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Synthesis and Polymerization Studies of New Azaethylene Monomers Carrying Electron-Acceptor Groups on Nitrogen

Jin-Bong Kim, Anne Buyle Padias, and H. K. Hall, Jr.*

C. S. Marvel Laboratories, Chemistry Department, University of Arizona, Tucson, Arizona 85721. *Received March 6, 1989; Revised Manuscript Received May 18, 1989*

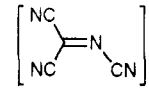
ABSTRACT: To explore the polymerizability of C=N monomers, the following compounds were synthesized: 2-phenylazaethylenecarbonitrile (benzylidenecyanamide; **1**), 2-*tert*-butylazaethylenecarbonitrile (pivalidenecyanamide; **2**), methyl 2-phenylazaethylenyl sulfone (*N*-(methylsulfonyl)benzylideneamine; **3**), ethyl 2-phenylazaethylenecarboxylate (*N*-carbethoxybenzylideneamine; **4**), and ethyl 2-*tert*-butylazaethylenecarboxylate (*N*-carbethoxypivalideneamine; **5**). Their electrophilic character was appraised using hydrolysis rates and NMR data. Monomer **1** homopolymerized in high yield under both anionic and free-radical conditions to yield a low molecular weight polymer (DP = 8). Monomer **2** polymerized poorly anionically and free radically. Monomer **4** oligomerized in low yield with weak bases. Compounds **3** and **5** did not polymerize. Low polymerizability of these compounds is ascribed to the required bulky substituent on carbon, and only the most electrophilic imine with a small cyano substituent on nitrogen and a phenyl substituent on carbon is able to oligomerize effectively.

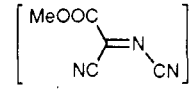
Introduction

Polymerizations involving C=C bonds are widely known. The same can be said of C=O bonds. In contrast, polymerizations involving C=N bonds are conspicuous by their rarity. With acid or base catalysis, common azaethylenes (imines) are known to cyclotrimerize, which, in analogy to the behavior of aldehydes, implies a tendency to polymerize. Moreover, azaethylenes with only one substituent on nitrogen prepared by flash vacuum pyrolysis are highly unstable and spontaneously polymerize.[1-4] Our studies of substituted 1- and 2-aza-1,3-butadienes showed that their C=N groups could indeed be polymerized. The best results were obtained for 1-phenyl-1-aza-1,3-butadiene and *N*-carbethoxy-3-methyl-1-aza-1,3-butadiene under anionic conditions,[5-7] but free radical reactions were also possible.

As to azaethylenes, we have already synthesized two imines with three electron-accepting substituents, tricyanoazaethylene and methyl 1,2-dicyanoazaethylene-2-carboxylate. These are so reactive that they can only be obtained in solution.[8,9] Attempted isolation gives oligomers. Mixing these monomers in solution with an electron-rich olefin such as *p*-methoxystyrene leads spontaneously to alternating copolymers.

In order to obtain azaethylene monomers, which can be isolated and purified and whose polymerization behavior can then be studied under controlled conditions, we have now synthesized electrophilic imines with one electron-accepting group on nitrogen in order to confer anionic





polymerizability and one substituent on carbon to provide thermal stability. The polymerization behavior of these imines was studied, mainly with anionic initiators.

Results

Monomer Synthesis. Because it is known that the unsubstituted CH_2=NX compounds are too reactive,[3] we selected the following electron-deficient imines with one β-substituent for study.

The easy tautomerization of electron-deficient imines with α-hydrogen-bearing alkyl groups to enamines[10] prevents use of methyl, ethyl, etc., alkyl groups and restricts us to aromatic and tertiary alkyl substituents.

