Pulsed Laser Polymerisation Studies of Methyl Methacrylate in the presence of AlCl_3 and ZnCl_2 – Evidence of propagation catalysis

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A series of pulsed laser polymerisation (PLP) experiments in conjunction with the size exclusion chromatography (SEC) was carried out to investigate the effect of Lewis acid AlCl_3 and ZnCl_2 on the propagation rate constants at a variety of conditions. The Arrhenius parameters were obtained from kinetics data over a temperature range of $\sim 0 - 60^\circ\text{C}$ at 5 mole % Lewis acid loading in bulk methyl methacrylate (MMA). The results showed that the Lewis acids are excellent propagation catalysts with catalysis increasing with the charge on the metal ion. The Lewis acids AlCl_3 and ZnCl_2 enhanced the propagation rate by around 80% and 40% respectively at 5 mol% loading, reducing the activation energy for the propagation step by $5.8\text{ kJ}\cdot\text{mol}^{-1}$ and $2.2\text{ kJ}\cdot\text{mol}^{-1}$. Propagation rate coefficient enhancements of up to 100% were obtained when AlCl_3 was used at a loading of 10 mol %. The presence of Lewis acid also affects the radical initiation process by complexing with the photoinitiator. This results in both catalysis of initiation and increased triplet lifetimes. These problems could be overcome through optimization of the initiator concentration and laser flashing rate to ensure that IUPAC quality criteria for PLP are met. Despite its strong influence to the kinetics of free radical polymerisation, limited evidence of stereocontrol was observed for both Lewis acids.

Introduction

One of the most important advances in polymer synthesis in recent decades has been the development of methods for controlling the molecular weight and architecture of polymers produced by free-radical polymerization¹⁻³. Whereas conventional free radical polymerisation gives rise to polymers with a broad molecular weight distribution and no control over chain end composition, controlled radical polymerisation allows for the synthesis of polymers with narrow molecular weight distributions, designer end groups and special architectures such as block copolymers^{4, 5}, graft polymers^{6, 7}, star polymers⁸ and so forth. These have found application in a wide array of functional materials with a variety of practical applications such as lubricants,⁹ catalysts,¹⁰ prosthetics¹¹ and drug delivery.^{12, 13} Controlled radical polymerisation does not alter nature of the propagating radical; instead its mechanism is based on altering the relative amounts of chain propagation to bimolecular termination by reversibly storing the propagating radical as a dormant species. As a result, the key advantages of conventional radical polymerisation, such as its broad scope, mild reaction conditions, tolerance of protic impurities, are retained. However, this also means some of the disadvantages of conventional radical polymerization are also retained. In particular, the majority of polymers produced via free-radical polymerization lack stereocontrol and contain defect structures, such as unsaturated groups and branch points. These defect structures are often detrimental to the thermal and photostability of the resulting polymer¹⁴ and are formed when the propagating radical undergoes side reactions such as head-head addition, inter- and intramolecular chain transfer and β -scission¹⁵. To minimise these defect structures, it is necessary to catalyse the propagation step, allowing it to better outcompete the side reactions. Moreover, if such propagation catalysis could be achieved without interfering with the control agent, it could also help improve controlled radical polymerization, as the ratio of propagation to termination provides a fundamental limit to control in a well optimized system.

Despite these potential advantages, propagation catalysis has been relatively unexplored. There have been a number of

anecdotal reports of polymerisation catalysis in the presence of Lewis acids, dating back to the 1950s.¹⁶ Studies of radical polymerisation in the presence of Lewis acids such as zinc chloride¹⁷ (ZnCl_2), magnesium bromide¹⁸ (MgBr_2), and rare earth metal triflates¹⁹ ($\text{M}(\text{OTf})_3$, $\text{M}=\text{Sc}, \text{Y}, \text{Yb}, \text{Lu}$) have been carried out intended to investigate their effect on polymer stereocontrol. Along with some influences on polymer stereochemistry, increases in conversions were also noted in these studies. However, due to the limited experimental methods available in the past, it was difficult to ascertain whether the catalysis resulted from effects on either propagation or initiation, or both. Indeed, a recent experimental and theoretical study showed that Lewis acids redshift the UV-absorption profile of acetophenone derivative initiators such as MMMP and DMPA, and alters their energetics and photostabilities.²⁰

The first unequivocal demonstration of propagation catalysis was made by Clark who carried out quantum chemical calculations to investigate the effect of metal complexation to alkenes more than 25 years ago.²¹ The study showed an increase in the rate of radical addition in the presence of a Li^+ metal cation, and this was attributed to electrostatic interactions. The theoretical investigation suggested that catalysis does not require covalent interaction between lithium and $\text{C}=\text{C}$ double bond, and can be observed at long distances when the cation is fully solvated. Later, Clark showed that Li^+ coordination to the $\text{C}=\text{C}$ double bond can allow propagation to outcompete transfer in propylene radical polymerisation.²² This prediction was subsequently verified experimentally by Michl²³ using lithium carborane complexes.

