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Controlled Polymerization of Methyl Methacrylate Using Lithium Aluminum Alkyls

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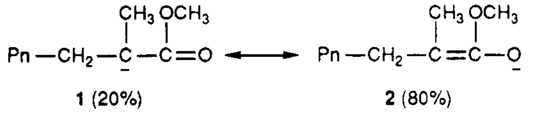
ABSTRACT: The important contribution of this paper is to show that certain combinations of lithium and aluminum alkyls enable polymerizations of alkyl methyl methacrylate to be carried out at elevated temperatures. The work also shows that both the lithium and aluminum components must contain alkyl groups which have cross-sectional areas as large as possible. Moreover, these initiators are only effective in hydrocarbon solvents in which they are soluble. Solvents which have previously been preferred for anionic and catalyzed anionic polymerization, such as tetrahydrofuran, dimethoxyethane, etc., inactivate these initiators. In hydrocarbon solvents the separation between the anionic and cationic components are minimized and the high cross-sectional area of the latter "screens" the propagating terminus of the polymer chain from side reactions. Thus we refer to this polymerization of methacrylate monomers as "screened anionic polymerization". Molecular weights in the range 2000–150 000 have been prepared with dispersions close to that described by the Poisson distribution. A variety of block copolymers have also been prepared. A model has been developed which accounts for the quantitative observations and is based on the known structure of lithium aluminum alkyls.

Introduction

Methyl methacrylate is an important monomer with a wide range of uses in materials and surface coating industries. It is also of considerable interest academically since it can be polymerized using radical or anionic initiators. The polymers formed have an unbranched structure and are probably the best example of an amorphous organic material. Moreover the microstructure and stereochemistry can be determined with reasonable precision.

The development of anionic initiators for the polymerization of styrene and butadiene, in which the activity of the propagating end of the polymer chain could be maintained indefinitely, has led to attempts to develop analogous initiators for methyl methacrylate and other methacrylates. To summarize a long story, the main conclusion from these early studies was that "living" propagation was only possible at temperatures in the range −40 to −100 °C and lithium alkyls were the preferred initiators. At higher temperatures termination reactions occur in which the carbanion reacts with ester groups.

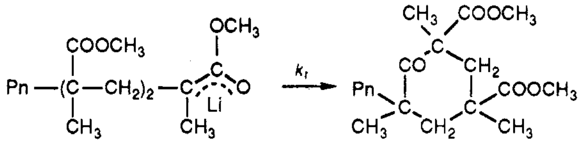
There are important differences between the carbanion propagating center in styrene polymerization and methyl methacrylate. Calculations show that the negative charge is highly delocalized, giving a classical resonant structure.



$$Pn-CH_2-\underset{-}{\overset{CH_3}{C}}-\overset{OCH_3}{C}=O \longleftrightarrow Pn-CH_2-\overset{CH_3}{C}=\overset{OCH_3}{C}-\underset{-}{O} \qquad (1)$$

1 (20%) 2 (80%)

Propagation can only occur by addition of the carbanion, 1, to the monomer, but structure 2 is the predominant conacal form because the negative charge prefers to reside on the most electronegative atom. It is a reasonable argument that in these circumstances one of the principle termination process at ambient temperatures is cyclization involving adjacent ester groups of the same molecule.



(2)

It is evident from recent publications that the stability of the propagating species is increased by increasing the cross-section of the gegenion. The first example of attempts to do this are due to Lochmann[1] who used a metallo ester of lithium or sodium with an excess of sodium *tert*-butoxide. The latter forms an ionic cluster in the region of the propagating end of the molecule, thereby inhibiting side reactions. In this way living polymerizations were possible at 0–20 °C. Although the detailed chemistry may be different, similar principles apply to group-transfer polymerization of methyl methacrylate,[2] where the $Si(CH_3)_3$ group screens the propagating terminus of the polymer chain. Also the use of the *tert*-butylammonium ion[3] and tetraphenylporphyrin[4] probably relies on similar principles.

In this paper we describe a group of initiators formed by the complex formation of organolithium and organoaluminum compounds[5] which are well-defined crystalline compounds. In solution, in solvents such as tetrahydrofuran, it has been demonstrated that compounds such as $Na[AlEt_4]$ are dissociated into discrete Na^+ and $[AlEt_4]^-$ ions. Lithium aluminates have some covalent character but are also ionic. The structures of potassium, rubidium, cesium,[6] and lithium[7] tetramethylaluminates have been determined by X-ray crystallography. The crystal lattices consist of alternating alkali-metal cations and tetraalkylaluminate anions in a chain structure. The simple lithium tetraorganoaluminates described above are known to polymerize methyl methacrylate monomers.[8] However, this is only possible at the very low temperatures of −78 °C. We have found that by increasing the cross-section of the alkyl groups in these lithium tetraorganoaluminates polymerizations can be carried out at temperatures in the range 0–40 °C in toluene solution, under isothermal conditions, and moreover, in the absence of solvent at temperatures in the excess of 100 °C. The propagating center is very stable, enabling block copolymers to be synthesized. Solvents which cause the complex

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to dissociate, such as tetrahydrofuran and dimethoxyethane, render the initiator inactive. Ethers are known to form very stable complexes with aluminum alkyls.[9] In these solvents therefore reaction 2 probably occurs and no polymerization is possible.

