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Alcohol mediated degenerate chain transfer controlled cationic polymerisation of *para*-alkoxystyrene†

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In this report we demonstrate methanol as an effective degenerative chain transfer agent to control the cationic polymerisation (initiated by triflic acid) of electron rich *p*-alkoxy-styrenes, such as *p*-methoxy-styrene (*p*-MOS). Kinetic analysis revealed that an induction period occurs initially during which free cationic polymerisation occurs at low monomer conversion before proceeding through the pseudo first order rate, analogous to the RAFT mechanism. Ethanol and isopropanol also demonstrated excellent control ($Đ$ > 1.30), however, with an apparent increase in experimental molecular weight. Furthermore, methanol controlled polymers were successfully chain extended upon sequential monomer addition, demonstrating the 'livingness' of the alcohol mediated cationic polymerisation.

Introduction

The advancement of macromolecular synthesis has enabled the creation of complex architectures and functional materials.[1–7] Although controlled radical polymerisation methods have dominated this area in general,[8,9,14] materials generated by cationic polymerisation offer unique properties that are not readily accessible by radical chemistry.[10,11] In contrast, controlled cationic polymerisation has gained less attention, due to the synthetic challenge in controlling the highly reactive propagating cationic species that often leads to more side reactions.[12] Historically, living cationic polymerisation has been classically controlled by atom transfer of the ω-capping halogen group to a catalytic Lewis acid activator.[13] However, more recently, Kamigaito and coworkers have demonstrated a genuinely new strategy to control the cationic polymerisation by degenerate chain transfer, a strategy that has been widely utilized in controlled radical polymerisation.[15]

The initial pioneering work was led by Kamigaito and co-workers, where his group reported cationic Reversible-Addition Fragmentation Chain Transfer (RAFT) polymerisation mediated by thiocarbonylthio-ester (Fig. 1) as a chain transfer agent (CTA), using ppm levels of triflic acid (TfOH) as a cationic initiator. This was proposed to proceed through equilibrium between the sulfonium intermediate and the degenerative chain transfer of growing cationic propagating chains, in a manner analogous to radical mediated RAFT polymerisation.[16] Furthermore, the Kamigaito group demonstrated a unique block copolymerisation generated from switching between cationic and radical RAFT block copolymerisation.[16,17] Fors and co-workers further demonstrated cationic RAFT by exploiting the redox properties of thiocarbonylthio-ester.[18] However, in contrast to the analogous reduction driven photoinduced electron transfer (PET)-RAFT,[19–21] Fors' group focused on oxidation driven cationic polymerisation. This oxidative initiation of the cationic RAFT was demonstrated both electrochemically and through photoredox catalysis.[18,22–25]

Investigating beyond thiocarbonylthio-esters, the Kamigaito group further demonstrated phosphates to mediate cationic-RAFT *via* a phosphonium intermediate (Fig. 1).[26] Similar to thiocarbonylthio ester, P═O bonds were proposed to add to the propagating cationic chain end and the reactivity was influenced by two Z-groups. The chain transfer constants (C_{tr}) of phosphates and phosphinate based RAFT agents were found to be between those of dithiocarbamates and trithiocarbo-

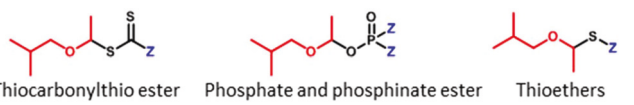

Fig. 1 Examples of degenerative chain transfer agents for cationic polymerisation, consisting of three components, the re-initiating R-group (red), chain transfer moiety (black) and Z-group (blue), which influences the reactivity of the chain transfer group.

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nates, for isobutyl vinyl ethers. Given the abundance of phosphate in biologically relevant materials, this phosphate-based cationic RAFT could offer a viable approach to prepare novel materials for bio-applications. Prior to this work, the Kamigaito group also showed that the sulfur atom alone as a thioether with a suitable re-initiating group can mediate cationic-degenerative chain transfer polymerisation (Fig. 1).[27] In this case, the propagating chain adds to the sulfur atom without any resonance stabilisation and controls the chain growth through the degenerative chain transfer process.[26]

As our major contribution to this emerging field, we previously reported methanol as an effective degenerative transfer agent (Fig. 2A) proceeding *via* an oxonium intermediate for the cationic polymerisation of an electron rich styrenic monomer, *para*-methoxystyrene (*p*-MOS).[28] This was discovered serendipitously with 2,4,6-tri(*p*-tolyl)pyrylium tetrafluoroborate as a photoredox initiator, where the molar mass of the polymers was observed to be dependent on the relative concentrations of methanol, and independent of the quantity of the initiator used. The ability of methanol as a degenerative chain transfer agent was based on a high affinity of carbocationic species for oxygen atoms in ethers and alcohols. Though alcohols are the commonly used nucleophiles to terminate cationic polymerisation, we proposed that the methyl ether terminated chains in our system were able to chain extend further upon sequential monomer addition, demonstrating the possible living nature of methanol terminated chain ends, for the polymerisation of *p*-MOS.[28] Our earlier report utilized a photoredox catalyst system which appeared to function solely as a cationic initiator (Fig. 2A); still, the importance of the catalyst in the control of polymerisation remains largely unexplored. To gain a deeper understanding of the nature of methanol as a degenerative chain transfer agent, we decided to de-couple the photoredox catalyst (presumably an initiator to generate cations) from the rest of the polymerisation; instead, we employed triflic acid as the initiator to generate cations 'cleanly'. Indeed, this triflic acid initiated polymerisation of *p*-MOS can be controlled using methanol, supporting our original claims (Fig. 2B).

