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Anionic Polymerization of Alkyl (Meth)acrylates Using Metal-Free Initiators: Effect of Ion Pairing on Initiation Equilibria

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ABSTRACT: Metal-free anionic polymerizations of alkyl (meth)acrylates using tetrabutylammonium salts of diethylphenylmalonate, fluorene, and 9-ethylfluorene as initiators were performed in THF at 30 °C. A poor control of molecular weights, inconsistent initiator efficiencies, and broad or bimodal molecular weight distributions were obtained. The effect of counterion nature was studied from the polymerization of methyl methacrylate using the 1,1-diphenylhexyl anion with tetrabutylammonium, tetramethyldiethylguanidinium, and lithium as counterions under otherwise identical conditions. Metal-free initiators resulted in incomplete initiation which is attributed to the fact that the initiation is an equilibrium reaction. In conjunction with possible side reactions such as Hofmann elimination and transfer reactions, this leads to broad and bimodal molecular weight distributions of the resulting polymers.

Introduction

The controlled anionic polymerization of acrylic monomers is characterized by a high degree of complexity due to the presence of ester groups that undergo side reactions with the initiator as well as with the propagating chain ends.[1] Webster and co-workers[2] demonstrated the possibility of a living polymerization of methacrylic esters at room temperature using silyl ketene acetals as initiator and nucleophilic or Lewis acid catalysts. Subsequently, several other initiating systems have been shown to give a controlled polymerization of methacrylic esters at room temperature, namely, metal-free cations,[3] phosphor ylide mediated metal-free cations,[3f−j] ligand-modified classical cations,[4] transition metal containing initiators,[5] and aluminum coordinated initiating systems.[6]

Of these, the metal-free initiators are of great interest owing to their low cost as well as their claimed ability to polymerize primary acrylates at room temperature. Reetz and co-workers[3] used, for the first time, metal-free carbon or nitrogen nucleophiles as initiators for the controlled anionic polymerization of *n*-butyl acrylate. Poly(*n*-butyl acrylate)s of moderately narrow molecular weight distribution were synthesized using tetrabutylammonium salts of malonates as initiators at room temperature. Using this strategy, several functional metal-free initiators consisting of tetrabutylammonium salts of oxazoline-functionalized malonates were prepared by us and others[7−9] for the polymerization of alkyl acrylates. Pietzonka and Seebach[7f] used the P_4-*tert*-butylphosphazene salt of ethyl acetate for the controlled polymerization of MMA in THF at elevated temperature. Recently, Börner and Heitz[7g] have shown the complexity of the polymerization of *n*-butyl acryate using the P_4-*tert*-butylphosphazene base/methyl isobutyrate initiating system.

Zagala and Hogen-Esch[3f,i] reported a living polymerization of methacrylates using the tetraphenylphosphonium counterion at ambient temperatures in THF. This system produces poly(methyl methacrylate) with predictable molecular weights with high initiator efficiencies and with narrow molecular weight distribution. It was found that this polymerization involves a phosphor ylide as a dormant species.[3g,h]

In contrast, the polymerization of alkyl (meth)acrylates using tetrabutylammonium counterion proceeds with a characteristic induction period, incomplete conversion, and inconsistent as well as low initiator efficiency ($f < 0.2$). In some cases, initiator eficiencies of more than 100% were observed.[7c] Preliminary kinetic results confirmed that this polymerization has considerable induction periods, nonlinear time conversion plot, and broader MWD's than reported before.[8]

This paper presents new data on the metal-free anionic polymerization of alkyl (meth)acrylates using initiators containing tetrabutylammonium and tetramethyldiethylguanidinium countercations in THF (Scheme 1) and discusses the problems associated with these polymerizations.

Experimental Section

Reagents. Tetrahydrofuran, toluene, and N_2 gas were purified as reported in the literature.[7] Methyl methacrylate (MMA, Aldrich), methyl acrylate (MA, Aldrich), *n*-butyl acrylate (nBA, Aldrich), and *tert*-butyl acrylate (tBA, Aldrich) were first vacuum distilled from CaH_2 and redistilled under reduced pressure in the presence of a small amount of triisobutylaluminum, just prior to the polymerization experiment. Diethylphenylmalonate (DEPM, Aldrich) and dimethylmalonate (DMM, Aldrich) were used as received. Fluorene (Fl, Merck, Bombay) was recrystallized in dry *n*-hexane or THF. 9-Ethylfluorene (9EFl, Fluka) was distilled under high vacuum and stored in a refrigerator. Diethylamine (Fluka) and dichloromethane (Aldrich) were distilled over CaH_2. *N*,*N*,*N*′,*N*′-tetra-

