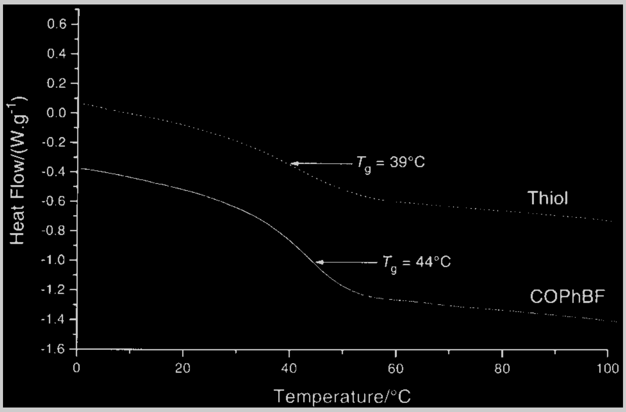
Full Paper: Batch solution terpolymerizations of styrene, methyl methacrylate and 2-hydroxyethyl methacrylate were carried out at 70 °C in the presence of either dodecanethiol or bis[(difluoroboryl)diphenylglyoximato]cobalt-(II) (COPhBF), to yield polymer products with a number average molecular weight of about 2 500. Conversion, molecular weight distribution and overall composition were monitored during the reaction, and the final products were investigated using differential scanning calorimetry and thermogravimetric analysis. It was found that the overall rates of polymerization do not differ significantly in the two systems, but that the molecular weight distribution of the polymer formed in the presence of the thiol becomes increasingly broader during the polymerization, whereas the COPhBF-mediated polymerization produces a relatively uniform product during the course of the reaction. The polymer product formed with COPhBF was found to be slightly less thermally stable than the product formed by the thiol, which can be explained by the formation of unsaturated endgroups in the case of the former product.



DSC thermograms showing the glass transition behaviour of the terpolymer oligomers generated in the thiol and COPhBF mediated reactions.

Preparation and characterization of oligomeric terpolymers of styrene, methyl methacrylate and 2-hydroxyethyl methacrylate: A comparison of conventional and catalytic chain transfer

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Introduction

One important aspect of organic coatings design is the volatile organics content (VOC) which is under constant review as legislation and industry best practice push for reductions. Ideally, high solids coatings (60–80% solids) would also have a sufficiently low viscosity to permit easy application procedures.[1] The major limiting factor in high solids coatings formulation is increased viscosity that can only be reduced by moving towards lower molecular weights, i. e. oligomers. This has two disadvantages: firstly, low molecular weights can only be attained using either high initiator or chain transfer agent concentrations, and secondly, the low molecular weight polymers display poor resilience and weak mechanical properties. Therefore, the oligomers must contain reactive functionality to allow crosslinking or chain extension on application. One aim of this study is to investigate catalytic chain transfer (CCT) as a potentially useful synthetic approach to oligomers for high solids coatings formulations. A secondary aim, is to compare the CCT polymerization process and final product properties with a conventional thiol transfer polymerization route. The formulation selected for study is a terpolymer of styrene, methyl methacrylate and 2-hydroxyethyl methacrylate which is a typical basic coatings formulation suitable for isocyanate curing.

Chain transfer

Low molecular weight polymers are commonly prepared by the addition of a chain transfer agent, X, to which the

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"radical activity" of the growing polymer chain is transferred, resulting in a dead polymer chain and a small radical (often) capable of re-initiation (Eq. (1)).[2–4]

$$R_n^{\bullet} + X \xrightarrow{k_{tr,X}} P_n + X^{\bullet} \qquad (1)$$

Here, $R_n^{\bullet}$ is the polymeric radical containing n monomer units, X is the chain transfer agent, and P_n is the dead polymer chain containing *n* monomer units. The transfer of "radical activity" occurs generally via the transfer of an atom, such as a hydrogen atom (e.g., thiols) or a halogen atom (e.g., CCl_4 and CBr_4), between the chain transfer agent and the growing radical chain, and its efficiency is expressed in the chain transfer constant, C_X, which is the ratio of the rate coefficient of the chain transfer reaction, $k_{tr,X}$, and the propagation rate coefficient, k_p:

$$C_X = \frac{k_{tr,X}}{k_p} \qquad (2)$$

A quantification of the effect of the addition of a chain transfer agent on the number average degree of polymerization, DP_n, is given by the Mayo equation:[4, 5]

