Polymer Chemistry

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

Journal:	*Polymer Chemistry*
Manuscript ID	PY-ART-04-2019-000480.R1
Article Type:	Paper
Date Submitted by the Author:	09-Jun-2019
Complete List of Authors:	Prasher, Alka; University of North Carolina at Chapel Hill, Biomedical Engineering Hu, Huamin; Univerisity of North Carolina at Chapel Hill, Chemistry Tanaka, Joji; University of North Carolina at Chapel Hill, Nicewicz, David; University of North Carolina at Chapel Hill, Chemistry You, Wei; University of North Carolina at Chapel Hill Campus Box 3290 Chapel Hill, NC 27599-3290, USA , Department of Chemistry

Journal Name

ARTICLE

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

Alka Prasher,[a] Huamin Hu,[a†] Joji Tanaka,[a†] David A. Nicewicz,[a] Wei You*[a]

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

In this report we demonstrate methanol as an effective degenerative chain transfer agent to control cationic polymerisation (initiated by triflic acid) of electron rich *p*-alkoxy-styrenes, such as *p*-methoxystyrene (*p*-MOS). Kinetic analysis revealed that, an induction period occurs initially during which free cationic polymerisation occurs at low monomer conversion before proceeding through pseudo first order rate, analogous to RAFT mechanism. Ethanol and isopropanol also demonstrated excellent control ($Đ$ > 1.30), however, with apparent increase in experimental molecular weight. Furthermore, methanol controlled polymers were successfully chain extended upon sequential monomer addtion, 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] materials generated by cationic polymerisation offers unique properties and that are not readily accessible by radical chemistry.[10, 11] However, controlled cationic polymerisation in contrast has had gained less attention, due to the synthetic challenge in controlling the highly reactive propagating cationic species that often leads to more side reaction.[12] Historically, living cationic polymerisation has been classically controlled by atom transfer of ω-capping halogen group to a catalytic Lewis acid activator.[13] However, more recently, Kamigaito and Fors have demonstrated genuinely new strategy to control the cationic polymerisation by degenerate chain transfer, a strategy that has been widely utilized in controlled radical polymerisation.[14, 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 (**Figure 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 sulfonium intermediate and 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 has 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] the 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]

Exploiting beyond thiocarbonylthio-esters, the Kamigaito group has further demonstrated phosphates to mediate cationic-RAFT via phosphonium intermediate (**Figure 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 constant (C_{tr}) of phosphates and phosphinate based RAFT agents were found to be between that of dithiocarbamates and trithiocarbonates, 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 material for bio-applications. Prior to this work, the Kamigaito group also showed that sulfur atom alone as a thioether with a suitable re-initiating group can mediate cationic-degenerative chain transfer polymerisation (**Figure 1**).[27] In this case, 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 have previously reported methanol as an effective degenerative transfer agent (**Figure 2A**) proceeding via an oxonium intermediate for 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 to the quantity of the initiator used. The ability of methanol as degenerative chain transfer agent was based on a high affinity

[a] *Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290, United States*
† These authors have contributed to the work equally
Electronic Supplementary Information (ESI) available: . See DOI: 10.1039/x0xx00000x

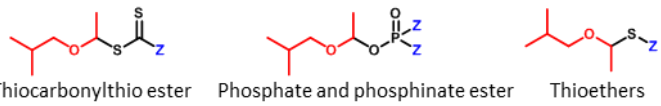


Figure 1. Examples of degenerative chain transfer agents for cationic polymerisation, consisting of three components, Re-initiating R-group (red), Chain transfer moiety (black) and Z-group (blue) that influences the reactivity of the chain transfer group.

of carbocationic species for oxygen atoms in ethers and alcohols. Though alcohols are commonly used nucleophiles to terminate cationic polymerisation, we proposed 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 (**Figure 2A**); still, the importance of the catalyst in the control of the polymerisation remains largely in the dark. To gain a deeper understanding of the nature of methanol as a degenerative chain transfer agent, we decided to de-couple the photredox catalyst (presumably an initiator to generate cations) from the rest of the polymerisation; instead, we employed triflic acid as the initiator to generate cation 'cleanly'. Indeed, this triflic acid initiated polymerisation of *p*-MOS can be controlled by methanol, supporting our original claims (**Figure 2B**).

