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Synthesis and Polymerization of 1-Azabutadiene Monomers

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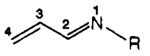
ABSTRACT: Four 1-aza-1,3-butadiene monomers carrying substituents at the 1-aza position have been synthesized, and their abilities to polymerize have been assessed. The most successful monomers are *N*-phenyl-1-aza-1,3-butadiene (**1**) and *N*-(2,4,6-trimethylphenyl)-1-aza-1,3-butadiene (**2**). Their polymerization behavior was examined under acid, base, and free-radical conditions. Base-initiated polymerizations were the most successful. Monomer **2** gave vinyl polymer, whereas the polymer of **1** had both vinyl- and 4,1-addition structures. Both of these monomers also polymerized with acidic initiators to yield polymers having both types of structural units. The various polymers were reduced with lithium borohydride to the corresponding saturated polyamines. Successful polymerizations of *N*-methoxy-1-aza-1,3-butadiene (**3**) and *N*-(dimethylamino)-3-methyl-1-aza-1,3-butadiene (**4**) were not achieved.

Introduction

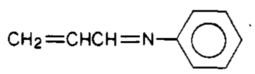
In contrast to extensive investigations of the polymerization of C=C and C=O compounds, very little is known about the addition polymerization of simple C=N compounds. Methyleneimine and its simple derivatives are too reactive to be isolated. Imines often give cyclic trimers,[1] indicating a tendency to polymerize. However, no well-defined polymers have been reported.

Vinyl groups can provide a handle for polymerization of functional groups. For example, vinylcyclopropane can polymerize in a ring-opening fashion, while cyclopropane itself cannot.[2] This concept led us to study the polymerization of conjugated imines, namely 1-aza-1,3-butadienes.

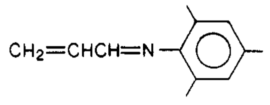


Although this diene system is not uncommon, only two reports have been published on the polymerization of 1-aza-1,3-butadienes. Sato and Tsuruta[3] reported that three *N*-alkyl-3-methyl-1-aza-1,3-butadienes and *N*-alkyl-1-aza-1,3-butadienes polymerized through 4,3-vinyl-type polymerization by anionic initiators. Smith and co-workers[4] found that *N*-alkyl-1-aza-1,3-butadienes did not polymerize with peroxides or boron trifluoride etherate.

In this work, four 1-azabutadienes having differing N-substituents were synthesized and investigated for their polymerizability. The substituents selected were aryl, methoxy, and dimethylamino groups, in order to widely modify the character of the nitrogen atom in this conjugated system. These monomers were subjected to anionic, cationic and radical initiation.



N-phenyl-1-aza-1,3-butadiene (**1**)



N-(2,4,6-trimethylphenyl)-1-aza-1,3-butadiene (**2**)

$CH_2{=}CHCH{=}NOCH_3$

N-methoxy-1-aza-1,3-butadiene (**3**)

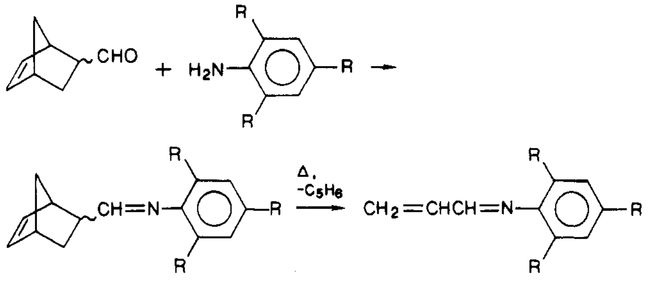
$CH_2{=}C(CH_3)CH{=}NN(CH_3)_2$

N-(dimethylamino)-3-methyl-1-aza-1,3-butadiene (**4**)

Results

Synthesis of Monomers. Direct synthesis of the 1-aryl derivatives by a dehydration reaction between an arylamine and acrolein or methacrolein was not successful, owing to competitive Michael additions and condensations.

N-Alkyl-1-aza-1,3-butadienes have previously been synthesized by thermolysis of anthracene adducts, although the experimental details did not appear in the literature.[3] We employed the more convenient thermolysis of cyclopentadiene adducts for the syntheses of *N*-aryl-1-aza-1,3-butadienes **1** and **2**, according to the procedure described for α-substituted acrylates[5] and 1,3-disubstituted butadienes.[6] The norbornene precursors were easily synthesized from the commercially available aldehyde and amine:



R = H, CH3

Thermolysis of the precursors was carried out in a quartz tube packed with quartz fragments at temperatures ranging from 400 to 650 °C and pressures from 0.1 to 5 mmHg. Best results were obtained at 580–600 °C, at which the thermolysate consisted almost completely of the monomer and cyclopentadiene. The monomers were purified by vacuum distillation. Monomers **1** and **2** were not very stable at room temperature, turning to dark brown viscous liquid, but could be stored at −50 °C at least for 1 month after vacuum distillation.