$$\frac{1}{DP_n} = \frac{1}{DP_{n,0}} + C_X \frac{[X]}{[M]} \qquad (3)$$

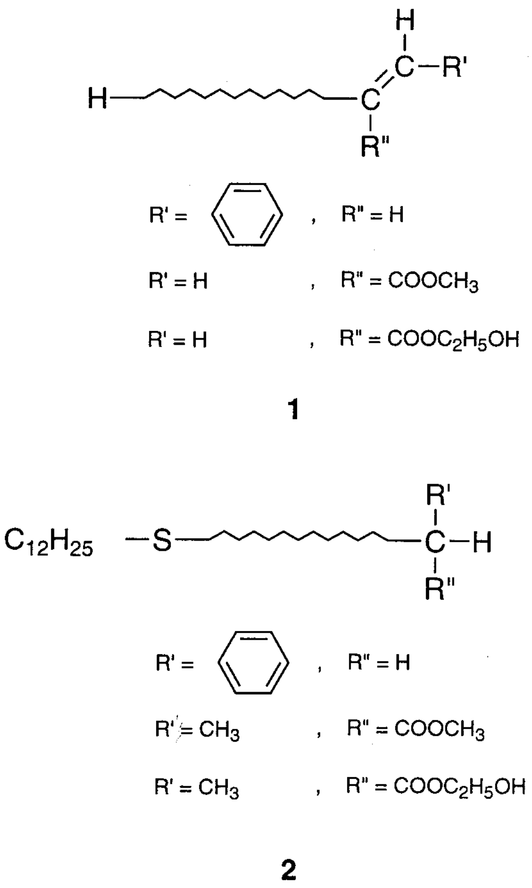
where $DP_{n,0}$ is the number average degree of polymerization which would be obtained in the absence of added chain transfer agent, ceteris paribus. In the case of a copolymerization, the kinetic parameters and concentrations should be based on overall radical and monomer concentrations.[6–8] Conventional chain transfer agents, such as thiols, have chain transfer constants in the range 10^{-2}–10; consequently high concentrations are required to significantly reduce the molecular weight of the polymer.[9] Since thiols are odorous and toxic, any residuals require removal from the polymer product.

Catalytic chain transfer (CCT) polymerization provides an alternative to the use of conventional chain transfer. CCT was originally discovered in the early 1980s by Enikolopyan and co-workers.[10–12] Certain low-spin Co(II) complexes, such as porphyrins and cobaloximes, catalyze the chain transfer to monomer reaction, yielding dead polymer chains with a vinyl end-functionality and a monomeric radical. The mechanism is generally assumed to proceed via a Co(III)—H intermediate:[10–12]

$$R_n^{\bullet} + \mathrm{Co(II)} \longrightarrow P_n + \mathrm{Co(III)}\text{—}H \qquad (4a)$$

$$\mathrm{Co(III)}\text{—}H + \mathrm{Mon} \longrightarrow R_1^{\bullet} + \mathrm{Co(II)} \qquad (4b)$$

It is evident from these two reactions that the Co(II) catalyst is not consumed during the reaction. This contrasts with the conventional chain transfer mechanism, described by Eq. (1). The catalytic nature of the reaction, together with chain transfer constants in the range 10^2–10^5,[10–12] results in very efficient molecular weight control in the presence of only ppm quantities of the catalyst. Since the mechanisms of conventional and catalytic chain transfer processes differ, it is important to know how this variation affects the polymerization kinetics and the final product properties.



Scheme 1.

Experimental part

Materials

The bis(methanol) complex of bis[(difluoroboryl)diphenylglyoximato]cobalt(II) (COPhBF), was prepared as described previously.[13, 14] Styrene (99%), methyl methacrylate (99%) and 2-hydroxyethyl methacrylate (99%), all kindly provided by Orica/Dulux Australia, were passed through a column of activated basic alumina (ACROS, 50–200 micron) and purged with high purity nitrogen (BOC) for 1.5 h prior to use. *n*-Dodecanethiol (DDM, Aldrich, 98%) was used without further purification and purged with high purity nitrogen gas for about 10 min prior to use. AIBN (DuPont) was recrystallized twice from methanol and used as initiatior. The solvents butyl acetate (Aldrich, 99 + %) and xylene (BDH, AnalaR) were used without any purification.

Polymerization procedure

A mixture (2:1 v/v) of butyl acetate and xylene was purged with high purity nitrogen (BOC) for approximately 1 h prior to use. Approximately 33 ml of MMA, 33 ml of S, 33 ml of HEMA and 200 ml of the solvent mixture were then charged into a two-neck roundbottom flask containing a magnetic stirrer bar, ~1.4 g of AIBN and the required amount of COPhBF (0–9 mg). The roundbottom flask was subjected to three vacuum-nitrogen purge cycles prior to charging with solvent, monomer, and, in the case of the mercaptan experiments, ~7 g of DDM. During the charging process, care was taken to exclude oxygen from the reaction mixture. Polymerizations were carried out with continuous stirring (magnetic) in a water bath thermostated at 72 °C.