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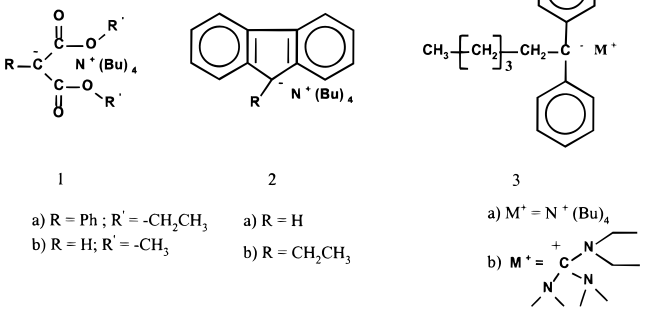
Scheme 1. Metal-Free Anionic Initiators Used for Alkyl (Meth)acrylate Polymerization



methylurea (Fluka) and oxalyl dichloride (Aldrich) were used as received without any further purification. *n*-BuLi (1.6 M in hexane, Aldrich) was used after determining its actual concentration by Gilman's double-titration method. Diphenylethylene (DPE, Aldrich) was titrated with a small amount of *n*-BuLi and distilled under high vacuum.

Tetra-*n*-butylammonium hydroxide (TBAOH, 20% solution in toluene/methanol, SD fine chemicals, Bombay) was used as received after determining its concentration by titration against standard acid solution. Tetra-*n*-butylammonium chloride (TBACl, Fluka) was twice recrystallized in THF and dried under dynamic high vacuum for 2 days and stored at room temperature in a glovebox. Tetramethyldiethylguanidinium chloride (GC) was synthesized in THF by reacting *N*,*N*,*N*′,*N*′-tetramethylchloroformamidinium chloride with diethylamine as reported in the literature.[14] *N*,*N*,*N*′,*N*′-Tetramethylchloroformamidinium chloride was prepared by the reaction of *N*,*N*,*N*′,*N*′-tetramethylurea and oxalyl dichloride in 1,2-dichloroethane as reported in the literature.[14] The pale yellow crystals of GC were found to be insoluble in THF. ^{13}C NMR in $CDCl_3$(100 MHz, ppm): 11.14 ($N-CH_2-CH_3$), 38.47 ($N-CH_3$), 41.74 ($N-CH_2-$), and 160.8 (C^+, cation).

Initiators. 1,1-Diphenylhexyllithium (DPHLi) was prepared by reacting a known amount of *n*-BuLi with a slight excess of DPE in THF at −40 °C. Fluorenylpotassium and 9-methylfluorenylpotassium were prepared by metalation of the hydrocarbons with potassium mirror in THF under vacuum. The concentration of these initiators was determined by Gilman's double-titration method. Tetrabutylammonium salts of diethylphenylmalonate, dimethylmalonate, and fluorene were prepared by deprotonation with Bu_4NOH (TBAOH) as reported earlier.[7a,b]

Initiators were obtained as pale crystals of tetrabutylammonium diethylphenylmalonate (**1a**), white crystals of tetrabutylammonium dimethylmalonate (**1b**), and dark-orange crystals of tetrabutylammonium fluorenide (**2a**). They were characterized by NMR and stored under N_2 in a refrigerator. The initiators were dissolved in a known amount of THF, and the concentration was determined by hydrolyzing with excess standard HCl acid of known concentrations and back-titration of residual HCl with standard NaOH solution using phenolphthalein as indicator.

Tetrabutylammonium diethylphenylmalonate (**1a**): pale crystals; ^{1}H NMR (300 MHz, DMSO-d_6) δ; 1.0 (t, $N-CH_2CH_2CH_2CH_3$), 1.5 (m, $N-CH_2CH_2CH_2-$), 1.7 (m, $N-CH_2CH_2-$), 3.4 (m, $N-CH_2-$), 4.2 (q, $-O-CH_2-$), 1.25 (t, $-O-CH_2CH_3$), and 7.4 (m, phenyls). ^{13}C NMR (75.5 MHz, in THF) ppm; 13.8 ($N-CH_2CH_2CH_2CH_3$), 23.1 ($N-CH_2CH_2CH_2-$), 27.1 ($N-CH_2CH_2-$), 61.5 ($N-CH_2-$), 81.1 (C^- anion), 171.5 (C=O), 59.2 ($-O-CH_2-$), 19.2 ($-O-CH_2CH_3$), phenyl carbons 148.4, 129.4, 135.6, 123.8 ppm.

Tetrabutylammonium fluorenide (**2a**): dark-orange crystals; ^{1}H NMR (300 MHz, DMSO-d_6) δ; 0.98 (t, $N-CH_2CH_2CH_2CH_3$), 1.49 (m, $N-CH_2CH_2CH_2-$), 1.7 (m, $N-CH_2CH_2-$), 3.5 (m, $N-CH_2-$), 5.82 (s, CH^- anion), 6.38 (t, aryl H-2,7), 6.78 (t, aryl H-3,6), 7.18 (d, aryl H-1,8), 7.78 (d, aryl H-4,5). ^{13}C NMR (75.5 MHz, in THF) ppm; 14.5 ($N-CH_2CH_2CH_2CH_3$), 20.6 ($N-CH_2CH_2CH_2-$), 24.4 ($N-CH_2CH_2-$), 58.2 ($N-CH_2-$), 84.4 (CH^- anion), 122.9 (C), 119.76 (C-1,8), 109.25 (C-2,7), 117.42 (C-3,6), 120.23 (C-4,5), and 137.7 (C).

