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Organoborazines.3.Homo- and Copolymerization of
p-Vinylphenylcyclotriborazines

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The polymerization and copolymerization with styrene of a series of unsymmetrically B-p-vinylphenyl-N-methyl, and N-phenyl borazines $(R^3(R^2)_2B_3N_3(R^1)_3$; R^1 = methyl, phenyl, R^2 = methyl phenyl, R^3 = p-vinylphenyl) has been studied. The polymerization of these monomers yielded both tractable and crosslinked materials. The polymers obtained were characterized by ^1H and ^{13}C NMR spectroscopy, elemental analysis, gel permeation chromatography and thermogravimeteric analysis. The reactivity ratios for the copolymerization reaction were calculated by the Mortimer-Tidwell method.

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Organoborazines. 3. Homo- and Copolymerization of p-Vinylphenylcyclotriborazines[1]

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Synopsis

The polymerization and copolymerization with styrene of a series of unsymmetrically B-p-vinylphenyl-N-methyl, and N-phenyl borazines ($R^3(R^2)_2B_3N_3(R^1)_3$; R^1 = methyl, phenyl, R^2 = methyl phenyl, R^3=p-vinylphenyl) has been studied. The polymerization of these monomers yielded both tractable and crosslinked materials. The polymers obtained were characterized by ^1H and ^{13}C NMR spectroscopy, elemental analysis, gel permeation chromatography and thermogravimeteric analysis. The reactivity ratios for the copolymerization reaction were calculated by the Mortimer-Tidwell method.

Introduction

Interest in hybrid inorganic-organic polymers has grown considerably in recent years.[2] Linear high polymers have been based on inorganic backbones with organic substituents, e.g. poly(phosphazenes), poly(siloxanes), poly(silanes), or systems based on inorganic ring systems. Inorganic ring system polymers include linear (cyclolinear) or crosslinked (cyclomatrix) polymers with an inorganic ring as part of the backbone and carbon chains with inorganic rings as substituents. Our group has explored the latter class of polymers in which the pendant inorganic ring is a cyclophosphazene and we have prepared a variety of homo and copolymers of this type.[3-9] Recently, we have become interested in related systems containing cycloborazines in place of cyclophosphazenes.[10] In addition to the fundamental interest in new types of polymeric materials, borazine containing polymers have attracted attention for applications as diverse as flame retardency, thermal stability and toner image support materials." With the recent recognition of the importance of polymer pyrolysis as a route to ceramic materials,[12] attention has been focused on borazine polymers as boron-nitride precursors.[13] Several groups have explored cyclolinear and cyclomatrix borazine polymers in this regard.[14-16] Of closer relevance to this study, is the work of Sneddon who showed that alkenyloborazines such as $N_3B_3H_5CH=CH_2$ undergo, in the presence of borazine itself, thermal polymerization to low molecular weight oligomers which can be converted to boron-nitride.[17] Previous studies have shown that trivinylborazine is easily polymerized but the products have not been examined in detail.[18] N-phenyl-B-trivinylborazine does not homopolymerize due to steric crowding of the phenyl groups but will undergo copolymerization.[19] Crude reactivity ratio determinations suggest that the reactivity of the N-phenyl-B-trivinylborazine is similar to that of styrene.[19] Similarly, B-

isopropenyl-pentamethylborazine undergoes radical copolymerization with styrene and 4-vinyl-pyridine.[20] In most cases, the resulting polymers received limited characterization.

We have previously shown that monofunctional borazine rings can be easily prepared bearing an alkenyl functionality which can allow for polymerization by standard techniques.[1,10] In this paper we described the polymerization and copolymerization of a series of p-vinylphenyl substituted cyclic borazines (Scheme 1).

EXPERIMENTAL

Materials. The p-vinylphenyl borazines were prepared by previously published procedures.[1] Styrene was distilled from calcium hydride and stored at 0 °C. Prior to use, a small quantity of styrene was added to an excess of methanol. If no turbidity was observed, it was assumed that no polymer was present. Azobis(isobutrylnitrile) (AIBN) was recrystallized twice from ethanol, dried under vacuum and stored at 0 °C. Benzene[21] was distilled directly from potassium metal before use.

