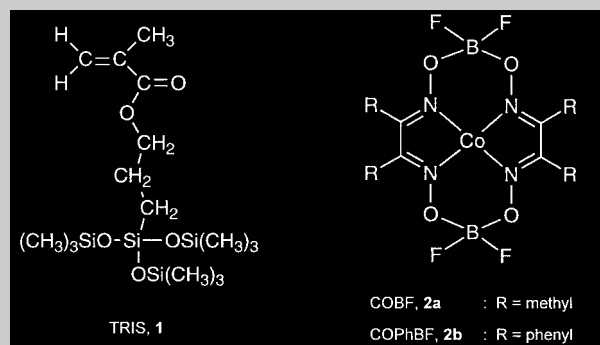


Full Paper: Macromers of 3-[tris(trimethylsilyloxy)silyl]propyl methacrylate (TRIS) were synthesised using catalytic chain transfer polymerization, and the kinetic parameters governing the reaction were evaluated. A study on the radical solution polymerization of TRIS in the presence of the catalytic chain transfer agent bis[(difluoroboryl)dimethylglyoximate]cobalt(II) (COBF) at 60 °C was conducted. Using appropriate Mark-Houwink-Kuhn-Sakurada constants for polyTRIS, the chain transfer constant (C_S) for COBF was found to be ~ 1400 in toluene solution. This low C_S value, as compared to the value reported for methyl methacrylate polymerization ($\sim 3.5 \cdot 10^4$), is only partly explained by a diffusion-controlled chain transfer reaction in the methacrylate series of monomers. A study on the influence of conversion on the molecular weight distribution indicated significant broadening and bimodality, consistent with reversible catalyst poisoning and chain transfer to the macromers. High oxy-

gen solubility in TRIS is hypothesised to play a role in the reversible catalyst poisoning making it difficult to obtain a controlled reaction under normal free-radical polymerization reaction conditions.



Synthesis of 3-[tris(trimethylsilyloxy)silyl]propyl methacrylate macromers using catalytic chain transfer polymerization: a kinetic and mechanistic study

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Introduction

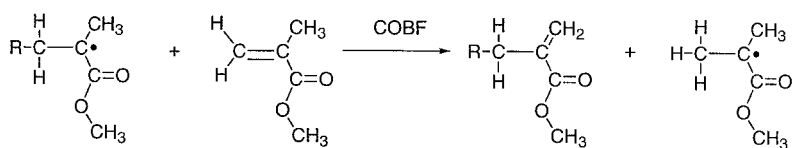
Polymers and copolymers containing the monomer 3-[tris(trimethylsilyloxy)silyl]propyl methacrylate (TRIS) are widely used in the contact lens industry, as it imparts significant oxygen permeability to lens materials. As a homopolymer, polyTRIS has limited value as it is difficult to machine, lacks wettability and suffers from protein deposition resulting in poor wear comfort. Therefore, the application of TRIS is restricted to co- and ter-polymeric formulations with hydrophilic monomers. In order to optimise these formulations, a number of research groups have found it advantageous to make relatively complex molecular architectures of TRIS and related compounds as prepolymers resulting in star, block or graft structures. A number of synthetic approaches to prepolymer synthesis have been taken, including group transfer and contiguous condensation – free radical polymerizations^{1–4}.

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This paper describes the application of catalytic chain transfer to synthesise TRIS macromers and deals primarily with the kinetic and mechanistic aspects of catalytic chain transfer that govern the controlled production of macromers. A preliminary paper outlining a study on the catalytic chain transfer polymerization of TRIS has recently been published by Steward and co-workers⁵.

Over the past decade, catalytic chain transfer polymerization has emerged as a very efficient tool for the production of oligomers with a vinyl end-functionality^{6–10}. This process is based upon the ability of certain low-spin Co(II) complexes, such as cobalt(II) porphyrins and cobaloximes, to catalyze the chain transfer to monomer reaction. In this particular process, a hydrogen atom is abstracted from a β -position in the growing radical (preferably from an α -methyl group) and transferred to a monomer molecule^{11–13}. Overall this process leads to a dead polymer chain with an unsaturated endgroup and a monomeric radical (see Scheme 1 for the case of methyl methacrylate polymerization).