Tetrabutylammonium salts of 1,1-diphenylhexane (DPHTBA), fluorene (FlTBA), and 9-methylfluorene (9MFlTBA) were prepared in situ by reacting its precursor metal salts with dry tetrabutylammonium chloride in THF at −40 °C. Similarly, tetramethyldiethylguanidinium salts of 1,1-diphenylhexane was prepared in situ by reacting DPHLi with tetramethyldiethylguanidinium chloride (GC). The red color of the DPHLi anion changed into a deep-purple color upon reaction with THF solution containing TBACl and to a wine-red color upon reaction with tetramethyldiethylguanidinium chloride at −40 °C, indicating the exchange of cations from Li^+ to TBA^+ and G^+, respectively.

Polymerization of Alkyl (Meth)acrylates. Batch polymerization was carried out in a flamed glass reactor under pure nitrogen atmosphere. The required amount of initiator solution in THF was added into the reactor containing 35 mL (or 70 mL) of THF. The purified alkyl (meth)acrylate neat (3 or 5 mL) or diluted in THF (1:2 v/v) was added to the initiator solution slowly (1 mL/min) at 30 °C. After 3−5 min of monomer addition, the reaction temperature rose by 10−15 °C. In all cases, the initiator color did not disappear completely and persisted throughout the polymerization. The reaction was terminated after 15 min and in some case 2 min with methanol containing a small amount of dilute HCl. The residual initiator color disappeared upon addition of termination agent.

Poly(methyl acrylate) (PMA), poly(*n*-butyl acrylate) (PnBA), and poly(*tert*-butyl acrylate) (PtBA) were recovered by evaporating THF and extracting the polymers in ether or CH_2Cl_2. After aqueous workup, the polymers were dried in high vacuum for 3 h. Poly(methyl methacrylate) (PMMA) was recovered by precipitation in *n*-hexane and dried under vacuum at 60 °C for 4 h.

Characterization of polymers was carried out by using a Waters SEC 150C equipped with 100, 500, 10^3, 10^4, and 10^5 Å μ-Ultrastyragel columns and THF as the eluent at a flow rate of 1 mL min^{-1} at 30 °C. Standard monodisperse poly(methyl methacrylate)s (Polymer Laboratories) were used for calibration. NMR was recorded on a Bruker 300 MHz spectrometer using D_2O as internal lock.

Results and Discussion

Polymerization of Alkyl (Meth)acrylates in the Presence of Tetrabutylammonium Counterion. The anionic polymerization of methyl acrylate (MA), *n*-butyl acrylate (nBA), *tert*-butyl acrylate (tBA), and methyl methacrylate (MMA) was performed using various tetrabutylammonium salts (**1a**, **2a**, and **2b**) in THF at 30 °C. The results are given in Table 1. In all cases, after 2 min of monomer addition, the temperature rose to 40−45 °C depending on the initiator and monomer concentrations, indicating the presence of a considerable induction period. A faint pale-yellow color of the initiator (**1a**), even after all monomer was added, was visible to the naked eye. The color persisted throughout the polymerization and disappeared only upon termination using methanol containing a small amount of diluted HCl. The polymerization of MMA using tetrabutylammoniumfluorenyl (**2a**) and tetrabutylammonium 9-ethylfluorenyl (**2b**) as initiator was characterized by an orange color of the residual initiator, indicating an incomplete initiation (Table 1, runs 7−9 using **2a** and runs 10 and 13 using **2b**).

The appearance of residual initiator color during the polymerization strongly depends on the initiator and the monomer concentration. Reetz and co-workers[9] had also observed the persistence of initiator color during polymerization. Warzelhan et al.[10a] reported an observation of unreacted initiator after complete monomer

Table 1. Data on the Anionic Polymerization of Alkyl (Meth)acrylate Monomers Using Various Tetrabutylammonium Salts in THF at 30 °C[a]

run	monomer	$[I]_0 \times 10^{-3}$, mol/L	$[M]_0$, mol/L	yield, %	$M_{n,cal}$[b]	$M_{n,SEC}$[c]	M_w/M_n[d]	f[e]
Initiator: Tetrabutylammonium Diethylphenylmalonate (**1a**)								
1[f]	MA	8.44	2.00	95	20 000	4 000	3.7	5.00
2[f]	MA	8.66	1.76	85	17 000	3 300	3.7	5.15
3	nBA	7.08	1.16	92	21 000	23 700	2.73[g]	0.88
4[f]	nBA	19.13	11.63	96	7 800	8 900	3.36[g]	0.87
5[f]	tBA	11.60	0.725	96	8 300	38 300	1.69	0.22
6	tBA	137.20	1.896	95	1770	7 000	1.62	0.25
Initiator: Tetrabutylammonium Fluorenide (**2a**)								
7[h]	MMA	13.80	0.790	100	5 700	4 350	1.44	1.31
8	MMA	10.76	0.659	100	6 100	4 140	1.32	1.47
9	MMA	5.67	0.688	100	12 200	7 060	1.45	1.72
Initiator: Tetrabutylammonium 9-Methylfluorenide (**2b**)								
10	MMA	10.00	0.685	96	6 360	6 900	bimodal	0.92
11	MMA	5.50	1.170	>95	21 300	13 500	bimodal	1.57
12	MMA	1.76	0.187	>95	10 600	16 100	1.47	0.66
13	MMA	10.20	0.163	100	1 600	5 800	1.94	0.27
14	MMA	2.75	0.425	>95	15 500	20 100	2.70	0.76