Experimental Section

(a) General Methods and Materials. Syntheses and manipulations of chemicals were carried out using standard Schlenk and syringe techniques under nitrogen. Methyl methacrylate was obtained from ICI Acrylics and was purified by passing down a column of activated basic alumina and up a column of activated 4-Å molecular sieve. Toluene and tetrahydrofuran (THF) were refluxed with a sodium dispersion in paraffin and distilled under nitrogen prior to use. Triisobutylaluminum was purchased from Aldrich as a 1 M solution in toluene and used directly. *tert*-Butyllithium was purchased from Aldrich as a 1.7 M solution in pentane and was titrated with diphenylacetic acid in THF prior to use to determine its concentration.

2,6-Di-*tert*-butyl-4-methylphenol (BHTH) (99+%) and 2,6-di-*tert*-butylphenol (BHBH) were obtained from Aldrich and used with no further purification. Methyl methacrylate-d_8 (98% D) was purchased from Cambridge Isotope Laboratories and was dried by vacuum distillation with triethylaluminum immediately prior to use.

The concentration of water in toluene and methyl methacrylate were determined by Karl Fischer titration.

(b) (2,6-Di-*tert*-butyl-4-methylphenoxy)diisobutylaluminum (Al(BHT)(iB)$_2$). 2,6-Di-*tert*-butyl-4-methylphenol (8.87 g, 4.02 × 10^{-2} mol) was dissolved in 25 mL of dry toluene. Triisobutylaluminum (8.03 g, 4.04 × 10^{-2} mol) was added by syringe with stirring under nitrogen. The temperature was allowed to rise to approximately 50 °C, and butane evolution was observed. The total volume of the solution was made up to 50 mL to give a 0.8 M solution. This was used as a stock solution for the polymerization reactions.

(c) (2,6-Di-*tert*-butylphenoxy)diisobutylaluminum (Al(BHB)(iB)$_2$). 2,6-Di-*tert*-butylphenol (7.88 g, 3.57 × 10^{-2} mol) was dissolved in 20 mL of dry toluene. Triisobutylaluminum solution, 1.0 M in toluene (35.7 mL, 3.57 × 10^{-2} mol), was added by syringe with stirring under nitrogen. The solution was allowed to increase in temperature to 56 °C with butane evolution. This was also used as a stock solution for the polymerization reactions.

(d) Polymer Evaluation. (i) NMR. Approximately 0.2 mL of the reaction solution was dissolved in approximately 1 mL of $CDCl_3$. ^1H NMR were recorded on a Bruker AM500 spectrometer at 500 MHz. Spectra are referenced relative to residual $CHCl_3$ at 7.24 ppm. The yield of the reaction was calculated by the relative integration areas of the peaks at 3.79 ppm (residual methyl methacrylate monomer) and 3.68 ppm (poly(methyl methacrylate)). The stereochemistry of the polymer backbone was calculated by looking at the peaks from the backbone methyl groups: syndiotactic triad, 0.81 ppm; atactic triad, 0.97 ppm; isotactic triad, 1.14 ppm. ^{13}C NMR were recorded at 125.7 MHz and used to confirm the triad stereochemistry observed by looking in the carbonyl region, 175–179 ppm.

(ii) GPC. Molecular weights were determined at 30 °C using chloroform as the elutent. Polymer Laboratories 10-μm PL gel in mixed gel columns were employed and calibrated with Polymer Laboratories PMMA standards, from 7.8–1400 K. A 64 K standard was used routinely to check the performance of the columns. Data are reported in the tables as the number average molecular weight (M_n) and polydispersity (D).

(e) Polymerization in Toluene Solution at Ambient Temperatures. All glass surfaces were freed from adsorbed water by flame drying in vacuum. The appropriate amount of stock solution, Al(BHT)(iB)$_2$ or Al(BHB)(iB)$_2$, was mixed with 40 mL of toluene and cooled to −5 °C. The appropriate amount of *tert*-butyllithium solution in pentane was then added with stirring.

Several minutes were allowed to elapse to permit complete complexation of the two metal alkyls. Methyl methacrylate was then added at a rate which allowed the temperature to remain within previously defined limits so that conditions approximated to an isothermal reaction. Initially, the addition of methyl methacrylate produces a pronounced yellow color in the solution. However, on completion of the polymerization the solution is colorless.

Table I
Dimensions of Some Gegenions Used in Anionic Polymerization

ion	diameter (Å)	ion	diameter (Å)
Li^+	1.20	$(NBu_4)^+$	7.00
Na^+	1.92	$(LiAl(BHT)(iB)_2)^+$ [a]	12.00[b]
K^+	2.66		

[a] This paper (Figure 4). [b] Cross section of gegenion normal to Li–Al axis.

Table II
Polymerization of Methyl Methacrylate[a]

R	$[M]_o/[BuLi]_o$	yield (%)	$10^{-3}M_n$	D	syn (%)	iso (%)
3.0	200	99	28.4	1.09	75	6
2.0	200	99	30.3	1.15	72	2
1.4	186	99	29.4	1.10	71	2
1.2	200	99	32.4	1.09	71	2
1.07	179	99	29.6	1.18		
0.75	200	75	19.9	1.12	68	2
0.43	179	46	17.1	1.28	50	20

[a] Effect of varying the ratio of aluminum alkyl to *tert*-butyllithium. R = $[Al(BHT)(iB)_2]_o/[BuLi]_o$. Conditions: toluene solution, $[M]_o$ = 1.87 mol/L, temperature 0 °C.