Scheme 1:

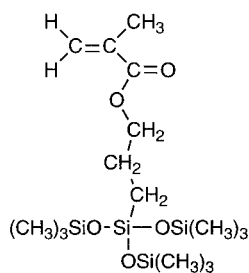


Since the functional oligomers which result from catalytic chain transfer polymerization are, in principle, macromers, they can be used subsequently for copolymerization with other monomers, resulting in graft, comb or star architectures^{14–16}; alternatively, these macromers can act as chain transfer agents^{9,10,17}. The mode of reaction (copolymerization or chain transfer) is dependent on the structure of the comonomers – acrylates tend to copolymerize whereas methacrylates undergo addition-fragmentation chain transfer⁸). The primary advantage associated with the use of catalytic chain-transfer is its simplicity. The reaction conditions required are generally identical to those used in normal free radical polymerization and the reaction is insensitive to moisture. In addition, the reaction leads to very high levels of chain end vinyl functionality without the necessity for any post-polymerization transformation.

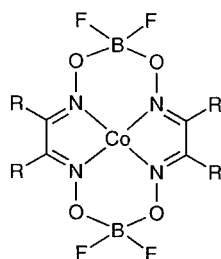
Experimental part

Materials

The bis(methanol) complexes of bis[(difluoroboryl)dimethylglyoximate]cobalt(II) (COBF, **2a**) and its tetra phenyl derivative CPhBF (**2b**) were prepared according to the method described by Bakač et al.¹⁸ The monomers TRIS (Aldrich, 98%) and methyl methacrylate (MMA; Aldrich, 98%) were passed through a column of activated basic alumina (ACROS, 50–200 micron) to remove inhibitor and purged with high purity nitrogen (BOC) for 1.5 h prior to use. AIBN (DuPont) was recrystallized twice from methanol and used as initiator. Toluene (Ajax Chemicals, Analytical Reagent) was used without further purification and purged with high purity nitrogen (BOC) for 1.5 h prior to use.



TRIS, 1

COBF, **2a** : R = methylCOPhBF, **2b** : R = phenyl

Chain transfer constant measurements

Chain transfer constants for COBF in the solution polymerization of TRIS (toluene:TRIS = 2:1 v/v) at 60 °C were determined as described in detail previously^{19–23}. The TRIS monomer has a very high boiling point making removal very difficult. Polymers were isolated from the reaction mixtures by precipitation in cold methanol – in some cases, isolation of the precipitate required centrifugation. The polymers were subsequently dried under reduced pressure at 50 °C.

Time dependent experiments

A mixture of monomer and toluene (1:2 v/v) was purged with high purity nitrogen gas for approximately 1.5 h before charging this solution into a Schlenk flask containing 2,2'-azobisisobutyronitrile (AIBN) ($2 \cdot 10^{-2}$ M; in both TRIS and MMA experiments) and COBF ($7.7 \cdot 10^{-5}$ M; only in TRIS experiment), which had been previously evacuated and subsequently purged with nitrogen for three times in order to exclude oxygen from the reaction mixture. In the case of the MMA experiment, a 10 ml solution of CPhBF ($4.3 \cdot 10^{-5}$ M in overall reaction mixture) in toluene, which had *not* been deoxygenated previously, was subsequently added to the reaction mixture. In both experiments, the Schlenk flask was placed in a water bath at 60 °C and polymerization was carried out under continuous magnetic stirring. Samples were withdrawn from the reaction mixture to determine conversion gravimetrically and to follow the molecular weight evolution.

Molecular weight analyses

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 (Å 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 $1 \text{ ml} \cdot \text{min}^{-1}$. Calibration of the SEC equipment was performed with narrow poly(methyl methacrylate) standards (Polymer Laboratories, molecular weight range: 200– $1.6 \cdot 10^6$), and the polymers were analyzed using Mark-Houwink constants for poly(methyl methacrylate) ($K = 12.8 \cdot 10^{-5} \text{ dl} \cdot \text{g}^{-1}$ and $a = 0.697$) and those previously determined for poly(TRIS) ($K = 1.67 \cdot 10^{-5} \text{ dl} \cdot \text{g}^{-1}$ and $a = 0.74$)²⁴.