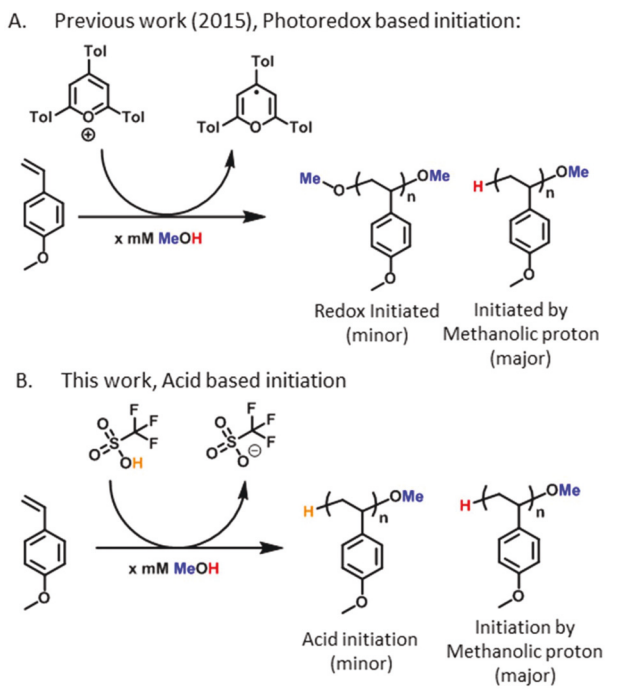


Fig. 2 (A) Previous work with methanol controlled photocationic polymerisation. (B) Current work using methanol controlled cationic polymerisation initiated by triflic acid.

Experimental

Materials and methods

All reagents were purchased from Sigma-Aldrich, Fischer Scientific, or Acros and were used without additional purification unless otherwise noted. Anhydrous dichloromethane was dried further over an activated alumina plug; 4-methoxystyrene was distilled under calcium hydride before use and stabilised using *tert*-butylcatechol as an inhibitor. The stock solution of triflic acid in diethyl ether (20 mg ml^{-1}) was prepared inside a glove box due to the hygroscopic and reactive nature of the acid.

Characterisation

Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on a Bruker AVANCE III 600 CaryoProbe 400 MHz spectrometer with a solvent residual peak as the internal standard (^{1}H NMR at 7.26 ppm for $CDCl_3$). Size Exclusion Chromatography (SEC) analysis was carried out using a Water Alliance 2695 instrument equipped with a refractive index detector (Waters 2414). Samples were passed through three columns (Waters Styragel HR5, HR4, and HR2) using THF as the mobile phase. All the experimental molar masses ($M_{n,SEC}$) and dispersities ($Đ$) were determined using polystyrene standards purchased from Polyscience Corporation.

General polymerisation procedure

In a typical polymerisation, monomer (*p*-MOS, 500 mg, 500 μL, 3.7 mmol, 50 eq.), chain transfer agent (methanol, 2.7 mg, 3.4 μL, 74.5 μmol, 1 eq.) and solvent (dichloromethane, 6.68 mL) were added *via* gastight syringe into a pre-flame dried and argon purged sealed scintillation vial equipped with a magnetic stirrer. The solution was allowed to stir at −10 °C, followed by addition of triflic acid solution prepared as a 20 mg ml^{-1} diethyl ether solution (140 μL, 1.9 μmol, 0.25 eq.) *via* a gastight syringe into the reaction mixture to initiate polymerisation. The polymerisation was left stirring for one hour. The polymerisation was sampled by quenching the aliquot into methanol with triethylamine. After confirming the full consumption of the monomer, the polymerisation was then quenched with triethylamine, and precipitated into cold methanol.

For *in situ* chain extension, after sampling the reaction mixture for GPC and NMR to confirm completion, an equivalent repeating unit of monomer solution (500 mg, 3.7 mmol, 50 eq. as 0.5 M solution in dichloromethane, 7.453 ml) was added into the reaction mixture through a syringe. The reaction was stopped after 1 hour by quenching with triethyl amine and precipitated into methanol.