[a] Monomer in THF (1:2 v/v) was added drop by drop. After 2−5 min of induction period, strong rise in temperature (∼10−15 °C) was noticed in all cases. [b] $M_{n,cal}$ = (grams of monomer/moles of initiator). [c] Obtained using calibrated with standard PMMA. [d] M_w/M_n obtained from SEC. [e] Initiator efficiency, $f = M_{n,cal}/M_{n,SEC}$. [f] Polymerization was conducted at 0 °C. [g] Bimodal distribution having a shoulder at peak maximum. [h] Initiator was prepared by deprotonation of fluorene using TBAOH in toluene.

consumption while using fluorenylsodium as initiator for the polymerization of MMA. They attributed this to a slow initiation. Similar results were obtained in the polymerization of MMA using the potassium and tetrabutylammonium fluorenyl salts.[3j] However, experiments carried out using low initiator concentration (<3 mmol/L) of **2b** showed that the color of initiator solution changed slowly to colorless upon addition of MMA (Table 1, runs 1, 12, and 14). This observation is consistent with the results obtained by Quirk and coworkers.[11] Using the Bu_4N^+ salt of 9-methylfluorene as initiator, at low initiator concentration (10^{-3} mol/L), they obtained PMMA of broad MWD ($M_w/M_n = 2.16$) in low yield (24%).

The eluograms of the obtained poly(methyl acrylate) (PMA), poly(*n*-butyl acrylate) (PnBA), and poly(*tert*-butyl acrylate) (PtBA) as well as PMMA are characterized by broad molecular weight distributions which in some cases were bimodal (PnBA, Table 1, runs 3 and 4). Although quantitative conversions were obtained in all cases, the observed residual initiator color suggests that not all of the added initiator participated in the polymerization. It should be noted that the initiator efficiencies are not consistent. In some cases, PMA and PMMA synthesized using **1a** and **2a**, respectively, shows a lower M_n than calculated from the feed ratio of monomer to initiator.[12] The alkoxide anions formed from the Claisen reaction between the ester enolate and the antepenultimate ester group ("backbiting") reactions may act as an initiator resulting in a larger number of polymer chains. This effect, which resembles spontaneous transfer, was observed first by Müller et al.[13a] in the polymerization of MMA with Cs^+ counterion at $T >$ 0 °C in THF. It was also reported in the polymerization of acrylates in the presence of metal-free cations in THF.[3i,7g,13f] Also, the presence of α-hydrogen in the backbone of the polyacrylate chains may lead to a transfer reaction, resulting in the formation of branched polymers. Generation of new initiating species during the polymerization and the formation of branched polymers would result in lower apparent SEC molecular weight. The MWD's of the obtained polymers are very broad and decrease in the order MA > *n*BuA > *t*BuA (Table 1). This is indicative of the presence of secondary reactions such as backbiting or transfer reaction and indicates that the rate of such termination reactions also follows in the same order.

UV spectroscopy of PMMA prepared using **2a** as initiator indicated much less fluorene present in the polymer than used for initiation. The number-average molecular weights of obtained polymers were much less than accounted for by the fluorene detected in the polymer. A possible transfer reaction to the fluorenyl group at the 9-position would result in a bifunctional growing chain leading to the formation of two polymer chains originating from the same fluorene moiety.[10] This may account for the decreased fluorene content in the polymer.

The rate of polymerization of MMA using **2a** and **2b** seems to be high as evident from a local polymerization resulting in precipitation of PMMA while adding MMA at high concentration of initiator (Table 1, runs 10 and 13). The polymers obtained using initiators **2b** as well as **3a** and **3b** (discussion follows, Table 2) have a higher M_n than the calculated ones. The obtained PMMAs exhibit a bimodal or broad molecular weight distribution with either low or high molecular weight tailings (Figure 1). This further confirms the presence of several side reactions that were discussed above such as backbiting or transfer reactions. Hofmann elimination (i.e., proton transfer from alkylammonium ion to the enolate anion) cannot be ruled out. This termination reaction was also observed by Bandermann and co-workers.[13f]

To confirm the presence of residual initiator, the Michael adduction of **2b** and MMA was performed, and the reaction mixture was analyzed by UV/vis spectroscopy before and after MMA addition. Absorption of initiator solution before mixing with MMA was considered as zero time intensity. A solution of MMA (1.17×10^{-2} mol/L) was added to THF containing **2b** (1.1×10^{-2} mol/L) within 2 s using nitrogen pressure at 30 °C, and the initiator concentration was measured by recording the UV/vis spectra with time.

