Unusual polymerization activities of bulky aluminum alkyl complexes

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Abstract

Sterically hindered aluminum alkyl complexes have been found to be active catalysts and/or initiators compared to sterically non-congested complexes in the polymerization of acrylates and styrene type of monomers to yield polyacrylates and polystyrene with high molecular weights. Electron-withdrawing groups on the ligands enhance the polymerization activity of the catalysts. Mechanistic investigations suggest that both radical and ionic active species are involved in the polymerizations depending on the monomers used. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Recently, aluminum alkyl complexes have been found to be active Ziegler–Natta polymerization catalysts [1–4]. This discovery has not only significantly expanded the capability of Ziegler–Natta catalysis, but also has spurred intensive interests in developing new aluminum based olefin polymerization catalysts [5,6]. Aluminum complexes have the advantages of low-cost, highly reactive and ease of synthesis compared to other transition metal complexes. Cationic metal complexes with *d*-zero electron configuration are in general extremely electrophilic, which has limited their utilization for the synthesis of functionalized polymers. One solution to enhance the functional group tolerance is to use neutral metal complexes [7]. Neutral aluminum alkyl complexes known to date, however, have little activity in the polymerization of olefins, and have been mainly used as co-catalysts to increase the activity of other transition metal complexes.

Aluminum alkyl complexes exist mainly in dimeric or polymeric forms, which might in part contribute to their diminished polymerization activities. Several sterically bulky aluminum alkyl complexes were synthesized and extensively studied as Lewis acids in catalyzing a number of useful organic transformations [8–10]. These complexes were found to be compatible with strong bases, radical species and carbonyl functional groups. The role of the Lewis acids is to bind to the carbonyl groups of the substrate and to enhance their reactivities. The steric hindrance of the ligands not only has increased the solubility of the complex, but also has been used to achieve the control of the steric outcome of reactions through the interaction with substrates. There is, however, no precedence in the literature on using these complexes in the study of polymerizations. We reason that these exceptional sterically bulky monomeric complexes should exhibit higher reactivity, and we report here the unusual polymerization activities of these complexes.

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Table 1
Experimental data for the polymerization of methyl acrylate[a]

Complex	T (°C)	t (h)	M_n	M_w[b]	Yield (%)[c]
1	70	20	190600	273600	89
1a	70	8.5	54800	105100	52.2
2a	70	20	742600	1054800	9.2
2b	70	20	445900	740500	15.3
2c	70	20	30600	184700	44

[a] Polymerizations were carried out in the presence of solvents, such as benzene, toluene and dichloroethane. Typical monomer concentration is 0.5–6.5 M and catalysts loading is 1%.

[b] Molecular weights were determined using gel permeation chromatography using polystyrene standards.

[c] Isolated yield. A typical polymerization procedure: in a nitrogen-filled drybox, with a glass tube equipped with a Teflon valve, was weighed 1–5% of the aluminum complexes. Calculated amount of, toluene, benzene or dichloroethane was added to dissolve the complexes. To the reaction mixture, calculated amount of monomer was added via a syringe. The tube was sealed and brought out of the box and stirred at room temperature or heated to 70 °C. The mixture was precipitated into methanol. The polymers collected were dried in vacuum.

Sterically bulky aluminum complexes (**1**, **1a** and **2a**–**c**) can be easily synthesized from the reaction of the corresponding phenols with trimethyl aluminum [11,12]. Complexes (**1**, **1a** and **2a**–**c**) are characterized

1: X = Br
1a: X = CH₃

2a: R = H **2b:** R = CH₃
2c: R = Br
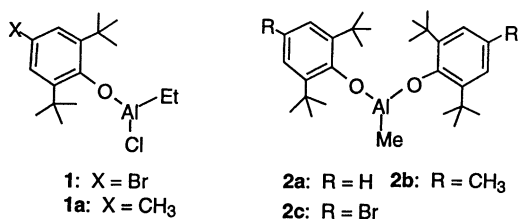
by ^{1}H, ^{13}C NMR spectroscopy and elemental analysis. We have found that these complexes are active in initiating the polymerization of acrylate to yield high molecular weight polyacrylate, a functionalized polymer (Table 1). NMR spectroscopy also shows that the polymer is atactic. Although the polymerization can be carried out both neat or in solution, higher polymerization rates were observed when the reaction was conducted in neat. The polymerization was observed at both ambient and elevated temperatures. Visible light does not enhance the polymerization activity. The activity of the complex also varies drastically with the ligand environment, which can be altered by different electron donating or withdrawing groups. As shown in Table 1, electron-withdrawing group on the ligand enhances the polymerization activity. For example, complex **2c** is more reactive than **2a** and **2b** as evidenced from better polymer yields observed. Among all the complexes, **1** and **1a** exhibit the highest reactivity, which correlates with their strong electrophilic

nature. These reactivity trends are consistent with the fact that electrophilic metal center facilitates the coordination of a carbonyl group of methyl acrylate, which promotes the activation of aluminum alkyl bond [13,14]. [1] In comparison, other strong electronic deficient but sterically non-hindered or less crowded aluminum complexes, such as $AlCl_3$, trialkyl aluminum, or dialkyl aluminum chlorides do not, however, initiate the polymerization of methyl acrylate. Thus, steric and electronic factors need to balance in order to achieve an optimized polymerization activity. Addition of oxygen does not increase the polymerization activity.

