

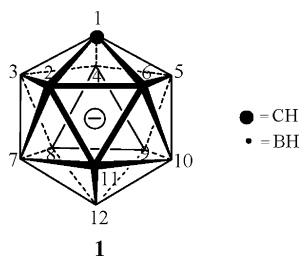
Li⁺-Catalyzed Radical Polymerization of Simple Terminal Alkenes

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Uncatalyzed radical polymerization of unsubstituted alkenes is only effective for ethylene at high pressure and temperature, only produces low-molecular-weight oligomers of other alkenes,¹ and has been eclipsed by transition-metal-catalyzed^{2,3} or cationic^{4,5} polymerization. Remarkably, in weakly ligating solvents under ambient conditions, Li⁺ salts of highly alkylated derivatives of the monocarbododecaborate anion **1** induce facile polymerization of terminal alkenes by the radical mechanism.



The first hint at possible Lewis acid catalysis of chain propagation in the radical polymerization of alkenes was apparently provided by Clark's calculation⁶ of the gas-phase activation energy of methyl radical addition to ethylene, which predicted a decrease from 14.4 to 6.0 kcal/mol when ethylene was complexed with Li⁺. Although such catalysis seems not to have been reported for unsubstituted alkenes so far, LiCl has been long known to catalyze the radical polymerization of acrylonitrile,⁷ and catalysis with other Lewis acids, presumably due to complexation of the acid to the activating substituent, has been used to modify monomer reactivity in radical copolymerizations and to influence polymer tacticity.^{8a-12}

To promote the polymerization of simple alkenes, Li⁺ needs to be in a poorly solvated ("naked") form. Li⁺ cations present in

solutions of LiCB₁₁(CH₃)₁₂^{13,14} in benzene¹⁵ and 1,2-dichloroethane accelerate pericyclic rearrangements¹³ far more than those in solutions of LiClO₄ in ether.¹⁶⁻¹⁹ Neat solid CH₂=CH(CH₂)_{n-2}C(BMe)₁₁⁻Li⁺ polymerizes spontaneously on the benchtop.²⁰ In the presence of air or another initiator, this and related salts also undergo radical polymerization in benzene unless 12-crown-4 is added, but not in THF.²¹

In a solution of 10% (by weight) LiCB₁₁(CH₃)₁₂ in 1,2-dichloroethane, unactivated alkenes polymerized in about 18 h (liquid alkenes were at 1 M concentration and gases at saturation at atmospheric pressure). The modes of initiation were (i) laboratory air at 25 °C, (ii) azoisobutyronitrile (AIBN) at 25 °C, (iii) di-*tert*-butyl peroxide (DTBP) at 80 °C, and (iv) DTBP at 25 °C under UV irradiation. Seven of the eight terminal alkenes that were examined, both 1,3-dienes, and both terminal acetylenes yielded polymers (Table 1). 3,3,3-Trifluoropropene did not react, nor did tetramethylethylene and the *Z* and *E* isomers of 2-butene.

Alkene polymers were characterized by size exclusion chromatography (SEC) against polystyrene standards and by comparison with published ¹H NMR²² and ¹³C NMR^{22,23} spectra (Supporting Information). The dienes yielded the *cis* 1,4-polymers (NMR^{22,24-26} and mp^{27,28}). In the air-initiated polymerizations of alkenes and alkadienes, one of the terminal groups was -CH₂OH, quantitated as the trichloroacetyl isocyanate adduct,²⁹ permitting an independent determination of the degree of polymerization. The polyacetylenes contained both *cis* and *trans* double bonds (¹H NMR^{30,31}) and had the expected^{32,33} UV-vis spectra. Polymer microstructures are under examination.

The high polydispersity of the polymers, the need for a radical initiator, the nature of the end group in air-initiated polymers, and the ¹H NMR spectra, which suggest atactic structures, are all compatible with radical mechanism.