For chain extension after isolation, the isolated polymer was azeotroped with toluene to remove trace methanol and water prior to the reaction. The polymer (500 mg) was re-dissolved in DCM (7.453 ml, equivalent to 0.5 M in repeat units). The solution was sealed and allowed to stir at −10 °C, followed by addition of triflic acid solution prepared as a 20 mg ml^{-1} diethyl ether solution (140 μL, 1.9 μmol, 0.25 eq.) *via* a gastight syringe into the reaction mixture. The sequential monomer (500 μL, 3.7 mmol, equivalent moles of repeat units) was then added dropwise through a gastight syringe.

Calculation of $M_{n,th}$

The theoretical number-average molar masses ($M_{n,th}$) were calculated as

$$M_{n,th} = \frac{\rho[M]_0 M_M}{[CTA]_0} + M_{CTA}, \quad (1)$$

where $[M]_0$ and $[CTA]_0$ are the initial concentrations (mol dm^{-3}) of the monomer and the chain transfer agent, respectively, ρ is the monomer conversion as determined by ^{1}H NMR, and M_M and M_{CTA} are the molar masses (g mol^{-1}) of the monomer and the chain transfer agent, respectively.

Results and discussion

Methanol is typically used as a nucleophile to quench cationic polymerisation and added at the end of the polymerisation. As our goal is to investigate the role of methanol as a RAFT agent, it was added at the beginning of the reaction before the addition of the polymerisation initiator. Following on closely from our previous work, we continued to use *p*-MOS as a model monomer and commenced the polymerisation with TfOH as the initiator. This was chosen as it was previously reported to initiate cationic polymerisation at low ppm concentration.[16] All the polymerisations conducted were cooled to −10 °C before adding the initiating acid solution and maintained at this temperature due to the reactive nature of our catalyst/monomer system. The monomer conversion was determined by ^{1}H-NMR spectroscopy by integrating the –CH***H*** vinylic proton at 5.57 ppm and using the phenyl-methoxy –OC$\boldsymbol{H}_3$ at 3.77 as the internal reference. The ^{1}H-NMR analysis of all the obtained polymers showed a full monomer conversion within 1 hour.

We then conducted a series of preliminary experiments to investigate the molar mass dependence on methanol concentration. The experiments were carried out using constant initial monomer ($[M]_0$) and initiator ($[I]_0$) concentrations of 500 mM and 2.5 mM, respectively, and a varying methanol concentration (0, 5, 10, 20, and 50 mM, Fig. 3). TfOH initiated cationic polymerisation, without the presence of methanol, generated high molecular weight polymers ($M_{n,SEC}$ = 22 480 g mol^{-1}) with a broad dispersity ($Đ$ = 3.44) (Fig. 3 and Table 1). The poor control with TfOH alone is due to the uncontrolled fast propagation of the monomer relative to the acid initiation, which is consistent with the results in the literature.[29] However, when methanol was added to the reaction mixture prior to the addition of the acid, a profound decrease in experimental molar mass ($M_{n,SEC}$) accompanied by narrow dispersity from SEC analysis ($Đ$ < 1.30) was observed (Fig. 3 and Table 1). The control was comparable to xanthate[29] and trithiocarbonate[25] based RAFT agents. Furthermore, the increasing MeOH concentration led to a decrease in molar mass, similar to our previous observation for the photoredox initiated MeOH controlled system.[28] In all cases, $M_{n,SEC}$ was in good agreement with the theoretical molar mass ($M_{n,th}$, Fig. 3) calculated from the targeted (Degree of Polymerisation) DP based on the monomer to CTA ratio ($[M]_0/[MeOH]$), eqn (1).

Furthermore, ^{1}H-NMR spectroscopy revealed an increased appearance of α-C$\boldsymbol{H}_3$ at 0.91–1.10 ppm with increasing methanol concentration (Fig. 3, $\boldsymbol{H}_a$), indicative of methanol initiation. This was accompanied by an increase in the ω-OC$\boldsymbol{H}_3$ end group (Fig. 3, $\boldsymbol{H}_d$) that appeared at 2.90–3.11 ppm equally with increasing methanol concentration when targeting a lower DP.

To ascertain whether the initiating protons are derived from methanolic protons, deuterated methanol (CD_3OD, or MeOH-d_4) was used as a CTA to unequivocally distinguish from TfOH initiated chains. As the ^{2}H-NMR signals are inherently weak, a relatively high concentration of CD_3OD was used ($[CD_3OD]$ = 50 mM, [*p*-MOS] = 500 mM) to target a DP of 10. ^{2}H-NMR spectroscopy revealed two broad ^{2}H signals at 2.55–3.25 ppm from the ω-OC$\boldsymbol{D}_3$ and at 0.70–1.30 ppm from α-$CH_2\boldsymbol{D}$ with the observed integral ratio of 3 : 0.7 which is consistent with the theoretical ratio of 3 : 1 with 100% deuterium initiation (ESI, Fig. S1†).