Throughout the polymerization, samples were taken in order to measure conversion by gravimetry, and to determine the molecular weight distribution and cumulative composition of the terpolymer. After 20–24 h, the reactions were stopped by addition of hydroquinone and solvent was removed with a rotary evaporator.

Polymer characterization

Molecular weight distributions were determined by size exclusion chromatography using a GBC Instruments LC1120 HPLC pump, a Shimadzu SIL-10A Autoinjector, a column set consisting of a Polymer Laboratories 3.0 μm bead-size guard column (50 × 7.5 mm) followed by four linear PL columns (10^6, 10^5, 10^4 and 10^3) and a VISCOTEK dual detector Model 250 differential refractive index detector. Tetrahydrofuran (BDH, HPLC grade) was used as eluent at 1 ml/min. Calibration of the SEC equipment was performed with narrow polystyrene (Polymer Laboratories, molecular weight range: $580–3.0 \cdot 10^6$) and poly(methyl methacrylate) (Polymer Laboratories, molecular weight range: $200–1.6 \cdot 10^6$) standards.

Average terpolymer compositions were determined by ^{1}H-NMR analysis with a 300 MHz (Bruker ACF 300) spectrometer using $CDCl_3$ (Aldrich, 99.8 atom% D) as a solvent.

The glass transition temperatures of the final polymer products were determined using a TA Instruments DSC 2010 Differential Scanning Calorimeter, at a heating rate of 10 °C min^{-1} using sample weights in the range 5–10 mg. Thermal degradation of the final polymer products was studied under nitrogen atmosphere using a TA Instruments TGA 2050 Thermogravimetric Analyzer at a heating rate of 20 °C min^{-1} using sample weights in the range 8–15 mg.

Results and discussion

Relative chain transfer agent concentrations

A specific molecular weight of 2 500 was targeted to permit a direct comparison of the two transfer processes. This value was chosen, as it is large enough to satisfy the long chain assumption in the kinetic analysis. The requisite amount of chain transfer agent was evaluated in preliminary experiments, shown in Fig. 1 where the final average degree of polymerization of the terpolymer is given as a function of the initial concentrations of COPhBF and DDM, respectively. It is evident that the target $\overline{M}_n$ of ~ 2500 is attained when using [COPhBF] ≈ $4.1 \cdot 10^{-5}$ M or [DDM] ≈ $1.1 \cdot 10^{-1}$ M. These specific concentrations were used in all the subsequent studies.

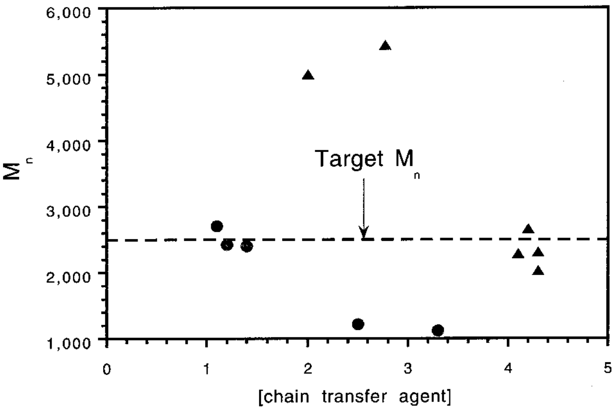


Fig. 1. Data from preliminary experiments targeting a molecular weight of 2500 using ● DDM (× 10^{-1} M) and ▲ COPhBF (× 10^{-5} M).

Polymerization rate

Polymerization conversions were monitored as a function of time by gravimetry for both the thiol and COPhBF-mediated polymerizations. The results, shown in Fig. 2 clearly indicate that there is no significant difference between the two systems. In both polymerization systems the gel effect is absent and the rate of polymerization (R_p) at every single point in time is given by the classical rate equation:[4]

$$R_p = \langle k_p \rangle \sqrt{\frac{fk_d[\mathrm{I}]}{\langle k_t \rangle}}[\mathrm{Mon}] \qquad (6)$$

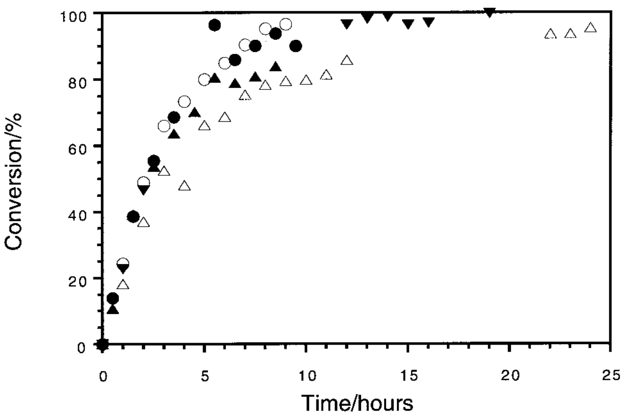


Fig. 2. Replicate time-conversion plots for the terpolymerization reaction with DDM (●, ○) and COPhBF(▲, ▼, △).