The UV/vis spectrum of the initiator solution showed broad absorption bands at 376 and 512.7 nm in the visible region. Figure 2 shows a plot of intensity of absorption bands of **2b** after addition of MMA with time. After an initial decrease, no appreciable change in the

Table 2. Data on the Anionic Polymerization of MMA[a] Using 1,1-Diphenylhexyl Anion with Tetrabutylammonium, Tetramethyldiethylguanidinium, and Lithium as Counterions in THF at −40 °C

run	[I] × 10^3, mol/L	[M], mol/L	yield, %	$M_{n,cal} \times 10^{-3}$	$M_{n,SEC} \times 10^{-3}$	$M_{w,SEC} \times 10^{-3}$	M_w/M_n[b]	f[c]
			Tetrabutylammonium Counterion (**3a**)					
1	6.7	0.340	94	5.1	28.9	48.2	1.66	0.17
2	4.5	0.374	>94	8.3	52.5	147.9	2.80	0.16
3	4.5	0.748	100	16.6	15.0	29.2	1.94	1.10
4[d]	4.5	0.374	98	8.3	9.6	37.2	3.87	0.86
			Tetramethyldiethylguanidinium Counterion (**3b**)					
5	4.5	0.374	100	8.3	11.6	31.8	2.73	0.71
6	9.71	0.802	100	8.3	9.6	27.7	2.88	0.86
			Lithium Counterion (DPHLi)					
7	2.43	0.534	>95	22.0	26.6	32.3	1.21	0.83

[a] Neat monomer was added within 10−15 s. Initiator color (very low in intensity) persisted throughout the polymerization. Reaction was terminated within 2 min. [b] Bimodal distributions with high molecular weight tailing. [c] Initiator efficiency, $f = M_{ncal}/M_{nSEC}$. [d] MMA was added drop by drop for 1−2 min.

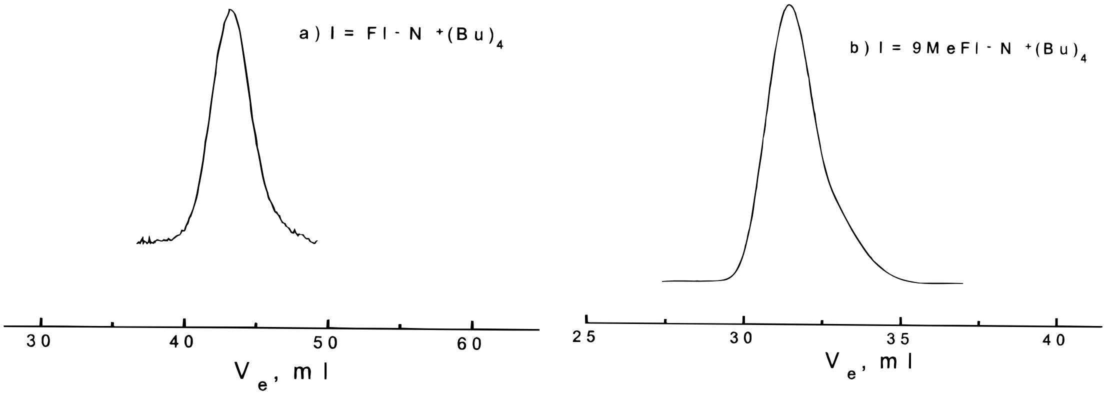


Figure 1. SEC traces of PMMA synthesized in THF at 30 °C using the following initiators: (a) **2a**, $M_{n,SEC} = 4140$, $M_w/M_n = 1.32$, and (b) **2b**, $M_{n,SEC} = 16\,100$, $M_w/M_n = 1.47$.

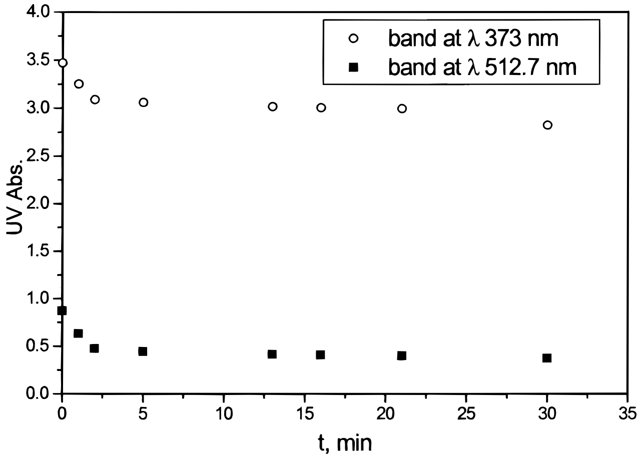


Figure 2. Change in absorptivity with time of initiator **2b** after mixing with MMA.