To probe further into the mechanism of polymerisation, the rate of monomer consumption was monitored over time (Fig. 4A, B and ESI, Fig. S2–S6†), targeting a DP of 50 ($[M]_0$ = 500 mM, [MeOH] = 10 mM). To obtain reliable kinetic data for such a fast reaction, the concentration of TfOH was reduced to 0.2 mM, purposely lowering the rate of polymerisation. It is important to note that an increase in acid concentration leads to a faster polymerisation rate, making it difficult to study the kinetics. Each aliquot was quenched with triethylamine to prevent further propagation after sampling. Interestingly, an induction period occurred during the initial 30 minutes, a key feature often observed prior to the RAFT main equilibrium with a typical (radical) RAFT mechanism, after which rapid monomer conversion was observed with first-order kinetics (Fig. 4A). During this induction period, a broad molecular weight distribution was observed (Fig. 4B, $Đ$ > 1.5), indicative of 'free' cationic polymerisation with triflic acid, in contrast to our photocationic polymerisation, where a low $Đ$ was observed even at a low conversion.[28] Our hypothesis is that during the

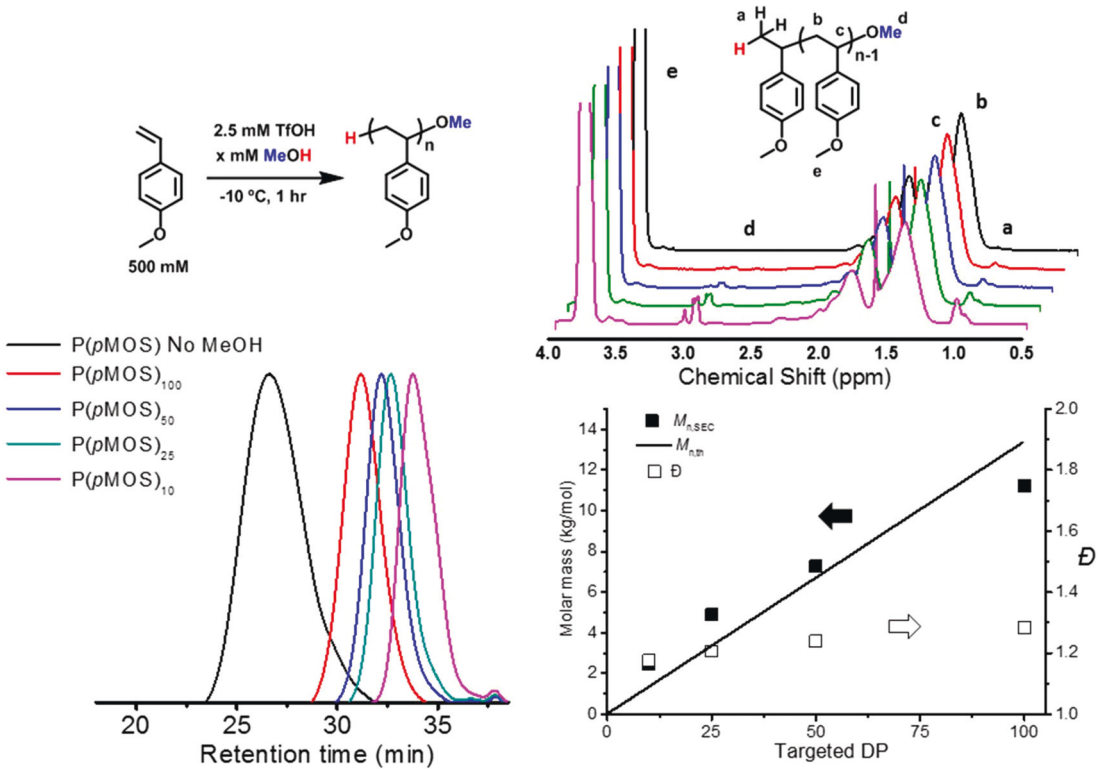


Fig. 3 Cationic RAFT polymerisation of *p*MOS with MeOH as the RAFT agent ([MeOH] = 0, 5, 10, 20, and 50 mM). Bottom left: SEC chromatograms (dRI, THF) of p(*p*-MOS) controlled by MeOH. The targeted DP is the ratio of monomer to CTA ([*p*MOS]/[MeOH]) assuming additional chains generated from the initiator to be negligible. Bottom right, the black line represents the theoretical molar mass calculated from eqn (1). The filled squares represent the experimental molar masses obtained by THF SEC with polystyrene as standards. The empty squares represent the dispersity values as determined by THF SEC. Top right, the ^{1}H-NMR spectrum shows the end groups of p(*p*-MOS).