Tab. 1. Evolution of molecular weight with conversion in the thiol-mediated terpolymerization (where M_p refers to the peak molecular weight).

Conversion %	M_p	$\overline{M}_n$	$\overline{M}_w$	PDI
27.3	2626	1651	2985	1.8
51.9	2974	1797	3384	1.9
69.0	3194	2011	3971	2.0
76.4	3461	2172	4502	2.1
83.0	3292	2254	4955	2.2
87.9	3531	2325	5542	2.4
93.4	3584	2515	6094	2.4
98.2	3638	2387	6076	2.5
99.6	4051	2707	6630	2.5

Tab. 2. Evolution of molecular weight with conversion in the COPhBF-mediated terpolymerization (where M_p refers to the peak molecular weight).

Conversion %	M_p	$\overline{M}_n$	$\overline{M}_w$	PDI
18.2	4674	2758	5708	2.1
37.1	4333	2713	5447	2.0
52.5	4763	2814	5561	2.0
66.3	4271	2470	5217	2.1
78.4	4150	2101	4974	2.4
81.5	3973	2273	4934	2.2
85.8	3915	2343	5015	2.1
93.7	4070	2361	5045	2.1
95.5	3954	2286	5081	2.2

where $\langle k_p \rangle$ and $\langle k_t \rangle$ are the average rate coefficients for propagation and termination, respectively, f the initator efficiency, k_d the initiator decomposition rate coefficient, and [I] the initiator concentration. The average termination rate coefficient is diffusion controlled, and is dependent on the average molecular weight produced, and the overall conversion (which determines the viscosity).[15] Since similar molecular weights are targeted in both experiments, the conversion-time plots are expected to be similar. Previous studies of catalytic chain transfer copolymerization have indicated that conventional copolymerization propagation kinetics are applicable to catalytic chain transfer polymerization.[14, 16] In summary, the results validate the long chain assumption and are consonant with conventional copolymerization kinetics.

Tab. 3. Final molecular weight data for all the terpolymerization experiments.

Quantity CTA[a) g]	n-Dodecanethiol $\overline{M}_n$	$\overline{M}_w$	M_p	PDI
8.45	2399	6663	3036	2.78
6.91	2707	6630	4051	2.45
6.97	3381	7584	4322	2.24

Quantity CTA[a) mg]	COPhBF $\overline{M}_n$	$\overline{M}_w$	M_p	PDI
8.3	2286	5081	3954	2.22
8.5	4140	10252	8937	2.48
8.6	2663	5742	4652	2.16

a) Amount per 300 ml of monomer solution.

Molecular weight evolution

As the chain transfer mechanism in the two systems differ, it is important to assess the influence of the chain stopping process on the development of the molecular weight distributions with time. The molecular weight distributions obtained in the thiol and COPhBF-mediated terpolymerizations are shown as a function of time in Tab. 1 and 2 respectively. It is evident from these results that there is a significant drift in the molecular weight distributions with conversion for the polymers prepared with the thiol, whereas with COPhBF, an invariant molecular weight distribution is formed during the course of the reaction. Assuming that there is no significant change in the relative fractions of the different types of propagating radicals (see the following section), then the drift in the thiol mediated polymerization is caused by disparate rates of thiol and monomer consumption. This results in a decreasing ratio of [DDM]/[monomer], and therefore an increasing DP_n (see Eq. (3)). An explanation for the invariant molecular weight distribution obtained with CCT is more elusive. However, these results are consistent with previous findings in the homopolymerizations of styrene[17] and methyl methacrylate[17, 18] with catalytic chain transfer. As the COPhBF catalyst is not incorporated into the oligomer chains, the [COPhBF]/[monomer] ratio should increase, resulting in a decreasing DP_n (see Eq. (3)). This is clearly not observed and a plausible explanation for this result[19] other than (fortuitous) catalyst poisoning,[20, 21] is not available at present. A summary of the final molecular weight parameters obtained from all the polymerizations is given in Tab. 3.