In recent decades, the development of pulsed laser polymerisation (PLP)²⁴ combined with molecular weight analysis via size exclusion chromatography (SEC) allowed quantitative measurements of kinetics data to become attainable.²⁵ Since then, there has been a renewed interest in investigating the catalysing the propagation step of radical polymerisation, typically by harnessing solvent effects²⁶⁻³⁰ on the rate of polymerisation. For example, enhancements in propagation rate constants were observed in organic solvents such as benzyl alcohol^{28, 30} and dimethyl sulfoxide³⁰, as well as ionic liquids such as $[\text{Tf}_2\text{N}]$ ³¹.

Recently, we used a combination of pulsed laser polymerisation and theoretical calculations were carried out to determine the effect of Lewis acid $\text{Li}(\text{NTf})_3$ on the rate of radical homopolymerisation of methyl methacrylate via PLP-SEC³². We observed a rate enhancement of 20-30 % in the presence of the lithium cation. Unlike the solvent and ionic liquids used in prior studies, the Lewis acid was used in catalytic instead of stoichiometric or excess amounts and the polymerisations can be carried out in bulk monomer. Furthermore, the theoretical models used to rationalize the mechanism of Lewis acid during polymerisation showed that catalysis is most likely to occur via the Li^+ bridge which holds the terminal carbonyl of the growing chain and the incoming monomer carbonyl.³² As a result, the interaction lowers the activation energy and facilitates radical addition, and consequently catalyses the propagation step of radical polymerisation. Propagation catalysis by Li^+ salts has also been demonstrated in a PLP study of ethoxy methacrylate,³³ while EPR studies have confirmed that Li^+ salts interact with the propagating radicals and alter the radical concentrations in the radical polymerization of MMA³⁴ and various acrylamides.^{35, 36}

While the precise origin of this propagation catalysis is complicated, there are strong indications that it has a significant electrostatic component.^{21, 22, 32} More generally, there is growing evidence that the electrostatic effects from both charged functional groups^{37, 38} and external electric fields³⁹ play a significant role in catalysis of chemical reactions⁴⁰. This suggests the possibility of increasing the catalytic effect by using Lewis acids with higher charges, provided that their complexation mechanism remains unchanged. To test this hypothesis, in the present work we examine the effect of zinc and aluminium chloride (ZnCl_2 , AlCl_3) on the propagation rate coefficient, k_p of bulk methyl methacrylate via PLP-SEC analysis. In course of this work, we observed that that these stronger Lewis acids have detrimental effects on the PLP experiment by interfering with the photoinitiation process.²⁰ Thus, as part of the present work, we also identify strategies to overcome these issues.

Experimental

Materials

Methyl methacrylate (Sigma-Aldrich, 99%) was passed through a column of alumina to remove the inhibitor, and stored in a freezer over 4 Å molecular sieves (Sigma-Aldrich); 2-methyl-4'-(methylthio)-2-morpholinopropiophenone (MMMP) (Sigma-Aldrich, 98%); 2,2-dimethoxy-2-phenylacetophenone (DMPA) (Sigma-Aldrich, 99%); zinc chloride (Sigma-Aldrich, 99%); aluminium chloride (Sigma-Aldrich, 99 %); deuterated chloroform (Cambridge Isotope Laboratories, 99.8%, stabilised with silver foil) and tetrahydrofuran (THF) (Merck LiChrosolv®) were used as received.

Method

Propagation rate coefficients, k_p , of methyl methacrylate polymerisation in the presence of AlCl_3 and ZnCl_2 were

determined via the IUPAC recommended PLP-SEC procedure. The experimental conditions were optimized in order to observe the PLP features in the molecular weight distribution such that it conformed to the IUPAC consistency criteria.⁴¹ This included ensuring that values of k_p were independent of laser pulse energy, initiator concentration, initiator identity. In addition, at least two inflections were required to be present in the molecular weight distributions; with the one inflection point at molecular weight double the other.

Solutions of methyl methacrylate (MMA) containing AlCl_3 or ZnCl_2 (ranging from 0 to 10 mol % relative to MMA) and photoinitiator (MMMP or DMPA) at concentration 2-4 mM were prepared and deoxygenated via freeze-pump-thaw degassing. This solution was then placed into a 10 mm pathlength Starna Type 65 jacketed cylindrical cell under a nitrogen blanket. The samples were allowed to equilibrate at the desired temperature and the internal temperature was monitored during laser pulsing (at 355nm, ~ 20mJ/pulse). The temperatures used ranged from 0-60 °C. The temperature variations measured inside the cell did not exceed 3 °C during each experiment. The molecular weight distributions of the resulting polymers were determined by the Agilent 1260 Infinity GPC/SEC system. A selection of samples were analysed via ¹H-NMR in chloroform-d to determine triad tacticities of PMMA. A complete description of the experimental procedures, including selected PLP traces can be found in the ESI.