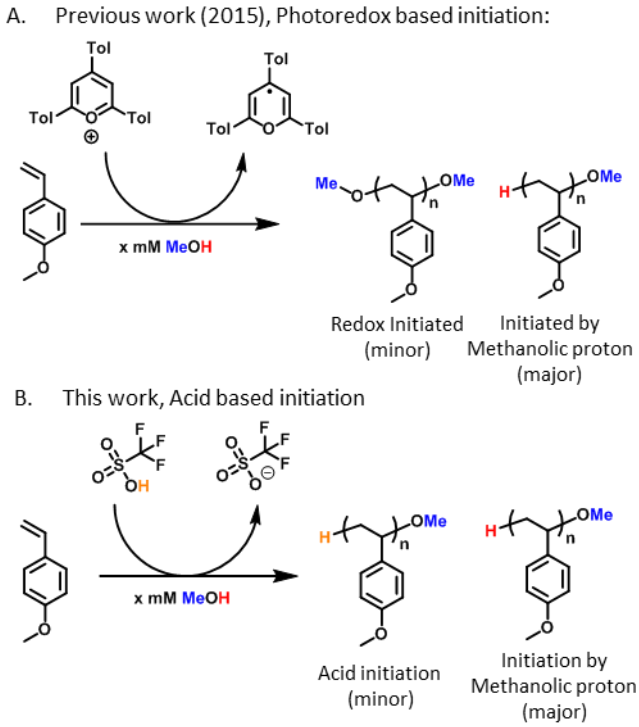


Figure 2. A) Previous work with methanol controlled photocationic polymerisation. B) Current work using methanol controlled cationic polymerisation initiated by triflic acid.

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) was prepared inside a glove box due to the hygroscopic and reactive nature and 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 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) was added via gastight syringe into pre-flame dried and argon purged sealed scintillation vial equipped with magnetic stirrer. The solution was allowed to stir at -10 °C, followed by addition of triflic acid solution prepared as a 20 mg/ml 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 for completion, 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 was 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 0.5M 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 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 has been previously reported to initiate cationic polymerisation at low ppm conentrations.[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 from ^{1}H-NMR spectroscopy by integrating the -CH***H*** vinylic proton at 5.57 ppm and using the phenyl-methoxy -OC***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, **Figure 3**). TfOH initiated cationic polymerisation, without the presence of methanol, generated high molecular weight polymers ($M_{n,SEC}$ = 22,480 gmol^{-1}) with a broad dispersity ($Đ$ = 3.44) (**Figure 3**, **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 literature.[29] However, when methanol was added to the reaction mixture prior to the addition of acid, a profound decrease in experimental molar mass ($M_{n,SEC}$) accompanied with narrow dispersity from SEC