Composition drift

In a copolymerization of multiple monomers, the compositional homogeneity of the polymer is governed by composition drift, originating from a non-proportional consumption of the comonomers. In the case of a chain-transfer-dominated copolymerization, a large composition drift would not only lead to compositional heterogeneity of the product, but could also lead to a significant broadening of the molecular weight distribution. The potential impact of drift is significant in this work as the reactivities of styrene and methacrylate radicals in chain transfer are quite disparate. The styrene radicals are about 20

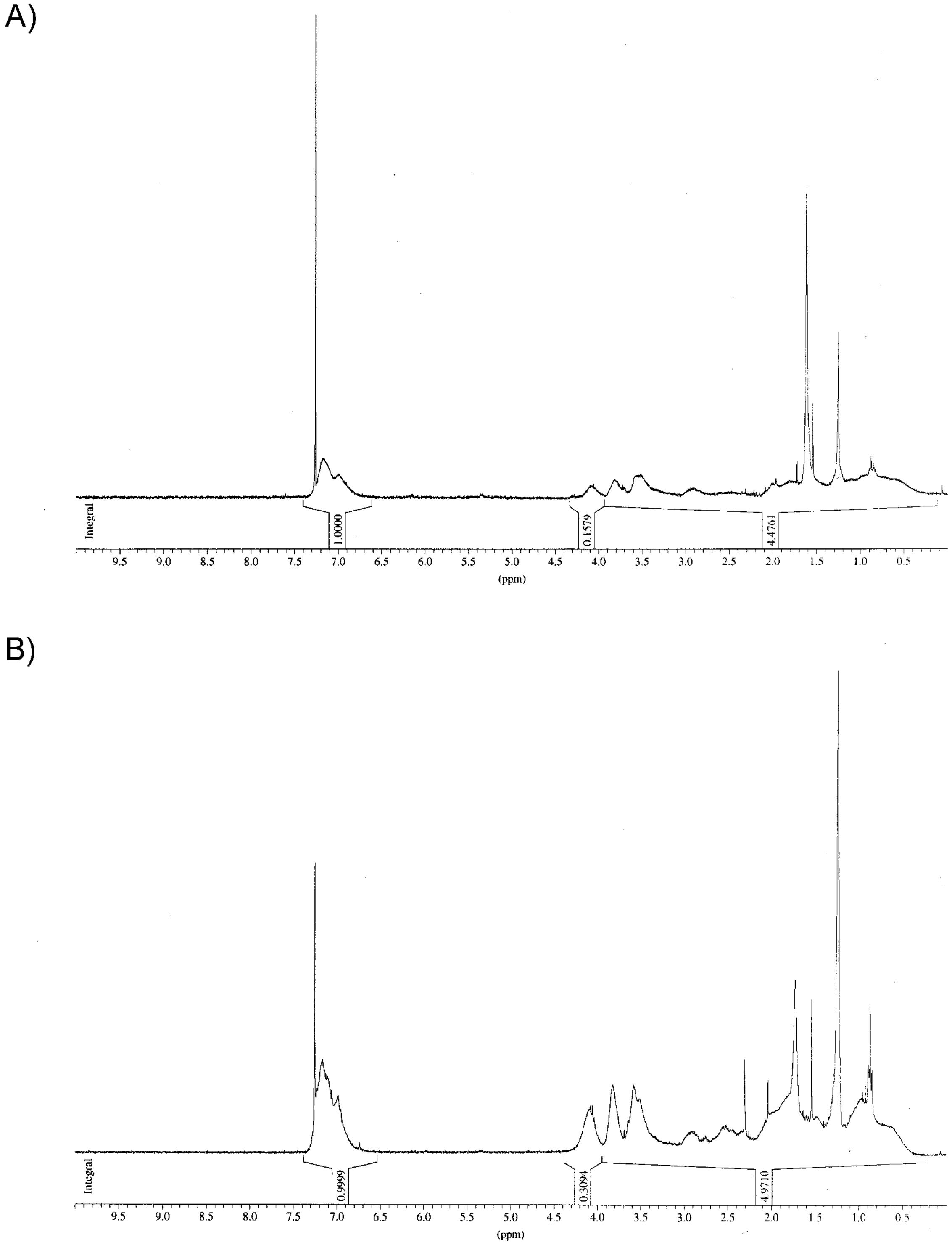


Fig. 3. NMR spectra for the thiol mediated (A) and the COPhBF(B) mediated terpolymers.

times more reactive than the methacrylate radicals towards thiols.[3] In contrast, the methacrylate radicals are about 20 times more reactive towards COPhBF[14, 22] (assuming that the HEMA and MMA radicals have a similar reactivity in chain transfer reactions). Consequently, significant composition drift, leading to different ratios of the propagating radicals, would result in a large drift in the molecular weight distributions.