Of our selected monomers, only **1** and **3** have been previously described in the literature. 2-Phenylazaethyl-

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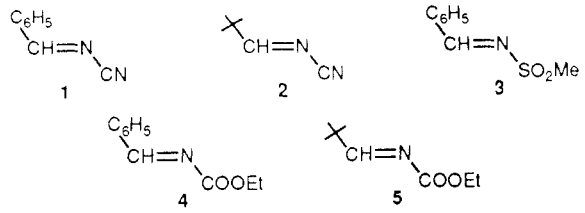


enecarbonitrile (benzylidenecyanamide; **1**) has been prepared by the reaction of the *N*-*tert*-butylimines with cyanamide in trifluoroacetic acid[11] or by pyrolysis of a 1,2,3,4-thiatriazole derivative.[12] Methyl 2-phenylazaethylenyl sulfone (*N*-(methylsulfonyl)benzylideneamine; **3**) has been synthesized by reaction of *N*-hydroxybenzylideneamine with methanesulfonyl chloride, followed by rearrangement.[13]

In this work, the *N*-cyanoimines **1** and **2** were synthesized from the reaction of the corresponding aldehydes with the appropriate bis-silylated amides in the presence of a catalytic amount of titanium tetrachloride (2–4 mol % relative to aldehyde).

$$\mathrm{RCHO + Me_3SiN{=}C{=}NSiMe_3 \xrightarrow[70\ ^\circ C]{\text{cat. } TiCl_4} RCH{=}NCN + (Me_3Si)_2O}$$

$$\mathrm{R = C_6H_5,\ \textit{t}\text{-Bu}}$$

$$\mathrm{C_6H_5CHO + (Me_3Si)_2NSO_2Me \xrightarrow[100\ ^\circ C]{\text{cat. } TiCl_4} C_6H_5CH{=}NSO_2Me + (Me_3Si)_2O}$$

The conversion of a carbonyl functionality to *N*-cyanoimines with bis(trimethylsilyl)carbodiimide has been described for ketones and *p*-quinones, using an equivalent amount of titanium tetrachloride.[14] We adapted it to aldehydes by using only a catalytic amount of $TiCl_4$. Addition of more $TiCl_4$ accelerated the reaction, but poor yields and complex side reactions occurred, making the purification of these imines very difficult. For *N*-(methylsulfonyl)benzylideneamine (**3**), a similar but novel reaction was accomplished using *N*-(methylsulfonyl)bis(trimethylsilyl)amine and a catalytic amount of $TiCl_4$.

The *N*-carbethoxyimines **4** and **5** were prepared from the corresponding aldehyde and ethyl carbamate, using an equivalent amount of $TiCl_4$.

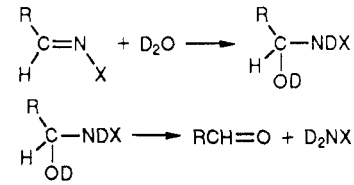
$$\mathrm{2RCHO + 2H_2NCOOEt + TiCl_4 \xrightarrow[\text{benzene}]{4Et_3N} 2RCH{=}NCOOEt + 4Et_3N{\cdot}HCl + TiO_2}$$

$$\mathrm{R = C_6H_5,\ \textit{t}\text{-Bu}}$$

This method is analogous to an enamine synthesis described in the literature.[15] Titanium tetrachloride, here used in equivalent amount, acts as a water scavenger and also activates the carbonyl function. The added base traps the hydrogen chloride. Ethyl carbamate was used instead of the methyl derivative for solubility reasons.

Properties of Monomers. The physical properties of the monomers **1–5** are summarized in Table I. They were relatively stable at room temperature in the absence of air but were sensitive to moisture.

The hydrolytic stability of these imines was evaluated by investigating their reaction with D_2O. Two sequential reactions can occur: hydration (eq 1) and/or hydrolysis (eq 2). The reactions of **1–5** with D_2O were followed by NMR. Imines **1–3** underwent complete hydrolysis: **2** in 1 h, **1** in 1 day, while **3** reacted much more slowly (15 days). Monomer **4** led to 60% hydration and 40% hydrolysis in 2 h, while **5** underwent almost total hydration in 5 days.