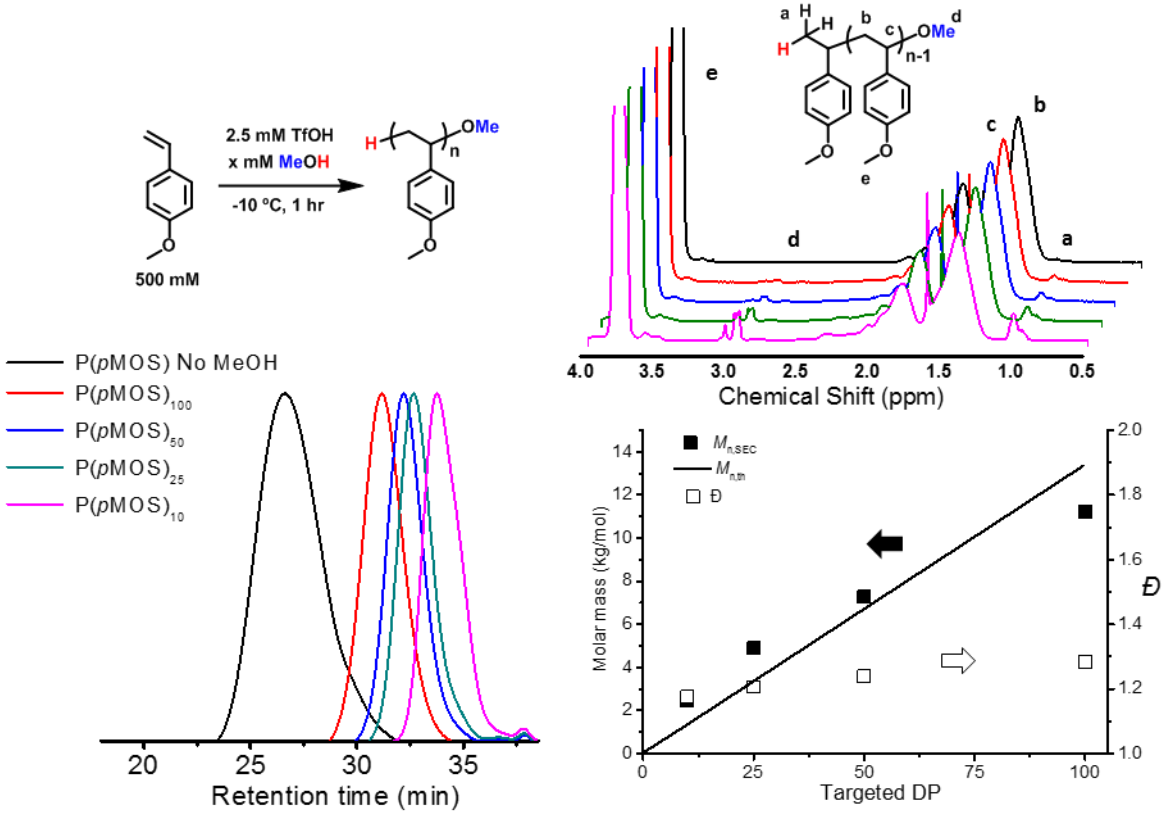


Figure 3. Cationic RAFT polymerisation of *p*MOS with MeOH as the RAFT agent ([MeOH] = 0, 5, 10, 20, and 50 mM). Bottom left: SEC chromatograms (dRI, THF) of p(*p*-MOS) controlled by MeOH. The targeted DP is ratio of monomer to CTA ([pMOS]/[MeOH]) assuming additional chains generated from the initiator to be negligible. Bottom right, the black line represents 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, ^{1}H-NMR spectrum shows the end groups of p(*p*-MOS).