Measurements. Infrared spectra were recorded as KBr pellets on a Perkin Elmer 1430 spectrometer. The ^{1}H and ^{13}C NMR spectra (in $CDCl_3$) were recorded on a Bruker 270 MHz FT NMR spectrometer operating at 270.13 and 67.93 MHz. Chloroform (^{1}H) and tetramethylsilane (^{13}C) were used as the internal references. Gel permeation chromatography (GPC) on a Waters 6000A HPLC system equipped with Waters 10^{4}- and 10^{5} microstyragel columns. Toluene solutions were employed for GPC determinations. Thermal analyses were carried out on a Perkin-Elmer TGS-2 thermogravimetric system (TGA) interfaced with a PETOS thermal analysis data station. Copolymer composition was determined from weight percent nitrogen. Elemental analysis were performed by Robertson Laboratories. Reactivity ratios for the systems following the terminal model were calculated by using the Mortimer-Tidwell nonlinear least-squares approach.[22]

Polymerization Reactions. Polymerization and copolymerization reactions were carried out by the following general method. Monomer or comonomers, along with 2% AIBN and benzene,[21] were placed in a glass ampule and subjected to three freeze-pump-thaw cycles. The ampules were then sealed under vacuum and place in a thermoregulated oil bath at 60 ± 2 °C. After heating the tubes were cooled and opened carefully. The reaction mixture were diluted slightly with methylene chloride and the polymer was precipitated from hexane. Using this method, homo and styrene copolymers of B-p-vinylphenyl-B-dimethyl-N-triphenylcycloborazines (Ic) were prepared (Table I). The polymers and copolymers are milk-white solids soluble in a wide variety of organic solvents. Alcoholic solvents cause decomposition of polymers as does long term exposure to the atmosphere.

The polymerization of B-p-vinylphenyl-B-dimethyl-N-trimethylcycloborazine (Ia) was performed in bulk at the melt temperature of the monomer. The monomer was placed in glass ampules and the tube was evacuated. The monomer was then heated to the melt temperature to allow for removal of trapped gases. This process was repeated twice. The ampules were then sealed under vacuum and heated in a thermoregulated oil bath at 60 ± 2 °C. It was not necessary to use an intiatior and polymerization to a crosslinked material was complete in 12 h. Attempted copolymerizations with styrene were performed by the same method only the tubes were not sealed under vacuum; cross-linked materials were also obtained. Solution polymerization of Ia in benzene also yielded cross-linked materials. Identical behavior was observed when the polymerizations of B-p-vinylphenyl-B-diphenyl-N-trimethylcyclotriborazine(Ib) and B-di(p-vinylphenyl)-B-methyl-N-trimethylborazine(II) were carried out.

RESULTS AND DISCUSSION

The organofunctional borazine monomers under investigation in this study, B-p-vinylphenyl-B-dimethyl-N-trimethylcycloborazine (Ia), B-p-vinylphenyl-B-diphenyl-N-trimethylcycloborazine (Ib), p-vinylphenyl-B-dimethyl-N-triphenylcycloborazine (Ic), and B-di(p-vinylphenyl)-B-methyl-N-trimethylborazine (II), can be considered as substituted styrenes with the borazine ring in the para position of the aromatic ring of the styrene. Radical initiation was chosen for these monomers since the Lewis base character of the ring nitrogen atoms would interfere with cationic processes and the Lewis acid character of boron atoms would effect anionic processes. Polymerization and copolymerization of these monomers yield polymers of the type shown in Scheme 1.