intensities of these absorption bands is noticed (even after 30 min). This observation is also consistent with the results obtained by Reetz and co-workers,[9] who noticed the persistence of initiator color during polymerization. A slow initiation was considered responsible for the presence of initiator color during polymerization. This confirms that initiation is incomplete and thus raises many questions on the effect of nonmetal cation on the initiation process of anionic polymerization. The presence of residual initiator indicates that the attack of initiator on the carbonyl groups of the monomer or the chain may be assumed to be less significant. The methoxide elimination reaction may have resulted from the attack of propagating species on the carbonyl groups of monomer or polymer (backbiting reaction). This is quite reasonable given the much greater basicity of the ester enolate compared to that of the fluorenyl anion.[17]

The effect of countercations on the anionic polymerization of MMA in THF was studied in the presence of tetrabutylammonium, tetramethyldiethylguanidinium, and lithium counterion using 1,1-diphenylhexyl anion as an initiator (**3a** and **3b**). The results of the polymerization are given in Table 2. The initiators, **3a** (deep purple) and **3b** (wine red), were prepared in situ by reacting the lithium salt of precursor anion (DPHLi) to the THF solution of the corresponding nonmetal chlorides at −40 °C.[15] Neat MMA was added into the initiator solution at −40 °C using a cannula. It was noted that the color of the initiators did not disappear completely even after all the monomer was added (Table 2, runs 1, 2 and 5, 6). A slight initiator color persisted throughout the polymerization and disappeared only upon the addition of methanol after 2 min. The conversions after 2 min were quantitative, indicating a fast polymerization in the presence of nonmetal counterions.

The PMMA's obtained using **3a** and **3b** possess broad/bimodal distributions with higher number-average molecular weights (Table 2, runs 1−6). The initiator efficiencies are lower and inconsistent. Slow, dropwise addition of monomer did not improve the results. The eluogram showed a very broad, bimodal distribution with equal areas of the two peaks (Table 2, run 4). Almost in all cases, a high molecular weight tailing or shoulder was observed in their respective eluograms. In contrast to tetrabutylammonium and guanidinium counterions, the lithium counterion gave better control on the polymerization at −40 °C. The red color of DPHLi immediately disappeared while adding MMA. Typical eluograms for various counterions at similar experi-

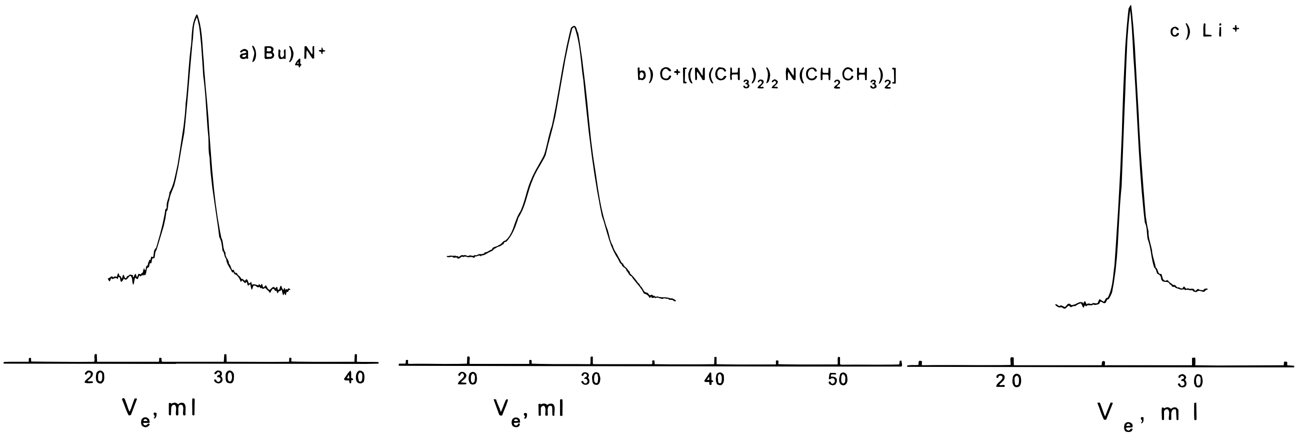


Figure 3. SEC traces of poly(methyl methacrylate) samples initiated with 1,1-diphenylhexyl anion in the presence of different countercations in THF at −40 °C: (a) tetrabutylammonium ion, (b) tetramethyldiethylguanidinium ion, and (c) lithium ion.

mental conditions are given for comparison (Figure 3). It can be seen that under similar conditions the use of lithium as a counterion (DPHLi initiator) resulted in PMMA with narrow molecular weight distribution ($M_w/M_n = 1.21$) at −40 °C in THF (Table 2, run 7). Unlike the lithium counterion, the residual initiator color was seen in non-metal-containing initiating systems depending on the initiator and monomer concentration.