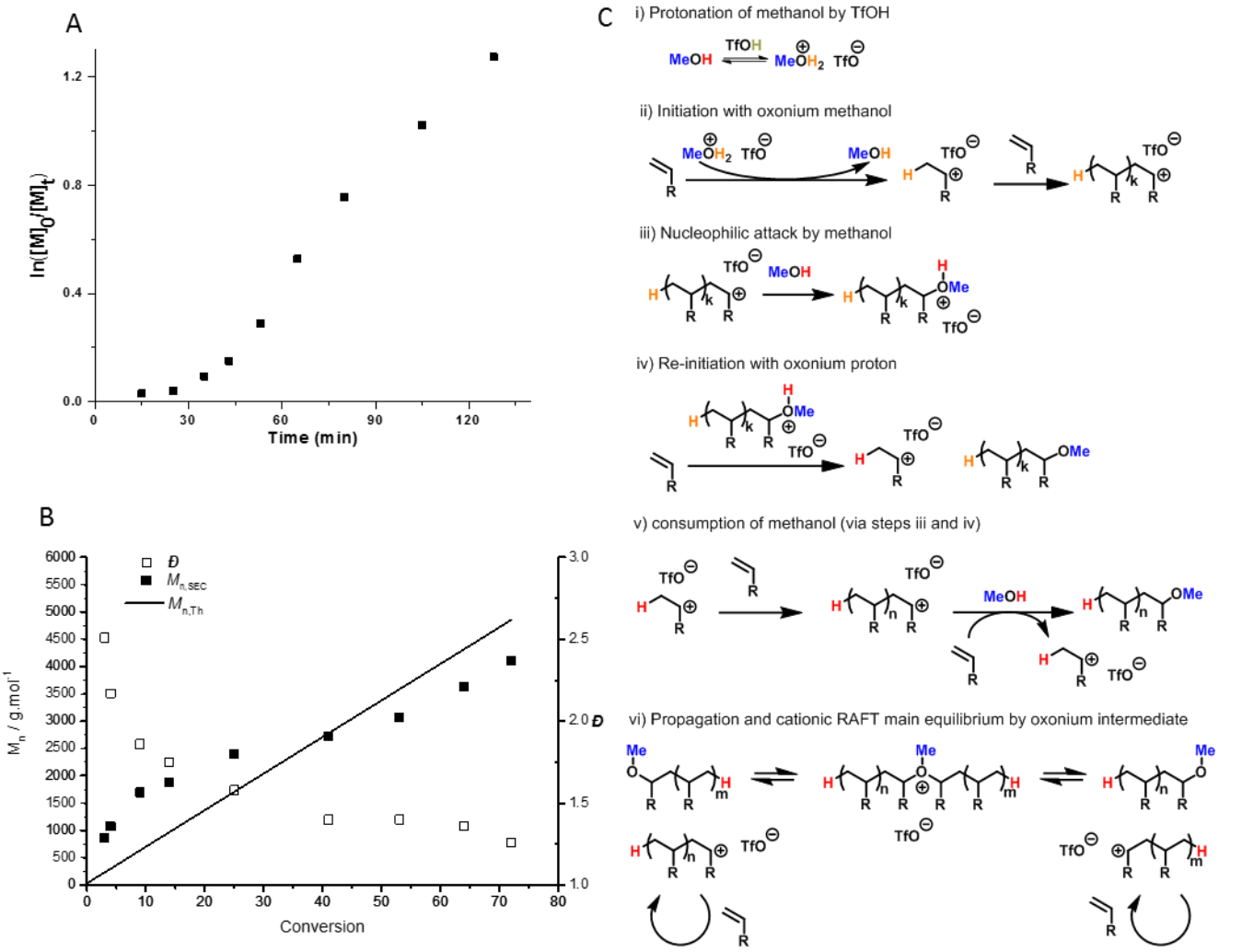


Figure 4. A, B) Kinetic analysis of triflic acid initiated Cationic-RAFT polymerisation of *p*MOS with MeOH as a RAFT agent. C) Proposed mechanism for methanol mediated cationic RAFT polymerisation: i) Protonation of methanol with TfOH, ii) initiation of monomer with oxonium methanol, iii) nucleophilic 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 oxonium intermediate.

analysis ($Đ$ < 1.30) was observed (**Figure 3**, **Table 1**). The control was comparable to xanthate[29] and trithiocarbonate[25] based RAFT agent. Furthermore, the increasing MeOH concentration led to 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 ($M_{n,th}$, **Figure 3**) calculated from the targeted (Degree of Polymerisation) DP based on monomer to CTA ratio ($[M]_0/[MeOH]$), Equation 1).

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

To ascertain 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, 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 reveals, two broad ^{2}H signals at 2.55-3.25 ppm from the ω-OC***D***$_3$ and 0.70 – 1.30 pm α -CH$_2$***D*** with observed

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

Entry	[p-MOS]:[MeOH]:[TfOH]	$M_{n,th}$[a] (gmol^{-1})	$M_{n,SEC}$[c] (gmol^{-1})	$Đ$[c]
1[d,e]	500 : 0 : 2.5	26,900[b]	22,480	3.44
2[d]	500 : 50 : 2.5	1400	2,230	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	13500	11250	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 chain length calculated from $[p\text{-MOS}]_0/[TfOH]_0$ ratio of 200:1. [c.] Determined by SEC in THF with polystyrene standards. [d.] GPC and NMR presented in Figure 3. [e.] GPC presented in Figure 6 and Table 2. [f.] GPC plotted in Figure 5.

integral ratio of 3:0.7 which is consistent with theoretical ratio of 3:1 with 100% deuterium initiation (supporting information, **Figure S1**).

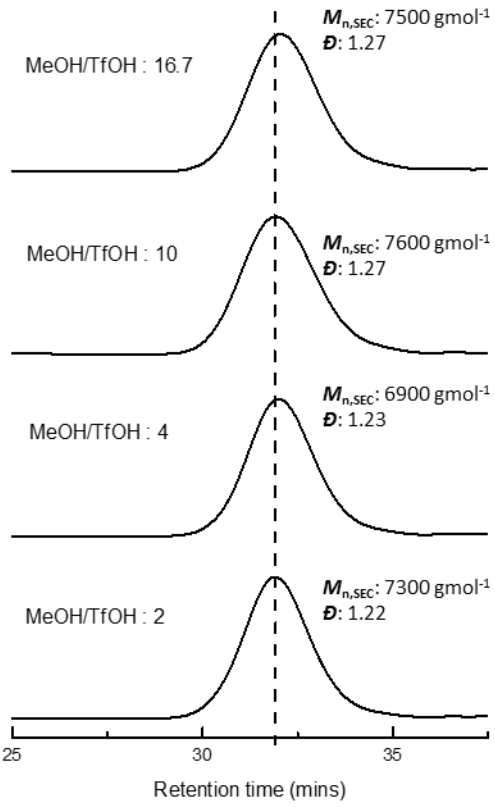


Figure 5. SEC chromatogram (dRI, THF) of p(*p*-MOS)$_{50}$ varying the triflic acid concentration.