N-Methoxy-1-aza-1,3-butadiene (**3**) and *N*-(dimethylamino)-3-methyl-1-aza-1,3-butadiene (**4**) were synthesized directly from acrolein and methacrolein, respectively, as described in the literature.[7,8]

Monomers **2** and **3** were obtained as isomeric mixtures of syn and anti forms, as evidenced by NMR spectra. NMR and IR spectra, as well as elemental analyses, supported the assigned structures for monomers **1**–**4**.

Polymerization of *N*-Aryl-1-aza-1,3-butadienes. Polymerization was attempted by anionic, cationic, and radical initiators. The results are summarized in Table I.

Anionic polymerization was the most effective method. Monomers **1** and **2** gave polymers by anionic initiators such as butyllithium (BuLi) and *tert*-butylmagnesium chloride (*t*-BuMgCl) in toluene. Polymerization of **1** by BuLi in tetrahydrofuran (THF) failed, but **2** gave polymer in similar yields in both toluene and THF. Polymerization at

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Table I
Polymerization of 1-Aryl-1-aza-1,3-butadienes[a]

monomer	mmol	initiator	μmol	solvent	temp, °C	time, h	precipitant	yield, %	color	MW (SEC)	softening pt, °C
1	0.5 mL	BuLi	80	tol[f]	−78	24	*b*	23.6	white	2100	160
	(3.7 mmol)	BuLi	80	tol	0	24	*b*	89.3	white	7200	210
		BuLi	125	THF	−78	30	*b*	0			
		t-BuMgCl	80	tol	−78	30	*b*	8.7	white	1600	140
		BF_3OEt_2	74	DCM[g]	−78	30	*c*	19.2	lt brown	960	160
		CF_3CO_2H	74	DCM	−78	30	*c*	34.5	lt brown	1900	
2	1 mL	BuLi	110	tol	−78	24	*d*	38.8	white	4800	100
	(5.45 mmol)	BuLi	110	tol	0	24	*d*	58.0	white	3200	100
		BuLi	110	THF	−78	24	*d*	30.8	white	1000	
		BuLi	110	THF	0	24	*d*	53.7	white	1000	
		t-BuMgCl	120	tol	−78	24	*d*	5.5	yellow-white	2400	90
		BF_3OEt_2	110	DCM	−78	24	*e*	60.6	yellow-white	1500	130
		CF_3CO_2H	110	DCM	−78	24	*e*	~9.9	yellow-white	1100	150

[a] Polymerizations were carried out in Y-shapted tubes with vacuum valve. Catalysts were added by syringe. Five milliliters of solvent was used. [b] One-hundred milliliters of hexane. [c] Washed with Na_2CO_3 (aq), dried over K_2CO_3, and poured into hexane. [d] One-hundred milliliters of methanol. [e] One-hundred milliliters of methanol plus 5 mL of concentrated ammonium hydroxide. [f] Toluene. [g] Dichloromethane.

Table II
IR and NMR Data for Poly-1 and Poly-2

	IR for poly-1		poly-2			
			IR		NMR intensity	
polymerization conditions	$\nu_{C=N}$	intensity[a]	$\nu_{C=N}$	intensity[b]	CH=N	=CH-N
BuLi/Tol[c]/78 °C	1644	0.73	1657	1.06	0.95	
BuLi/Tol[c]/0 °C	1644	0.39	1657	1.07	0.92	
BuMgCl/Tol[c]/−78 °C	1644	0.43	1659	1.03	0.65	0.19
BF_3OEt_2/CH_2Cl_2/−78 °C	1651	0.36	1651	0.93	0.53	0.41

[a] Relative to a peak at 1600 cm^{-1}. [b] Relative to a peak at 1479 cm^{-1}. [c] Toluene.

0 °C in toluene gave better yields and higher molecular weight polymer than at −78 °C. Molecular weights ranged from 1000 to 7000 (by SEC).

Poly-1 and poly-2 were soluble in toluene, benzene, chloroform, dichloromethane, carbon tetrachloride, acetone, THF, and *N,N*-dimethylformamide. Poly-2 was also soluble in acetonitrile, hexane, ethyl acetate, ethyl ether, and triethylamine, while poly-1 was not. Common nonsolvents for both polymers were methanol, ethanol, and 2-propanol. Softening points, observed on a "Kofler Heizbank" heating bar, of poly-1, 140-210 °C, were higher than those of poly-2, 90–130 °C.

Monomers 1 and 2 could also be polymerized by cationic initiators such as BF_3OEt_2 and CF_3COOH to give slightly yellow powdery polymer, but the molecular weights were rather low.

