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Synthesis and Polymerization of *N*-Carbethoxy-3-methyl-1-aza-1,3-butadiene

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ABSTRACT: An azabutadiene with a highly electron-withdrawing group, carbethoxy, at the N-position was synthesized, and its polymerizability toward various initiators was investigated. *N*-Carbethoxy-3-methyl-1-aza-1,3-butadiene (CEMAB) gave highly pure 4,1-addition polymer under anionic conditions and, with free radicals, gave polymers with mixed structures in low conversion. During the radical homopolymerization of CEMAB and copolymerization with electron-rich olefins, cycloaddition reactions involving carbon double bonds and imine linkage occurred to give inverse Diels–Alder type compounds. CEMAB is very sensitive to moisture and easily changed to a hydrate through addition of water to the imine double bond. The polymers were obtained as low-melting solids.

Introduction

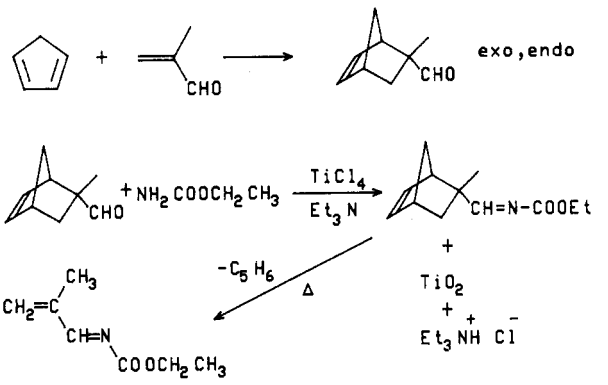
In previous publications, 1-aza-1,3-butadiene[1] and 2-aza-1,3-butadienes[2] carrying aryl substituents at the 1-position were examined as monomers for possible anionic polymerization through C=N bond opening. Though the participation of the C=N bond in the polymerization was higher than achieved in earlier literature,[3,4] these monomers did not undergo efficient C=N bond opening. Stabilization of the growing species at nitrogen by aryl was not quite sufficient to efficiently polymerize through C=N bond opening.

Pursuing this point of view, we have now introduced a more effective substituent for anionic polymerization, the carbethoxy group, at the N-position of the azabutadiene system. In this paper, we investigate the polymerizability of *N*-carbethoxy-3-methyl-1-aza-1,3-butadiene, CEMAB, under different polymerization modes and its reaction with electron-rich olefins.

Results

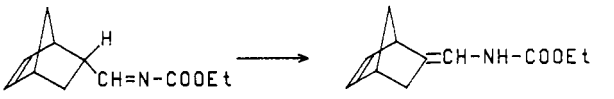
Synthesis. The monomer was synthesized by the route shown in Scheme I. Diels–Alder cycloaddition of methacrolein to cyclopentadiene proceeded readily in good yield. The resulting α-methylcarboxaldehyde condensed with ethyl carbamate in the presence of titanium tetrachloride in triethylamine under absolutely dry conditions. We preferred ethyl carbamate over methyl carbamate for its better solubility in the reaction mixture. All other attempts for preparing this norbornenyl imine by general methods,[5] such as azeotropic dehydration or acid, base, or organotin catalytic condensation, failed, owing to unusual instability of imines with an electron-withdrawing group on nitrogen toward moisture and other side reactions.

Scheme I



N-Carboethoxy-3-methyl-1-aza-1,3-butadiene (CEMAB)

Our first experiments, starting from acrolein, were unsuccessful because the intermediate imine underwent a tautomeric CH → NH shift to form the enamide:



This tautomerization places limitations on the types of C=N–A compounds, where A is an electron-accepting group, which can be synthesized.

The pyrolysis of the precursor was carried out in a quartz column at 580 °C with benzene as solvent and all the purification procedures were carried out under absolutely

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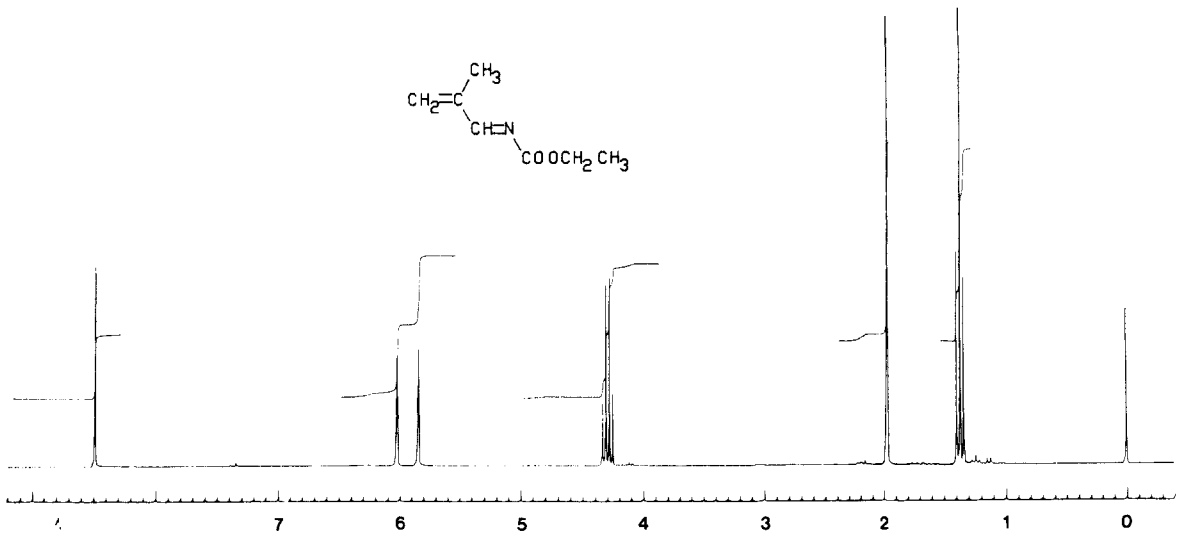