Table III
Polymerization of Methyl Methacrylate[a]

alkyl	$[M]_o/[BuLi]_o$	P_n	D	syn (%)	iso (%)
Al(BHT)(iB)$_2$	40	59	1.16		
Al(BHT)(iB)$_2$	40	59	1.17		
Al(BHT)(iB)$_2$	40	64	1.19	72	2
Al(BHT)(iB)$_2$	100	136	1.12	70	2
Al(BHT)(iB)$_2$	100	172	1.18	71	
Al(BHT)(iB)$_2$	300	441	1.11		
Al(BHT)(iB)$_2$	300	411	1.10	70	3
Al(BHT)(iB)$_2$	400	590	1.17	71	3
Al(BHT)(iB)$_2$	400	617	1.14	76	2
Al(BHB)(iB)$_2$	100	153	1.20	73	1
Al(BHB)(iB)$_2$	202	225	1.15	69	4
Al(BHB)(iB)$_2$	300	421	1.18	73	2

[a] Relationship between the ratio of monomer to *tert*-butyllithium and the degree of polymerization (P_n) of the polymer formed. Conditions: toluene solution, $[M]_o$ = 1.87 mol/L, temperature 0 °C. Complete reaction of monomer in each case.

The reaction can be followed using ^1H NMR which is ideal for determining the concentration of MMA. This technique showed that all the MMA reacts in times which vary from a few minutes to 2 h, depending on the molecular weight of the polymer being produced.

The samples removed during the polymerization were also studied using GPC and showed a progressive increase in molecular weight of the polymer with a decrease in the monomer concentration. At the end of the polymerization methanol was added, destroying the metal alkyls, and the polymer was precipitated in *n*-hexane and dried at 120 °C in vacuum. In Tables II and III the data obtained relating the composition of the reaction mixture to the final composition of the polymers formed are summarized.

To demonstrate the stability of the propagating center, a series of experiments were carried out in which equal aliquots of MMA were added to the initiator solution in toluene at 60-min intervals after complete reaction. To 80 mL of dry toluene, in a 250-mL jacketed reaction vessel, was added 2.46 × 10^{-3} mol of Al(BHT)(iB)$_2$ as a solution described above. The reaction mixture was cooled to −10 °C, and 1.23 × 10^{-3} mol of *tert*-butyllithium was added as a solution in pentane. To this cooled solution was added 10 mL of MMA, at such a rate that the temperature of 0 °C was maintained.

Within 5 min all the monomer had been converted to polymer, as determined by NMR. The reaction mixture was allowed to stand for a further 60 min before addition of an additional 10 mL of MMA. The above procedure was then repeated, and on

Table IV
Demonstration of Living Nature of Propagating Centers[a]

time (min)	total MMA reacted (mol/L)	$[M]_0/[BuLi]_0$	$10^{-3}M_n$	$10^{-3}M_n$ increment	D
65	1.06	75	11.7	11.7	1.09
130	2.12	150	23.2	11.5	1.10
195	3.18	225	33.9	10.7	1.11
260	4.24	300	44.1	10.2	1.11

[a] Conditions: toluene solution; 0 °C; $[BuLi]_0$ = 0.0141 mol/L; $[Al(BHT)(iB)_2]_0/[BuLi]_0 = 2$. Aliquots of 1.06 mol/L monomer were added over a 5-mins period. The mixture was left for a further 60 min before the next addition.

Table V
Adiabatic Polymerization of Methyl Methacrylate[a]

alkyl	reaction time (s)	final temp (°C)	yield (%)	$10^{-3}M_n$	D	α
$Al(BHB)(iB)_2$	5	85	83	61.1	1.6	0.54
$Al(BHB)(iB)_2$	8	75	85	58.7	1.6	0.55
$Al(BHT)(iB)_2$	7	125	82	49.5	1.44	0.66
$Al(BHT)(iB)_2$	6	105	85	50.7	1.54	0.66

[a] Conditions: pure MMA, initial temperature 0 °C; ratio of aluminum alkyl to *tert*-butyllithium 2:1; $[M]_0/[BuLi]_0 = 396$. Note: Experiments carried out at ambient pressures therefore vaporization of monomer reduces the final temperature and gravimetric yield.

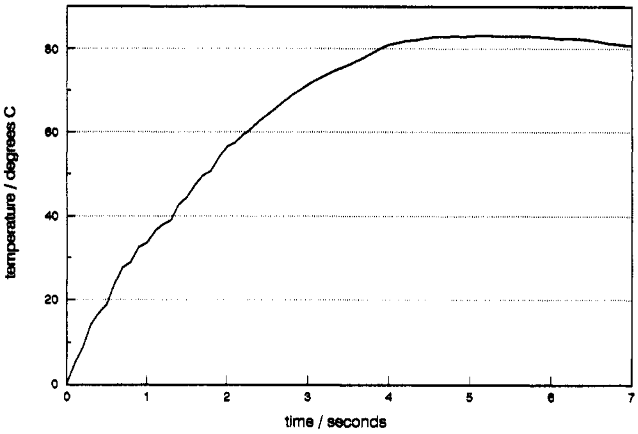


Figure 1. Exotherm for the polymerization of methyl methacrylate in the absence of solvent. $[M]_0/[BuLi]_0 = 397$; $[Al(BHB)(iBu)_2]_0/[BuLi]_0 = 2$.

completion two further aliquots of MMA were added. The total duration of the experiment was 260 min. The results are summarized in Table IV.