The composition drift was analysed by following the average terpolymer composition as a function of conversion using ^{1}H NMR.[23, 24] In Fig. 3a and 3b, the ^{1}H NMR spectra at ~70% conversion are shown for terpolymers prepared by COPhBF and DDM, respectively; very similar spectra were obtained during the entire course of polymerization in both systems. It is clear from these spectra that the average terpolymer compositions obtained in all the experiments are similar. In Tab. 4, a summary is given of the ^{1}H NMR results and the corresponding compositions of the terpolymers, that were determined using the following expressions:

$$F_S = \frac{A_{\text{phenyl}}/5}{A_{\text{phenyl}}/5 + A_{\text{hydroxyl}} + (A_H - 3 \times (A_{\text{phenyl}}/5) - 9 \times A_{\text{hydroxyl}} - \Phi_T)/8} \tag{6a}$$

$$F_M = \frac{(A_H - 3 \times (A_{\text{phenyl}}/5) - 9 \times A_{\text{hydroxyl}} - \Phi_T)/8}{A_{\text{phenyl}}/5 + A_{\text{hydroxyl}} + (A_H - 3 \times (A_{\text{phenyl}}/5) - 9 \times A_{\text{hydroxyl}} - \Phi_T)/8} \tag{6b}$$

$$F_H = \frac{A_{\text{hydroxyl}}}{A_{\text{phenyl}}/5 + A_{\text{hydroxyl}} + (A_H - 3 \times (A_{\text{phenyl}}/5) - 9 \times A_{\text{hydroxyl}} - \Phi_T)/8} \tag{6c}$$

where F_i is the mole fraction of monomer i in the copolymer (i = S, H or M), A_{phenyl} is the peak area of the 5 phenyl protons of styrene (δ = 7.5–6.5), A_{hydroxyl} is the peak area of the one hydroxyl proton of HEMA (δ = 4.4–4.0), A_H is the peak which contains all aliphatic protons in the terpolymer (δ = 4.0–0.4), and Φ_T is an approximate correction for the contribution to A_H by the aliphatic protons contributed by the thiol fragment, given by:

$$\Phi_T = \begin{cases} 0 \text{ for polymer prepared with COPhBF} \\ 0.11 \times (A_{\text{phenyl}} + A_{\text{hydroxyl}} + A_H) \text{ for polymer prepared with DDM} \end{cases} \tag{7}$$

The expression for Φ_T is derived assuming that on average there will be one thiol unit (i.e., 26 aliphatic protons) per chain with an average chain length of 25 units. It is assumed (in retrospect) that on average there will be 8 styrene units (= 8 × 8 = 64 H), 8 MMA units (= 8 × 8 = 64 H) and 8 HEMA units (= 8 × 10 = 80 H) per chain. Hence the signals arising from the protons of the incorporated thiol comprise about 11% of the total signal.

It is evident from the results in Tab. 4 that no significant composition drift occurs under the specified reaction conditions. This provides an explanation for the absence of any significant drift in the molecular weight distributions other than that caused by thiol consumption.

Tab. 4. Experimental (NMR) variation of terpolymer composition with conversion.

Conversion	A_{Phenyl}	A_{OH}	A_H	F_{STY}	F_{HEMA}	F_{MMA}
COPhBF						
39.2	1	0.2338	4.0584	0.33	0.39	0.28
63.7	1	0.1675	3.8865	0.34	0.28	0.38
70.2	1	0.178	4.3441	0.31	0.28	0.41
80.6	1	0.2145	3.9004	0.34	0.37	0.29
83.9	1	0.1874	4.1336	0.32	0.30	0.37
DDM						
27.3	1	0.2298	4.8846	0.32	0.37	0.31
69.0	1	0.2736	4.9234	0.32	0.44	0.24
76.4	1	0.2885	4.7003	0.34	0.49	0.18
93.4	1	0.2563	4.7441	0.33	0.42	0.24
99.6	1	0.2429	4.7283	0.33	0.40	0.27

These experimental results were compared to theoretical expectation by utilising a kinetic model based on the Q–e Scheme.[3, 25] Within the Q–e Scheme, the monomer reactivity ratio r_i can be approximated as a function of four parameters Q_i, Q_j, e_i and e_j which reflect certain intrinsic molecular properties of the monomers i and j:[3]

$$r_i = \frac{k_{ii}}{k_{ij}} = \frac{Q_i}{Q_j} \exp\{-e_i(e_i - e_j)\} \tag{8}$$

In this equation, k_{ii} and k_{ij} are the rate coefficients for the addition of a radical with a terminal unit of type i to monomers i and j, respectively. Using the conventional (terminal) copolymerization kinetics and Eq. (8) to express all involved monomer reactivity ratios, the following expression can be derived for the instantaneous fraction of a particular monomer in the terpolymer (F_i for monomer i):[25]

$$F_1 = \frac{f_1 Q_1 \left\{\sum_{i=1}^{3} f_i Q_i \exp(-e_1 e_i)\right\}}{\sum_{i=1}^{3} \sum_{j=1}^{3} f_i Q_i f_j Q_j \exp(-e_i e_j)} \tag{9}$$