Table 1. LiCB₁₁(CH₃)₁₂-Catalyzed Polymerization in 1,2-Dichloroethane^a

monomer	aerobic, 25 °C					AIBN, 25 °C				DTBP, 80 °C				DTBP/UV, 25 °C			
	<i>M_w</i> /10 ³	<i>M_n</i> /10 ³	<i>n^b</i>	<i>r^c</i>	Y (%)	<i>M_w</i> /10 ³	<i>M_n</i> /10 ³	<i>n^b</i>	Y (%)	<i>M_w</i> /10 ³	<i>M_n</i> /10 ³	<i>n^b</i>	Y (%)	<i>M_w</i> /10 ³	<i>M_n</i> /10 ³	<i>n^b</i>	Y (%)
CH ₂ =CH ₂	3.00	1.15	41	40	75	3.40	1.20	43	82	6.20	2.00	71	88	1.40	0.53	19	88
MeCH=CH ₂	8.85	3.45	82	80	83	9.15	3.60	90	88	20.4	7.15	170	92	4.45	2.30	55	93
Me ₂ C=CH ₂	4.90	1.70	30	27	70	5.25	2.10	37	78	7.75	2.70	47	90	2.75	1.70	30	95
EtCH=CH ₂	6.60	2.35	42	41	80	9.60	3.10	55	84	33.5	11.9	212	92	3.25	1.90	34	98
<i>t</i> -BuCH=CH ₂ ^d	3.50	1.25	15	13	68	9.05	2.60	31	79	12.2	3.40	40	85	2.28	1.49	18	85
<i>n</i> -BuCH=CH ₂	2.50	1.15	14	14	65	10.3	4.90	53	75	23.8	9.50	110	85	8.10	2.90	35	94
Me ₃ SiCH=CH ₂	9.80	4.00	38	35	75	24.1	10.5	100	78	35.2	11.4	109	86	10.8	4.25	43	98
CH ₂ =CMeCH=CH ₂	8.00	3.50	51	50	82	13.2	4.90	72	86	18.5	6.40	94	90	12.4	4.59	68	99
CH ₂ =CMeCMe=CH ₂	10.2	4.40	53	50	75	18.5	6.10	74	85	22.2	7.20	87	89	9.55	3.98	48	99
C ₆ H ₅ -C≡CH ^e	9.00	2.70	26		82	14.0	6.00	76	85	28.9	9.05	88	94	13.5	5.25	51	90
<i>n</i> -Bu-C≡CH ^f	12.4	4.10	48		88	16.2	5.50	67	90	24.0	7.05	85	95	15.9	5.59	68	94

^a Unoptimized results with commercial alkenes. LiCB₁₁(CH₃)₁₂, AIBN, and DTBP at 10 wt %. Degassed samples, except for aerobic initiation, done in ambient air. The polymers were precipitated with CH₃OH, and the catalyst was recovered almost quantitatively after filtration or sedimentation and solvent evaporation, with no noticeable loss of activity. Without catalyst, no polymer was formed. ^b Average degree of polymerization (SEC in THF with polystyrene standards). ^c From ¹H NMR spectra; quantitated after treatment of the polymers with trichloroacetyl isocyanate. The -CH₂O-CO-NHCO-CCl₃ protons were a doublet at 3.77-4.03 ppm (*J* = 6.1-6.3 Hz) and the -NH protons a broad singlet at 10.42-10.47 ppm. Protons of -CRHO-CO-NH-CO-CCl₃ groups, expected at 5.15-5.22 ppm, were not detectable. Peaks in the vinylic region were extremely weak or absent. ^d This polymer contains no CH₂ groups, and its structure is under investigation. ^e UV-vis (dichloromethane): λ_{max} = 248 nm (ε = 6100 M⁻¹ cm⁻¹), 328 (3100), 380 (2900). ^f UV-vis (hexane) λ_{max} = 285 nm (ε = 1900 M⁻¹ cm⁻¹), 330 (1700). The absorption coefficients are per monomer.