(1)

(2)

Table I
Properties of Electron-Deficient Azaethylene Monomers[a]

monomer	mp, °C	IR (C=N), cm^{-1}	NMR (HC=N), ppm ^1H	NMR (HC=N), ppm ^{13}C
PhCH=NCN (**1**)	71	1607	9.00	182.5
t-BuCH=NCN (**2**)	26	1623	8.57	198.6
$PhCH{=}NSO_2Me$ (**3**)	92	1604	9.05	171.5
PhCH=NCOOEt (**4**)	liq	1630	8.93	170.6
t-BuCH=NCOOEt (**5**)	liq	1657	8.15	180.8

[a] Elemental analyses of **2–5** are within 0.3% of the calculated values for C, H, and N.

The NMR spectra confirmed the electrophilic character of these monomers. The chemical shifts of the –HC=N– proton and carbon are at a much lower field than for ordinary imines (^1H, 6.5–8.0 ppm; ^{13}C for aliphatic imine, 168–175 ppm; ^{13}C for aromatic imine, 157–163 ppm). As can be seen in Table I, the proton shifts for imines **1–5** are between 8.15 and 9.05 ppm, and the ^{13}C shifts vary from 170 to 198 ppm. This is an identification of the extreme electrophilic character of these imines.

According to these properties of the monomers, their relative electrophilic character is as follows:

^1H NMR	3 > 1 > 4 > 2 > 5
^{13}C NMR	2 > 1 > 5 > 3 > 4
reactivity in hydrolysis	2 > 1 > 3 > 4 > 5

Probably the reactivities in hydrolysis are the best indicator of their expected reactivities in anionic polymerization, as hydrolysis involves nucleophilic attack of water on the electrophilic C=N bond.

Homopolymerizations. Azaethylene monomers **1–5** were treated with initiators of free-radical and anionic polymerization. The results are summarized in Table II. All polymerizations were very slow and were continued until a viscosity buildup could be visually observed, usually 2–3 days.

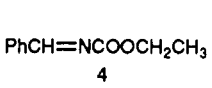
Anionic initiators gave the best results. Under these conditions, 2-phenylazaethylenecarbonitrile (**1**) was the best monomer. High yields were obtained after 2 days with a variety of initiators, although the oligomer had a very low molecular weight (DP = 8). For monomer **2**, rather low yields of oligomers were first obtained (see Table II), but further polymerization occurred during workup. Also, monomer **2** without initiator oligomerized after 5 days when exposed to air. Sulfone monomer **3** leads to only a low yield of polymer in the presence of *n*-butyllithium. With *n*-BuLi, monomer **4** gives only a very low yield of polymer; with less nucleophilic initiators, such as potassium *tert*-butoxide, moderate yields of low molecular weight polymer are formed. Curiously, if this monomer is mixed with *n*-butyllithium and exposed

Table II
Homopolymerizations

monomer	g	initiator (mol %)	solvent (mL)	temp, °C	time, day	conv,[b] %	MW,[c] (SEC)	softening points,[e] °C
1	0.5	AIBN (2)	neat	75	3	70	1100	170–235
	0.4	DTBP (2)[a]	Tol (1)	100	3	51	950	155–245
	0.5	KCN (1.5)	DMF (2)	0	2	88	1050	174–244
	0.4	BuLi (4)	Tol (2)	0	2	76	800	155–245
	0.4	BuLi (4)	THF (2)	0	2	82	780	162–214
2	0.36	AIBN (2)	neat	70	3	17	800	>250
	0.30	BuLi (2)	Tol (1.5)	0	2	4	700	>250
	0.31	KCN (2)	DMF (1.5)	0	2	17	750	>250
	0.20	TEA (4)	neat	28	1.5	12		>250
3	0.5	AIBN (2)	neat	95	3	trace		
	0.5	BuLi (3)	THF (2)	0	2	6	660	140–210
	0.5	KCN (3)	DMF (2)	0	2	trace		
4	0.2	AIBN (3)	acetone (0.2)	70	3	trace		
	0.5	BuLi (3)	Tol (2)	0	2	trace		
	0.5	BuLi (3)	THF (2)	0	2	1		
	0.5	BuLi (3)	THF (2)	−50	2	3	620	150
	0.5	KCN (3)	DMF (2)	0	2	16		
	0.5	*t*-BuOK (3)	THF (0.6)	0	2	18	700	
	0.5	BuLi (3)	THF (2)	28	2	>90[d]	600	35
5	0.46	AIBN (3)	neat	70	3	0		
	0.46	BuLi (3)	THF (2)	0	2	trace		
	0.46	BuLi (3)	Tol (2)	0	2	0		
	0.46	KCN (3)	DMF (2)	0	2	trace		
	0.46	*t*-BuOK (3)	THF (0.3)	0	2	trace		