To probe further into the mechanism of polymerisation, the rate of monomer consumption was monitored over time (**Figure 4A,B**, supporting information, **Figure 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 (**Figure 4B**, *Đ* >1.5), indicative of 'free' cationic polymerisation with triflic acid, in contrast to our photocationic polymerisation, were low *Đ* was observed even at a low conversion.[28] Our hypothesis is that during the 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 the alcohols are consumed, the propagation is accelerated with pseudo first-order kinetics after 40 % monomer conversion, where controlled chain growth was observed (*Đ* < 1.3). This is indicative of steady state controlled chain growth through the RAFT equilibrium between the propagating chains and oxonium intermediate (**Figure 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 formation of several distinct solvated propagating species in the beginning of 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 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 relatively low CTA/initiator ratio, the theoretical mass should consider the amount of initiator (i.e., 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 the TfOH as low as 0.6 mM, which furnished relatively $M_{n,SEC}$ of 7500 gmol^{-1} with theoretical [MeOH]/[TfOH] ratio as high as 16.7 **(Figure 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 [MeOH]/[TfOH] ratio as low as 2 ([TfOH] = 5 mM), 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 molar mass measured ($M_{n,SEC}$ 7300 gmol^{-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 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 oxygen present in the system (**Scheme S1**) without generating additional chains from excessive TfOH. In addition, surprisingly lower *Đ* at higher TfOH suggests protonated oxonium methanol to act as the main initiator and hence initiation is accelerated at higher TfOH loading, thus leading to lower *Đ*. We suspect this phenomenon to also

contribute towards the lack of the molar mass dependency of on the synthesized polymers on the quantity of TfOH.

Table 2 Alcohol additive study

Entry[a]	Alcohol	$M_{n,th}$ (gmol^{-1})[b]	$M_{n,SEC}$ (gmol^{-1})[c]	$Đ$[c]
A1	Methanol	6700	7200	1.28
A2	Ethanol	6800	10200	1.24
A3	Isopropanol	6800	20400	1.28
A4	Tert-Butanol	6800	88500	1.55
A5	Trifluoroethanol	6800	26400	1.71
A0	None	26900[d]	22480	3.44

[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 chain length calculated from $[p\text{-MOS}]_0/[\text{TfOH}]_0$ ratio of 200:1

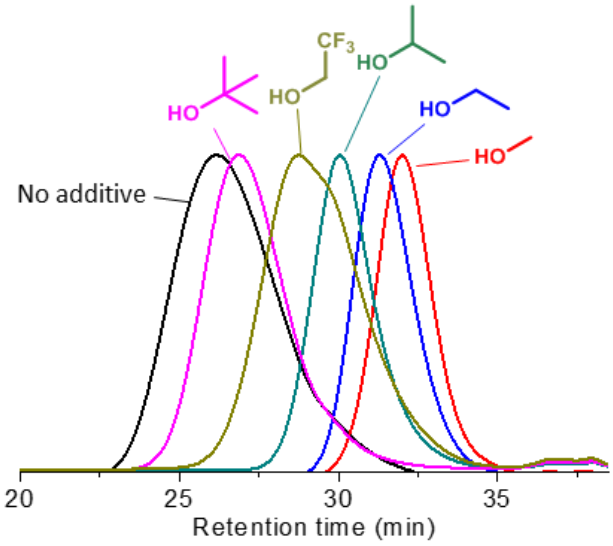
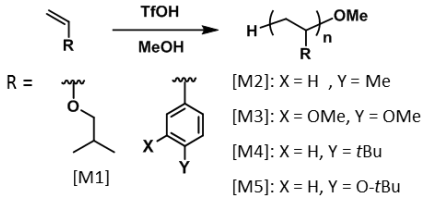


Figure 6. SEC chromatogram (dRI, THF) of p(*p*-MOS)$_{50}$ (targeted DP of 50, in all case) controlled with different alcohol, $M_{n,SEC}$ and $Đ$ tabulated in Table 2.