Figure 1. ^{1}H NMR spectrum of CEMAB, 250 MHz.

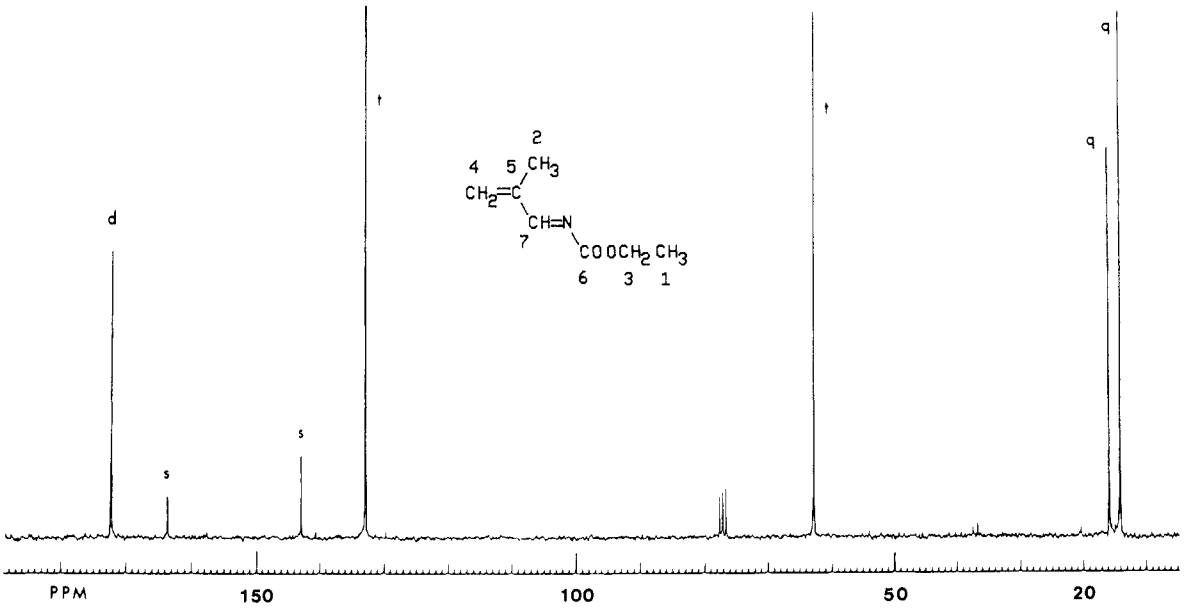


Figure 2. Decoupled ^{13}C NMR spectrum of CEMAB.

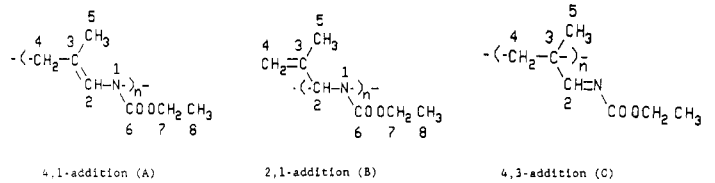
Table I
Polymerization of CEMAB under Various Conditions

sample no.[a]	solvent mL	initiator, nmol	temp, °C	time, h	conv, %	MW, SEC max peak	softening point, °C	polymerization mode
1	neat	AIBN, 0.025	80	48	25	1000	110	4,1; 2,1; 4,3-type addition structure mixture
2	toluene, 1.0	AIBN, 0.05	70	48	23	1400	135	
3	toluene, 1.0	DTBP,[b] 0.05	105	24	15	1300	130	
4	toluene, 1.0	TBPB,[b] 0.05	105	22	17	1300	135	
5	neat	TEA,[b] 0.036	25	24	70	1300	50	pure 4,1-type polymerization structure or
6	toluene, 2.0	TEA, 0.022	25	48	95	1250	90	abundant 4,1-addition structure
7	DMF, 2.0	KCN, 0.033	0	24	96	2000	55	
8	DMF, 2.0	KCN, 0.055	−50	48	8	1100		
9	DMF, 2.0	KCN, 0.006	0	120	45	2100	60	
10	DMF, 2.0	TEA, 0.07	−50	48	22	850	45	
11	toluene, 2.0	BuLi, 0.08	−78	24	4			
12	THF, 2.0	BuLi, 0.08	−78	24	5	800	43	
	comonomer							
13	styrene, 1.0	none	105	48				styrene homopolymer[c]
14	EVE,[b] 1.0	AIBN, 0.05	80	48				CMAB homopolymer[c]