Insert Scheme 1

The first monomer to be examined was the B-p-vinylphenyl-B-dimethyl-N-trimethylcycloborazine (Ia). The homopolymerization of this monomer in bulk and in benzene, with or without an initiator (AIBN) present, resulted only in crosslinked material. We have previously reported that this monomer readily under goes thermal polymerization during purification.[1] The bulk monomer crosslinked to a clear transparent glass at 60 ±2 °C over a period of 12 h. Similar crosslinking of the material resulted upon heating at 250 °C for 15 min. Shorter polymerization times yielded rubbery material which could be further polymerized to a glassy material by heating, presumably reflecting an increase in the crosslinking density. The crosslinked materials (rubber or glass) were insoluble in all common solvents except methanol which effects borazine ring degradation. Copolymerization with styrene yielded similar crosslinked materials. In order to obtain some information on structural features responsible for the crosslinking reaction, the effect of a systematic variation of substituents on the borazine ring was examined. The

replacement of methyl groups by phenyl groups on the boron atoms not containing the p-vinylphenyl function gives monomer **Ib** which undergoes crosslinking reactions exactly analogous to those noted for **Ia**. On the other hand if the N-methyl, rather than B-methyl, groups are replaced by the phenyl moiety to give monomer **Ic**, facile polymerization and copolymerization are observed without crosslinking (vide infra).

The intractable mixture of the crosslinked products (from **Ia, b**) limits the characterizational methodologies which can be applied to the elucidation of the nature of the crosslinks. The chemical evidence given above strongly implicates the N-methyl groups. Slight changes are noted in the methyl region of the IR spectra between the monomers and crosslinked polymers of **Ia,b** but these changes were not significant enough to draw firm conclusions. The more diagnostic CH_2 modes are masked by the strong boron-nitrogen ring mode. One does note the expected loss of the olefinic stretch. Derivatization of the N-methyl carbon atom of organoborazines has been previously noted in thermolysis reactions[23] and hydrogen abstraction from N-alkyl groups occurs by the addition of organic radicals,[24] photochemically[25] and under conditions of the mass spectrometry experiment.[26] A reasonable model for the crosslinking behavior involves chain transfer to polymer. The radical center derived from the vinyl group can abstract an N-methyl hydrogen atom. The new radical center then adds to the vinyl group of **Ia** or **Ib** leading to the observed crosslinking. The polymerization of a monomer with two vinyl groups (**II**) was carried out in order to explore a system which could undergo crosslinking at two vinyl sites in addition to the process described above. The bulk polymerization of **II** occurs, even in the absence of an initiator, immediately as the melt temperature is approached. The resulting material is hard, glassy and insoluble in all common solvents.

The homopolymerization of B-p-vinylphenyl-B-dimethyl-N-triphenylcycloborazine, **Ic**,

and copolymerization with styrene using AIBN as an initiator was found to occur readily and resulted in good conversion to polymer. The polymers and copolymers produced were all white powders, soluble in a variety of common organic solvents. Long term exposure to the atmosphere resulted in decomposition of the materials. The reactions of Ic with stryene lead to copolymers with a wide range of compositions (Table I). Incorporation of the borazine monomer, Ic, into the polymers ranged from 10 to 100 %. The presence of the borazine ring para on the styrene functionality did not substantially effect the amount of borazine monomer incorporated into the copolymer; i.e., similar feed ratios of Ic lead to polymers of similar composition as determined by elemental analysis. Lower incorporations of Ic into the polymers were not attempted. Relative molecular weight of the copolymers of Ic and styrene, as determined by GPC, were observed to increase with increasing Ic content. The increase in volume occupied by a poly(styrene) fragment with a terminal N-phenyl(borazine) over that of poly(styrene) suggest that polystyrene standards are not particularly accurate for this system. The generally low values for the molecular weights suggests a chain transfer process leading to termination.

The reactivity ratios of Ic with styrene as the comonomer were calculated by using the Mortimer-Tidwell nonlinear least-squares approach. The value calculated for r_1 was 0.93 (M_1 = Ic) and r_2 was 0.70 (M_2 = STY). However, the variability inherent in determination of copolymer composition by elemental analysis leads to variability in the values of r_1 and r_2. If one examines the 95% joint confidence limit calculated for this data set, it is found that the values for r_1 and r_2 both lie within this interval and are consequently indistinguishable. Thus at the level of accuracy afforded by the compositional data r_1 is virtually equal to r_2. This observation is consistent with the spectroscopic properties of Ic.[1]