Table 1 Triflic acid initiated methanol controlled polymerisation of *p*-MOS

Entry	[*p*-MOS] : [MeOH] : [TfOH]	$M_{n,th}$[a] (g mol^{-1})	$M_{n,SEC}$[c] (g mol^{-1})	$Đ$[c]
1[d,e]	500 : 0 : 2.5	26 900[b]	22 480	3.44
2[d]	500 : 50 : 2.5	1400	2230	1.23
3[d]	500 : 20 : 2.5	3400	3270	1.22
4[d,e]	500 : 10 : 2.5	6700	6230	1.22
5[d]	500 : 5 : 2.5	13 500	11 250	1.22
6[f]	500 : 10 : 0.6	6700	7530	1.27
7[f]	500 : 10 : 1	6700	7620	1.27
8[f]	500 : 10 : 2.5	6700	6920	1.23
9[f]	500 : 10 : 5	6700	7340	1.22

[a] The molar mass calculated from eqn (1). [b] The molar mass determined by the chain length calculated from the $[p\text{-MOS}]_0/[\text{TfOH}]_0$ ratio of 200 : 1. [c] Determined by SEC in THF with polystyrene standards. [d] GPC and NMR presented in Fig. 3. [e] GPC presented in Fig. 6 and Table 2. [f] GPC plotted in Fig. 5.

initial induction period, free cationic polymerisation is terminated rapidly by nucleophilic attack of the methanol, followed by chain transfer of methanol derived protons to re-initiate new chains. Once all of the alcohols are consumed, the propagation is accelerated with pseudo first-order kinetics after 40% monomer conversion, where controlled chain growth is observed ($Đ < 1.3$). This is indicative of steady state controlled chain growth through the RAFT equilibrium between the propagating chains and oxonium intermediate (Fig. 4C), analogous to the radical-mediated RAFT polymerisation. Interestingly, SEC analysis revealed the convergence of a polymodal distribution into a monomodal distribution with increasing conversion (Fig. S6†). Sauvet *et al.* reported a similar phenomenon of the formation of several distinct solvated propagating species in the beginning of the free cationic polymerisation of *p*-MOS leading to polymodal distribution.[30] However, as the reaction proceeds, the slower "solvent-free" chain ends stabilized by the intramolecular coordination of the residual aromatic ring becomes dominant. In contrast, monomodal distribution was observed even at low monomer conversion in our previous work.[28]

Our next objective was to investigate the effect of acid concentration on polymerisation control. According to the (radical) RAFT mechanism, the M_n should be proportional to the sum of the CTA and initiator consumed during polymerisation. In most cases, the initiator generated chains are often neglected due to a high CTA/initiator ratio.[31,32] In this work, however, since we used a relatively low CTA/initiator ratio, the theoretical mass should consider the amount of initiator (*i.e.*,