Results and Discussion

Lewis acid solubility in bulk methyl methacrylate

Solubility experiments were carried out in order to determine the suitable concentrations for the subsequent PLP experiments. AlCl_3 and ZnCl_2 with concentrations of 2.5 mol %, 5 mol %, 7.5 mol% and 10 mol % in bulk MMA were prepared to observe the solubility of the LAs in the monomer. It was found that AlCl_3 was soluble at concentrations of up to 10 mol % in MMA, while ZnCl_2 was soluble up to 5 mol %. Furthermore, Lewis acids of high purity were required for the subsequent PLP experiments to be successful. It was found that Lewis acids' prolonged exposure to air causes absorption of water or oxidation to occur, and hence the transfer of Lewis acids and the prepared solution needed to be carried out under nitrogen. Oxidation of Lewis acids causes its solubility in the bulk MMA monomer to decrease, and absorption of water results in inconsistent inflection points to occur to be present in the molecular weight distribution in the subsequent experiments. These aspects needed to be taken into consideration when preparing samples for the following PLP experiments.

Optimisation of pulsed-laser polymerisation conditions

As the photoinitiators 2,2-dimethoxy-2-phenylacetophenone (DMPA) and 2-methyl-4-(methylthio)-2-morpholinopropiophenone (MMMP) interact with AlCl_3 and ZnCl_2 via complexation at the carbonyl in solution,²⁰ optimization of the PLP conditions was not straightforward and many of our initial samples failed to meet IUPAC consistency criteria and were not

included here It was found that in general the presence of LAs resulted in a “smearing” of the MWD as seen in Figure 1. This was particularly a problem in our PLP experiments at higher pulse rates, which also had a greater tendency to yield molecular weight distributions (MWDs) with no secondary inflection points. The reason for these problems is the interaction between the photoinitiator and Lewis acid, which alters the UV-Vis spectrum by relatively stabilizing the π - π^* transitions, and destabilizing the $n\pi^*$ transitions that lead to homolysis.²⁰ The net result is a decrease in the initiation rate and an increase in the triplet lifetimes, which becomes problematic at low initiator concentrations and high flashing rates.

To overcome these problems, we found that it was necessary to restrict the laser flashing rate to at or below 25 Hz for temperatures at or below 22 °C. These limits varied slightly with temperature with higher pulse rates able to be used at higher temperatures. We also observed that successful PLP experiments required higher initiator concentrations than equivalent experiments performed in the absence of Lewis acid. With these precautions, samples meeting all IUPAC consistency criteria could be obtained. The experimental conditions for the final data set is provided in the ESI, along with the UV-Vis spectra for these systems.

Figure 1: The molecular weight distribution of the poly(MMA) in the presence and absence of Lewis acid AlCl_3

Effect on the Propagation Rate Coefficients

PLP experiments with AlCl_3 concentrations of 2.5 mol %, 5 mol % and 10 mol %, and ZnCl_2 with concentrations of 2.5 mol % and 5 mol % were carried out at 22 °C with MMMP and DMPA initiators to observe the effect of Lewis acid concentration on the k_p of MMA. The results are summarised in Figure 2.

Figure 2: The effect of Lewis acid concentration on the k_p of MMA polymerisation at 22°C. Bulk MMA data is based on ⁴².

The experiments showed an overall enhancement of k_p with increasing Lewis acid concentrations, with AlCl_3 achieving greater catalysis (~80 %) in comparison to ZnCl_2 (~40 %) at 5 mol %. The k_p increases at increasing Lewis acid concentration as reflected by the shifting molecular weight distribution during PLP as shown in Figure 2. At a concentration of 10 mol % of AlCl_3 it was found that the k_p of MMA at 22°C was increased by around 100 % over the uncatalysed system.

It is important to note that a substantial portion of undissolved product was present when THF was used to dissolve the polymer for molecular weight analysis. The undissolved portion was reduced via rinsing with and re-precipitating in methanol. This portion arises from residual Lewis acid attached to the polymer, thus making it less soluble in THF. It is important that the residual Lewis was fully washed off from the polymer such that it completely dissolves in THF for the desired features (two inflection points) in the molecular weight analysis to become distinctive. The presence of Lewis acid also causes a general increase in MMA to PMMA conversion in the PLP experiments. The rate of conversion and the amount of undissolved portion of product when the polymer was initially dissolved in THF increased at higher Lewis acid concentrations for both AlCl_3 and ZnCl_2 systems. The significant amount of undissolved product resulting from DMPA initiated polymerisations meant that all solutions needed to be passed prior to molecular weight analysis.