Attempted radical homopolymerization, or copolymerization with methyl methacrylate, was unsuccessful with 1 or 2. Similar observations were reported for *N*-cyclohexyl-1-aza-1,3-butadiene.[3]

Structure of Poly-2. Determination of the structure of the polymers by NMR and IR spectroscopy was aided by the symmetrical 2,4,6-trimethylphenyl structure. The spectroscopic data for both poly-1 and poly-2 are summarized in Table II.

Figure 1a shows ^1H NMR spectrum of poly-2 prepared with BuLi. The clarity of the aromatic absorption allowed us to assign a broad singlet signal at 7.5 ppm to the imine proton, whose intensity, relative to the phenyl proton signal, nearly corresponds to one hydrogen. A small difference in shift is observed between the *o*- and *p*-methyl protons. ^{13}C NMR also clearly showed the imino carbon signal at 169 ppm whose intensity was comparable to those for substituted aromatic carbons, although quantitative measurements were not done. In the IR spectrum of the polymer, a strong C=N stretching vibration band at 1657 cm^{-1} was observed, slightly stronger than the phenyl absorption (Figure 2a).

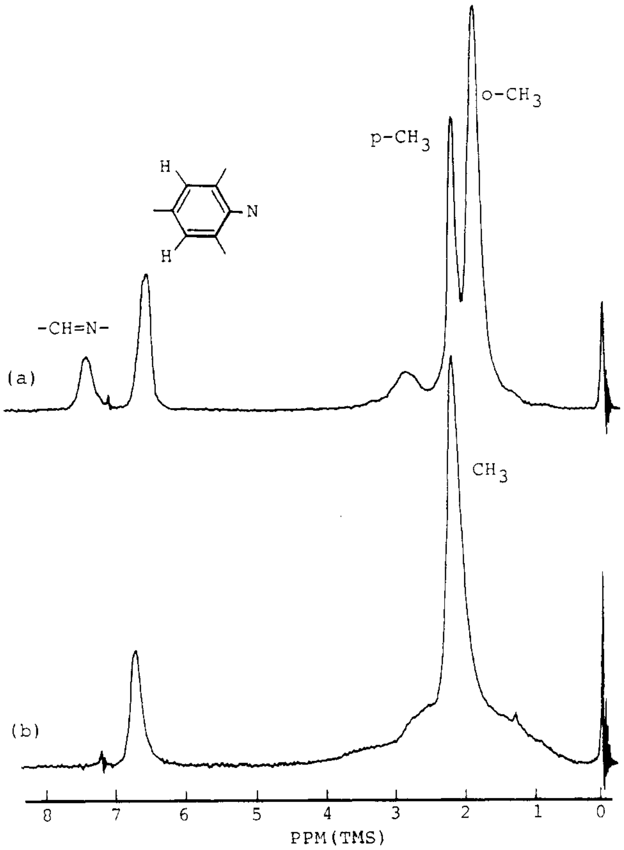


Figure 1. ^1H NMR spectra of poly-2 prepared with BuLi in toluene at 0 °C (a) and reduced poly-2 by $LiBH_4$ (b).

Reduction of BuLi-initiated poly-2 with $LiBH_4$ was conducted in refluxing THF. The ^1H NMR spectrum of the resulting polymer (Figure 1b) showed that the CH=N group was completely reduced. One broad signal for all methyl protons was observed in the spectrum of the re-

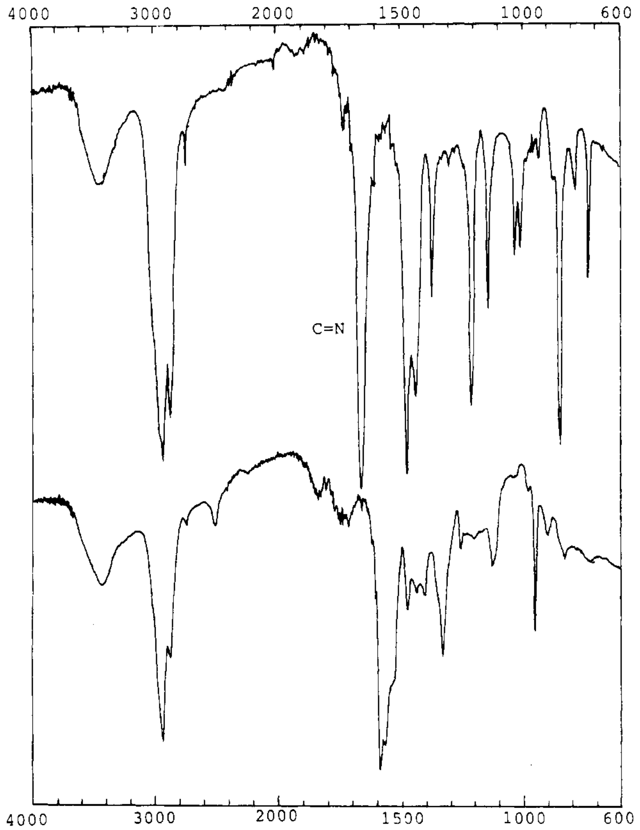
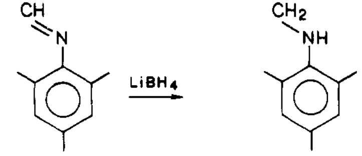