Viscosity measurements

The absolute viscosities of pure monomer and a toluene-monomer mixture (2:1 v/v) at 60 °C were measured using an Ostwald viscometer (size A) immersed in a temperature-controlled water bath²⁵. The calibration of the capillary was verified by cross-checking the viscosity of MMA with the value reported by Stickler et al.²⁶ Values of 2.00 and 0.55 centipoise were obtained for the pure monomer and the monomer solution, respectively.

Results and discussion

Determination of chain transfer constants

The chain transfer constant of COBF in the free-radical polymerization of TRIS at 60 °C was measured using both the Mayo²⁷ and chain-length-distribution (CLD)²⁸ procedures. The Mayo approach (Eq. (1)), requires the measurement of the reciprocal average degree of polymerization (\overline{DP}_n^{-1}) as a function of the ratio of chain transfer agent and monomer concentrations ([COBF]/[TRIS]), after which the chain transfer constant (C_S) is obtained as the proportionality constant of the two parameters.

$$\frac{1}{DP_n} = (1 + \lambda) \frac{\langle k_t \rangle [R^*]}{k_p [TRIS]} + C_M + C_S \frac{[COBF]}{[TRIS]} \quad (1)$$

In Eq. (1), λ is the fraction of termination by disproportionation, $\langle k_t \rangle$ is the average termination rate coefficient, k_p is the propagation rate coefficient, $[R^*]$ the total radical concentration and C_M the chain transfer constant to monomer. The average degree of polymerization is experimentally determined from the molecular weight distribution either from the number average molecular weight (\overline{M}_n) or half the weight average molecular weight ($\overline{M}_w/2$), where the latter procedure has been found to yield more reliable results^{19, 23, 29–31}.

The CLD procedure, based upon Eq. (2), was originally derived by Clay and Gilbert²⁸, and requires the measurement of the slope of a molecular weight distribution (A), plotted as the natural logarithm of the number distribution ($\ln(P(M))$) against the molecular weight, as a function of [COBF]/[TRIS]:

$$\lim_{M \rightarrow \infty} \frac{d \ln P(M)}{dM} = A = - \left\{ \frac{\langle k_t \rangle [R^*]}{k_p [M]} + C_M + C_S \frac{[COBF]}{[TRIS]} \right\} m_0^{-1} \quad (2)$$

where m_0 is the mass of the monomer. A plot of $-A m_0$ vs [COBF]/[TRIS] (called a CLD-plot in the remainder of this paper) yields a straight line with a slope equal to the chain transfer constant C_S . Although Eq. (2) is only

strictly valid in the high molecular weight region of the molecular weight distribution, it has been found that more reliable results seem to be obtained when A is determined in the region of the peak molecular weight^{19, 30, 31}. In the present study both the high and peak molecular weight slopes, denoted as A_{high} and A_{peak} respectively, are utilised in the analyses.

Comments on the SEC calibration

In order to obtain accurate results from Eq. (1) and (2) using size exclusion chromatography (SEC), it is imperative to construct a universal calibration curve. Typically, the Mark-Houwink-Kuhn-Sakurada (MHKS) parameters, K and a , of the calibrant and analyte polymers are utilised to avoid the necessity of measuring the intrinsic viscosities $[\eta]$ of all the polymer samples. These parameters, K and a are empirical parameters which relate the intrinsic viscosity $[\eta]$ of a polymer to its molecular weight M (see Eq. (3))³².

$$[\eta] = K \cdot M^a \quad (3)$$

This relationship can be used with the universal calibration principle, Eq. (4), to yield Eq. (5).

$$[\eta]_1 \cdot M_1 = [\eta]_2 \cdot M_2 \quad (4)$$

$$M_2 = \left(\frac{K_1}{K_2} \right)^{\frac{1}{1+a_2}} M_1^{\frac{1+a_1}{1+a_2}} \quad (5)$$