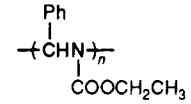
[a] DTBP = 2,6-di-*tert*-butylpyridine. [b] Polymers precipitated in hexane. [c] Molecular weight of soluble fraction in $CHCl_3$. [d] Exposed to air, semirigid sticky material soluble in common solvents; conversion was checked by NMR. [e] Softening points measured on a Kofler Heizbank; two transformations could be observed in most cases.

Table III
NMR Data for *N*-Carbethoxy Monomers 4 and 5 and Reference Compounds

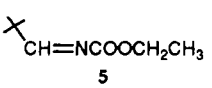


4

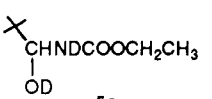
4a



poly(4)



5



5a

compd	CH_{imine}	CO	CH_2	CH_3	phenyl	*tert*-butyl
			^{1}H NMR Data			
4	8.93 (s)		4.33 (9)	1.38 (t)	7.42–7.92 (m)	
4a	6.25 (dd)		4.09 (9)	1.19 (t)		
poly(4)	6.22 (m)		4.02 (9)	1.18 (t)	7.26–7.42 (m)	
5	8.15 (s)		4.24 (9)	1.33 (t)		1.14 (s)
5a	4.88 (s)		4.11 (9)	1.24 (t)		0.95 (s)
			^{13}C NMR Data			
4	170.6 (d)	163.3 (s)	62.7 (t)	13.9 (9)	133.5 (s), 129.9 (d)	
4a	80.8 (d) 79.6 (d)	155.6 (s)	60.9 (t)	14.2 (9)	128.5 (d), 133.4 (s)	
poly(4)	79.0 (d)	155.2 (s)	59.9 (t)	14.5 (9)	128.0 (d), 126.1 (d) 127.4 (s)	
5	180.8 (d)	162.9 (s)	62.0 (t)	13.5 (9)		36.5 (s), 25.2 (9)
5a	81.2 (d)	156.4 (s)	60.5 (t)	14.0 (9)		34.6 (s), 24.5 (9)

to air, a very high yield of oligomer is obtained. Monomer **5** did not polymerize with any of the anionic initiators.

Under free-radical conditions, only the two *N*-cyano monomers **1** and **2** polymerized. For **1**, high yields of a low molecular weight polymer were obtained. This oligomer gradually became insoluble. For **2** a low yield was obtained. Again, spontaneous reactions took place during workup, and product continued to precipitate. Monomers **3**–**5** did not polymerize under free-radical conditions.

As noted above, all the products were obtained in low molecular weight, regardless of the type of initiator. The oligomers were not completely soluble in common solvents such as chloroform and ether. The insoluble fraction increased with time, most notably for poly(**1**) obtained with *n*-butyllithium as initiator. Poly(**1**) and poly(**3**) softened at about 160 °C, then slowly resolidified, possibly due to a crystallization, and softened again at about 230 °C. Decomposition started at 260 °C. Polymer **2** did not soften.

The structure of the *N*-cyano polymers from **1** and **2** is rather complicated. The NMR and IR spectra indicate that numerous side reactions occur, but the main reaction was at the C=N bond. Several peaks are observed for the C*H*–N proton in the NMR spectrum, between 5.2 and 6.2 ppm for poly(**2**). The oligomers are asymmetric (chiral) at the carbon centers, complicating the NMR spectra. Two peaks are observed in the IR spectrum for CN at 2200 cm^{-1}.