To gain insight to the polymerization process, we conducted the polymerizations of methyl acrylate in the presence of catalytic amount of radical scavengers, such as TEMPO and Galvinoxyl free radicals and found that polymerizations were completely inhibited. These observations suggest that radical active species might be involved in the polymerization reaction. We also examined the effect of solvent polarity on the polymerization. There is, however, little change in polymerization rates when solvents of different polarities are used. [2]

We further investigated the kinetics of the polymerization using NMR spectroscopy. The disappearance

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[1] We speculate that the radical is generated through the homolysis of Al–Me bond facilitated by the presence of acrylate at elevated temperature or through an oxidative process by the presence of trace amount of oxygen.

[2] Polymerizations were carried out in dichloroethane, benzene and dichlorobenzene, and polymers with similar molecular weights and yields were obtained.
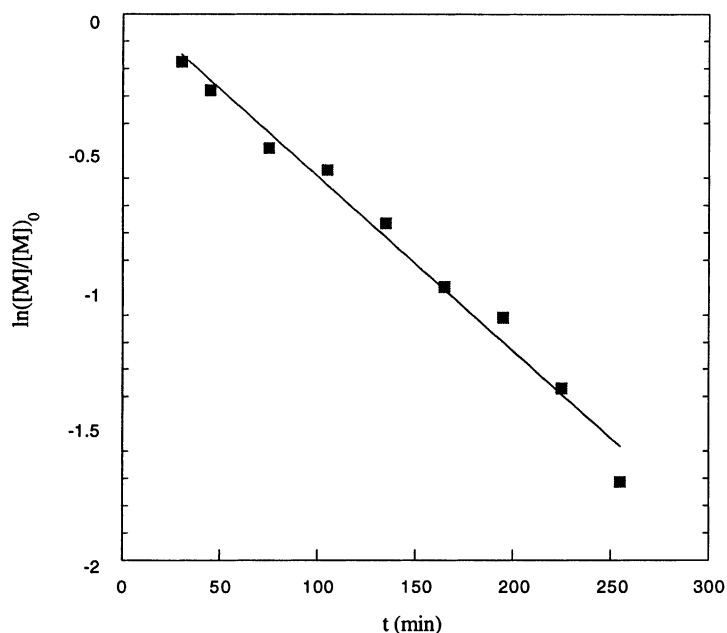
Fig. 1. Plot the monomer concentration with time at 23 °C. Typical experimental conditions: [M] = 6.18 M, [I] = 0.0496 M in toluene at 70 °C with a final conversion of 82–94%.

of the monomer concentration was followed at different time intervals. A plot of logarithm of the monomer concentration versus time yields a straight line (Fig. 1).

Quadrupling the concentration of catalyst while maintaining the same initial monomer concentration results in doubling the rates of the polymerization. These results indicate that the rate of the polymerization is first order with respect to the monomer concentration and half order with respect to the catalyst concentration, which is also consistent with a radical polymerization mechanism. Based on the experimental evidence, kinetic equation was derived (Eq. (1)), where [M] and [I] are the concentrations of monomer and complex, respectively, and k_p, k_i, k_t and k_{obs} are propagation, initiation, termination and observed rate constants, respectively. The observed polymerization rate constant is calculated ($k_{obs} = 0.029\,M^{-1/2}min^{-1}$) from the equation. This result coupled with the trapping experiment strongly suggests that sterically bulky aluminum complexes function as radical initiators in the polymerization of acrylate type of monomers. We speculate that the increase of molecular weight with time may be a result of the termination of the propagating radicals being hindered by the presence

of certain stable radical species originated from the bulky aluminum complexes.

$$-\frac{d[M]}{dt} = k_{obs}[M][I]^{1/2}, \qquad k_{obs} = k_p \left(\frac{k_i}{k_t}\right)^{1/2} \quad (1)$$

We also examined the polymerization of styrene. All the complexes can initiate the polymerization of styrene both in neat and solution to yield high molecular weight polystyrenes (Table 2). Low polymer yields are usually observed when reaction is conducted in bulk as compared to those in solution. Electron-withdrawing groups also facilitate the reactions (entry 7 versus 9; entry 3 versus 1, 2). Elevated temperature and extended reaction time are also required. Complex **1** and **1a**, however, can initiate the polymerization of styrene at room temperature to produce polystyrene with high yields. It is also interesting to note that polymers synthesized using the aluminum complexes have much higher molecular weights ($M_n = 100,000–600,000$) than those prepared using AIBN under similar conditions, which indicates that highly reactive species might have involved during the polymerization. The polymerization is also not inhibited in the presence of an excess amount of