Mechanistically, as the key functional group is the alcohol motif, a series of experiments were carried out to investigate whether other alcohols could achieve same level of control on this cationic polymerisation, i.e., effectively investigating the influence of Z-group. Experimentally, for easy comparison, we maintained identical experimental condition (e.g., the same ratio of [alcohol]:[TfOH]:$[p\text{-MOS}]_0$) for different alcohols based polymerisations. Specifically, increasing the substituent to ethyl-alcohol (A2, **Table 2**), the control was maintained ($Đ$ = 1.24) with unimodal molecular weight distribution (**Figure 6**), yet the $M_{n,SEC}$ was almost doubled ($M_{n,SEC}$ = 10200 gmol^{-1}) in comparison to methanol controlled polymerisation. Increasing the substituent of the Z-group further using a secondary alcohol, isopropyl alcohol (A3, **Table 2**) still maintained good control over the molecular weight ($Đ$ = 1.28), however, this was accompanied with a further shift in $M_{n,SEC}$ (**Figure 6**, $M_{n,SEC}$ = 20400 gmol^{-1}). This was remarkably consistent with our previous findings where 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 with 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 of the Z-group to tertiary alcohol was found to be detrimental on the polymerisation control (A4, **Table 2**, $M_{n,SEC}$ = 88500 gmol^{-1}, $Đ$ = 1.55). Consistent with our previous work, trifluoroethanol was not able to control the polymerisation, as a result of decreased nucleophilicity of the alcohol (A5, **Table 2**). Additionally, no presence of fluorine was detected by ^{19}F-NMR (**Figure S7**).

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 typical vinyl ether family of monomers such as Isobutyl vinyl ether (entry M1, **Table 3**). Lack of control was also observed in styrenic monomers with the absence of stabilising electron donating *para*-alkoxy group such as 4-methyl styrene (M2, **Table 3**) and *tert*-butyl styrene (M4, **Table 3**). Whereas good control were found for *para*-alkoxy group containing styrene monomers such as 1,2 methoxy styrene (M3, **Table 3**) and *tert*-butyloxy styrene (M5, **Table 3**). Indicating that the absence of *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]

Table 3: Cationic of Polymerisation in presence of methanol with various monomers



Entry[a]	$M_{n,th}$ (gmol^{-1})[b]	$M_{n,SEC}$ (gmol^{-1})[c]	$Đ$[c]
M1	5000	3300	1.80
M2	5900	5300	1.87
M3	8200	6700	1.29
M4	8000	4400	1.54
M5	8800	13200	1.23

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

To further demonstrate the retention of the livingness of our system, a series of chain extensions from initial block with targeted DPs of 25, 50 and 100 were carried out, aiming to extend with an equal block length, respectively. Experimentally, this was done by sequentially adding new monomer solution without the addition of more TfOH. In theory, if no base was used to quench the 'living' cationic polymerisation, no