[a] Amount of monomer used for each experiment was 0.5 g (3.54 mmol). [b] Abbreviations: EVE, ethyl vinyl ether; DTBP, di-*tert*-butyl peroxide; TBPB, *tert*-butyl peroxybenzoate; TEA, triethylamine. [c] Both accompanied by cyclic adducts.

dry conditions at mild temperature to give a 67% yield. The monomer was easily hydrated in the presence of water and dimerized at or above room temperature but was stable at −50 °C under dry atmosphere. All the spectra and chemical analyses were consistent with the expected structure of monomer (Figures 1 and 2).

Table II
NMR Analysis of Polymer Stucture[a]



4,1-addition (A) 2,1-addition (B) 4,3-addition (C)

	position						
	2	3	4	5	6	7	8
			^{1}H NMR Data				
structure A	5.80 (s)	none	3.95 (s)	1.57 (s)	none	4.14 (q)	1.25 (t)
structure B	5.45–6.05	none	4.65–5.15	1.67–1.78	none		
D_2O addition product	5.54 (s)	none	5.21, 4.94 (s)	1.78 (s)	none	4.13 (q)	1.25 (t)
structure C	8.42	none		0.90–1.07			
			^{13}C NMR Data				
structure A	124.9 (d)	129.8 (s)	61.2 (t)	14.2 (q)	154.9 (s)	61.1 (q)	14.1 (q)
structure B	77.2 (d)	139.9–140.5	111.7–112.2	19.5–19.8	155.5		
D_2O addition product	76.6 (d)	142.6 (s)	112.1 (t)	18.1 (q)	156.3 (s)	60.9 (t)	14.2 (q)
structure C	179.8	48.0, 47.2, 49.4	38.1, 35.5, 30.6	21.1			

[a] Data for structure A obtained from sample 7. Structure B from samples 5 and 6. Because the fraction of 4,3-structure (C) was low, the peaks could not be determined exactly; solvent, $CDCl_3$.

Table III
Structure Characterization of Polymer Samples

	% composition of structure[a]			typical IR, cm^{-1}		
sample	4,1-type	2,1-type	4,3-type	C=O (ν)	CH_2=< (γ, 2.1-type)[b]	–CH=< (γ, 4,1-type)[b]
no. 7	>93			1700	none	843
no. 5	75	16	1.7	1702	903	844
no. 6	49	24	18	1701	921	none
no. 2			31–45	1702	921	none
monomer				1721	882	none, C=N (γ, 789)

[a] Calculated from ^{1}H NMR integrations of 3-methyl protons. [b] Out-of-plane bonding absorptions showing typical carbon unsaturated structures were compared qualitatively.

Table IV
Thermal Reaction of CEMAB with Electron-Rich Olefins

olefin (0.15 mL)	CEMAB, mL	solvent[a] $CDCl_3$, mL	temp, °C	time, days	result[b]
CEMAB, neat	0.1	0.4	70	2	CEMAB dimer, 70%
p-ethoxystyrene	0.1	0.4	70	2	CEMAB dimer, CEMAB/*p*-ethoxystyrene adduct, and unreacted olefins
p-methoxystyrene	0.1	0.4	70	5	CEMAB dimer, 45%; CEMAB/*p*-methoxystyrene adduct, 55%
isobutyl vinyl ether	0.1	0.4	70	5	CEMAB dimer, 27%; CEMAB/isoBVE adduct 73%

[a] Reaction was carried out in a septum-sealed NMR tube. [b] Conversion and yield were measured by proton NMR.

Polymerization. Polymerization was carried out by radical and anionic initiators. The results are summarized in Table I. Anionic polymerization, especially when initiated by weak nucleophiles such as triethylamine or cyanide anion, gave moderate yield of polymers with rather low molecular weight (1200–2000 by size exclusion chromatography (SEC)). The monomer was polymerized by moisture after several days of standing in air at room temperature, but the resulting material was found to have a very low molecular weight (ca. 800 by SEC) with about 50% conversion. Though most radical initiators effectively polymerize CEMAB, the conversions were low and found to be restricted by competitive dimerization of the monomer. Attempts to copolymerize CEMAB with electron-rich olefins both with and without radical initiators were unsuccessful, giving only the cycloaddition products of CEMAB with olefins.