(f) Polymerization under Adiabatic Conditions without Solvent. The required amount of initiator solution usually less than 1 mL was transferred rapidly by syringe to 5 mL of vigorously stirred MMA at 0 °C under an atmosphere of nitrogen. A yellow coloration was produced immediately followed by rapid polymerization yielding a foamed polymer. The polymer was dissolved in dichloromethane (~30 mL), precipitated in a large excess of hexane (~800 mL), removed by filtration, and dried under vacuum at 100 °C for 3 h. Polymer yields were determined gravimetrically. Not all the monomer was converted to polymer because the heat generated vaporized 10–20% of the MMA.

The rapid exotherm during this type of polymerization was monitored using a fast response thermocouple (response time 10 ms) linked via a termination unit to a Strawberry Tree ACPC-12-8 data acquisition card located inside an IBM-compatible personal computer. Temperature versus time data were accumulated employing the "Labtech Notebook" software package with a Strawberry Tree driver (available from Laboratory Technologies).

Data capture rates of up to 50 Hz were possible. Data files were generated in ASCII code for further manipulation. A typical curve is shown in Figure 1.

(g) Investigation of the Initiating Species by ^1H NMR End Group Analysis. For this purpose MMA-d_8 (98 at %) was used to prepare deuterated PMMA using tBuLi and $Al(BHB)(iB)_2$ as initiator in toluene solution. The intention was to determine which of the three types of alkyl groups became covalently bonded to the PMMA-d_8 formed as a result of the initiation reaction.

$Al(BHB)(iB)_2$ (7×10^{-5} mol) was premixed in 2.4 mL of toluene with 3.4×10^{-5} mol of tBuLi at 0 °C. MMA-d_8 (5.6×10^{-3} mol) was added to this solution so as to maintain the temperature at 0 °C. The polymer was isolated by repeated precipitation in acidic methanol to remove all initiator residues. ^1H NMR (500 MHz) of the polymer showed there was an absence of resonances with the splitting pattern expected of an isobutyl group and for aromatic protons. Therefore, it can be concluded that the alkyl groups originating from the organoaluminum compounds do not become incorporated into the polymer chain. This is confirmed by the well-defined singlet ~0.8 ppm characteristic of the $-C(CH_3)_3$ moiety. This is strong evidence that the *tert*-butyl anion derived from tBuLi is the entity responsible for the initiation.

Table VI
Random Copolymerization[a]

$[MMA]_0 + [BMA]_0$ (mol/L)	feed composition MMA, BMA	polymer composition MMA, BMA	$10^{-3}M_n$	D
2.11	40, 60	38, 62	43.6	1.08
2.37	65, 35	66, 34	49.0	1.27
1.92	37, 63	36, 64	39.8	1.16

[a] Mixtures of MMA and *n*-butyl methacrylate (BMA). Conditions: toluene solution; 0 °C; $[Al(BHT)(iB)_2]_0/[BuLi] = 2$; $[BuLi]_0 = 7.1 \times 10^{-3}$ mol/L. Compositions of initial monomers added and polymers produced in molar percentages.

Table VII
Block Copolymerization[a]

block type	feed composition MMA, BMA	polymer composition MMA, BMA	$10^{-3}M_n$	D
AB	40, 60	41, 59	86.0	1.15
AB	89, 11	92, 8	48.6	1.10
AB	89, 11	94, 6	67.3	1.12

block type	feed composition MMA, BMA, MMA	polymer composition MMA, BMA	$10^{-3}M_n$	D
ABA	40, 20, 40	84, 16	71.0	1.12
ABA	45, 15, 40	87, 13	51.5	1.27

[a] Mixtures of MMA and *n*-butyl methacrylate (BMA). Conditions: toluene solution; 0 °C; $[Al(BHT)(iB)_2]_0/[BuLi] = 2$; $[BuLi]_0 = 7.1 \times 10^{-3}$ mol/L. Compositions of initial monomers added and polymers produced in molar percentages. Procedure as described in Table IV.

(h) Synthesis of Copolymers. (i) Random Copolymers. Conditions used were identical with those for homopolymerization. A solution in toluene of *n*-butyl methacrylate and methyl methacrylate, premixed in the required proportions, was added to a toluene solution of the initiator. The temperature was maintained at 0 °C and the progress of the copolymerization followed using H NMR. On completion of the reaction the copolymer was isolated using the same procedure as for the homopolymer. The composition, molecular weight, and polydispersity were determined using H NMR and GPC. The results are summarized in Table VI.

(ii) Block Copolymers. Initially, methyl methacrylate was homopolymerized and H NMR used to determine when all the monomer had reacted. To the preformed living homopolymer was added the appropriate amount of *n*-butyl methacrylate. On complete reaction the AB-type block copolymer was isolated in the manner previously described. These procedures were repeated to produce AB copolymers of different composition and molecular weight. Also if a preformed AB block copolymer is used to initiate the polymerization of a further quantity of methyl methacrylate, an ABA triblock copolymer is obtained. Some of the different types prepared are described in Table VII.