The spectra for the *N*-carbethoxy oligomers from **4** and **5** are very simple. Due to the extremely low molecular weight of poly(**4**), possible impurities, such as $C_6H_5CH(NHCOOEt)_2$, could not be easily removed. The

NMR data for these monomers, their hydration products, and poly(4) are summarized in Table III. The chemical shifts of the imine proton and the methylene of the ethyl ester function are almost identical. This indicates that the propagation does occur through reaction at the C=N bond as expected.

Discussion

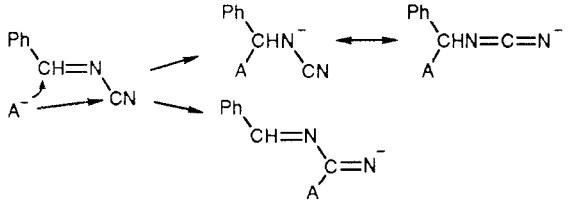
Electrophilic azaethylenes cannot be synthesized as easily as normal imines, because the electron-accepting substituent on nitrogen reduces the nucleophilic character of the nitrogen. Therefore, more reactive derivatives of the amine have to be used and/or a catalyst has to be used to activate the carbonyl function of the aldehyde. The use of $TiCl_4$ to activate the aldehyde C=O function and also to scavenge the water formed in the reaction is sufficient in the synthesis of the *N*-carbethoxy monomers **4** and **5**. In the case of the stronger acceptors, i.e., CN and SO_2Me, the silylated derivatives of the amines have to be used, and $TiCl_4$ again is added to activate the aldehyde carbonyl, this time only in catalyatic amount.

From our results, we can conclude that 2-phenylazaethylenecarbonitrile (**1**) oligomerizes in high yield, while 2-*tert*-butylazaethylenecarbonitrile (**2**) and ethyl 2-phenylazaethylenecarboxylate (**4**) oligomerize only in low yield.

The hydrolysis rates of the imines can be compared to the observed polymerization tendencies. The most electrophilic imines, **1** and **2**, undergo complete hydrolysis, while the less reactive, **4** and **5**, only undergo hydration.

Steric effects also help dictate the observed polymerizability sequence. The substituent on carbon was introduced to confer higher stability to CH_2=NX monomers. This aim was accomplished, because imines **1**–**5** could be isolated at room temperature. The phenyl and *tert*-butyl groups are rather bulky, but smaller alkyl groups could not be used because of tautomerization to enamines. Thus, only the most electrophilic and least hindered imines homopolymerize, namely with a CN substituent on nitrogen and a phenyl on carbon.

Weak bases are more effective initiators for the anionic oligomerization of **2** and **4** than the strong base BuLi. In fact, oligomerization of **4** initiated by BuLi is only observed after the mixture has been exposed to air and the strong base has been hydrolyzed. The monomer has two electrophilic centers, namely the C=N bond and the electrophilic substituent, -C≡N.



A possible explanation for the low reactivity of the hard base BuLi is that it preferentially attacks the electrophilic substituent instead of the imine C=N bond. The observed cross-linking, which occurs upon standing, could also be due to attack of a terminal nitrogen anion on the CN substituent of another chain.

In conclusion, we can state that the C=N bond in simple azaethylenes does participate in propagation reactions and oligomers with a DP of about 8 can be obtained. Radical and anionic initiators are most effective if the imine bond is electron-poor, which can be accomplished by a nitrile substituent on nitrogen. A phenyl on carbon allows such imines to be isolated and purified.