Polymer Structure. Three kinds of polymerization modes, such as the 4,1-type, 2,1-type (C=N bond opening), and 4,3-type (C=C bond opening), are possible in the polymerization of the azabutadiene system (Figure 3). The NMR spectra showed differences in polymer structure according to the polymerization conditions (Figure 4). The typical spectral data of each polymer structure were determined and are summarized in Table II. The model compound for the 2,1-addition type was prepared from

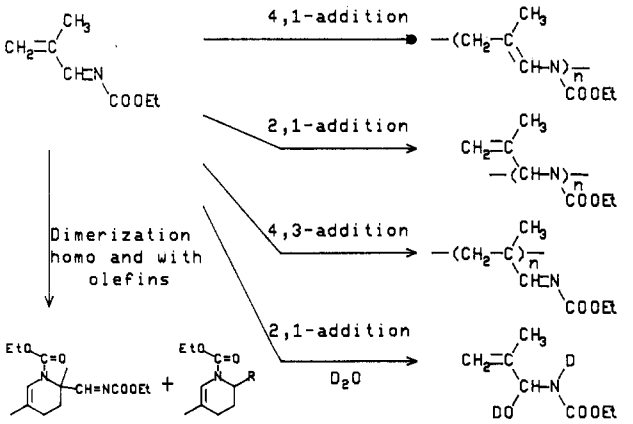
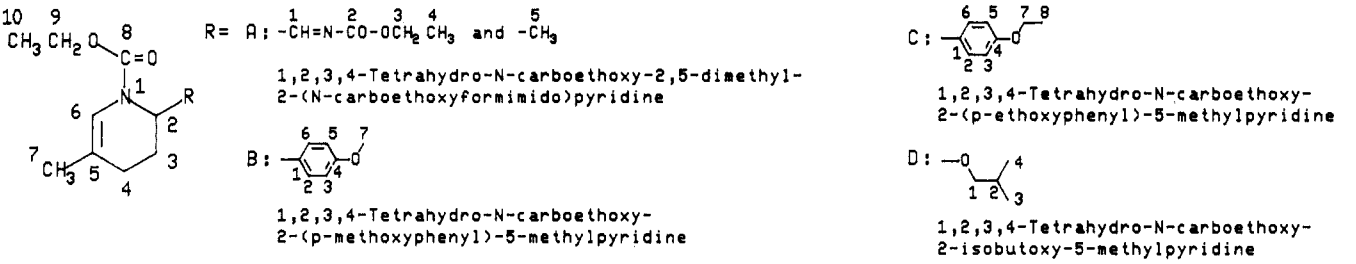


Figure 3. Feasible structures obtained during the polymerization and reactions.

Table V
NMR Spectra of Cycloaddition Compounds from CEMAB and Electron-Rich Olefins[a]



		proton or carbon position, main skeleton									proton or carbon position, substituent (R)							
NMR	compd	2	3	4	5	6	7	8	9	10	1	2	3	4	5	6	7	8
^{1}H			+m	+m		*m	s		q	*t	*s		q	q	s			
	A		1.54–1.85	1.91–2.25		6.61	1.72	4.19	1.28		8.41		4.28	1.35	1.44			
		+m	*m	*m		+m	*s		*m	+m		*2,6/m	3,5/d				s	
	B	5.31	1.73	2.01		6.83	1.68		4.15	1.22		7.07	6.83				3.78	
		+m	*m	*m		+m	*s		*m	+m		*2,6/m	3,5/d				*q	*t
	C	5.28	1.74	2.02		6.82	1.67		4.13	1.18		7.02	6.79				4.00	1.37
		+m	m	+m		+m	s		*q	*t	*m	m	d	d				
	D	5.48	1.80	1.97		6.50	1.67		4.21	1.31	3.27	1.62	0.86	0.87				
^{13}C		s	t	t	s	*d	q	*s	t	*q	*s	s	t	q	*q			
	A	59.2	23.2	31.4	113.2	118.9	20.6	153.0	62.2	14.3	179.6	163.2	62.9	14.1	17.5			
		+d	*t	*t	+s	+d	q	*t	*t	*q	*s	2,6/d	3,5/d	s			q	
	B	52.9	22.6	27.6	114.8	119.5	20.9	153.8	61.7	14.6	133.9	113.6	126.6	158.3			55.2	
		+d	*t	*t	+s	*s	q	*s	*t	*q	s	2,6/d	3,5/d	s			t	q
	C	52.8	22.2	27.1	114.9	119.0	20.6	153.6	61.3	14.5	133.4	113.8	126.1	157.3			61.7	14.2
		d	+t	t	+s	+d	q	*s	*t	q	+t	*d	3,4/9					
	D	78.4	22.3	26.5	115.9	117.1	20.8	153.7	61.7	14.5	74.2	28.4	19.3					

[a] s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, *, peak broadening; + peak splitting. Results were measured on room temperature. Split or broadened peaks might be combined or sharpened depending on the temperature.