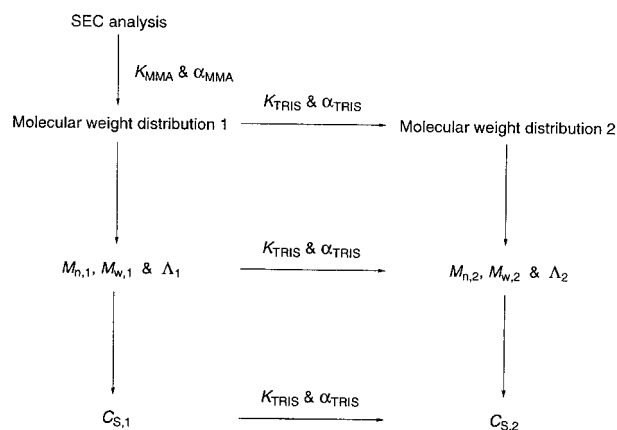
In Eq. (4) and (5) the subscripts 1 and 2 refer to the calibrant and analyte polymers, respectively.

One problem with this calibration approach is that the empirical parameters K and a are known to vary over different molecular weight ranges³². Hence it is important to determine the ‘best’ approach to transforming a molecular weight distribution, minimizing errors. There are two possible approaches: directly changing the molecular weight averages obtained against a poly(methyl methacrylate) calibration curve into the desired ones and, alternatively, converting the entire molecular weight distribution first, and subsequently calculating the molecular weight moments (see Scheme 2). Furthermore, it is of practical value to investigate whether the MHKS parameters can be used to directly convert the slopes of CLD plots into the correct values, without recourse to the original molecular weight distributions. Eq. (1) and (2) clearly suggest the following relationship between \overline{M}_n and A :

$$-\frac{1}{A} \approx M_n \quad (6)$$

It was shown by Moad and Moad³⁰ that this approximate relationship turns into an equality if the polymerization system is completely dominated by chain transfer.

Scheme 2:



The implication is that the slopes of CLD plots are likely to conform to Eq. (7).

$$-\frac{1}{A_2} = \left(\frac{K_1}{K_2}\right)^{\frac{1}{1+\alpha_2}} \left(-\frac{1}{A_1}\right)^{\frac{1+\alpha_1}{1+\alpha_2}} \quad (7)$$

Scheme 2, summarizes the different approaches that can be taken. Eq. (8). Can also be derived.

$$\frac{m_0}{C_{S,2}} \approx \left(\frac{K_1}{K_2}\right)^{\frac{1}{1+\alpha_2}} \left(\frac{m_0}{C_{S,1}}\right)^{\frac{1+\alpha_1}{1+\alpha_2}} \quad (8)$$

This intuitive expression originates from the notion that $DP_n^{-1} = \bar{M}_n/m_0 \propto C_S$, and if Eq. (8) is valid it would be of practical utility for recalculating published chain transfer constants in the absence of molecular weight data.

Tab. 1. Effect of the molecular weight conversion sequence on the final molecular weight parameters obtained in a series of experiments to determine C_S

| Parameter | pMMA K and α | pTRIS K and α | |
|-------------|-----------------------|------------------------|-----------------------|
| | | direct conversion | MWD conversion |
| \bar{M}_n | $116 \cdot 10^3$ | $281 \cdot 10^3$ | $291 \cdot 10^3$ |
| | $46 \cdot 10^3$ | $115 \cdot 10^3$ | $119 \cdot 10^3$ |
| | $36 \cdot 10^3$ | $88 \cdot 10^3$ | $91 \cdot 10^3$ |
| | $22 \cdot 10^3$ | $57 \cdot 10^3$ | $58 \cdot 10^3$ |
| \bar{M}_w | $180 \cdot 10^3$ | $430 \cdot 10^3$ | $442 \cdot 10^3$ |
| | $76 \cdot 10^3$ | $185 \cdot 10^3$ | $189 \cdot 10^3$ |
| | $60 \cdot 10^3$ | $146 \cdot 10^3$ | $149 \cdot 10^3$ |
| | $34 \cdot 10^3$ | $84 \cdot 10^3$ | $86 \cdot 10^3$ |
| A_{high} | $-10.1 \cdot 10^{-6}$ | $-4.2 \cdot 10^{-6}$ | $-4.3 \cdot 10^{-6}$ |
| | $-22.7 \cdot 10^{-6}$ | $-9.2 \cdot 10^{-6}$ | $-9.9 \cdot 10^{-6}$ |
| | $-31.3 \cdot 10^{-6}$ | $-12.6 \cdot 10^{-6}$ | $-12.8 \cdot 10^{-6}$ |
| | $-62.9 \cdot 10^{-6}$ | $-24.8 \cdot 10^{-6}$ | $-26.0 \cdot 10^{-6}$ |
| A_{peak} | $-12.0 \cdot 10^{-6}$ | $-4.9 \cdot 10^{-6}$ | $-4.9 \cdot 10^{-6}$ |
| | $29.3 \cdot 10^{-6}$ | $-11.8 \cdot 10^{-6}$ | $-11.8 \cdot 10^{-6}$ |
| | $40.7 \cdot 10^{-6}$ | $-16.2 \cdot 10^{-6}$ | $-16.3 \cdot 10^{-6}$ |
| | $70.5 \cdot 10^{-6}$ | $-27.7 \cdot 10^{-6}$ | $-28.1 \cdot 10^{-6}$ |