These results confirm that the polymerization of alkyl (meth)acrylates using tetrabutylammonium as counterion is uncontrolled and leads to polymers with broad molecular weight distribution and low initiator efficiency. Recently, Fieberg et al.[13f] have found long induction periods in the polymerization of MMA initiated with tetrabutylammonium diethyl-2-ethylmalonate. They obtained polymers with broad MWD and low initiator efficiencies. This confirms our results of MMA polymerization using **2b**, tetrabutylammonium 9-ethylfluorenide (Table 1, runs 12−14). It appears that the reactivity of a PMMA or PBA enolate with a nonmetal countercation is much higher than initiators **1, 2**, and **3**. A reasonable explanation for incomplete initiation as well as for lower initiator efficiency comes from the experimental observation that the polymerization is very fast compared to initiation with a characteristic induction period in the presence of a nonmetal counterion. Hence, the course of the polymerization is primarily determined by the rate of mixing (monomer to initiator solution), the apparent rate of initiation, and the formation of active centers whose proportions are all set at the initial stages of polymerization.

Kinetic investigation on the metal-free anionic polymerization of MMA using the tetrakis[tris(dimethylamino)phosphoranylidenamino]phosphonium salt of the diphenylhexyl anion at room temperature shows evidence of termination, and the obtained PMMA possesses broad molecular weight distribution with low initiator efficiency ($f = 0.2$).[18] A first-order time conversion plot showed a downward curvature, indicating the presence of termination. The plot of the number-average degree of polymerization vs conversion is linear, indicating the absence of transfer reactions. However, the initiator efficiency, f, was very low ($f = 0.20$) in all cases irrespective of the initial initiator concentration. Since the experiment was done using a flow-tube reactor with short mixing time (<0.5 ms) and the stability of the initiator at room temperature was also confirmed by NMR spectroscopy,[18] it appears that the monomer was depleted by rapid polymerization before the rest of the initiator had a chance to react and thus did not participate in the polymerization. Thus, the reactivity of the propagating enolate anion with nonmetal counterion differs considerably from the initiator in terms of charge distribution.

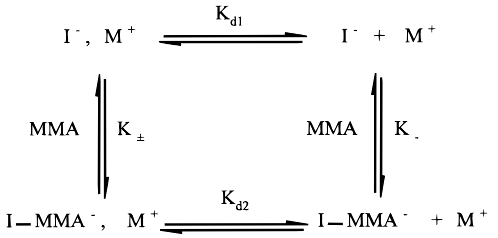
Low initiator efficiencies and induction periods in anionic polymerization have frequently been attributed to slow initiation, i.e., the rate of initiation being considerably smaller than that of propagation ($k_i < k_p$). However, these experimental phenomena can also arise from initiation equilibria. In addition, the fractions of anions, ion pairs, and associates in the initiator and the propagating chain end as well as their reactivities may differ to a large extent. The effect of these conditions on initiator efficiencies and induction periods will be discussed in the next paragraph.

Initiation Equilibria and Effect of Ion Pairing. The ion-pair effect is a most significant factor in the initiation processes of anionic polymerization. We believe that the main reason for often-encountered irreproducibility in metal-free anionic polymerization is because of the inability to achieve rapid and complete initiation with nonmetal necleophiles.[16] This is partly because of the fact that the pK_a values for the C−H dissociation of the malonic esters (~16) and fluorene (~23) compounds are lower compared to that of the esters enolates. The pK_a value of ethyl acetate was calculated by Bordwell[17] to be ca. 30−31. This suggests that initiation is not an irreversible process (though slow compared to propagation, $k_i < k_p$) but an equilibrium process where the equilibrium is shifted to the left-hand (initiator) side ($K_i < 1$):

$$\mathrm{I} + \mathrm{M} \rightleftharpoons \mathrm{I{-}M}^*; \quad K_i = k_i/k_{-i}$$

Evidence for the reversibility of the intiation step can be drawn from “disproportionation” studies of Lochmann amd Müller.[19] When they lithiated the Michael adduct of methyl isobutyrate and MMA (MMA dimer), they observed the formation of methyl α-lithioisobutyrate, oligo(MMA), and oligomers which then undergo Claisen condensation to form cylcic β-keto esters. This was attributed to the retroaddition of MMA from the lithiated dimer to form initiator and MMA. The latter is than added to the residual lithio dimer to form oligomers. In a similar experiment, Bandermann et al.[13f] observed the formation of diethyl tetrabutylammonium ethylmalonate and PMMA when preparing the tetrabu-

Scheme 2. Initiation Equilibrium and Their Ion-Pairing Effects



I^- = malonate or fluorenyl or diphenylhexyl anion

$M^+ = Li^+, Na^+, K^+, Cs^+, N^+(Bu)_4$ or $C^+[(N(CH_3)_2)_2(N(CH_2CH_3)_2)$

tylammonium salt of the malonate–MMA Michael adduct.

The observation that initiator efficiency strongly decreases with increasing ionic radius can now be discussed in light of the initiation equilibrium being driven to the left-hand side with increasing ionic radius. The results suggest that ion pairing of initiator and of the enolate formed plays an important role in the initiation equilibrium.