Experimental Section

General Methods. ^1H NMR and ^{13}C NMR spectra were taken on Varian EM360L and Bruker WM-250 NMR spectrometers at 60 and 250 MHz. IR spectra were recorded on a Perkin-Elmer 983 spectrometer. Number-average molecular weights were measured on Du Pont Zorbax PSM 60S and PSM 300S and IBM GPC/SEC Pore Type A columns, calibrated with polystyrene standards with chloroform as eluent, a Spectra Physics detector at 254 nm, and a Hewlett-Packard 3392A integrator. Elemental analyses were performed by Desert Analytics, Tucson, AZ. All melting points were obtained from a Thomas–Hoover capillary melting point apparatus and are uncorrected. Thermal measurements were done on a Kofler Heizbank.

Chemicals. Solvents for monomer syntheses and polymerizations were dried by general methods: tetrahydrofuran, benzene, and toluene were distilled from sodium hydride, and dimethylformamide was distilled from P_2O_5 and kept over a 3-Å molecular sieve.

Initiator 2,2′-azobis(isobutyronitrile) (AIBN), was purchased and purified by standard methods. *n*-Butyllithium (2.5 N) was used as obtained from Aldrich. Potassium cyanide was purified by recrystallization from ethanol–water and saturated in dimethylformamide. Potassium *tert*-butoxide was saturated in tetrahydrofuran. Triethylamine (TEA) was refluxed over CaH_2 and distilled.

N,*N*-Bis(trimethylsilyl)carbodiimide was prepared from the reaction of cyanamide with trimethylchlorosilane and triethylamine[16] in diethyl ether in 70% yield [bp 49 °C (15 mmHg)].

N,*N*-Bis(trimethylsilyl)methanesulfonamide was synthesized via a modified literature method.[17] Methanesulfonamide (19.0 g, 0.2 mol) in THF (400 mL) was stirred at room temperature with trimethylchlorosilane (54.3 g, 0.5 mol) and triethylamine (50.6 g, 0.5 mol). The silylation reaction reached about 1.5 substitution after overnight stirring. The reaction mixture was filtered to remove the precipitated triethylamine hydrochloride, and then additional trimethylchlorosilane (36.1 g, 0.2 mol) and sodium hydride (4.5 g, 0.15 mol) were added to the THF filtrate. The reaction mixture was stirred for an additional 1 day, and the precipitated salts were filtered off. After evaporation of solvent and removal of the salts by filtration, the liquid was distilled to give 76% yield of *N*,*N*-bis(trimethylsilyl)methanesulfonamide, which is highly sensitive to moisture and was easily hydrolyzed in air: bp 78 °C (1.5 mmHg); ^1H NMR δ 0.41 (s, 18 H), 2.91 (s, 3 H).

Monomers. Cyano- and sulfonylimines were synthesized from the corresponding aldehydes and silicone compounds [*N*,*N*-bis(trimethylsilyl)carbodiimide or *N*,*N*-bis(trimethylsilyl)-methanesulfonamide] with a catalytic amount of $TiCl_4$. These electron-deficient imines are very sensitive to moisture; therefore, all the procedures were carried out under anhydrous conditions.

2-Phenylazaethylenecarbonitrile (Benzylidenecyanamide) (1). Benzaldehyde (7.96 g, 0.075 mol) and *N*,*N*-bis(trimethylsilyl)carbodiimide (13.98 g, 0.075 mol) were placed in a tightly capped flask under nitrogen atmosphere and cooled to 0 °C. Titanium tetrachloride (0.36 g, 1.88 mmol) was introduced dropwise using a syringe while stirring well. After 1 h, the reaction mixture was heated to 70 °C. As the reaction was proceeding, phase separation occurred. After 7 h at 70 °C, the reaction mixture was cooled. The lower layer solidified and the upper layer, mostly hexamethyldisiloxane, was discarded. The lower layer was recrystallized in dry diethyl ether and sublimed at 72 °C (1 mmHg) to give 5.9 g of **1** (60% yield).

2-*tert*-Butylazaethylenecarbonitrile (Pivalidenecyanamide) (2). The synthesis procedure was almost identical with the procedure for imine **1**. A mixture of pivaldehyde (8.61 g, 0.1 mol), *N*,*N*-bis(trimethylsilyl)carbodiimide (16.8 g, 0.9 mol) and titanium tetrachloride (0.47 g, 2.5 mmol) was stirred at 70 °C for 18 h, and the final reaction mixture was fractionally distilled to give 6.7 g of **2** [bp 52 °C (5.5 mmHg), 68% yield].