Table 2
Experimental data for the polymerization of styrene

Entry	Catalyst/Initiator[a]	T (°C)	t (h)	M_n	M_w	Yield (%)
1	**2a**[b]	70	20	365200	599700	2.8
2	**2b**[b]	70	20	291900	513700	4.3
3	**2c**[b]	22	20	8600	53800	82.5
4	**2c**[c]	70	24	208	32200	100
5	**2c**[d]	70	24	412	16800	100
6	**2c**[e]	70	24	130000	276000	15.1
7	**1**[b]	22	0.5	1600	43200	94
8	**1**[e]	70	20	4700	14400	62
9	**1a**[b]	22	0.5	1800	44300	82.1
10	AIBN[f]	70	20	5700	11700	77.8

[a] Typical catalyst loading is 1–5%.
[b] Reactions were carried out in bulk.
[c] Reaction was carried out in dichloroethane.
[d] Reaction was conducted in dichlorobenzene.
[e] Reaction was carried out in benzene.
[f] Reaction was initiated using 5% AIBN in benzene.

radical scavenger, such as galvinoxyl free radical, but completely stopped when a sterically bulky tertiary amine (e.g. quinuclidine) was added. The polymerization was also favorable in the presence of polar solvents, such as dichlorobenzene or dichloroethane as exemplified by the higher yields (entry 4 and 5).[3] These results rule out the involvement of radical active species and further imply the presence of polar active centers, presumably cationic species during the polymerization [15]. The polymers produced are, however, atactic as evidenced by ^{13}C NMR spectroscopy, and are similar to those prepared by radical polymerization. We also synthesized sterically less hindered phenoxy ethylaluminum chloride and ethoxy ethylaluminum chloride analogs and found that they are, however, much less reactive than **1**, **1a** or **2a–c**, which indicates that steric bulk on the ligand also enhances the reactivity of the complexes.

We have discovered that sterically bulky aluminum alkyl complexes are active in the polymerization of styrene and acrylates to produce high molecular weight polystyrene and polyacrylates as compared to conventional radical and cationic polymerizations. Preliminary results suggest that either a radical or a cationic polymerization process is involved depend-

ing on the monomers used. Electron-withdrawing and sterically bulky ligands apparently enhance the reactivity of the catalysts. This has provided possibility for fine tuning the reactivity to develop other active polymerization catalysts, and to prepare a variety of functionalized polymers.

Acknowledgements

References

[1] C.E. Radzewich, I.A. Guzei, R.F. Jordan, J. Am. Chem. Soc. 121 (1999) 8673.
[2] C.E. Radzewich, M.P. Coles, R.F. Jordan, J. Am. Chem. Soc. 120 (1998) 9384.
[3] E.Y. Ihara, G. Victor Jr., R.F. Jordan, J. Am. Chem. Soc. 120 (1998) 8277.
[4] J.S. Kim, L.M. Wojcinski II, S. Liu, J.C. Sworen, A. Sen, J. Am. Chem. Soc. 122 (2000) 5668.
[5] M. Bruce, V.C. Gibson, C. Redshaw, G.A. Solan, A.J.P. White, D.J. Williams, Chem. Commun. (1998) 2523.
[6] M. Bochmann, Top. Catal. 7 (1999) 9.
[7] D.J. Crowther, R.F. Jordan, Makromol. Chem. Macromol. Symp. 66 (1993) 121.
[8] Y. Kita, Y. Yoshida, S. Kitagaki, S. Mihara, D.-F. Fang, A. Furukawa, K. Higuchi, H. Fujioka, Tetrahedron 55 (1999) 4979.

[3] For example, a quantitative yield of polymers was obtained when the polymerization was carried in dichloroethane, as compared to less than 15% yield of polymers when done in benzene.

[9] K. Maruoka, Lewis Acid Reagents, Oxford University Press, New York, 1999, pp. 5–29.

[10] H. Yamamoto, S. Saito, Pure Appl. Chem. 71 (1999) 239.

[11] M.D. Healy, D.A. Wierda, A.R. Barron, Organometallic 7 (1988) 2543.

[12] T. Ooi, K. Maruoka, H. Yamamoto, Org. Syn. 72 (1995) 95.

[13] H. Umeyama, K. Morokuma, J. Am. Chem. Soc. 98 (1976) 7208.

[14] A. Almenningen, S. Halvorsen, A. Haaland, Acta Chem. Scand. 25 (1971) 1937.

[15] G. Odian, Principles of Polymerization, 3rd Edition, Wiley, New York, 1991.