In this expression f_i denotes the mole fraction of monomer i in the monomer feed. Since the comonomers may not be consumed with similar rates, it is important to take into account how the monomer feed composition changes with conversion, and at any given fractional conversion of x_θ the monomer feed composition is given by:[25]

$$f_{i,\theta} = \frac{(f_{i,0} - x_\theta \overline{F}_{i,\theta})}{1 - x_\theta} \tag{10}$$

where $\overline{F}_{i,\theta}$ is the cumulative fraction of monomer i in the oligomer, which is given by:[25]

$$\overline{F}_{i,\theta} = \frac{\sum_{m=1}^{\theta} \Delta x_m F_{i,m-1}}{x_\theta} \tag{11}$$

and Δx_m is the change in conversion between two consecutive "sample points":[25]

$$\Delta x_m = x_m - x_{m-1} \tag{12}$$

Use of Eqs. (9)–(12) permits the calculation of instantaneous and cumulative terpolymer compositions if the Q and e parameters for the three monomers are known. For

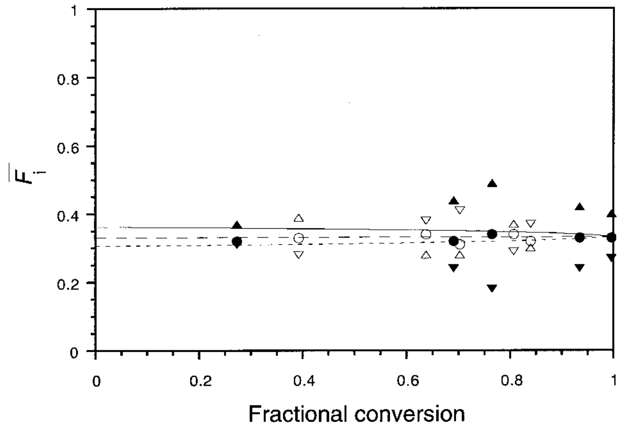


Fig. 4. Terpolymer compositional drift plotted as cumulative mole fraction of STY, MMA and HEMA in the terpolymer versus conversion. The solid lines represent the calculated drift. The symbols indicate experimental measurements. The filled characters indicate thiol-mediated reactions whereas the open symbols indicate COPhBF-mediated reactions with △ F_{HEMA}, ○ F_{STY}, ▽ F_{MMA}.

Tab. 5. $Q-e$ values used in the composition drift calculation.

	STY	MMA	HEMA
Q	1	0.78	0.88
e	−0.8	0.4	0.2
f_0	0.33	0.33	0.33

the current study literature values were selected (see Tab. 5). It should be borne in mind that in the case of monomers such as HEMA, the Q and e parameters are very solvent dependent.

A comparison of the theoretical predictions with the experimental values for both experimental systems is shown in Fig. 4, and it is clear that the kinetic model (Eq. (9)–(12)) in combination with the parameters listed in Tab. 5 adequately reproduces the experimental results. Combining this theoretical approach with previously reported models[14, 16] used to predict chain transfer kinetics in copolymerization extends the theoretical framework to multi-component polymerizations in the presence of chain transfer agents.

Thermal properties

The thermo-mechanical properties of coatings remain important design criteria. Therefore it is pertinent to investigate how the polymerization protocol affects the thermal properties of the product polymers.[26] In Fig. 5, differential scanning calorimetry (DSC) curves (above 0 °C) are shown for the two different oligomers. Both thermograms are similar with a T_g around 42 °C; the T_g for the thiol-derived polymer was found to be 39 ± 1 °C (average of two different polymer samples) and the T_g for the CCT-derived polymer was found to be 45 ± 1 °C (average of two different polymer samples). These low values for the glass transition temperature are consistent with a molecular weight dependence of T_g reported by Sanayei and O'Driscoll.[27] However, the values obtained in this work seem low in comparison; Sanayei and O'Driscoll[27] reported a T_g of 70 °C for PMMA oligomers of DP_n = 23. The small difference between the two T_gs obtained in the current work can be partly attributed to the small differences in the molecular weights and polydispersities of the two polymers. However, it is more likely to be caused by the different end-groups of the polymers (See Scheme 1). The thiol-initiated chains (**2**) should contain a long alkyl chain end-group that has the potential to act as a plasticizer. In contrast, the CCT-derived polymer contains no extraneous functionality.

