if the composition variation in a polymer is coupled to its hydrodynamic volume distribution.[27] In the event that the polymer is compositionally heterodisperse about the same mean composition for every hydrodynamic volume fraction of the SEC, no apparent compositional heterogeneity will be measured by the SEC/LALLS method. As a result, the SEC/LALLS/UV data reported herein were used to qualitatively assess the compositional heterogeneity of the SVB copolymers.

From the comparison of overlayed normalized UV chromatograms shown in Figure 6, copolymers containing greater than 77 wt % styrene (SVB4) exhibited near perfect overlap of the 259- and 230-nm chromatograms. The compositional variation as a function of hydrodynamic volume was, therefore, judged to be negligible. For copolymers containing less than 77 wt % styrene, the 230-nm chromatogram deviated slightly from the 259-nm chromatogram in the high molecular weight region. Poorer overlap was noted when the styrene content reached 68 wt % (SVB2). In every case, excess absorbance at 230 nm was found in the higher molecular weight region of the UV chromatograms when the chromatograms displayed a lack of overlap. This indicates that the high molecular weight end of the molecular weight distribution is enriched in *B*-vinylborazine relative to styrene. As a result, the use of a constant d*n*/d*c* obtained from Figure 5 is not rigorously correct for the SEC/LALLS molecular weight determination. The magnitude of the d*n*/d*c* inaccuracy was evaluated by calculating UV absorbance ratios, A_{230}/A_{259}, across the UV chromatograms. In the case of maximum compositional variation (resin SVB2 in Figure 6), A_{230}/A_{259} was nearly constant across the chromatograms except in the region of the highest molecular weight chains. The contribution of this fraction to the total polymer mass represented a maximum of 15–20 wt %. Since the fraction of molecules that exhibited a significant compositional difference from the bulk of the copolymer was relatively small, the overall compositional heterogeneity is not severe and the calculated molecular weights listed in Table III are good estimates of the true values.

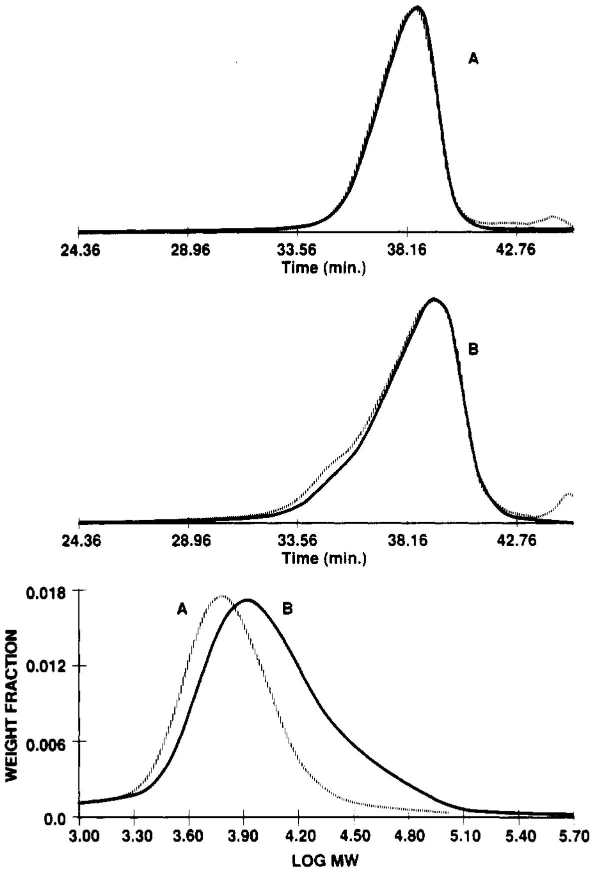

Figure 7. Overlay of normalized ultraviolet chromatograms and molecular weight distributions. (Top, A) SVB7 (88% styrene, 12% *B*-vinylborazine, 4.8% conversion); UV chromatograms (solid line) 259 nm, (hatched line) 230 nm. Middle, B) SVB9 (84% styrene, 16% *B*-vinylborazine, 32.5% conversion); UV chromatograms (solid line) 259 nm, (hatched line) 230 nm. (Bottom) Overlayed molecular weight distributions: (A) SVB7; (B) SVB9.

Molecular weight distributions (MWD) calculated for the set of copolymers in Table III were characterized by increased skewing toward high molecular weight with increasing average *B*-vinylborazine content. The comparison of MWD for the 0, 14, 32, and 100 wt % *B*-vinylborazine-containing copolymers, shown in Figure 2, depicts the dramatic change in the shape of the MWD as a function of composition. For SVB copolymers prepared with constant monomer feed and different percent conversion (resins SVB7–SVB9), skewing of the MWD increased with increasing percent conversion as shown in Figure 7. In addition, greater apparent compositional heterogeneity was also observed for the copolymers prepared at higher conversion as shown in Figure 7.