(i) Molecular Models. Molecular mechanics models of $Al(BHB)(iB)_2$ were created using locally derived force field parameters for the sp^2-hybridized aluminum center. The structures

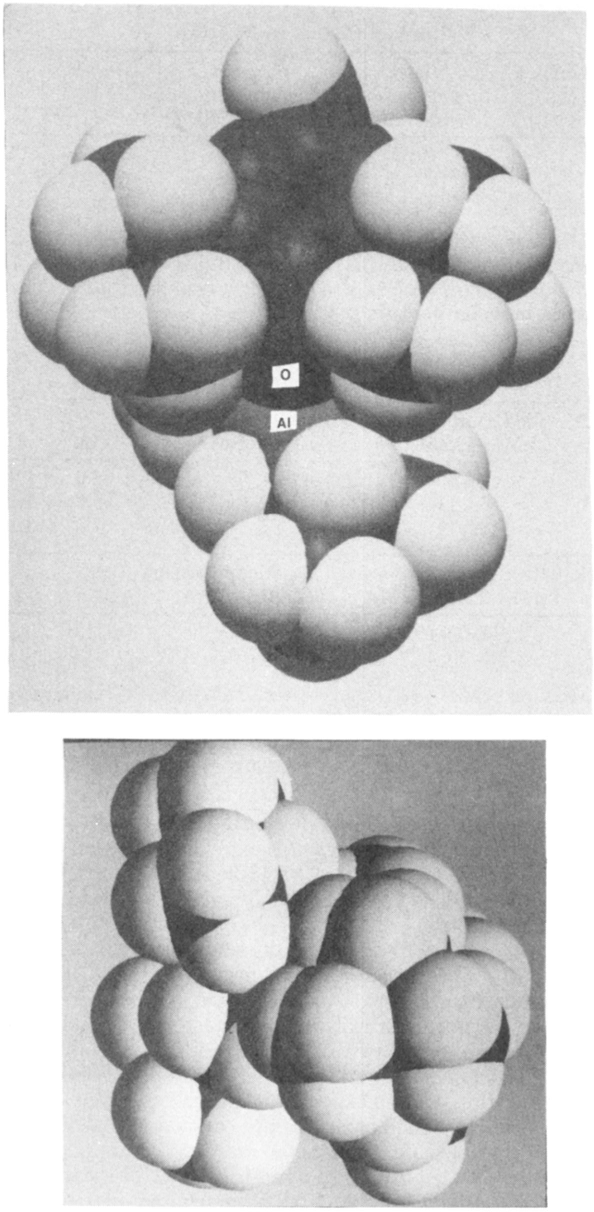
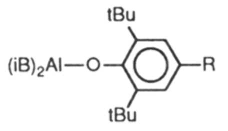


Figure 2. Molecular models of Al(BHB)(iB)$_2$: (a, top) screening of the aluminum (Al) and oxygen (O) atoms by adjacent alkyl groups, (b, bottom) rear view of the molecule.

were optimized to their global energy minima by standard minimization techniques. Solid rendered CPK and van der Waals images of the models were demonstrated and are discussed in the text.

Results

Initiating System. The aluminum alkyl which is most effective in allowing the polymerization temperature to be increased to an economically sensible range incorporates the aryloxy substituent and has the structure **3** (R = H, Me).



3

The structure of **3** is given in Figure 2 and shows that access to the aluminum alkyl for complexation with the lithium cation is restricted to one side of the molecule. This structure was obtained using recently developed computer graphics software.

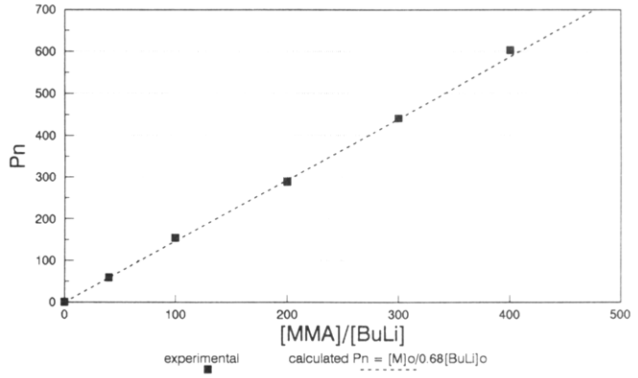


Figure 3. Comparison of the number average molecular weight determined (P_n) with that predicted from the ratio of $[M]_o/[BuLi]_o$: experimental points (□); (- - -) computed from eq 17 for $\alpha = 0.68$. Data are from Table III for Al(BHT)(iB)$_2$ only. $[Al(BHT)(iB)]_o/[BuLi]_o = 2$; $[M]_o = 1.87$ mol/L.

It is evident from Figure 2 that the oxygen atom is not shielded by the Al atom from this side of the molecule and would be equally accessable to the lithium atom within the hydrocarbon cavity. Whereas computer graphics show the hydrocarbon ligands at the rear of the molecule, they totally enclose the Al atom which is therefore not accessable from this side. The screen effect of these aluminum alkyls increases the stability of the propagating end where the lithium cation is located. In toluene solution, the stability of the complex is such that the systems have lifetimes in excess of 48 h at temperatures −5 to +15 °C. In Table I dimensions of known gegenions are compared with lithium aluminates derived from **3**.

Characteristics of the Polymerization. In Table II is summarized a series of experiments which shows the effect of the proportion of aluminum alkyl on the course of the polymerizations in the presence of *tert*-butyllithium. Experimental details are given under (e), and the aluminum alkyl **3** (R = Me) is represented in the abbreviated form as Al(BHT)(iB)$_2$.

In these experiments when the concentration of the aluminum alkyl exceeds that of the *tert*-butyllithium, polymerization proceeds to completion. There seems to be little advantage to having an excess of **3** except to remove adventitious impurities introduced during handling of the reactants. It is also evident from Table II that when $[Al(BHT)(iB)_2]_o < [BuLi]_o$ that reaction efficiency declines. Moreover, the microstructure of the polymer changes from 70% syndiotactic to 50% with a corresponding increase in isotacticity.