A summary of the molecular weight data obtained from one of the chain transfer constant determinations is given in Tab. 1. It is clear from these results that direct conversion of the molecular weight moments via Eq. (5) yields results that are generally within 5% of the molecular weight averages that are obtained by firstly converting the entire molecular weight distributions via Eq. (5). The same conclusion is also valid for the slopes of the $\ln P$ plots, indicating the applicability of Eq. (7). These results are important for practical reasons as they suggest that

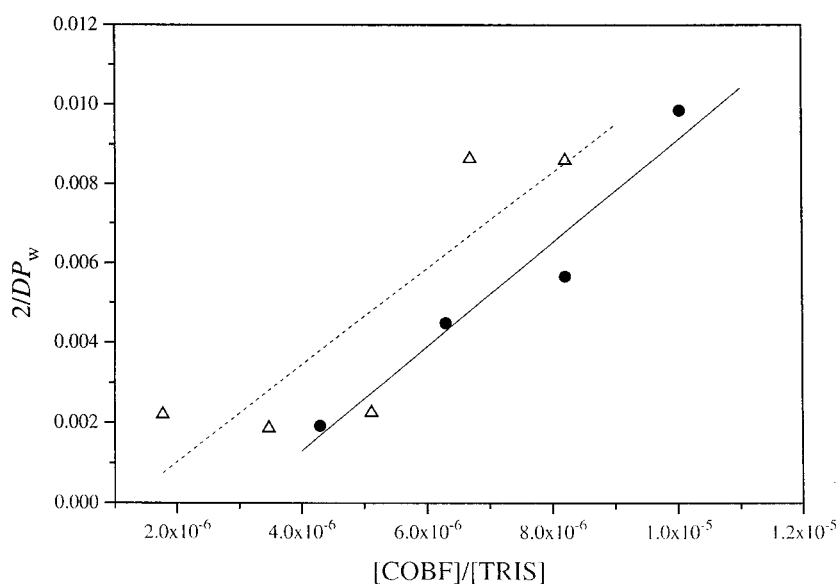


Fig. 1. Two replicate Mayo plots for TRIS based on $\bar{M}_w/2$. (Δ) Data from run a shown in Tab. 2. (\bullet) Data from run b shown in Tab. 2

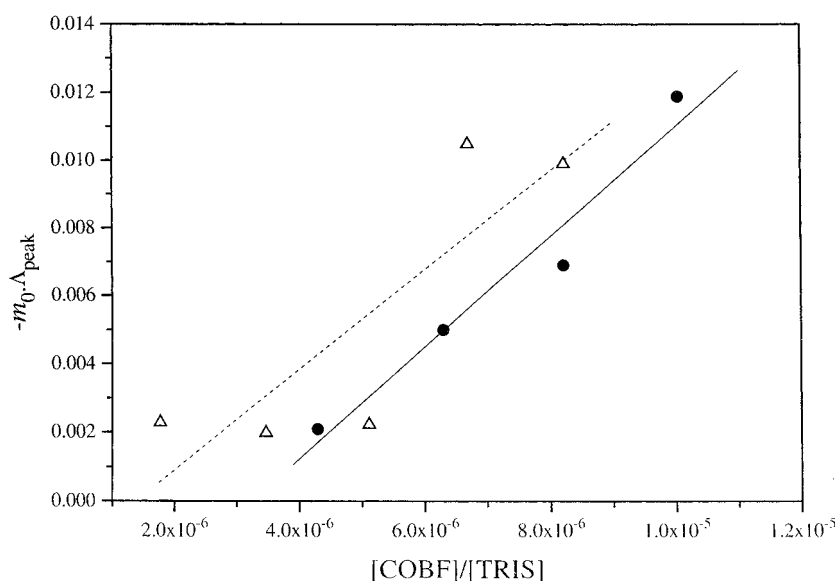


Fig. 2. Two replicate CLD plots for TRIS. (Δ) Data from run *a* shown in Tab. 2. (\bullet) Data from run *b* shown in Tab. 2