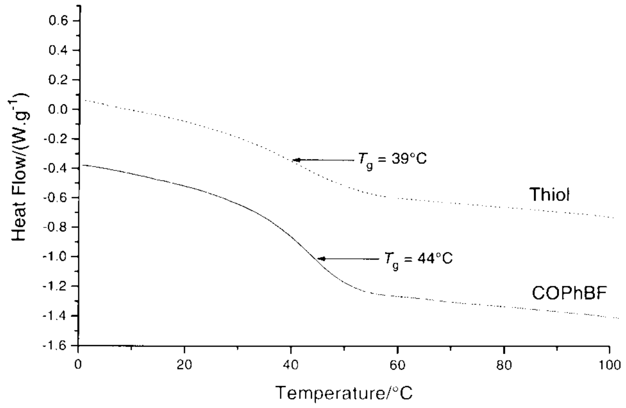
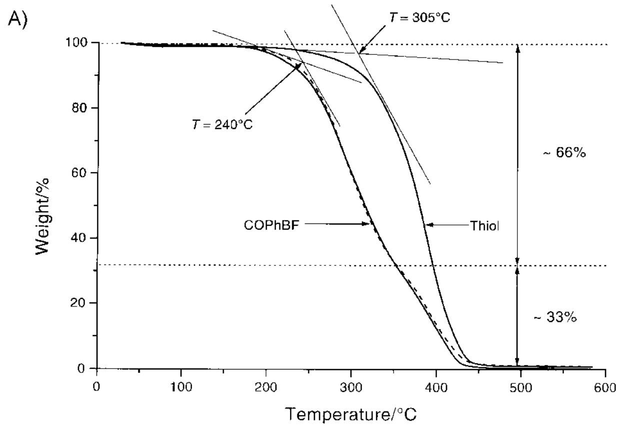


Fig. 5. DSC thermograms showing the glass transition behaviour of the terpolymer oligomers generated in the thiol and COPhBF mediated reactions.

The thermal degradation behaviour of both oligomers in nitrogen analysed by thermogravimetric analysis (TGA) is shown in Fig. 6a and 6b. The degradation of the thiol-derived terpolymer starts at a higher temperature (~305 °C) than that of the CCT-derived polymer (~240 °C). It is noteworthy that the degradation process is dependent on the nature of the diverse end-groups introduced by the different chain transfer mechanisms. The thiol-derived polymer degrades in a single stage leading to 100% weight loss. In contrast, the CCT-derived polymer degrades in two contiguous steps, initially a 66% weight loss is followed by a 33% weight loss. Both of these observations are explicable by considering the nature of the end-groups in the two polymers. The thiol-derived terpolymer contains saturated end-groups which are known to be stable up to 300 °C regardless of the monomer end-group.[28–34] However, the unsaturated end-groups in the CCT-derived polymer are significantly less thermally stable.[29, 31, 34] Vinyl-terminated poly(methyl methacrylate) is known to undergo degradation reactions at around 250 °C,[29, 31, 32] and it appears that unsaturated HEMA end-groups are similar.[35] The unsaturated styrene



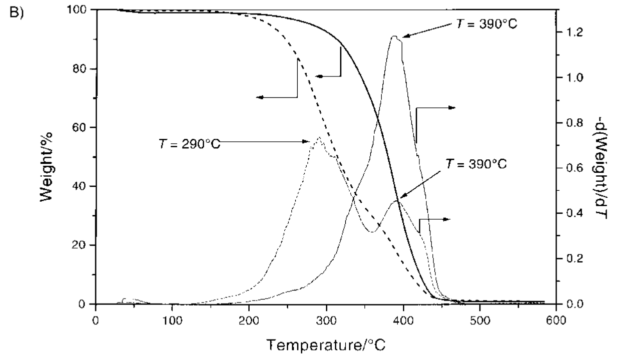


Fig. 6. TGA Thermograms showing the thermal degradation of the terpolymer oligomers generated in the thiol and COPhBF mediated reactions. (a) The onset degradation is highlighted, (b) shows the differential trace, clearly illustrating the two-step degradation of the polymer synthesised using COPhBF.

end-groups are more stable and degrade around 300 °C.[34] Since it was shown that in a styrene-methyl methacrylate catalytic chain transfer copolymerization the fraction of unsaturated styrene endgroups is proportional to the mole fraction of styrene in the monomer feed,[14, 36, 37] it is expected that approximately 66% of all unsaturated end-groups will be methacrylic and about 33% styrenic. This assessment implies that approximately 2/3 of the chains should start to degrade at a 65 °C lower temperature than the remaining 1/3 of the chains. The results shown in Fig. 6b are indeed consistent with this analysis, confirming the potential of TGA as a tool for quantifying oligomer end-groups.

Finally, the effect of residual COPhBF on the thermal stability of the polymer product was investigated. The results clearly indicated that the COPhBF does not significantly affect the thermal stability of the polymer product.

Conclusions

Catalytic chain transfer polymerization is a clean and efficient method for synthesising oligomers suitable for coatings applications. The polymerization proceeds to high conversion without molecular weight drift. The glass transition temperature of the polymer and the thermal degradation behaviour is dependent on the oligomer end-groups. Previous work[14, 16] on utilising CCT to control end-group chemistry could be combined with this work to target thermally stable oligomers.

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