The presence of the borazine ring in the polymers and copolymers was confirmed by ^{1}H and ^{13}C NMR and elemental analysis. The ^{1}H NMR spectrum of the homopolymer of **lc** consisted of broad resonances. The protons of the methyl groups of the attached to the boron atoms of the ring were found centered at 0.0 ppm. The resonances for the aromatic protons were observed between 6.2 and 7.5 ppm as a set overlapping resonances. A broad weak shoulder of the aromatic resonances was observed between 5.3 and 6.2 ppm. The resonances for the polymer backbone protons were observed between 1.0 and 2.0 ppm as expected. The ^{13}C NMR spectrum of the homopolymer of **lc** consisted of broad resonances. The resonances for the methyl carbons attached to the borazine ring were observed as moderately broadened signals at 2.5 ppm. The broad resonances for the methylene carbons of the polymer backbone were observed centered at 36.8 ppm. The resonances for the aromatic carbons of the styrene functionality and the phenyl rings attached to ring nitrogen were observed found as broad resonances between 123 and 150 ppm. Confirmation of the borazine ring came from the observation of two resonances, at 149.6 and 147.3 ppm, assigned to the carbon atoms of the phenyl rings attached directly to the ring nitrogen atoms. These resonances were not as broadened as in the rest of the spectrum due to free rotation of the borazine and phenyl rings in the polymer.

The TGA data for thermal decomposition of the polymers derived from **lc** are found in Table I. The decomposition of the materials consisted of a two-step transition with the onset roughly at 400 °C and leading voltalization of all solids by 530°. Unfortunately these transitions are not clearly defined so assigning each to a particular monomer unit is not possible. Two transitions were observed for both the homo- and copolymers of **lc** suggesting that the two transition are a result of cleavage of the borazine ring from the

polymer and cleavage of the polymer chain. Decomposition can occur by a number of different pathways. Obviously thermal chain scission can occur, however cleavage and decomposition of the borazine ring from the polymer chain is also a viable mode of decomposition. It was noted for all of the samples that at the decomposition temperatures a white insoluble sublimate collect in the TGA probe suggesting borazine decomposition. The thermal decomposition of the crosslinked solids derived from **Ia,b** is essentially identical to that of the soluble polymers. This suggests a low crosslink density in these materials. By way of contrast, the thermal decomposition of the crosslinked material derived from **II** leaves a 40% char above 450°. This observation demonstrates the necessity for extensive crosslinking to prevent loss of borazine in the inert atmosphere pyrolysis of polymers with pendant organoborazine rings. Pyrolysis processes which occur in a reactivity atmosphere (e.g. ammonia) may be expected to follow a different pathway[17] and will be explored in subsequent publications.

In summary, we have identified the structural features needed for preparation of linear polymers with pendant organoborazine rings from monomers which can be conveniently prepared and handled under normal laboratory conditions. A crosslinking process involving alkylborazines has also been identified and a model involving chain transfer to polymer has been proposed to rationalize this process.

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Scheme 1

crosslinked solid

R=Me; R'=Me(Ia),

Ph(Ib)

$C_6H_5CH=CH_2$ AIBN

$[(CH-CH_2)_x (CH-CH_2)_y]_n$
$\overset{|}{C_6H_5}$

R=Ph, R'=Me

$(CH-CH_2)_n$

AIBN

R=Ph, R'=Me(Ic)