An important quantitative aspect to these polymerizations is that the number average degree of polymerization (P_n) of the polymer obtained exceeds that predicted from the ratio $[M]_o/[BuLi]_o$ by a significant amount. The values of P_n are not affected by the amount of aluminum alkyl present provided $[Al(BHT)(iB)_2]_o \geq [BuLi]_o$. A more detailed study of this aspect is summarized in Table III using aluminum alkyls with two different aryloxy ligands. The average figures from Table III are plotted in Figure 3 which shows that there is a linear relationship between values of P_n obtained and the ratio $[M]_o/[BuLi]_o$. Moreover, it is evident from this data that not every *tert*-butyllithium present at the beginning of the polymerization is forming a polymer chain. This will be considered in detail later.

It is evident from the values of D given in Tables II and III, that the molecular weight distributions are close to those described by Poisson statistics. In kinetic terms this means that the initial reaction of *tert*-butyllithium aluminum alkyl complex with the monomer is rapid compared to the subsequent polymer growth reaction and there are no processes which inactivate the propagating centers. These conclusions are confirmed by the experiment described in Table IV, the details of which are given in experimental section e. Four equal aliquots of monomer were added to a toluene solution of the catalyst system described in Table I whilst the temperature was maintained close to 0 °C. After each addition, which took place over a period of 5 min, a 1-h interval was allowed. As will be seen from the fourth column in Table IV, the increase in molecular weight following each addition was the same within experimental error. This shows that the propagating centers persist throughout these experiments with no loss in concentration. In separate studies in which reactions are carried out on a kilogram scale and contamination by oxygen and water in the atmosphere is at a very minimum, propagating centers can be kept for a considerable time at 0 °C without loss of activity. This is demonstrated by the observations that subsequent additions of monomer, after prolonged storage, give the expected increase in molecular weight with no broadening of the molecular weight distribution.

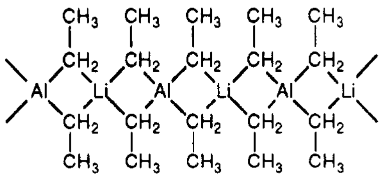
These initiator systems are able to polymerize methacrylate monomers in which the alkyl ester group differs from methyl. When such mixtures of MMA with other methacrylates are added to the toluene solution, random copolymerization occurs because of the close similarity of the reactivity ratios with MMA. A typical copolymerization between MMA and *n*-butyl methacrylate is given in Table VI. It should be noted that the molecular weight distribution obtained is similar to that for the homopolymerization, showing that the propagating center is stable. The synthesis of block copolymers of MMA with other methacrylates is therefore possible. The stability of the propagating species makes it possible to synthesize block copolymers in which the block length can be varied, examples are given in Table VII.

Discussion

Structure of the Initiation Species. The initiator system is formed by premixing the lithium alkyl with aluminum alkyl at 0 °C in toluene solution. This process is accompanied by an exotherm indicating that compound formation of some type has occurred. Reactions between lithium alkyls and aluminum alkyls are well established. An important system is the reaction of ethyllithium and triethylaluminum[5] which produces a crystalline solid from benzene solution in accordance with the equation

$$LiC_2H_5 + Al(C_2H_5)_3 = Li(AlC_2H_5)_4 \qquad (3)$$

This has been studied in some detail and the structure defined using wide-angle X-ray scattering. Lithium aluminum alkyls belong to a group of organometallic compounds[7] in which the two metal atoms are alternately linked through carbon bridges. $LiAl(C_2H_5)_4$ is oligomeric and should be written $[LiAl(C_2H)_4]_n$. Molecular dimensions measured show that there is no direct bonding between Li and Al and that the solid-state structure can be represented by **5**. Dissolution of the solid in an organic solvent will be accompanied by depolymerization. The extent to which this occurs will be dictated by the nature of the solvent. Strongly coordinating solvents such as tetrahydrofuran and dioxan will result in total disruption of the compound into lithium and aluminum alkyls, these will be separately coordinated to the cyclic ether. In hydrocarbon solvents such as benzene, toluene, and cyclohexane dissolution of **5** will occur, giving low molecular weight species. This process is more facil at higher temperatures, but in hydrocarbon solvents the oligomeric form **5** may persist.



5

It is evident from the molecular weight studies described in Table III that not all the *tert*-butyllithium added at the beginning of the polymerization is available for initiation. The degree of polymerization (P_c) computed from the ratio $[M]_0/[BuLi]_0$ is less than that obtained from molecular weight measurements (P_n). In fact P_n/P_c is approximately 1.5 and of the several catalysts we have studied[10] this ratio is never an integer and has values defined by

$$1 < P_n/P_c < 2 \qquad (4)$$

Clearly, there are two species present derived from an oligomer structure related to **5**. These differ structurally and we define them as L_2 and L_1 to represent dimeric and monomeric species.

L_2 has two lithium atoms but only one is accessible for polymerization; the other is totally screened and not available for reaction. L_1 has only one lithium atom and this is accessible for polymerization. We can with this model write the following statements:

$$[BuLi]_0 = 2[L_2] + [L_1] \qquad (5)$$

$$P_n = [M]_0/([L_2] + [L_1]) \qquad (6)$$

$$P_c = [M]_0/[BuLi]_0 \qquad (7)$$

The terms in square brackets represent the molar concentrations of these species. With the data in Table III and eqs 5–7 we can compute the concentrations of L_1 and L_2 and the proportion of active lithium given by (8) and

$$\alpha = ([L_1] + [L_2])/[BuLi]_0 \qquad (8)$$

the results are given in Table VIII. By comparison of the relative amounts of L_2 and L_1, it is evident that they are present in concentrations which are of similar order of magnitude but vary over a significant range. In the initial formation of the lithium aluminum alkyl in toluene, it seems that the formation of L_1- and L_2-type structures are equally probable and variations in mixing procedure could account for the random fluctuations in the relative amounts of L_1 and L_2 within the range.