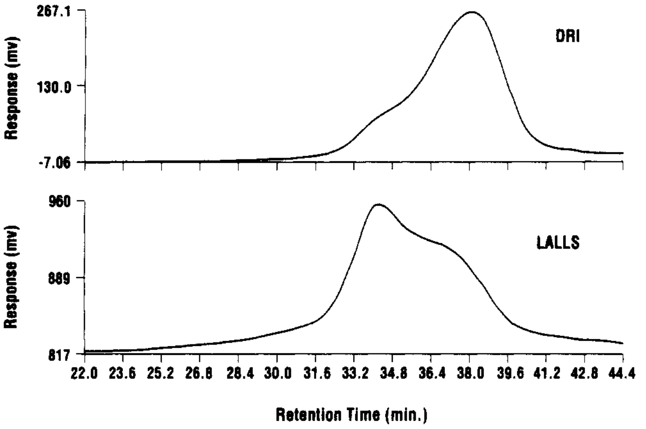

Figure 8. SEC/LALLS chromatograms showing high molecular weight fraction, copolymer SVB9 (84% styrene, 16% *B*-vinylborazine). (Top) DRI chromatogram; (bottom) LALLS chromatogram.

The pattern of MWD skewing in SVB copolymers closely followed the observations made for poly(*B*-vinylborazine). SEC/LALLS chromatograms for SVB copolymers, like that of poly(*B*-vinylborazine), are characterized by strong LALLS response resulting from a high molecular weight fraction. In the case of copolymers SVB8 and SVB9, this high molecular weight fraction produced clearly bimodal DRI and LALLS chromatograms as shown in Figure 8. The nature of the high molecular weight fraction is suggested by the corresponding UV chromatograms to be *B*-vinylborazine-rich copolymer molecules. The possibility that the high molecular weight mode contains some pure branched poly(vinylborazine) cannot be ruled out on the basis of SEC/LALLS data. A fraction of branched poly(*B*-vinylborazine) in the copolymer could be masked by strong overlap of its molecular weight distribution with that of the copolymer. Further work, such as solvent/nonsolvent fractionation of the copolymers according to composition, will be needed to resolve this issue.

On the basis of SEC/LALLS and fluorescence data for both poly(*B*-vinylborazine) and the SVB copolymers, ascribing the high molecular weight fractions in these polymers to branched polymer chains would account for all experimental observations. Given that *B*-vinylborazine can act as a branching agent in the free-radical polymerization of *B*-vinylborazine through dehydropolymerization, the same mechanism might be expected to occur to a lesser extent in SVB copolymer. However, due to the higher reactivity of styrene relative to that of *B*-vinylborazine and the relatively high percent conversion used to prepare SVB copolymers, branching reactions might become favorable at the end of the polymerization when the monomer feed mixture would be enriched in *B*-vinylborazine relative to styrene.

The fraction of branched chains in each copolymer was not accurately determined, but on the basis of DRI detector response of the high molecular weight fraction relative to the signal for the remainder of the copolymer, the high molecular weight fraction probably represents no greater than 15–20 wt % of the copolymer mass in the case of copolymers with high average *B*-vinylborazine content.

Conclusions. Soluble poly(*B*-vinylborazine) homopolymers can now be produced in a controlled fashion in solution by using free-radical initiation of *B*-vinylborazine with AIBN. A small fraction of the high molecular weight polymer may consist of branched or lightly cross-linked polymer chains resulting from dehydrocoupling reactions of the borazine ring. Since poly(*B*-vinylborazine) has previously been shown[3,4] to serve as an efficient ceramic precursor to boron nitride and boron nitride/carbide ceramics, this new capability to produce soluble processable polymers with higher molecular weights should expand the use of these preceramic polymers to a variety of new applications.

Copolymers of *B*-vinylborazine and styrene (SVB) with a range of compositions and molecular weights can also be prepared by solution free-radical polymerization. Reactivity ratios and excimer fluorescence of SVB copolymers indicate that styrene is more reactive in the copolymerization. The copolymers are characterized by isolated *B*-vinylborazine units separated by styrene sequences of random length.

Molecular weight characterization by SEC/LALLS/UV indicates that the SVB copolymers prepared in this study were compositionally heterodisperse. In addition, the *B*-vinylborazine monomer may act as a branching agent yielding branched SVB copolymers, particularly for copolymers containing greater than 23 wt % *B*-vinylborazine.

These studies further suggest that a wide range of new hybrid organic/inorganic copolymers derived from *B*-vinylborazine should now be attainable by using free-radical initiation, and we are currently in the process of examining these possibilities.

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