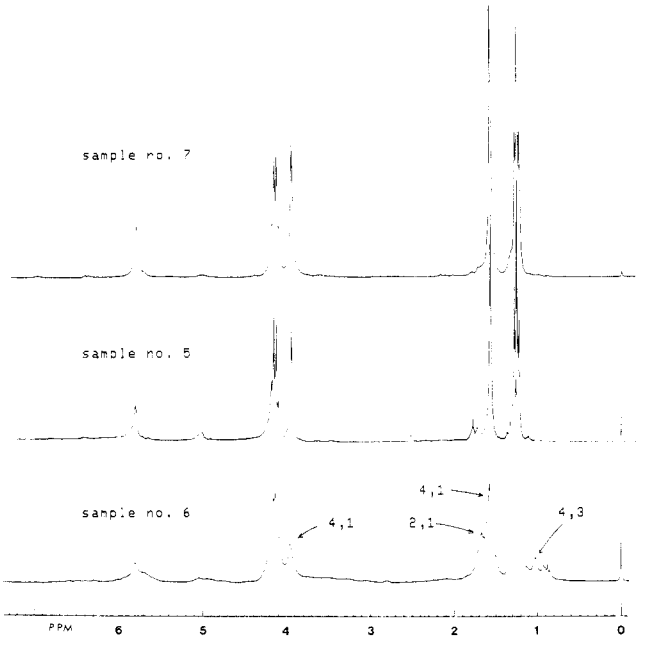
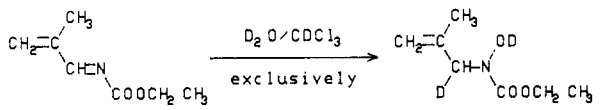


Figure 4. Comparison of ^{1}H NMR spectra of polymer samples showing structural differences.

CEMAB with D_2O addition and was used to confirm the 2,1-type polymer structure (Table II). From these data,



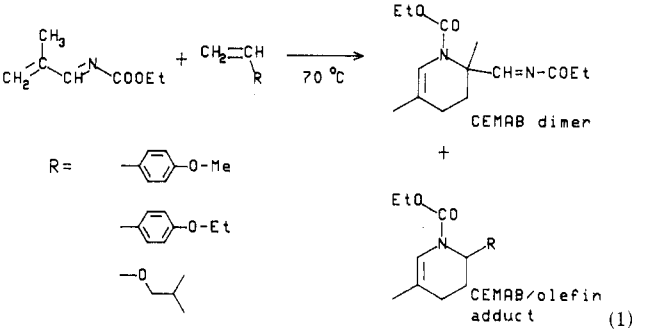
we could determine the contribution of the possible polymer structures in each sample (Table III).

In the case of anionic polymerization of CEMAB, the structures obtained corresponded almost completely to C=N bond opening (4,1-type predominant over 2,1-type). Sample number 7, obtained by KCN in DMF, showed highly pure 4,1-addition structure (Figures 4 and 5).

On the other hand, the homopolymer samples prepared by radical initiators showed structures resulting from mixed polymerization modes. ^{13}C and ^{1}H NMR spectra of these samples showed remaining imine peaks at 179.8 (^{13}C) and 8.42 ppm (^{1}H). The infrared spectra did not give enough information as the remaining C=N peak absorbs around 1650 cm^{-1}, and superposition of the carbonyl and carbon–nitrogen double bonds occurs.

Polymer Properties. The molecular weights obtained ranged from 1000 to 2100 (SEC). The polymer was soluble in most common solvents, except in nonpolar hydrocarbon solvents. Softening temperature varied according to the polymer structure. The 4,1-structured polymer has a much lower softening temperature than other structures, but most of them started to decompose at around 250 °C.

Thermal Side Reactions of CEMAB with Electron-Rich Olefins. During the radical polymerization of CEMAB and attempted copolymerizations with electron-rich olefins (Table I), inverse Diels–Alder type cycloaddition occurred (eq 1). This cycloaddition reaction is a typical inverse Diels–Alder reaction of α,β-unsaturated



(1)