CH=CH₂

MeN   NMe

MeB   B

N

Me

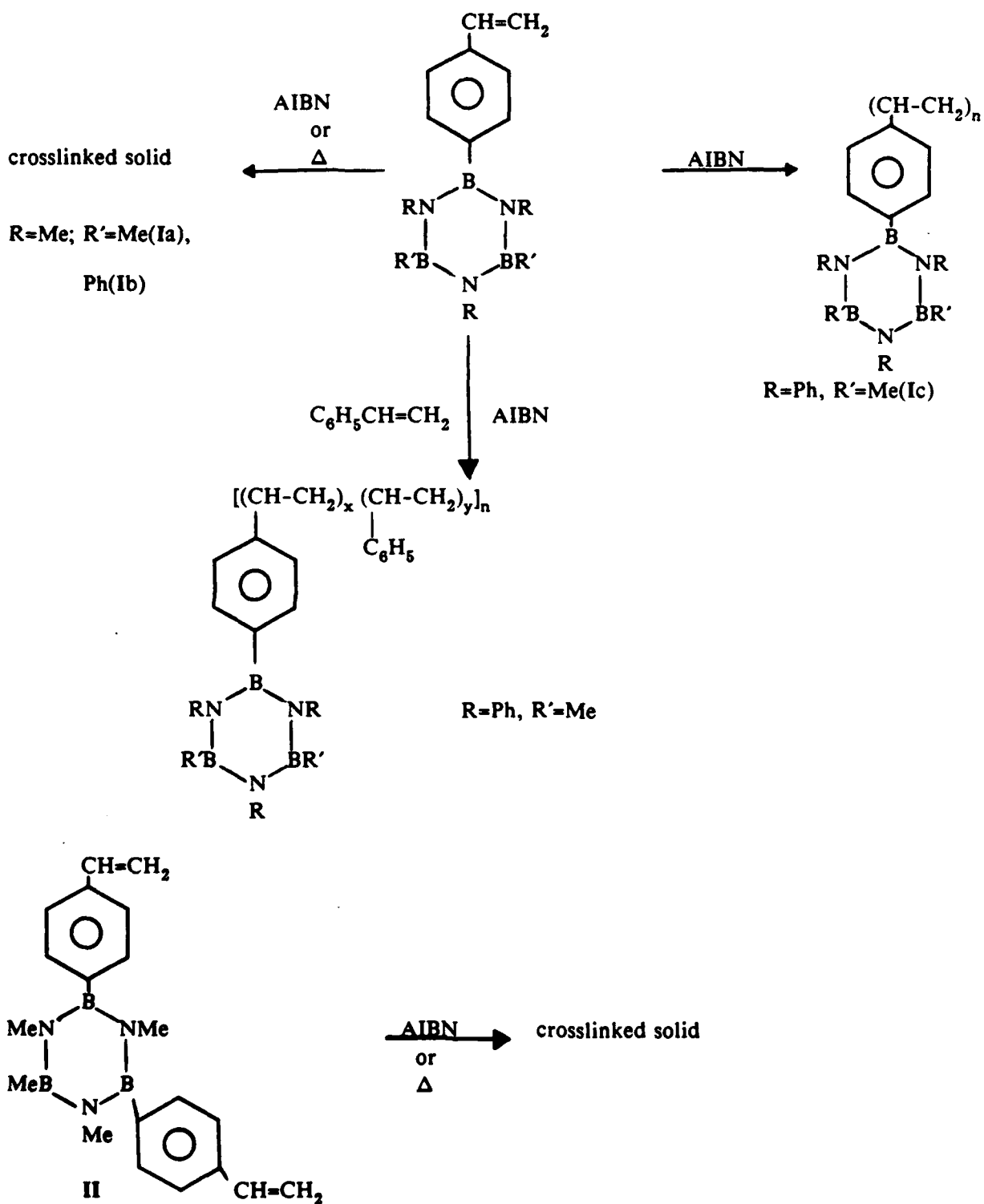II   CH=CH₂

AIBN   crosslinked solid
or
Δ

Table I

Composition, Conversion, Molecular Weight[a] and Differential Thermal Analysis Data for Homo-and Copolymerization of B-p-Vinylphenyl-B-Dimethyl-N-Triphenylborazine (Ic).

Feed	Ic, Mol % Polymer[b]	% Conversion	$\overline{M}_n$	$\overline{M}_w$	$T_{onset}(°c)$	$T^c_{50}(°c)$
100.00	100.00	78.0	18,612	48,445	410	440
9.09	10.25	18.8	10,472	14,257	391	420
20.03	17.38	47.0	8,617	29,398	394	432
33.33	30.95	49.1	6,934	10,169	400	435
49.95	49.02	57.4	10,622	17,224	412	442
59.85	59.17	52.6	18,787	36,920	415	432
76.00	68.49	64.3	26,002	74,365	408	428
78.08	72.46	66.6	10,934	63,282	410	427

a. Molecular weights determined by GPC.
b. Copolymers are with styrene as the componomer.
c. All polymers ultimately give 100% weight loss.