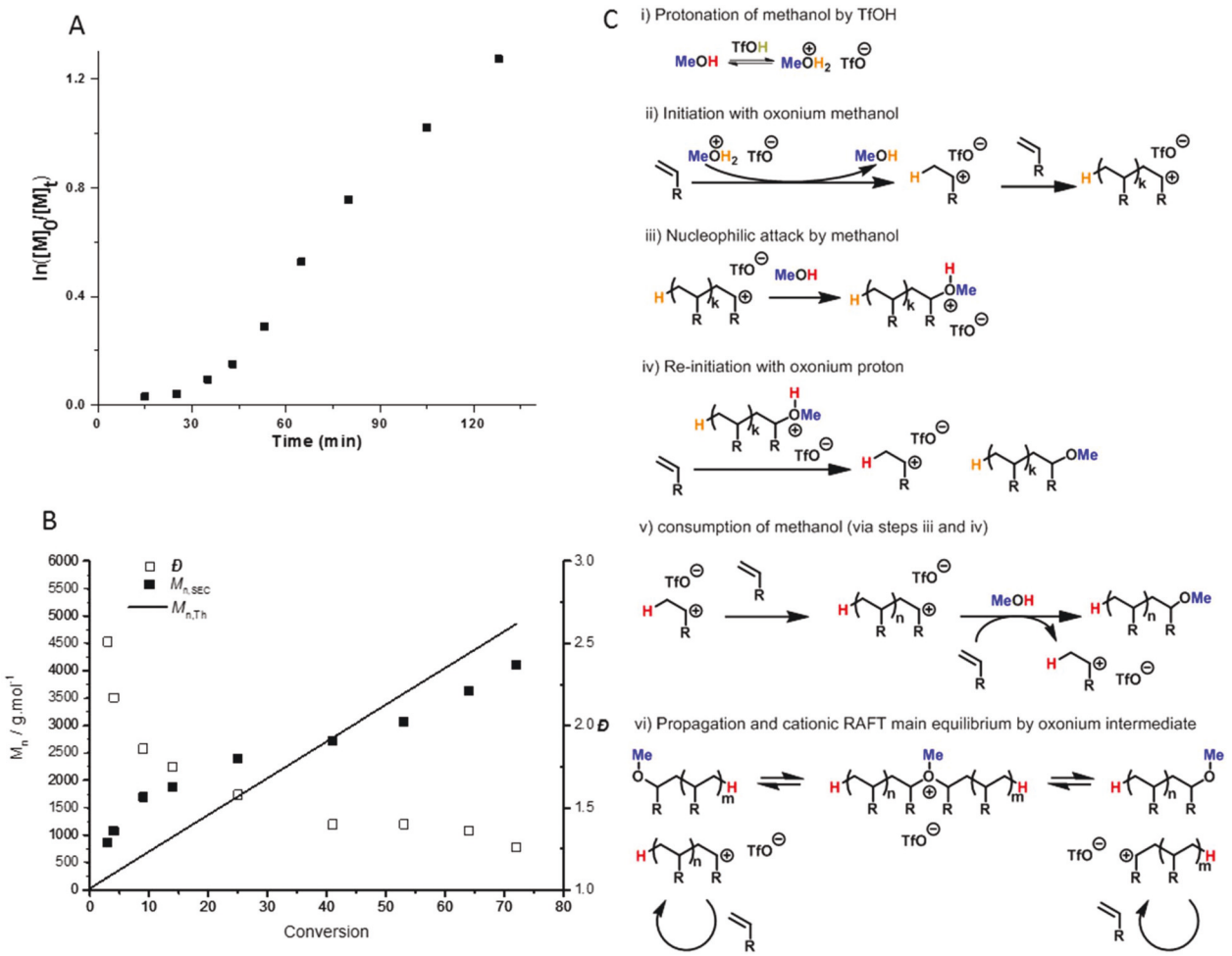


Fig. 4 (A, B) Kinetic analysis of triflic acid initiated cationic-RAFT polymerisation of *p*MOS with MeOH as a RAFT agent. (C) Proposed mechanism for methanol mediated cationic RAFT polymerisation: (i) protonation of methanol with TfOH, (ii) initiation of the monomer with oxonium methanol, (iii) nucleophilic attack by methanol (iv) re-initiation *via* chain transfer (v) consumption of the methanol through steps (iii–iv, vi) Controlled propagation of the monomer through reversible chain transfer *via* an oxonium intermediate.

TfOH) added to account for the chains that were initiated by the initiator. Yet our findings clearly show that the molar mass was solely dependent on the amount of methanol (*i.e.*, CTA) added, regardless of the amount of TfOH used. To further investigate the effect of initiator loading on the molar mass, a range of different TfOH concentrations ([TfOH] = 0.6, 1, 2.5, 5 mM, Table 1) were screened, whilst keeping the monomer and MeOH concentration constant ($[M]_0$ = 500 mM, [MeOH] = 10 mM, target DP = 50). A quantitative monomer consumption was achieved within 1 hour with the concentration of TfOH as low as 0.6 mM, which furnished relatively a $M_{n,SEC}$ of 7500 g mol^{-1} with the theoretical [MeOH]/[TfOH] ratio as high as 16.7 (Fig. 5, $M_{n,SEC}$ = 7500 g mol^{-1}, $Đ$ = 1.27). Clearly, in our methanol controlled cationic polymerisation, the initiator concentration did not affect the $M_{n,SEC}$. Even with the [MeOH]/[TfOH] ratio as low as 2 ([TfOH] = 5 mM), a considerably lower $M_{n,SEC}$ should be expected taking into account 1/3 of the polymer chains initiated from the TfOH. However, no considerable difference was observed with the molar mass measured ($M_{n,SEC}$ 7300 g mol^{-1}, $Đ$ = 1.22). In contrast, Kamigaito reported that increasing TfOH concentration with respect to the CTA markedly lowered the $M_{n,SEC}$ by SEC analysis, due to the increasing number of additional chains generated from TfOH.[16] We attribute this 'unusual' behaviour (*i.e.*, $M_{n,th}$ largely independent of high initiator concentration) to the free proton exchange occurring between other divalent oxygens present in the system (Scheme S1†) without generating additional chains from excessive TfOH. In addition, a surprisingly lower $Đ$ at higher TfOH suggests protonated oxonium methanol to act as the main initiator and hence initiation is accelerated at a higher TfOH loading, thus leading to a lower $Đ$. We suspect this phenomenon to also contribute towards the lack of the molar mass dependency of the synthesized polymers on the quantity of TfOH.

Mechanistically, as the key functional group is the alcohol motif, a series of experiments were carried out to investigate whether other alcohols could achieve the same level of control on this cationic polymerisation, *i.e.*, effectively investigating