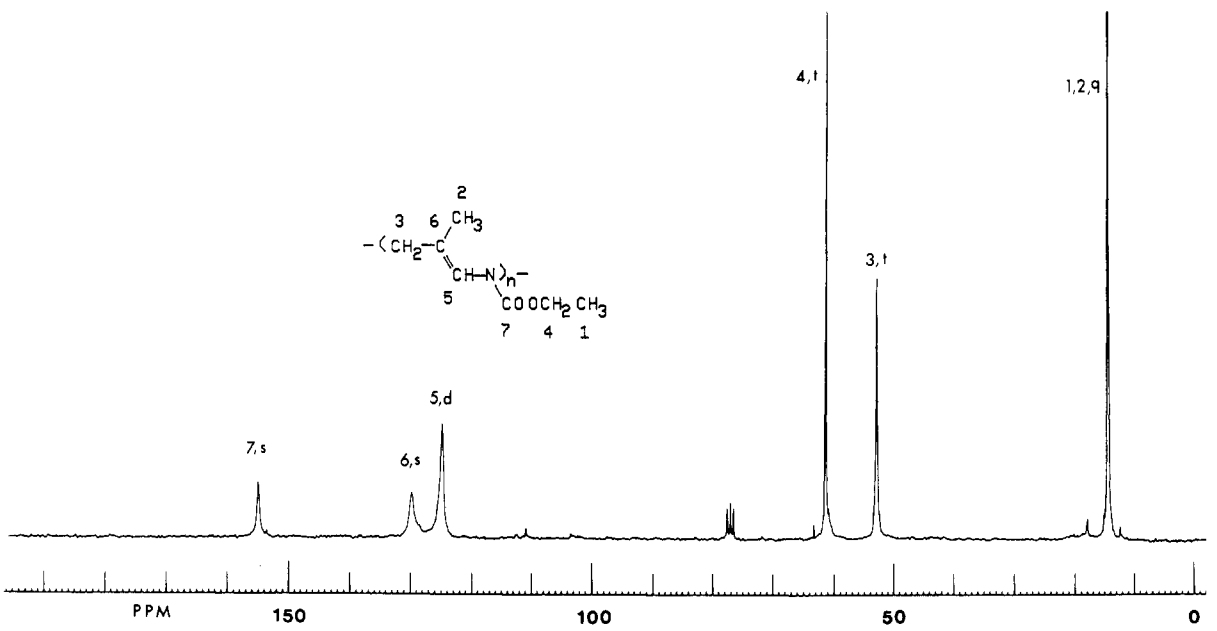


Figure 5. Decoupled ^{13}C NMR spectrum of 4,1-addition polymer (obtained from sample number 7).

imines and is considered to be the major factor why no radical copolymerization was observed. The obtained cyclic compounds were separated and purified by preparatory TLC, except CEMAB dimer, which decomposed during chromatography. The cyclic dimerization of CEMAB progressed slowly at room temperature, but the reaction was faster at higher temperature and the conversion reached 70% within 2 days at 70 °C. Thermal dimerizations were almost complete within 5 days in $CDCl_3$ and no other side reactions were found during the dimerization. The cycloadditions of CEMAB with electron-rich olefins were somewhat faster than the self-dimerization of CEMAB. The structures of these cycloadducts were confirmed by analysis of their NMR spectra (Table V).

Discussion

Anionic Polymerization. In earlier work with 1-azabutadienes, the CN double bond in the azabutadiene system played a role mainly as an electron-withdrawing substituent adjacent to the CC double bond.[1,2] The resulting polymers from those azabutadienes were predominantly vinyl polymers (4,3-addition structure). But CEMAB, which has a strong electron-withdrawing group at the N-position, always gives C=N bond-opened polymers. 4,1-Type and 2,1-type polymerization modes are competitive in the anionic polymerization of CEMAB, with the former dominant.

The factors that control the polymerization mode in these anionic systems are as follows: (1) stabilization of the growing anionic species by the N-substituent; (2) solvent, aprotic polar solvents further stabilize the ionic growing species and perhaps polarize the monomer's resonance structures; (3) initiators, a weak nucleophile is more selective than strong base. More reactive nucleophiles such as BuLi were not suitable, due to side reactions such as proton abstraction.

Free Radical Polymerization. In the case of radical polymerization, the carbethoxy group positioned at N was not sufficient to stabilize the growing radical species, although it was much more effective than alkyl or aryl substituents, which did not give radical polymerization at all.

Side reactions during radical polymerization were found to be of the Diels–Alder type. This reaction was a case of C=C and C=N bond participation in cycloaddition reaction.

Purity. Although the CEMAB monomer was reactive enough to give high conversion in anionic polymerization, high molecular weight samples were not obtained. The exact reason is not certain. However, the reactive nature of this monomer and the necessity of working with small quantities did not allow exhaustive purification.

Experimental Section

Methods. ^1H and ^{13}C NMR spectra were taken on a Bruker WM 250 spectrometer at 250 and 62.9 MHz, respectively. IR spectra were obtained from 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 with chloroform as eluent. Elemental analyses were performed by Desert Analytics, AZ. Thermal measurements were measured on Perkin-Elmer DSC-4 differential scanning calorimeter and Kofler Heizbank heating plate.

Source of Materials. Solvents. Tetrahydrofuran and toluene were dried over NaH and distilled. Dimethylformamide was dried over a 3-Å molecular sieve.

Initiator. 2,2′-Azobisisobutyronitrile (AIBN), di-*tert*-butyl peroxide (DTBP), and *tert*-butyl peroxybenzoate (TBPB) were purchased and purified by standard methods; *n*-butyllithium was obtained commercially. Potassium cyanide was recrystallized from ethanol–water mixed solvent, dried under vacuum, and then saturated in DMF solvent. Triethylamine (TEA) was refluxed over CaH_2 and distilled.