Tab. 2. Summary of CS values determined using the Mayo and the CLD procedures and different SEC calibrations

| <i>K</i> and <i>a</i> | Exp. | Chain transfer constant ^{a)} | | | |
|-----------------------|------|---------------------------------------|----------------------------|----------------------------|----------------------------|
| | | \bar{M}_n | \bar{M}_w | A_{high} | A_{peak} |
| PMMA | a | $(2.2 \pm 0.6) \cdot 10^3$ | $(3.0 \pm 1.0) \cdot 10^3$ | $(3.4 \pm 1.2) \cdot 10^3$ | $(3.6 \pm 1.3) \cdot 10^3$ |
| | b | $(2.5 \pm 0.3) \cdot 10^3$ | $(3.3 \pm 0.5) \cdot 10^3$ | $(3.7 \pm 0.8) \cdot 10^3$ | $(4.1 \pm 0.6) \cdot 10^3$ |
| | c | $(2.1 \pm 0.5) \cdot 10^3$ | $(3.2 \pm 0.9) \cdot 10^3$ | $(4.2 \pm 1.3) \cdot 10^3$ | $(4.1 \pm 1.1) \cdot 10^3$ |
| pTRIS-I | a | $(0.9 \pm 0.3) \cdot 10^3$ | $(1.2 \pm 0.4) \cdot 10^3$ | $(1.3 \pm 0.5) \cdot 10^3$ | $(1.4 \pm 0.3) \cdot 10^3$ |
| | b | $(1.0 \pm 0.1) \cdot 10^3$ | $(1.3 \pm 0.2) \cdot 10^3$ | $(1.4 \pm 0.3) \cdot 10^3$ | $(1.6 \pm 0.3) \cdot 10^3$ |
| | c | $(0.8 \pm 0.2) \cdot 10^3$ | $(1.3 \pm 0.3) \cdot 10^3$ | $(1.6 \pm 0.5) \cdot 10^3$ | $(1.6 \pm 0.3) \cdot 10^3$ |
| pTRIS-II | a | $(0.9 \pm 0.3) \cdot 10^3$ | $(1.2 \pm 0.4) \cdot 10^3$ | $(1.5 \pm 0.5) \cdot 10^3$ | $(1.5 \pm 0.5) \cdot 10^3$ |
| | b | $(1.0 \pm 0.1) \cdot 10^3$ | $(1.3 \pm 0.2) \cdot 10^3$ | $(1.5 \pm 0.3) \cdot 10^3$ | $(1.6 \pm 0.4) \cdot 10^3$ |
| | c | $(0.8 \pm 0.2) \cdot 10^3$ | $(1.2 \pm 0.3) \cdot 10^3$ | $(1.7 \pm 0.3) \cdot 10^3$ | $(1.6 \pm 0.5) \cdot 10^3$ |
| Eq. (8) | a | $0.6 \cdot 10^3$ | $0.9 \cdot 10^3$ | $1.0 \cdot 10^3$ | $1.0 \cdot 10^3$ |
| | b | $0.8 \cdot 10^3$ | $1.0 \cdot 10^3$ | $1.1 \cdot 10^3$ | $1.2 \cdot 10^3$ |
| | c | $0.6 \cdot 10^3$ | $1.0 \cdot 10^3$ | $1.2 \cdot 10^3$ | $1.2 \cdot 10^3$ |

^{a)} Quoted errors are standard errors.

chain transfer constants determined, using SEC, against any polymer standard can be readily converted into an accurate value once appropriate (or improved) MHKS parameters are known.