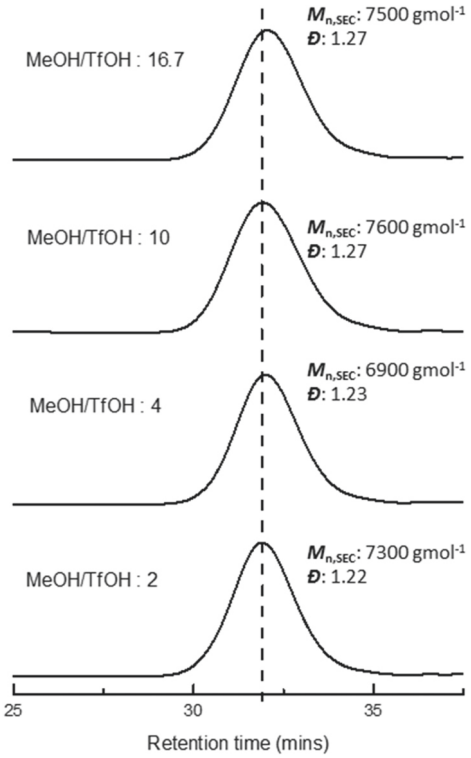


Fig. 5 SEC chromatogram (dRI, THF) of p(*p*-MOS)$_{50}$ varying the triflic acid concentration.

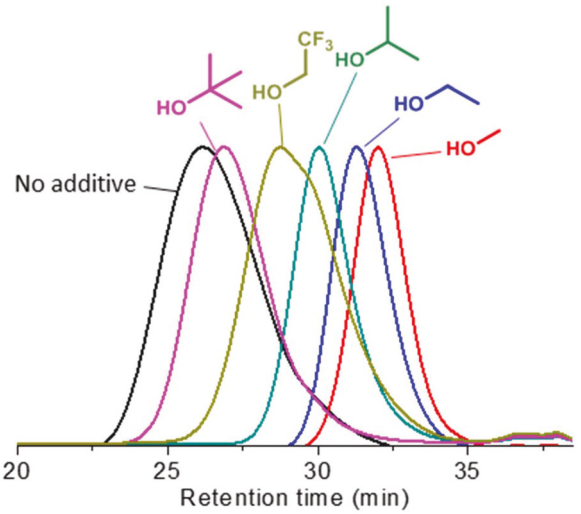


Fig. 6 SEC chromatogram (dRI, THF) of p(*p*-MOS)$_{50}$ (targeted DP of 50, in all cases) controlled with different alcohols, $M_{n,SEC}$ and $Đ$ tabulated in Table 2.

the influence of the Z-group. Experimentally, for easy comparison, we maintained identical experimental conditions (*e.g.*, the same ratio of [alcohol] : [TfOH] : [*p*-MOS]$_0$) for different alcohol-based polymerisations. Specifically, when the substituent was increased to ethyl-alcohol (A2, Table 2), the control was maintained ($Đ$ = 1.24) with unimodal molecular weight distribution (Fig. 6), yet the $M_{n,SEC}$ was almost doubled ($M_{n,SEC}$ = 10 200 g mol^{-1}) in comparison to methanol controlled polymerisation. When the substituent of the Z-group was increased further using a secondary alcohol, isopropyl alcohol (A3, Table 2), good control was still maintained over the molecular weight ($Đ$ = 1.28), however, this was accompanied by a further shift in $M_{n,SEC}$ (Fig. 6, $M_{n,SEC}$ = 20 400 g mol^{-1}). This was remarkably consistent with our previous findings where a photocationic initiator was used.[27] However, typically an increase in molecular weight is indicative of a decrease in chain transfer activity (for example, less CTA being consumed), and is usually accompanied by a loss of control (*i.e.*, higher Đ). Thus, observing a high molecular weight yet a low dispersity as we change the Z-group in this polymerization is rather strange and needs further investigation. Nevertheless, increasing further the steric effect of the Z-group to a tertiary alcohol was found to be detrimental for polymerisation control (A4, Table 2, $M_{n,SEC}$ = 88 500 g mol^{-1}, $Đ$ = 1.55). Consistent with our previous work, trifluoroethanol was not able to control the polymerisation, as a result of a decreased nucleophilicity of the alcohol (A5, Table 2). Additionally, no presence of fluorine was detected by ^{19}F-NMR (Fig. S7†).

Table 2 Alcohol additive study

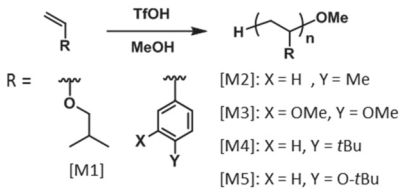
Entry[a]	Alcohol	$M_{n,th}$[b] (g mol^{-1})	$M_{n,SEC}$[c] (g mol^{-1})	$Đ$[c]
A1	Methanol	6700	7200	1.28
A2	Ethanol	6800	10 200	1.24
A3	Isopropanol	6800	20 400	1.28
A4	*tert*-Butanol	6800	88 500	1.55
A5	Trifluoroethanol	6800	26 400	1.71
A0	None	26 900[d]	22 480	3.44

[a] A molar ratio of [*p*-MOS] : [Alcohol] : [TfOH] of 500 : 10 : 2.5 was used. [b] Molar mass calculated from eqn (1). [c] Determined by SEC in THF with polystyrene standards. [d] The molar mass determined by the chain length calculated from the [*p*-MOS]$_0$/[TfOH]$_0$ ratio of 200 : 1.