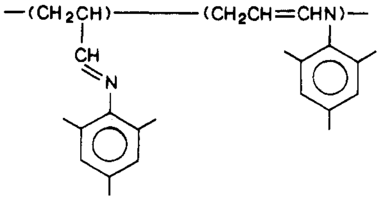
Figure 2. IR spectra of poly-2 prepared with BuLi in toluene at 0 °C (a) and reduced poly-2 by $LiBH_4$ (b).

duced polymer. In the IR spectrum of reduced poly-2, the C=N band at 1657 cm^{-1} disappeared (Figure 2b), also indicating successful reduction.

The above results indicate that BuLi-initiated poly-2 is formed through 4,3-addition (vinyl) polymerization and has the indicated structure



Next, we studied the structure of poly-2, prepared using BF_3OEt_2 (Figure 3a). In this NMR spectrum, a broadened but distinguishable signal around 7.5 ppm is assigned to an imine proton. However, the intensity for the signal is lower and corresponds to only 0.54 proton. On the other hand, a new broad signal was observed at 5.6 ppm, whose intensity corresponded to 0.41 proton. The latter signal may be ascribed to a vinyl proton. The IR spectrum of the polymer showed a strong C=N band, similar to BuLi-initiated poly-2, at 1651 cm^{-1}. These data indicate that the polymer contains at least two types of repeating units in the chain, which form through 4,3- and 4,1-additions.



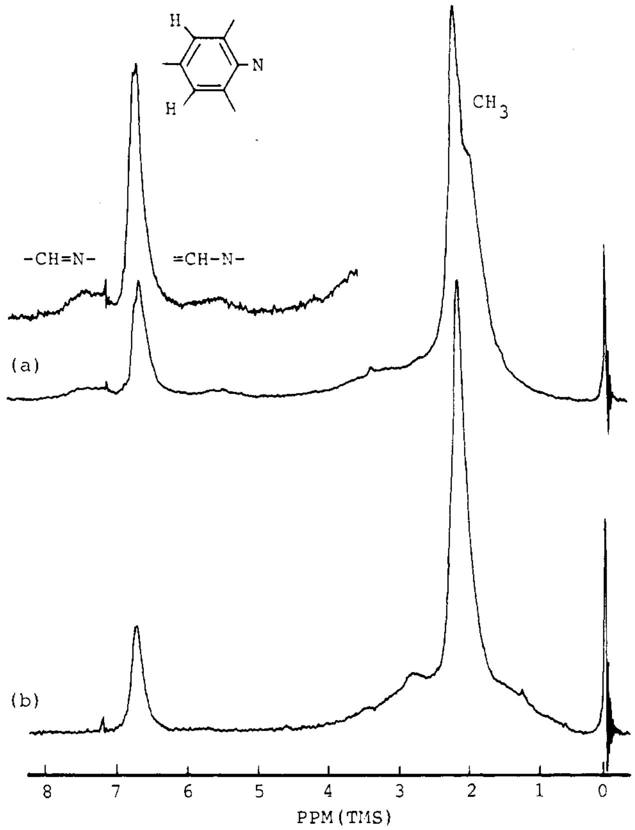
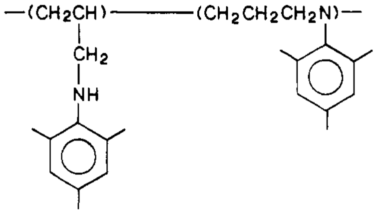


Figure 3. ^1H NMR spectra of poly-2 prepared with BF_3OEt_2 in dichloromethane at −78 °C (a) and reduced poly-2 by $LiBH_4$ (b).

Cationic poly-2 was also reduced by using $LiBH_4$. The ^1H NMR spectrum of the resulting polymer is illustrated in Figure 3b. Interestingly, even though poly-2 contained both 4,3- and 4,1-units, the polymer was almost completely reduced, as seen in the lower magnetic field part of the spectrum. Reduction of enamine as well as imine links occurs. The IR spectrum also showed the disappearance of C=N band upon reduction. This indicates the following type of polymer:



Structure of Poly-1. In the ^1H NMR spectra of poly-1, a broad aromatic signal prevents us from distinguishing the imine proton signal. ^{13}C NMR spectra of poly-1 showed the C=N carbon signal at 169$\sim$170 ppm, whose intensity was very low compared with the signal in the poly-2 spectrum, indicating a high proportion of 4,1-addition. In the IR spectrum of poly-1, obtained with BuLi at −78 °C, the C=N stretching band was observed at 1644 cm^{-1}; the intensity of this peak was two-thirds of the intensity of the aromatic band (1600 cm^{-1}), also indicating less C=N groups (compare to poly-2) (Figure 4a). There were no peaks of substantial intensity aroung 900 cm^{-1}, where CH_2= in a vinyl group would show the wagging frequency, excluding significant 2,1-addition (C=N opening). The C=N band disappeared upon $LiBH_4$ reduction (Figure 4b), confirming the assignment. The spectroscopic data for poly-1, prepared with BuLi at −78 °C, show that poly-1 contains both 4,1- and 4,3-structural units. Poly-1, prepared with BuLi at 0 °C, showed an even

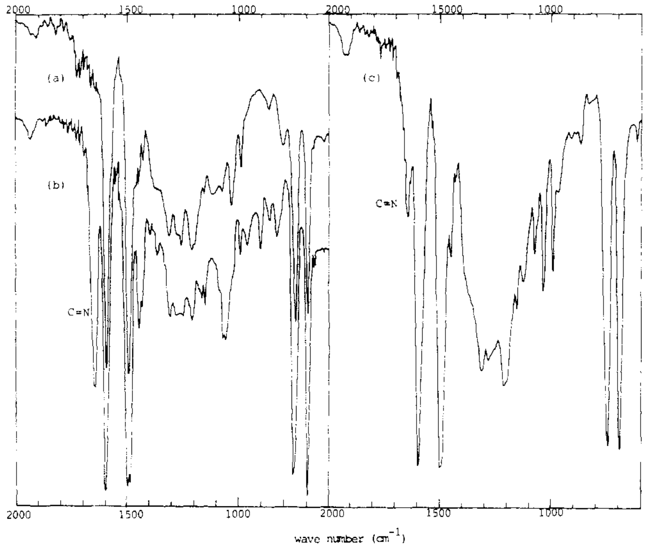


Figure 4. IR spectra of poly-1 prepared with BuLi in toluene at −78 °C (a) and reduced poly-1 (b) and poly-1 prepared with BuLi in toluene at 0 °C (c).

weaker C=N band at 1644 cm^{-1} (Figure 4c).

Cationically prepared poly-1 also exhibited a weak C=N band, whose infrared absorption wavenumber was a little higher (1651 cm^{-1}). The content of 4,1-unit in these last polymers is higher than in poly-1 prepared with BuLi at −78 °C.

Attempted Polymerizations of *N*-Methoxy-1-aza-1,3-butadiene (3) and *N*-(Dimethylamino)-3-methyl-1-aza-1,3-butadiene (4). Anionic or radical initiators, tested from −78 to 60 °C, caused no polymerization of these monomers.

Treatment of 3 with acids in catalytic amounts gave only salt formation.[3] Mixed in equivalent amounts with trifluoroacetic or sulfuric acid, 3 gave oils after neutralization. The stronger triflic acid led, on similar treatment, to a yellow powder (MW < 1000). Its elemental analysis was not in agreement with that of an oligomer or polymer, and it was not further investigated.

Monomer 4 with acids gave, after salt formation, even less evidence of cationic oligomerization or polymerization. Although small molecules in trace amounts were noted, there was not enough material to investigate.

Discussion

A summary of the polymerizability of the 1-aza-1,3-butadiene monomers studied is presented in Table III.

N-Aryl-1-aza-1,3-dienes could be polymerized best by anionic initiators. This is attributable to stabilization of the propagating anion by the aromatic substituent. Monomer 2 polymerized in both toluene and THF, in contrast to 1 which polymerized in toluene but not in THF. Steric hindrance between the trimethylphenyl group and C=N group in monomer 2 probably suppresses addition of BuLi to C=N bond and results in the successful polymerization of 2. Because BuLi is more nucleophilic in THF than in toluene, inability of 1 to polymerize in THF by BuLi can be explained by the more favored reaction of BuLi at the C=N bond.

BuLi-initiated polymerization of 2 proceeds preferentially by 4,3-addition, while poly-1 formed under the same conditions had 4,1-units as well as 4,3-units. Steric hindrance of the trimethylphenyl group in 2 prevents the active site on nitrogen from adding the next monomer, which results in preference for 4,3-addition.

For monomer 2, cationic polymerization proceeded by both 4,1- and 4,3-addition, which means that stabilization of the cation at nitrogen by the aromatic substituent overcomes the above-mentioned steric hindrance. Greater stabilization for the cation is due to the electron-donating character of the 2,4,6-trimethylphenyl group.

Table III
Summary of Polymerization of Various 1-Aza-1,3-butadienes[a]

initiator	monomer 1	2	3	4
anionic				
BuLi	+	+	–	–
t-BuMgCl	+	+	–	
cationic				
BF_3OEt_2	+	+		
CF_3COOH	+	+	–	–
CF_3SO_3H			olig.[b]	–
radical				
AIBN	–	–	–	–

[a] + = polymerization occurs, – = no polymerization. [b] Oligomer.