Chemicals for Monomer Synthesis. Commercially available chemicals such as cyclopentadiene dimer, methacrolein, ethyl carbamate, titanium tetrachloride, and common solvents were used without further purifications. Cyclopentadiene was obtained by cracking of cyclopentadiene dimer at 170 °C, with a Vigreux column maintained at a 42–45 °C distillation temperature range.

2-Methyl-5-norbornene-2-carboxaldehyde was prepared through a Diels–Alder reaction between cyclopentadiene and a slight excess of methacrolein, at room temperature with stirring for 2 days. The reaction mixture was pure enough to be used after removal of unreacted feeds by evaporation under reduced pressure. The obtained yield was over 90%.

Synthesis and Reaction. Precursor for Monomer *N*-(Ethoxycarbonyl)(2-methyl-5-norbornen-2-yl)methylidenimine. 2-Methyl-5-norbornene-2-carboxaldehyde, (34.1 g, 0.25 mol), 33.4 g (0.375 mol) of ethyl carbamate, and 83.6 mL (0.6 mol) of triethylamine were placed in a 3-L three-necked round-bottom flask, equipped with a mechanical stirrer, dropping funnel, and nitrogen purging adapter. Benzene (1 L) was added, and the

mixture cooled to 0 °C or less. Titanium tetrachloride (0.138 mol) in 250 mL of benzene was added dropwise to the solution during 1 h, maintaining the reaction temperature below 10 °C. The mixture was stirred at room temperature for several hours. After the completion of the reaction, the reddish brown reaction mixture was filtered to remove titanium oxide and amine salt, and the filtrate was concentrated by using a rotary evaporator. The concentrated mixture was distilled by using a Kugelrohr apparatus, and then the distillate was fractionally distilled to give 18.9 g of imine compound (exo and endo isomers): yield 36.5%; bp 70–71 °C (0.5 mmHg). All the procedures were carried on under absolutely dry conditions, because the imine compound is sensitive to moisture.

Anal. Calcd for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.68; H, 8.13; N, 6.51. IR (neat): 3060, 2971, 2872, 1721 (C=O), 1650 (C=N), 1446, 1368, 1231 (C–O), 1041, 955, 819, 727 cm^{-1}. ^1H NMR: (250 MHz, $CDCl_3$) δ 8.39 (s) and 8.09 (s, CH=N); 6.08–6.28 (m, CH=CH); 4.25 (q) and 4.21 (q, OCH_2); 2.69–2.92 (m, 2CH), 2.32 (dd) and 0.85 (dd, CH_2); 1.41–1.73 (m, CH_2, norbornenyl); 1.33 (t) and 1.31 (t, CH_3CH_2); 1.06 (s) and 1.38 (s, CH_3). ^{13}C NMR: (62.9 MHz, $CDCl_3$) δ 181.4 (d, CH=N) and 182.8 (s, C=O); 138.4 (d), 132.8 (d), 137.0 (d), 133.8 (d, CH=CH, two isomers); 62.0 (t) and 61.9 (t, CH_2O); 49.5 (d) and 51.6 (d), 47.6 (s) and 47.7 (s), 42.7 (d) and 42.4 (d), 47.0 (t) and 46.9 (t), 35.7 and 37.6 (t, norbornenyl carbons), 21.9 (q) and 23.3 (q), (CH_3, two isomers) 13.5 (q, CH_3CH_2O).

Monomer *N*-Carbethoxy-3-methyl-1-aza-1,3-butadiene. The monomer was synthesized by using pyrolysis of the precursor with an electrically heated vertical quartz tube (2 × 40 cm) packed with quartz fragments, equipped with an addition funnel and a trap. The system was evacuated and purged with dry nitrogen, then the pressure was adjusted to 2–3 mmHg, and the oven temperature was maintained at 580 °C before the reaction. The precursor (10.4 g, 0.05 mol) mixed with 6–9 times the amount of benzene by volume was introduced dropwise into the hot tube at the top. The feeding rate was 10–15 mL of solution/min. The pressure was adjusted to 4–5 mmHg during the pyrolysis. The pyrolysate was collected and solidified in the trap cooled with a dry ice–acetone bath. The solidified pyrolysate mixture was freeze-dried at 3–5 mmHg of pressure to remove cyclopentadiene, benzene, and other volatile impurities. When the pyrolysate changed to yellow liquid, the bath was slowly warmed to 50 °C to remove residual impurities. This temperature is close to the boiling point of the monomer. The sufficiently concentrated pyrolysate was distilled off by lowering the pressure to 0.5 mmHg and collected at -78 °C. The monomer was very sensitive to moisture and easily dimerized at higher temperature, so the procedures were carried out under dry and mild temperature conditions. The obtained yield was 4.7 g (67%).