Chain transfer data

In Fig. 1, Mayo plots based upon the weight average molecular weights are shown for two different experiments. It is evident that in one case (circles) the expected linearity is observed. This contrasts with the second data set (triangles), where very poor molecular weight control was obtained at lower values of [COBF]/[TRIS]. This poor control was observed in many subsequent experiments involving macromer syntheses targeting molecular

weights in the intermediate ranges of this plot. Results obtained by the CLD procedure (Fig. 2) display similar characteristics. This lack of control in the catalytic chain transfer polymerizations of methacrylates is atypical and this consequently became a focus for study in subsequent work.

A comparison of the chain transfer constants (listed with their standard error) obtained in three experiments using the Mayo method based upon \bar{M}_n and \bar{M}_w , and the CLD procedure using A_{high} and A_{peak} is shown in Tab. 2. It is evident that the results obtained by the Mayo method based upon \bar{M}_w and those obtained by the CLD procedure using either A_{high} or A_{peak} show generally good agreement; the chain transfer constants obtained by the Mayo method based upon \bar{M}_n are generally significantly smaller (this

may reflect the loss of some low molecular weight polymer during the polymer isolation via precipitation in methanol). Furthermore, the chain transfer constants obtained from the direct conversion of the average molecular weights and λ values (i.e., the polyTRIS-I entries in Tab. 2) are generally within 10% of those obtained from the converted molecular weight distributions (i.e., the polyTRIS-II entries in Tab. 2); this outcome confirms the results listed in Tab. 1. The use of the relationship given as Eq. (8) yields disappointing results (errors of about 50%). This result clearly indicates the importance of reporting average molecular weight data alongside chain transfer constants to facilitate subsequent reanalysis.

From the results listed in Tab. 2 (ignoring those based upon \bar{M}_n) a chain transfer constant of approximately $(1.4 \pm 0.3) \cdot 10^3$ is obtained (this value is, of course, subject to considerable error). Previously, Steward and co-workers published a value for C_S of $\sim 8 \cdot 10^3$ against a poly(methyl methacrylate) calibration curve⁵⁾, which yields values of $3 \cdot 10^3$ and $5 \cdot 10^3$ when using Eq. (5) to convert their reported \bar{M}_n and \bar{M}_w values, respectively. These disparate C_S values again indicate some problems in controlling the catalytic chain transfer polymerization of TRIS. The data reported by Haddleton and co-workers were also clearly subject to some problems as polydispersities as low as 1.3 were reported⁹⁾. Notwithstanding these differences, all C_S values for TRIS are remarkably low when compared to the C_S value observed in the free-radical polymerization of methyl methacrylate, which is about a factor of 25 higher^{21,23,33–35)}. This effect cannot be explained by the different propagation rate coefficients of TRIS and MMA alone, as the former is only $\sim 30\%$ higher than the latter^{24,36)}.

One obvious explanation for this low C_S value is that the TRIS monomer has a higher viscosity than methyl methacrylate, and the very high chain transfer rate coefficients determined from the chain transfer constants ($\sim 10^6$ – $10^7 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$) suggest that the chain transfer reaction may be diffusion-controlled. The higher viscosity of TRIS would then lead to a lower rate chain transfer coefficient as was previously shown in a series of methacrylates^{35–37)}. This would also be consistent with a previous study of temperature effects on the catalytic chain transfer polymerizations of methyl, ethyl and butyl methacrylate³⁵⁾. The Arrhenius parameters for the rate determining step in the chain transfer reactions involving cobaloxime and methacrylates are consistent with a diffusion-controlled reaction. The following relationship was found to be valid in methacrylate systems³⁵⁾:

$$C_S k_p \eta \approx \text{constant} \quad (9)$$

where η is the viscosity of the reaction medium. The applicability of Eq. (9) to the present system can be readily tested using Eq. (10):

$$\frac{C_{S,\text{TRIS}}}{C_{S,\text{MMA}}} \approx \frac{(k_p \eta)_{\text{MMA}}}{(k_p \eta)_{\text{TRIS}}} \quad (10)$$

Evaluation of the LHS and RHS of Eq. (10), using $k_{p,\text{MMA}} = 830 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ and $\eta_{\text{MMA}} = 0.37$ centipoise, yields values of ~ 0.04 and ~ 0.5 , respectively. On the basis of Eq. (9), a $C_{S,\text{TRIS}}$ value of about $16 \cdot 10^3$ would be expected as both k_p and η are similar to those found for butyl methacrylate, which has a C_S value of $16 \cdot 10^3$ ³⁵⁾. Hence, the very low catalytic chain transfer constant in TRIS cannot be attributed to viscosity effects alone.