To investigate the generality of this method in controlling the cationic polymerisation of different monomers, a series of comparable monomers were screened. Preliminary results suggest that this chemistry is not applicable for the typical vinyl ether family of monomers such as isobutyl vinyl ether (entry M1, Table 3). A lack of control was also observed in styrenic monomers with the absence of a stabilising electron donating *para*-alkoxy group such as 4-methyl styrene (M2, Table 3) and *tert*-butyl styrene (M4, Table 3), whereas good control was found for *para*-alkoxy group containing styrene monomers such as 3,4-dimethoxy styrene (M3, Table 3) and *tert*-butyloxy styrene (M5, Table 3). This indicates that the absence of the *para*-alkoxy group appears to be detrimental, thus highlighting the importance of stabilization of the propagating carbocation by electron rich aromatic groups for this methanol controlled polymerisation.[33,34]

To further demonstrate the retention of the livingness of our system, a series of chain extensions from the initial block with targeted DPs of 25, 50 and 100 were carried out, aiming

Table 3 Cationic polymerisation in the presence of methanol with various monomers



Entry[a]	$M_{n,th}$ [b] (g mol^{-1})	$M_{n,SEC}$ [c] (g mol^{-1})	$Đ$[c]
M1	5000	3300	1.80
M2	5900	5300	1.87
M3	8200	6700	1.29
M4	8000	4400	1.54
M5	8800	13 200	1.23

[a] A molar ratio of [Monomer] : [MeOH] : [TfOH] of 500 : 10 : 2.5 was used. [b] Calculated from eqn (1). [c] Determined by SEC in THF with polystyrene standards.

to extend with an equal block length, respectively. Experimentally, this was done by sequentially adding a new monomer solution without the addition of more TfOH. In theory, if no base was used to quench the 'living' cationic polymerisation, no termination should occur. In this scenario, the total number of active chains should remain constant through the polymerisation and be able to continue to propagate once new monomers are added. Pleasingly in all cases, a clear shift in $M_{n,SEC}$ was observed by SEC analysis (Fig. 7). Although unimodal, we found broader molecular weight distributions to be apparent ($Đ$ > 1.3) when targeting longer blocks (DP = 100). When attempting to extend this polymer by an equally long block (DP = 100), it resulted in a broader distribution ($Đ$ > 1.4), however the shift in molecular weight distribution was still noticeable (Fig. 7). The chain extendibility of our system after base mediated termination and isolation was also investigated. To ensure no additional chain transfer from the residual solvents, the isolated polymers were azeotroped with toluene prior to chain extension. Pleasingly, when the monomer was added after the addition of TfOH to the re-solubilised polymer ($M_{n,SEC}$ = 3800 g mol^{-1}, $Đ$ = 1.31, Fig. S8†), a shift in molecular weight distribution was observed by SEC analysis ($M_{n,SEC}$ = 5800 g mol^{-1}, $Đ$ = 1.42, Fig. S8†), indicative of chain extension by chain transfer between dormant chains with newly formed propagating species.

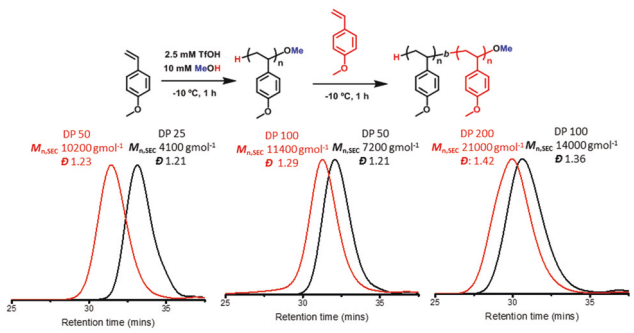


Fig. 7 SEC chromatogram (dRI, THF) of a series of chain extensions (in red) of various chain lengths.

Conclusions

Alcohols have been commonly used as a nucleophilic quencher for cationic polymerisation; however, in this work, we show that the cationic polymerisation of *p*-MOS with TfOH can be controlled with methanol as the chain transfer agent through a RAFT-like mechanism. From our spectroscopic measurements, we have shown that alcoholic protons can generate new chains, following the initial nucleophilic attack. Generally, a well-controlled polymerisation was observed after 40% monomer conversion where the polymerisation follows the pseudo first order rate following the initial induction period. The 'livingness' of our system was further demonstrated by chain extension *via* sequential monomer addition. While methanol provides the best control, ethanol and isopropyl alcohol have also shown good control as CTAs. However, it is important to note that this phenomenon is very specific to electron rich styrenic monomers. How to extend this unique cationic polymerisation methodology to other monomers, in particular, the vinyl ether family, remains a challenge that would need further investigation. Nevertheless, this study offers a new contribution to the field of controlled cationic polymerisation.

Conflicts of interest

There are no conflicts to declare.

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