Under the appropriate conditions, 1 and 2 polymerize in both 4,3- and 4,1-fashion. 4,1-Addition points to polymerizability of a C=N group, as already seen in its cyclotrimerization.

The strong electron-donor substituents, methoxy and dimethylamino, prevented polymerization. Anionic polymerization was suppressed, possibly due to electron repulsion between the electron pairs of the substituent and the putative anionic propagating species. On the cationic side, the strong donor substituents OCH_3 and $N(CH_3)_2$ rendered the system too basic/nucleophilic. A similar situation is found for *p*-(dimethylamino)styrene whose powerful donor substituent allows only oligomer formation under cationic initiation.[9]

Experimental Section

Methods. ^{1}H NMR spectra were taken on a Varian EM 360 L and a Bruker WM 250 spectrometers at 60 and 250 MHz, respectively. ^{13}C NMR spectra were obtained from the latter instrument at 62.9 MHz. All coupling constants are given in hertz. In every measurement, tetramethylsilane was used as an internal reference. IR spectra were recorded on a Perkin-Elmer 983 spectrometer. Average molecular weights were measured on Du Pont ZORBAX 60S, PSM 300S, and IBM GPC/SEC PORE type A columns calibrated with polystyrene standards using chloroform as eluent and a Spectra Physics detector at 254 nm. Elemental analyses were performed by MicAnal, Tucson, AZ. Thermal measurement was performed on a Kofler Heizbank heating plate.

Source of Materials. Aldehydes and amines were purified by distillation. BuLi and *tert*-butylmagnesium chloride were purchased from Aldrich as hexane and ether solutions, respectively. Acidic initiators, BF_3OEt_2, CF_3COOH, and CF_3SO_4H, were distilled and diluted with dichloromethane. Toluene was refluxed over sodium and distilled. Dichloromethane was successively washed with sulfuric acid, water, $NaCO_3$ (aq), and water, dried over $CaCl_2$, refluxed over CaH_2, and distilled.

Monomer Syntheses. Precursors of *N*-arylazadienes were synthesized from 5-norbornene-2-carboxyaldehyde (5) and corresponding amines. The products were mixtures of endo and exo compounds.

***N*-Phenyl-5-norbornen-2-ylmethylidenamine (6).** A mixture of 5 (91 g, 0.745 mol) and aniline (70.5 g, 0.765 mol) in 150 mL of benzene was refluxed for 5 h to remove water azeotropically. Distillation of the product under reduced pressure gave 147 g (91.2%) of 6. BP: 99.6–100.2 °C/0.4 mmHg. IR (neat): 3058, 2968, 2867, 1644 (C=N), 1594 (aromatic), 1486 (aromatic), 762, 718, 696 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.76 (d, J = 5.5) and 7.39 (d, J = 6.0), CH=N; 7.22 (m), 7.07 (m), 6.96 (m), aromatic H; 6.16 (d-d, J = 5.7, 3.1), 5.95 (d-d, J = 5.7, 2.6), 6.10 (d-d, J = 1.5, 1.6), HC=CH; 1.2∼1.5 (m, 3 H), 1.84–2.03 (m, 1 H), 2.36 (quint, J = 4.4, 0.4 H), 2.87∼3.07 (m, 2.6 H), norbornenyl residue. ^{13}C NMR ($CDCl_3$): δ 169.71 (d), 168.85 (d), CH=N, 152.35 (s), 152.27 (s), substituted phenyl C; 137.89 (d), 137.71 (d), 135.75 (d), 132.12 (d), CH=CH; 128.78 (d), 125.08 (d), 120.45 (d), aromatic CH; 49.59 (t), 45.61 (t), CH_2 (bridge head); 30.32 (t), 29.82 (t), CH_2; 46.70 (d), 46.37 (d), 45.69 (d), 44.99 (d), 42.73 (d), 42.08 (d), CH (norbornenyl residue). Anal. Calcd for $C_{14}H_{15}N$: C, 85.24; H, 7.66; N, 7.10. Found: C, 85.53; H, 7.70; N, 7.13.