Arrhenius parameters were obtained using non-linear regression to fit the k_p versus temperature data directly via customised scripts in *Matlab_2014b*. Details on the nonlinear least squares regression, which was based on the F-distribution and assumed constant relative errors in k_p , can be found in the ESI. The Arrhenius parameters are summarised in Table 1, and their 95% joint confidence intervals (JCI) are shown in Figure 3. It is clear that the presence of Lewis acids significantly change Arrhenius parameters. The activation energies are decreased by 5.8 kJ.mol⁻¹ and 2.2 kJ.mol⁻¹ for AlCl_3 and ZnCl_2 , respectively. These trends are consistent with the notion that electrostatic

effects are important; with aluminium, being a stronger Lewis acid and a smaller cation with a greater charge, giving greater k_p enhancements than the zinc cation. The catalysis of Lewis acids is offset to a minor extent by a reduction of the pre-exponential frequency factor. The decrease in pre-exponential factor, which is consistent with a more ordered transition state for both Lewis acids.

Figure 3: 95 % Joint Confidence Interval for Arrhenius parameters A and E_A . a: Bulk MMA data based on ⁴¹

These observations indicate that the Lewis acids enhance k_p for MMA polymerisation with rate enhancement of around 100% when AlCl_3 was used at a loading of 10 mol %. It is likely that the catalysis is electrostatic in nature with the larger charge on the Al^{3+} being responsible for the increase when compared to Zn^{2+} .

Table 1: Arrhenius parameters. N : number of data points.; A : pre-exponential factor; E_A : activation energy; ^b: bulk MMA data is taken from ⁴²

Catalyst	N	Temperature (°C)	$A \times 10^{-6}$ (L.mol ⁻¹ .s ⁻¹)	E_A (kJ.mol ⁻¹)	k_p (L.mol ⁻¹ .s ⁻¹) at 25 °C
none ^b	16	10.3 – 64	5.4	24.3	299
ZnCl_2	26	-0.4 – 61.1	3.1	22.1	416
AlCl_3	26	1.9 – 60.8	0.95	18.5	545

The effect of Lewis acid on Stereocontrol

Selected samples were subjected to NMR analysis to examine whether the Lewis acid affected the extent of stereocontrol in the MMA polymerisation. The samples were rinsed by methanol and dissolved in chloroform to ensure that the samples are suitable for ¹H-NMR analysis. Table 2 summarises the resulting triad fractions, which remained relatively constant across the two temperatures. The presence of Lewis acid showed a slight increase in the (rr) syndiotactic triad in comparison to PMMA generated in bulk; however, the effects

are minor and not sufficient to provide significant control of polymer tacticity. This is consistent with our previous study of Li^+ mediated polymerization, where theoretical calculations indicated that catalysis arises from chelation of the monomer and terminal side chains, a binding mode that does not influence tacticity control.³² Successful stereocontrol requires binding modes that chelate the terminal and penultimate unit^{43, 44}, which is anti-catalytic.³² It would seem that Lewis acids capable of chelating or bridging all three side chains are needed for effective stereocontrol in this system.

Table 2: Tacticity of Poly(MMA) formed via Lewis acid mediated radical polymerisation. mm , mr , rr refer to fractions of isotactic, heterotactic and syndiotactic triads. P_m refers to the probability of forming a meso diad. ^a Data for bulk MMA polymerisation taken from ⁴⁵

Catalyst	Temperature (°C)	mm	mr	rr	P_m
none ^a	25	0.069	0.349	0.582	0.244
AlCl_3	22	0.034	0.277	0.689	0.173
ZnCl_2	22	0.030	0.294	0.676	0.177
none ^a	80	0.037	0.356	0.607	0.215
AlCl_3	60	0.056	0.312	0.632	0.212
ZnCl_2	60	0.028	0.311	0.661	0.184

Figure 4: k_p (L.mol⁻¹.s⁻¹) at 25 °C with 5 mol% Lewis acid. Bulk MMA data taken from ⁴¹, LiNTf_2 data taken from³², ZnCl_2 and AlCl_3 data taken from the Arrhenius parameters in the present work.

Conclusions

The Lewis acids AlCl_3 and ZnCl_2 have the potential to be useful propagation catalysts for methyl methacrylate polymerisation. Both AlCl_3 and ZnCl_2 enhance k_p by lowering the activation energy, with AlCl_3 demonstrating greater catalytic effects via increased electrostatic stabilization of the transition state (Figure 4). The presence of Lewis acid affects initiation and the resulting PLP characteristics of the resulting polymer. In

contrast to the significant influence on kinetics, the Lewis acids have limited influence on the stereocontrol. This work provides a basis for investigating other the influence of other Lewis acids on the kinetics of free radical polymerisation.

Conflicts of interest

There are no conflicts to declare.

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