The proportion of lithium used in the polymerization, computed using eq 8, is more consistent. This accounts for the linear relationship between P_n and $[M]_0/[BuLi]_0$ described in Figure 3. The average value of α shows that 68% of the *tert*-butyllithium is utlized in initiating the polymerization.

The theoretical line in Figure 3 has been computed using this result. It is evident from eq 8 that if $[L_1] = 0$ then α will have a value of 0.5 whereas if $[L_2] = 0$ then $\alpha = 1$. None of the initiation systems studied has had values of α as high as the latter. On the other hand values of α of 0.53 are obtained with initiators derived from aluminum alkyls with ligands which do not include the phenoxy group.[10] In these systems polymerization by the L_2 species

Table VIII
Computation of the Concentration of Propagating Centers, L_1 and L_2, and the Fraction of Active Lithium Species, α, Using Equation 8 and Data from Table III for Al(BHT)(iB)$_2$[a]

P_c	P_n	10^3[BuLi]$_o$ (mol/L)	10^3[L_2] (mol/L)	10^3[L_1] (mol/L)	α
40	59	46.8	15.1	16.6	0.68
40	59	46.8	15.1	16.6	0.68
40	64	46.8	17.5	11.7	0.63
100	136	16.7	4.95	8.8	0.74
100	172	18.7	7.83	3.0	0.58
300	411	6.23	1.68	2.87	0.73
300	385	6.23	1.38	3.48	0.78
400	590	4.68	1.51	1.66	0.68
400	617	4.69	1.68	1.39	0.65

[a] Averages: Active lithium = 68.1%; [L_1]/[BuLi]$_o$ = 36.3%; [L_2]/[BuLi]$_o$ = 31.9%.

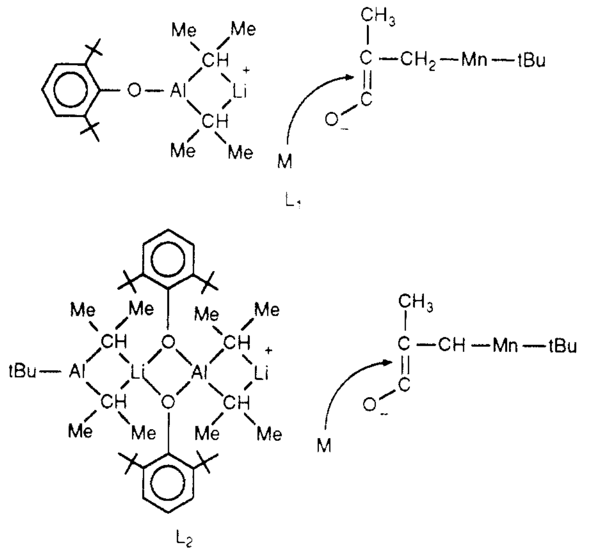


Figure 4. Proposed structures of the propagating centers L_1 and L_2 based on the X-ray structure of Li[Al(Et)$_4$].

dominates. Values of $\alpha < 0.5$ would imply the presence of higher oligomers of L_1 than L_2. This has not been observed.

Possible structures for the propagating centers are shown in Figure 4. The structure of L_2 shows the two lithium atoms have different environments. One of these is identical with that in L_1 and is the atom at which monomer addition to the growing end of the polymer chain occurs. The propagation reaction is by insertion in which the lithium cation does not change its position relative to the gegenion. Precoordination to the lithium is not excluded.

The structures shown in Figure 4 are consistent with the polymerization of MMA-d_8 described in experimental section g. NMR analysis of the deuterated polymer shows that the alkyl group bonded to the polymer chain is the $(CH_3)_3C$ moiety derived from the *tert*-butyllithium. None of the alkyl groups attached to aluminum are involved in the initiation process.

The second lithium atom in L_2 is not involved in the polymerization. Molecular graphics show that the screening by the surrounding groups in L_2 isolates the lithium atom completely and is therefore not accessible to the monomer.

The overall rate of polymerization will therefore be

$$-\frac{d[M]}{dt} = k_1[L_1][M] + k_2[L_2][M] \qquad (9)$$

where k_1 and k_2 are the velocity constants for polymer growth at species L_1 and L_2, respectively.

Molecular Weight Distributions

The PMMA molecules are produced from two centers L_1 and L_2. The rate of formation of a chain X_n containing n units of MMA is as follows

$$2\frac{d[X_n]}{dt} = (k_1 + k_2)[X_{n-1}][M] - (k_1 + k_2)[X_n][M]$$
$$= (k_1 + k_2)[M]([X_{n-1}] - [X_n]) \qquad (10)$$

the factor 2 derives from the fact that both L_1 and L_2 produce a polymer of n units. Combining with (9) gives

$$\frac{d[X_n]}{d[M]} = \frac{k_1 + k_2}{2(k_1[L_1] + k_2[L_2])}([X_{n-1}] - [X_n]) \qquad (11)$$