***N*-(2,4,6-Trimethylphenyl)-5-norbornen-2-ylmethylidenamine (7).** Yield: 100%. Bp: 90~93 °C/0.1 mmHg. IR (neat): 3135, 3058, 2968, 2864, 1659~1610 (br, C=N, C=C), 1479 (aromatic), 853, 718 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.57 (d, J = 4.9), 7.19 (d, J = 5.3); CH=N, 6.76 (s), 6.73 (s), aromatic CH; 6.12 (m), 5.93 (m), CH=CH; 2.20 (s), 2.18 (s), p-CH_3; 2.02 (s), 1.99 (s), OCH_3; 2.8~3.1 (m), 2.40 (m), 1.9~2.1 (m), 1.3~1.5 (m), norbornenyl residue. ^{13}C NMR ($CDCl_3$): δ 171.04 (d), 170.42 (d), 170.42 (d), CH=; 148.34 (s), =NC (aromatic); 137.38 (d), 137.12 (d), 135.34 (d), 131.79 (d), CH=CH; 131.62 (s), 125.93 (s), CH_3C (aromatic); 128.10 (d), 128.03 (d), CH (aromatic); 49.18 (t), 45.21 (t), CH_2 (bridge head); 46.09 (d) 45.77 (d), 45.01 (d), 44.51 (d), 42.24 (d), 41.65 (d), CH (norbornenyl residue); 29.51 (t), 29.04 (t), CH_2; 20.14 (q), p-CH_3; 17.66 (q), OCH_3. Anal. Calcd for $C_{17}H_{21}N$: C 85.31; H, 8.84; N, 5.85. Found: C, 85.16; H, 8.84; N, 6.06.

***N*-Aryl-1-aza-1,3-butadiene.** Monomers **1** and **2** were synthesized by thermolysis of their precusors. Thermolysis was carried out with a vertical quartz tube (2 × 40 cm) packed with quartz fragments (packing height, 25~30 cm), heated with an electric jacket and equipped with an addition funnel and a trap. The whole apparatus was evacuated at 0.05 mmHg before use. Precursors were introduced dropwise into the hot tube at the top. The pressure rose to 0.3–1.0 mmHg during thermolysis. Thermolysate was collected in the trap cooled with dry ice/methanol at the bottom and extracted with benzene. The benzene extract was washed with aqeous $NaCO_3$, dried over NaOH, filtered, concentrated, and distilled in vacuo by using Kugelrohr apparatus. The product was then distilled from CaH_2.

***N*-Phenyl-1-aza-1,3-butadiene (1).** The precursor **6**, 17.5 g (88 mol), was thermolyzed at 580 °C under vacuum (0.1~1.0 mmHg) during 20 min. An amber thermolysate obtained was worked up as described. Distillation gave a yellow liquid. Bp: 37~38 °C/0.2 mmHg. Yield: 8.8 g (76%). IR (neat): 3058, 3025, 2863, 1866 (C=C, overtone), 1632 and 1598 (C=N, C=C), 1486 (C=C), 996, 939, 765, 695 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.94 (d, J = 8.9), CH=N; 7.32 (m), 7.20, 7.12 (m), phenyl; 6.62 (ddd, J = 8.9, 10.1, 17.4), NCH=; 5.72 (d, J = 10.1), 5.68 (d, J = 17.4), CH_2=. ^{13}C NMR ($CDCl_3$): δ 161.94 (s), CH=N; 151.57 (s), substituted phenyl C; 137.51 (d), NCH=; 129.07 (d), 126.12 (d), 120.75 (d), phenyl; 128.75 (t), CH_2=. Anal. Calcd for C_9H_9N: C, 82.41; H, 6.92; N, 10.68. Found: C, 82.40; H, 6.83 N, 10.54.

***N*-(2,4,6-Trimethylphenyl)-1-aza-1,3-butadiene (2).** The precursor **7**, 19.8 g (82.6 mmol), was thermolyzed at 595 °C under vacuum (0.1~1.0 mmHg) during 10 min. Bp 58–59 °C/0.05 mmHg. Yield: 12.5 g (87%). The product was an isomeric mixture of syn and anti isomers. The ratio was 1:7 from ^1H NMR intensities for two imine protons at 8.09 and 7.72 ppm. The major component is believed to be the anti isomer, though not confirmed. IR (neat): 3008, 2915, 2958, 1884 (C=C, overtone), 1638 and 1607 (C=N, C=C), 1479 (C=C), 1210, 998, 938, 853 cm^{-1}. ^1H NMR ($CDCl_3$): δ *8.09 (* for minor isomer) (d, J = 8.8), 7.92 (d, J = 8.8), CH=N; 6.80 (s), aromatic; 6.71 (m), =CHN; 5.82 (d, J = 10.3), 5.70 (d, J = 17.4), CH_2=; 2.22 (s), p-CH_3; 2.06 (s), OCH_3. ^{13}C NMR ($CDCl_3$): δ 164.60 (s), CH=N; 148.28 (s); NC (aromatic); 139.96 (s), 132.66 (s), CH_3C (aromatic); 137.14 (d), =CH; 128.57 (s), 128.44 (s), HC (aromatic); 126.37 (t), CH_2=; 20.44 (q), 17.89 (q), 17.23 (q), CH_3 (minor components were not shown). Anal. Calcd for $C_{12}H_{15}N$: C, 83.19; H, 8.73; N, 8.08. Found: C, 82.97; H, 8.75; N, 8.21.