Methyl 2-Phenylazaethylenyl Sulfone (*N*-(Methylsulfonyl)benzylideneamine) (3). Again, the same procedure was

used. A mixture of benzaldehyde (10.6 g, 0.1 mol), *N,N*-bis(trimethylsilyl)sulfonamide (22.5 g, 0.094 mol), and titanium tetrachloride (0.76 g, 4 mmol) was stirred at 100 °C for 24 h. The lower layer solidified in the refrigerator. It was recrystallized in diethyl ether and sublimed at 95 °C (1 mmHg). The obtained yield was 13.7 g of **3** (75% yield).

Ethyl 2-Phenylazaethylenecarboxylate (*N*-Carbethoxybenzylideneamine) (4). Benzaldehyde (21.2 g, 0.2 mol), urethane (17.8 g, 0.2 mol), triethylamine (40.5 g, 0.4 mol), and 300 mL of benzene were placed in a 2-L three-necked round-bottom flask, equipped with a mechanical stirrer and dropping funnel under dry nitrogen. The mixture was cooled to 0 °C, and then titanium tetrachloride (20.9 g, 0.11 mol) dissolved in 150 mL of benzene was introduced dropwise into the solution during 1.5 h. After the mixture was stirred for an additional 1 h at 0 °C, the reaction mixture was warmed to room temperature, and the reaction continued for 12 h. The resulting mixture was filtered, concentrated, and distilled off under vacuum. Fractional distillation gave 15 g of **4** [80–81 °C (0.2 mmHg), 42% yield].

Ethyl 2-Phenylazaethylenecarboxylate (*N*-Carbethoxypivalideneamine) (5). The procedure for **5** was identical with the procedure for **4**. To a mixture of pivaldehyde (21.53 g, 0.25 mol), urethane (22.27 g, 0.25 mol), triethylamine (50.6 g, 0.5 mol), and 300 mL of benzene was added dropwise 26.6 g (0.14 mol) of titanium tetrachloride in 100 mL of benzene during 1.5 h. After 12 h of stirring at room temperature, the precipitated salts were filtered off and the filtrate was concentrated and fractionally distilled at 42–43 °C (0.1 mmHg). The obtained yield was 12.9 g (33%).

Model Reaction for C=N Bond Reaction. The solutions of imines, prepared from 50 mg of imine and 0.3 mL of $CDCl_3$, were placed in NMR tubes. D_2O (0.1 mL) was added to each NMR tube, which were then capped and kept at room temperature with shaking. The spectra are checked at certain intervals.

Polymerizations. Polymerization reactions were carried out in dry nitrogen atmosphere using syringe techniques for introduction of the liquid reactants and the solvents. The reactions performed in NMR tubes were easily checked by NMR. In the case of monomer **4**, solvent casting polymerization on a glass plate was used to obtain higher conversions. The reagents were mixed at −78 °C, and the mixture was then warmed up to room temperature and spread on a glass plate in air. The polymerization occurred slowly as the solvent evaporated to yield a semirigid sticky polymer.

All of the polymers were purified by precipitating in nonsolvents and dried under vacuum.

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Registry No. **1**, 64704-20-7; **1** (homopolymer), 123812-23-7; **2**, 123812-21-5; **2** (homopolymer), 123812-24-8; **3**, 14674-34-1; **3** (homopolymer), 123812-25-9; **4**, 27593-62-0; **4** (homopolymer), 123812-26-0; **5**, 123812-22-6; benzaldehyde, 100-52-7; *N,N*-bis(trimethylsilyl)carbodiimide, 1000-70-0; pivaldehyde, 630-19-3; *N,N*-bis(trimethylsilyl)sulfonamide, 71877-45-7; urethane, 51-79-6.

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