Since the molecular weight distributions are narrow it follows, therefore, that in any given polymerization the relative amounts L_1 and L_2 are constant. It follows therefore from (5) and (8) that (11) can be amended as follows

$$\frac{d[X_n]}{d[M]} = \frac{k_1 + k_2}{2[k_1(2\alpha - 1) + k_2(1 - \alpha)]}\frac{[X_{n-1}] - [X_n]}{[BuLi]_o} \qquad (12)$$

and rearranged to give

$$\frac{d[X_n]}{d[M]} + \frac{[X_n]}{[X]_o} = \frac{[X_{n-1}]}{[X]_o} \qquad (13)$$

where

$$\frac{1}{[X]_o} = \frac{k_1 + k_2}{2[k_1(2\alpha - 1) + k_2(1 - \alpha)]}\frac{1}{[BuLi]_o} \qquad (14)$$

The term $[X]_o$ is a constant and independent of conversion. Equation 13 is the well-known form of the differential of the Poisson distribution.[11] Successive integration of (13) gives the distribution for the polymer produced with this initiation system. On complete reaction this is

$$\frac{[X_n]}{[X]_o} = \left(\frac{[M]_o}{[X]_o}\right)\frac{\exp(-[M]_o/[X]_o)}{(n-1)!} \qquad (15)$$

It can be shown from eq 15 that the number average degree of polymerization is $[M]_o/[X]_o$. Stated in a simpler form $[X]_o$ must be identical to the term α[BuLi]$_o$.

This is possible in eq 14 if $k_1 = k_2$. Moreover if [L_1] = 0, then (14) becomes $[X]_o$ = 0.5[BuLi]$_o$ and, finally, when $(2\alpha - 1) = (1 - \alpha)$, $[X]_o$ = 0.67[BuLi]$_o$. The latter is observed with the initiator system reported here. Notwithstanding the fact that the polymerization is occurring at two centers, a narrow molecular weight distribution is possible even if their rates differ. This type of distribution is not strictly of the Poissan type as is evident from Tables II–IV.

Effect of Temperature on Polymerization Rates

It is possible to obtain an approximate value for the overall velocity constant k_p in the equation

$$-\frac{d[M]}{dt} = k_p\alpha[BuLi]_o[M] \qquad (16)$$

When (16) is compared with (9) and since, from Table VIII, [L_1] ≈ [L_2], we arrive at the approximation that

$$k_p \approx (k_1 + k_2)/2$$

Table IX
Comparison of Values of k_p[a]

	k_p [L/(mol s)]	half-life
adiabatic	73	0.9 s
isothermal	0.23	16.3 min

[a] Orders of magnitude computed from initial rate data for PMMA M_n = 61 000.

Also from eqs 6 and 8 the degree of polymerization of the polymer at complete reaction is

$$P_n = [M]_0/\alpha[BuLi]_0 \qquad (17)$$

Initial rate studies at 0 °C have enabled 1 order of magnitude values of k_p to be obtained. These are compared in Table IX for solution polymerizations and those carried out in the absence of solvent. Also given are approximate values for the half-life of the monomer.

It is evident from Table IX that in the absence of a solvent, polymerization is extremely fast, occurring in a matter of a few seconds. There is no induction period preceding this extremely rapid reaction and thermocouple readings given in Table V show that temperatures well in excess of 100 °C are rapidly achieved. Reactions in a pressurized reactor show temperatures of 150 °C can be reached with similar reaction times. It has been shown that in toluene the normal lifetime of the propagating species declines rapidly above 40 °C. This conflicting behavior can only be explained if the rate of polymerization is very fast compared to reactions of the type shown in eq 2, which lead to a loss of propagating centers.

At temperatures normally used to synthesize PMMA by anionic initiation (−78 °C), the polymerization is extremely slow and low molecular weight polymers are obtained. The reasons for this are not clear since the reduction in rate is larger than the expected dependence of k_p on temperature would predict. A possible explanation is that the proportion of lithium atoms available for initiation is reduced due to the formation of oligomers of the type L_n where $n > 2$.

Concluding Remarks

The important contribution of this paper is to show that certain combinations of lithium and aluminum alkyls enable polymerizations of methyl methacrylate to be carried out at ambient temperatures and above.

The work also shows that both the lithium and aluminum components must contain alkyl groups which have cross-sectional areas as large as possible. Moreover, these initiators are only effective in hydrocarbon solvents in which they are soluble. Solvents which have previously been preferred for anionic and catalyzed anionic polymerization, such as tetrahydrofuran, dimethoxyethane, etc., inactivate these initiators. In hydrocarbon solvents the separation between the anionic and cationic components are minimized and the high cross-sectional area of the latter screens the propagating terminus of the polymer chain from side reactions. Thus we refer to this polymerization of methacrylate monomers as screened anionic polymerization.

A model has been developed which accounts for the quantitative observations given in the Experimental Section. This is based on the known structures of lithium aluminum alkyls[7] and previous studies of the anionic polymerization of styrene[12] where two propagating centers are involved but narrow molecular weight distributions are obtained.

NMR studies show that solutions of these lithium aluminum alkyls are complex and not readily interpreted. Additional studies using deuterated species may be of value in understanding this initiator system better.

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Registry No. (MMA)(BMA) (copolymer), 25608-33-7; (MMA)(BMA) (block copolymer), 107404-23-9; PMMA, 9011-14-7; Al(BHT)(iB)$_2$, 56252-56-3; (iB)$_3$Al, 100-99-2; Al(BHB)(iB)$_2$, 76229-55-5; 2,6-di-*tert*-butyl-4-methylphenol, 128-37-0; 2,6-di-*tert*-butylphenol, 128-39-2; *tert*-butyllithium (2:1), 594-19-4.