***N*-Methoxy-1-aza-1,3-butadiene (3).** The monomer **3** was synthesized by condensing acrolein and N-methoxyamine as described in the literature.[7] Yield: 68%. Bp: 72–74 °C [lit. bp 76.5–75.5 °C]. The product was an isomeric mixture. IR (neat): 3094, 2940, 2902, 2820, 1625 (C=N), 1584 (C=C), 1464, 1418, 1057 (CO), 996, 939 (NO), 903 cm^{-1} (CH_2=). ^1H NMR ($CDCl_3$): δ 7.69 (d, J = 10.0, 0.7 H), CH=N (anti isomer); 6.85–7.00 (m, 0.6 H), CH=N (syn isomer), and NCH= (syn isomer); 6.32–6.47 (m, 0.7 H), NCH= (anti isomer); 5.44–5.57 (m, 2 H), CH_2=; 3.85, 3.88 (two s, 3H), OCH_3. ^{13}C NMR ($CDCl_3$): δ 150.30 (d), 167.74 (d), CH=N; 130.99 (d), 125.51 (d), NCH=; 124.84 (t), 123.46 (t), CH_2=; 61.90 (q), 61.69 (q), OCH_3. Anal. Calcd for C_4H_7NO: C, 56.45; H, 8.29; N, 16.46. Found: C, 56.14; H, 8.47; N, 16.37.

***N*-(Dimethylamino)-3-methyl-1-aza-1,3-butadiene (4).** Condensation of methacrolein and N,N-dimethylhydrazine gave **4**. Yield: 70%. Bp: 41.5–42 °C/15 mmHg [lit.[8] bp 56 °C/29 mmHg]. IR (neat): 3081, 2954, 2921, 2857, 2785, 1618 (C=N), 1563 1468, 1445, 1264, 1040 (CN), 894 cm^{-1} (CH_2=). ^1H NMR ($CDCl_3$): δ 7.00 (s), CH=N; 5.03 (br s), CH_2; 2.85 (s), $N(CH_3)_2$; 1.87 (s), CH_3. ^{13}C NMR ($CDCl_3$): δ 142.08 (s), $C(CH_3)$; 135.55 (d), CH=N; 114.23 (t), CH_2=; 41.92 (q), $N(CH_3)_2$; 17.12 (q), CH_3. Anal. Calcd for $C_6H_{12}N_2$: C, 64.24; H, 10.78; N, 24.97. Found: C, 64.15; N, 10.87; N, 26.89.

Polymerization. Polymerization of **1** and **2** was carried out in a Y-shaped tube equipped with a vacuum valve and filled with nitrogen. Monomer and initiator solutions in each side arm of the tube were maintained at the required temperature and then mixed to initiate the reaction. After a certain reaction time, the reaction mixture was poured into a selected precipitant. Polymer formed was collected by filtration, washed with the precipitant solvent, and dried in vacuo. The attempted polymerizations of **3** and **4** were carried out in serum capped tubes filled with nitrogen. A typical reaction procedure giving an oligomeric product is described below.

To a stirred mixture of trifluoromethanesulfonic acid (10 mmol) and dichloromethane (5 mL) was added monomer **3** (10 mmol) at 0 °C. After 1 day at room temperature, the mixture containing insoluble material was neutralized with aqueous Na_2CO_3, extracted with dichloromethane, dried over $MgSO_4$, and concentrated. The resulting orange syrup was washed with hexane thoroughly to give yellow powder, which was then filtered and dried in vacuo. Yield: 51%.

Reduction of Polymers by Lithium Borohydride. Poly-**1** and poly-**2** were reacted with $LiBH_4$ in refluxing THF under nitrogen. Typical example for poly-**2** was as follows.

Poly-**2**, prepared with BuLi in toluene at 0 °C, 91.3 mg, was dissolved in 5 mL of THF. Two milliliters of $LiBH_4$–THF solution (2.0 M) was added to the solution. The mixture was refluxed for 3 days, quenched with water, and extracted with chloroform. After drying over $MgSO_4$, the extract was concentrated and poured into 100 mL of methanol. A white precipitate formed and was collected by filtration and dried in vacuo. Yield: 57.3 mg. An elution time in SEC chromatography (15.55 min) agreed well with that of the unreduced original polymer (15.47 min).

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Registry No. **1**, 41819-47-0; **2**, 108347-15-5; **3**, 52302-97-3; **4**, 16713-45-4; **5**, 5453-80-5; **6**, 22442-31-5; **7**, 108347-16-6; poly-**1**, 108347-17-7; poly-**2**, 108347-18-8; $C_6H_5NH_2$, 62-53-3; $(CH_3)_2NNH_2$, 57-14-7; $H_2C{=}C(CH_3)CHO$, 78-85-3.

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