Anal. Calcd for $C_7H_{11}NO_2$: C, 59.56; H, 7.85; N, 9.92. Found: C, 59.66; H, 8.02, N, 9.72. IR (neat): 3089, 2982, 1721 (C=O), 1632 and 1613 (C=C, C=N conjugated), 1452, 1365, 1348, 1234 (C-O), 1030, 934, 882, 789 cm^{-1}. ^1H NMR: ($CDCl_3$) δ 8.49 (s, CH=N); 6.02 (m) and 5.84 (m, CH_2=C); 4.30 (q, CH_2O); 1.97 (s, CH_3, allylic); 1.37 (t, CH_3CH_2O). ^{13}C NMR ($CDCl_3$): 172.2 (d, CH=N); 163.5 (s, C=O); 142.9 (s, =C); 132.8 (t, CH_2=); 62.7 (t, CH_2O); 15.7 (q, CH_3, allylic); 13.9 (q, CH_3CH_2O).

Model Compound for 2,1-Type Polymer. Monomer (10 mg) and 0.3 mL of $CDCl_3$ were placed in an NMR tube. Two drops of D_2O was added, and the tube tightly stoppered with a rubber septum. The NMR tube was held at room temperature overnight. The resulting compound was exclusively the 1,2-position (imine moiety) deuteriated product. The ^1H and ^{13}C NMR spectra of this compound were checked and compared with those of polymers obtained from various polymerization conditions (Table II).

Thermal Dimerization of *N*-Carbethoxy-3-methyl-1-aza-1,3-butadiene and Reactions of Azabutadiene with Electron-Rich Olefins. Four NMR tubes containing 0.1 mL of azabutadiene and 0.15 mL of electron-rich olefins, such as *p*-ethoxystyrene, *p*-methoxystyrene, and isobutyl vinyl ether, in 0.3 mL of $CDCl_3$ solvent were prepared under nitrogen atmosphere and stoppered tightly with a rubber septum. The sample tubes were kept at 70 °C. The reactions were checked by NMR. After the reactions progressed or were completed, the reaction products were separated and purified by preparatory silica gel TLC. The eluent was the mixture of *n*-pentane and ethyl ether (2:1 by volume). The positions of separated components were determined by 250-nm UV light. The measured R_f values were 0.23 (azabutadiene dimer), 0.43 (*p*-methoxystyrene and *p*-ethoxystyrene adducts), and 0.68 (isobutyl vinyl ether adduct). But the azabutadiene dimer decomposed during the chromatography, because the imine moiety of the dimer is unstable in acidic conditions such as silica gel. The reaction products were identified as inverse Diels–Alder-type heterocyclic compounds. NMR spectroscopic data are shown in Table V. The NMR spectral data were obtained from 250 MHz (^1H) and 62.9 MHz (^{13}C) NMR. IR: A: 3099, 2981, 2919, 1704 (C=O, C=N, C=C, br), 1464, 1446, 1401, 1373, 1340, 1312, 1236, 1189, 1078, 1035, 987, 922, 840, 767 cm^{-1}. B: 2955, 2921, 2834, 1701 (C=O), 1611 (C=C), 1511 (C=C), 1406, 1371, 1335, 1313, 1247, 1173, 1108, 1060, 1035, 1003, 973, 834, 765 cm^{-1}. C: 2976, 2919, 1701 (C=O), 1611 (C=C), 1509 (C=C), 1405, 1371, 1335, 1245, 1173, 1108, 1060, 1003, 973, 837, 764 cm^{-1}. D: 3097, 2957, 1708 (C=O), 1681 (C=C), 1465, 1409, 1372, 1320, 1306, 1267, 1211, 1180, 1082, 986, 837, 767 cm^{-1}.

Polymerization. Polymerizations were carried out by radical and anionic initiators under nitrogen in sealed tubes. The prepared reaction tubes were maintained at a certain temperature for the required reaction time and poured into a large volume of *n*-pentane to precipitate the polymers. Radically prepared samples were easily precipitated in pentane, but the pure 4,1-type polymer samples prepared anionically formed tacky material in pentane, even though the molecular weights of the latter samples were larger. The polymers obtained were purified by reprecipitation and dried in vacuo.

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Registry No. CEMAB, 34724-63-5; CEMAB (homopolymer), 114379-09-8; CEMAB (dimer), 114379-05-4; 1,3-cyclopentadiene, 542-92-7; methacrolein, 78-85-3; ethyl carbamate, 51-79-6; 6-formyl-6-methylbicyclo[2.2.1]hept-2-ene, 40441-67-6; 6-methyl-6-((carboethoxyimino)methyl)bicyclo[2.2.1]hept-2-ene, 114379-01-0; 1,2,3,4-tetrahydro-5-methyl-2-(4-methoxyphenyl)-*N*-(ethoxycarbonyl)pyridine, 114379-02-1; 1,2,3,4-tetrahydro-5-methyl-2-(4-ethoxyphenyl)-*N*-(ethoxycarbonyl)pyridine, 114379-03-2; 1,2,3,4-tetrahydro-5-methyl-2-((2-methylpropyl)-oxy)-*N*-(ethoxycarbonyl)pyridine, 114379-04-3.

References and Notes

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