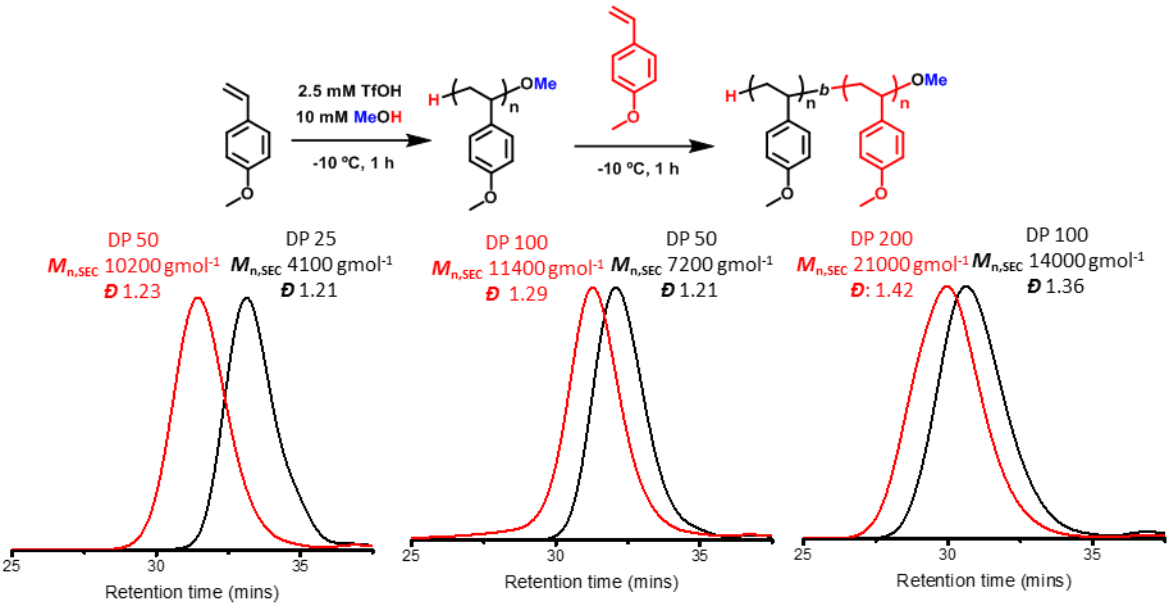


Figure 7. SEC chromatogram (dRI, THF) of series of chain extensions (in red) of various chain length.

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, clear shift in $M_{n,SEC}$ was observed by SEC analysis (**Figure 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 broader distribution ($Đ$ > 1.4), however the shift in molecular weight distribution was still noticeable (**Figure 7**). The chain extendibility of our system after base mediated termination and isolation was also investigated. To ensure no additional chain transfer from 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 gmol^{-1}, $Đ$ = 1.31, **Figure S8**), a shift in molecular weight distribution was observed by SEC analysis ($M_{n,SEC}$ = 5800 gmol^{-1}, $Đ$ = 1.42, **Figure S8**), indicative of chain extension by chain transfer between dormant chains with newly formed propagating species.

Conclusions

Alcohols has been commonly used as nucleophilic quencher for cationic polymerisation; however, in this work, we show that 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 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 CTA. 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, 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.

Acknowledgements

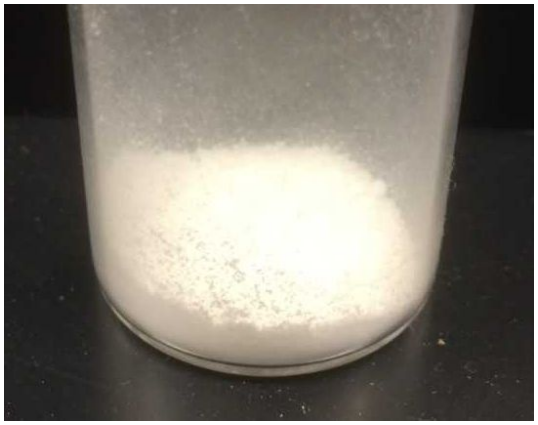
This work was financially supported by the University of North Carolina at Chapel Hill. AP, HH, DAN and WY acknowledge Eastman Chemical for financial support. JT was supported by the National Science Foundation under Award CHE-1808055.

Notes and references

1. P. Gurnani, C. Sanchez-Cano, K. Abraham, H. Xandri-Monje, A. B. Cook, M. Hartlieb, F. Lévi, R. Dallmann and S. Perrier, *Macromol. Biosci*, 2018, **0**, 1800213.
2. J. Zhang, J. Tanaka, P. Gurnani, P. Wilson, M. Hartlieb and S. Perrier, *Polymer Chemistry*, 2017, **8**, 4079-4087.
3. P. Gurnani, A. M. Lunn and S. Perrier, *Polymer*, 2016, **106**, 229-237.