Table 2. LiCB₁₁(CH₃)₁₂-Catalyzed Copolymerization^a

monomers ^b	<i>M_w</i>	<i>M_n</i>	ratio ^c	<i>n</i> ^d	Y (%)
<i>n</i> -BuCH=CH ₂ /ViAc	5100	2100	30/70	7/17	88
<i>n</i> -BuCH=CH ₂ /Meth	8150	2500	27/73	8/18	90
Me ₃ SiCH=CH ₂ /ViAc	6800	3000	37/63	11/22	85
Me ₃ SiCH=CH ₂ /Meth	8500	2700	40/60	10/16	92

^a With AIBN, 25 °C. SEC, relative to polystyrene. ^b Equimolar ratio of monomers. ^c By mass, quantified by ¹H NMR. ^d Degree of polymerization for each component.

To test the need for naked Li⁺ and to exclude the distant possibility of Li⁺-induced cationic polymerization, additional controls were run with 1-hexene. Air did not initiate its polymerization when 12-crown-4 was added, when Li⁺ was replaced with Na⁺ or Cs⁺, or when 1,2-dichloroethane was replaced with THF. Deaerated 1-hexene did not polymerize (i) with LiCB₁₁(CH₃)₁₂ without initiator or with DTBP at 25 °C without irradiation, (ii) with AIBN at 25 or 65 °C without LiCB₁₁(CH₃)₁₂, and (iii) in the presence of 0.1 M hydroquinone with AIBN in 1,2-dichloroethane at 25 or 50 °C. It took longer (26 h) to polymerize in the presence of 0.1 M *t*-BuOLi, which presumably ties up Li⁺ partially as *t*-BuOLi₂⁺. CHD (δ 0.85 ppm in ²D NMR) was incorporated into the polymer in the presence of 1% CD₃OD, but not CH₃OD.

At the temperatures used, AIBN and DTBP do not ordinarily yield radicals at a useful rate in the dark. However, like other Lewis acids,^{8b} LiCB₁₁Me₁₂ catalyzes the thermal decomposition of both initiators. The decay of AIBN in benzene-*d*₆ at 25 °C has been reported²¹ to be first order in AIBN and in LiCB₁₁Me₁₂, with an observed rate constant of *k*_{obs} = 0.49[LiCB₁₁Me₁₂]/L mol⁻¹ s⁻¹. The rate of decomposition of DTBP (initial concentration, 0.015 M) in 1,2-dichloroethane-*d*₄ at 80 °C is first order in DTBP and in LiCB₁₁Me₁₂, with *k*_{obs} = 0.63[LiCB₁₁Me₁₂]/L mol⁻¹ s⁻¹.

1-Hexene and trimethylvinylsilane copolymerize with vinyl acetate (ViAc) and methyl methacrylate (Meth) (Table 2).

To compare the effectiveness of Li⁺ salts of various anions in promoting the propagation step at a constant initiation rate, samples containing degassed 1-hexene, 10% DTBP, and a 10% Li⁺ salt³⁴ (both by weight) in 1,2-dichloroethane were exposed to the same UV photon flux (450-W medium-pressure Hg lamp with a Pyrex filter) in a merry-go-round apparatus at 25 °C, where this initiator is inactive in the dark. The *M_w* (*n*, polydispersity) values obtained with Li(1-Hx-CB₁₁Et₉Me₂),³⁵ Li(1-H-CB₁₁Et₉Me₂),³⁵ LiCB₁₁Me₁₂,^{13,14} Li(1-H-CB₁₁Me₁₁),³⁶ Li[(7-12)-I₆-CB₁₁H₆],³⁵ LiCB₁₁H₁₂, and no catalyst were 13 500 (55, 2.9), 11 200 (46, 2.9), 9500 (41, 2.8), 8600 (36, 2.8), 6700 (26, 3.1), 5600 (23, 2.9), and no polymer, respectively (SEC, polystyrene standards). Thus, Li⁺ catalyzes both initiation and propagation, the latter presumably by complexing the alkene as suggested by calculations.⁶

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Supporting Information Available: Experimental details and the ¹H, ¹³C, and APT NMR spectra of the polymers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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