Chang and Hogen-Esch[20] reported a significant ion-pairing effect on the equilibrium addition of 9-methylfluorenyl ($9MeF^-M^+$) carbanion alkali salts to 1-phenyl-1-(4-pyridyl)ethylene (PPE) in THF using Li^+, Na^+, and Cs^+ as counterions. This process only differs from initiation by the fact that PPE cannot homopolymerize. The apparent equilibrium constant, K_i, calculated using UV/vis spectroscopy, is higher for Li^+ than for Cs^+ by 4 orders of magnitude. The authors explained this effect to the different ion-pairing tendencies of the different carbanions and cations. They derived that the apparent equilibrium constant (which at high concentrations is approximately equal to that of ion pairs) is related to the dissociation constants of the ion pairs by eq 1.

$$K_i \approx K_\pm = \frac{K_{d1}}{K_{d2}}K_- \qquad (1)$$

Since K_- is independent of the cation, the ratio K_{d1}/K_{d2} determines the position of the addition equilibrium.

Obviously, similar ion-pairing effects must be operative in the initiation equilibrium in anionic polymerization (Scheme 2). Let us first consider the initiation by fluorenyl salts. Since the difference in Bronsted basicities of the initiator and polymer carbon acids is large (about 8 units), the free ion equilibrium constant would be decreased significantly, $K_{i,-} \ll 1$ L/mol. The metal-free cations are quite large, and all ion pairs, independent of the anion structure, have a large interionic distance, $a \approx 5-6$ Å. Even if the enolate anions "penetrate" into the tetrabutylammonium ion, coordinating with the α-carbon atom, this distance will be much larger than that with an alkali cation ($a \approx 1.5$ Å for Li^+). According to the theory of Fuoss,[23] the dissociation constant increases exponentially with a, so that both ion pairs will have rather high dissociation constants, $K_{d1} \approx K_{d2}$, which are estimated to be on the order of 10^{-5} mol/L.[21a] According to eq 1, $K_{i,\pm} \approx K_{i,app} \ll 1$ L/mol. Thus, initiation by metal-free fluorenides is expected to be incomplete and slow.

With small counterions, especially Li^+, fluorenyl salts form solvent-separated ion pairs with rather high interionic distance, a, and $K_{d1} \approx 10^{-5}$ mol/L.[21b] However, ester enolates form very tight bonds with Li^+ with very low estimated $K_{d2} \approx 10^{-9}$ mol/L.[22] Thus, $K_{d1}/K_{d2} \gg 1$, compensating the low $K_{i,-}$ value. The reported dissociation constant of initiator (K_{d1}) as well as enolate anion (K_{d2}) in the polymerization of MMA using florenyl anion with Li^+ and Cs^+ counterion in THF at −78 °C show that the ratio of the dissociation contants, K_{d1}/K_{d2}, amounts to $\approx 5 \times 10^4$ in the case of Li^+ and ≈ 30 in the case of Cs^+.[21,22] Thus, with smaller cations the initiation equilibrium is shifted more to the right-hand (polymer) side, as a result of the stabilization of enolate anion through ion pair formation. This effect is even enhanced by the well-known tendency of alkali enolates to associate into dimers or tetramers which was shown to also occur for living PMMA–Li.[24] Thus, initiation for Li^+ is fast and complete.

The situation is different when the salts of alkylmalonate esters are used as initiators, since for these enolates K_{d1} is also expected to be very small and independent of the cation, $K_{d1}/K_{d2} \approx 1$. Thus, $K_{i,\pm} \approx K_{i,app} \ll 1$, and in a first approximation, $K_{i,app}$ will be independent of the size of the cation. Thus, initiation with malonates will be incomplete and slow. However, the initiation with anion of higher pK_a value, e.g., diphenylhexyl in the presence of metal-free counterion, also shows an incomplete initiation. This is confirmed by the presence of residual initiator and low initiator efficiencies in our experiments in the presence of a bulky nonmetal counterion. This is attributed to the ion-pairing effects on the initiation equilibria which leads to an incomplete initiation in the metal-free anionic polymerization of alkyl (meth)acrylates.

Surprisingly, PMMA with high initiator efficiency and narrow molecular weight distribution is obtained in the presence of the tetraphenylphosphonium counterion.[3f,g] The driving force for complete initiation in this case is the formation of a phosphor ylide, which is in equilibrium with the enolate ion pair and thus stabilized the polymer chain end.[3g,h]

Conclusions

Metal-free initiators result in incomplete initiation of (meth)acrylates, which is attributed to the fact that the initiation is an equilibrium reaction. The position of this equilibrium depends on the relative pK_a values of the initiator and the enolate chain ends formed and on the tendency of the counterion to form ion pairs or even associates with the respective anions. For initiators with low pK_a (e.g., malonates and fluorenides) and metal-free cations, the equilibrium is strongly shifted to the initiator side, leading to slow and incomplete initiation. In conjunction with side reactions such as Hofmann elimination and transfer reactions, this leads to broad and bimodal molecular weight distributions of the resulting polymers. In contrast, with small alkali cations (and even more with anions of higher pK_a, e.g., diphenylhexyl) the resulting enolate anion becomes stabilized by the increased formation of ion pairs and associates, leading to fast and complete initiation.

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