4. J. Tanaka, S. Tani, R. Peltier, E. H. Pilkington, A. Kerr, T. P. Davis and P. Wilson, *Polymer Chemistry*, 2018, **9**, 1551-1556.
5. C. Footman, P. A. de Jongh, J. Tanaka, R. Peltier, K. Kempe, T. P. Davis and P. Wilson, *Chemical Communications*, 2017, **53**, 8447-8450.
6. A. B. Cook, R. Peltier, M. Hartlieb, R. Whitfield, G. Moriceau, J. A. Burns, D. M. Haddleton and S. Perrier, *Polymer Chemistry*, 2018, **9**, 4025-4035.
7. R. Whitfield, A. Anastasaki, N. P. Truong, A. B. Cook, M. Omedes-Pujol, V. Loczenski Rose, T. A. H. Nguyen, J. A. Burns, S. Perrier, T. P. Davis and D. M. Haddleton, *Acs Macro Letters*, 2018, **7**, 909-915.
8. A. Anastasaki, V. Nikolaou and D. M. Haddleton, *Polymer Chemistry*, 2016, **7**, 1002-1026.
9. G. Moad, *Polymer Chemistry*, 2017, **8**, 177-219.
10. H. Mach and P. Rath, *Lubrication Science*, 1999, **11**, 175-185.
11. A. J. Teator and F. A. Leibfarth, *Science*, 2019, **363**, 1439-1443.
12. S. Aoshima and S. Kanaoka, *Chemical Reviews*, 2009, **109**, 5245-5287.
13. J. P. Kennedy, *J. Polym. Sci. Part A Polym. Chem.*, 1999, **37**, 2285-2293.
14. S. Perrier, *Macromolecules*, 2017, **50**, 7433-7447.
15. M. Kamigaito, K. Satoh and M. Uchiyama, *Journal of Polymer Science Part A: Polymer Chemistry*, 2019, **57**, 243-254.
16. M. Uchiyama, K. Satoh and M. Kamigaito, *Angewandte Chemie International Edition*, 2015, **54**, 1924-1928.
17. M. Guerre, M. Uchiyama, E. Folgado, M. Semsarilar, B. Améduri, K. Satoh, M. Kamigaito and V. Ladmiral, *Acs Macro Letters*, 2017, **6**, 393-398.
18. V. Kottisch, Q. Michaudel and B. P. Fors, *Journal of the American Chemical Society*, 2016, **138**, 15535-15538.
19. J. Yeow, R. Chapman, A. J. Gormley and C. Boyer, *Chemical Society Reviews*, 2018, **47**, 4357-4387.
20. G. Ng, J. Yeow, R. Chapman, N. Isahak, E. Wolvetang, J. J. Cooper-White and C. Boyer, *Macromolecules*, 2018, **51**, 7600-7607.
21. J. Yeow, R. Chapman, J. Xu and C. Boyer, *Polymer Chemistry*, 2017, **8**, 5012-5022.
22. B. M. Peterson, S. Lin and B. P. Fors, *Journal of the American Chemical Society*, 2018, **140**, 2076-2079.
23. V. Kottisch, Q. Michaudel and B. P. Fors, *Journal of the American Chemical Society*, 2017, **139**, 10665-10668.
24. Q. Michaudel, T. Chauviré, V. Kottisch, M. J. Supej, K. J. Stawiasz, L. Shen, W. R. Zipfel, H. D. Abruña, J. H. Freed and B. P. Fors, *Journal of the American Chemical Society*, 2017, **139**, 15530-15538.
25. B. M. Peterson, V. Kottisch, M. J. Supej and B. P. Fors, *ACS Central Science*, 2018, **4**, 1228-1234.
26. M. Uchiyama, K. Satoh and M. Kamigaito, *Polymer Chemistry*, 2016, **7**, 1387-1396.
27. M. Uchiyama, K. Satoh and M. Kamigaito, *Macromolecules*, 2015, **48**, 5533-5542.
28. A. J. Perkowski, W. You and D. A. Nicewicz, *Journal of the American Chemical Society*, 2015, **137**, 7580-7583.
29. S. Sugihara, S. Okubo and Y. Maeda, *Polymer Chemistry*, 2016, **7**, 6854-6863.
30. G. Sauvet, M. Moreau and P. Sigwalt, *Makromolekulare Chemie. Macromolecular Symposia*, 1986, **3**, 33-46.
31. G. Gody, T. Maschmeyer, P. B. Zetterlund and S. Perrier, *Macromolecules*, 2014, **47**, 3451-3460.
32. G. Gody, T. Maschmeyer, P. B. Zetterlund and S. Perrier, *Macromolecules*, 2014, **47**, 639-649.
33. A. Kanazawa, S. Shibutani, N. Yoshinari, T. Konno, S. Kanaoka and S. Aoshima, *Macromolecules*, 2012, **45**, 7749-7757.
34. N. Kolishetti and R. Faust, *Macromolecules*, 2008, **41**, 3842-3851.

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



Alka Prasher,[a] Huamin Hu,[a] Joji Tanaka,[a] David A. Nicewicz,[a] Wei You[a]*

[a.]Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290, United States.