The combination of poor control, disparity in results between different research groups and a low C_S value indicate that the catalytic chain transfer polymerization of TRIS may be especially sensitive to impurities which are either benign or absent in the other methacrylates. As TRIS is specifically utilised to impart high oxygen permeability to biomaterials, it is possible that a very high oxygen equilibrium concentration in monomeric TRIS is not completely removed by nitrogen sparging or routine freeze-pump-thaw procedures. Catalytic chain transfer catalysts are vulnerable to poisoning by direct oxidation and/or attack by oxygen centred radicals³⁸⁾ and this explanation for the inconsistent results obtained was pursued by investigating changes in the molecular weight distribution with conversion.

Polymerization rate and molecular weight evolution

The rate of polymerization observed in the catalytic chain transfer polymerization of TRIS at 60°C is shown in Fig. 3, for a solution polymerization in toluene (33% solids) with an initiator concentration of $2 \cdot 10^{-2} \text{ M}$ and a $[\text{COBF}]/[\text{TRIS}]$ ratio of $1.1 \cdot 10^{-4}$. It is evident that very high conversion is reached after about 6 h. Replotting the data as a first-order kinetic plot, which maintains linearity throughout the course of polymerization, yields a value of $1.9 \cdot 10^{-4} \text{ s}^{-1}$ for the product of k_p and $[\text{R}^\bullet]$. This value indicates an overall radical concentration of about $1.8 \cdot 10^{-7} \text{ M}$, which is an order of magnitude higher than those previously observed in the catalytic chain transfer polymerizations of styrene and methyl methacrylate under similar conditions²⁰⁾. If initiator decomposition rate and efficiency do not significantly differ in the current system, the large difference in overall radical concentrations can only result from a lower average termination rate coefficient $\langle k_t \rangle$ in TRIS polymerization. A lower value of $\langle k_t \rangle$ is consistent with the fact that TRIS has a higher viscosity than either MMA or styrene. Furthermore, the observation is in accord with an explanation recently proposed by Olaj and Vana³⁹⁾, who measured $\langle k_t \rangle$ for styrene⁴⁰⁾ and methyl methacrylate³⁹⁾ under similar conditions and found that the former was a factor of 2 larger than the latter. This difference was explained by greater steric shielding in MMA restricting the mobility

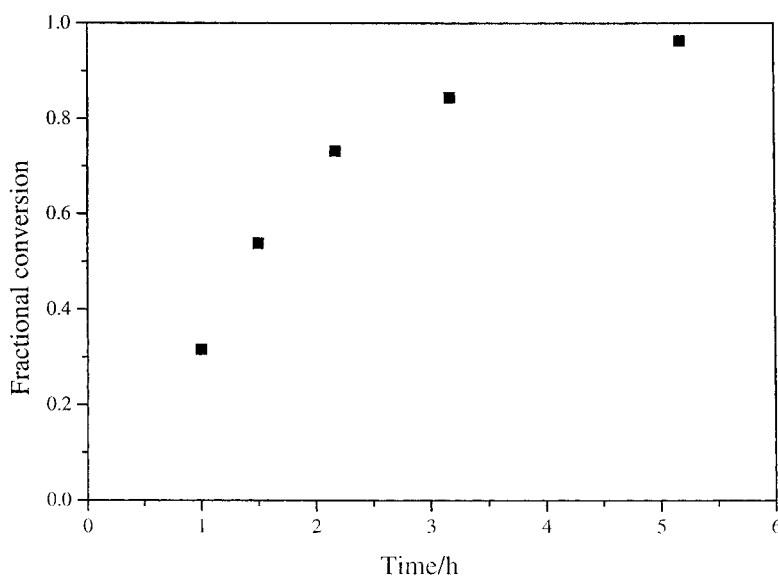


Fig. 3. Fractional conversion versus time for TRIS catalytic chain transfer polymerization

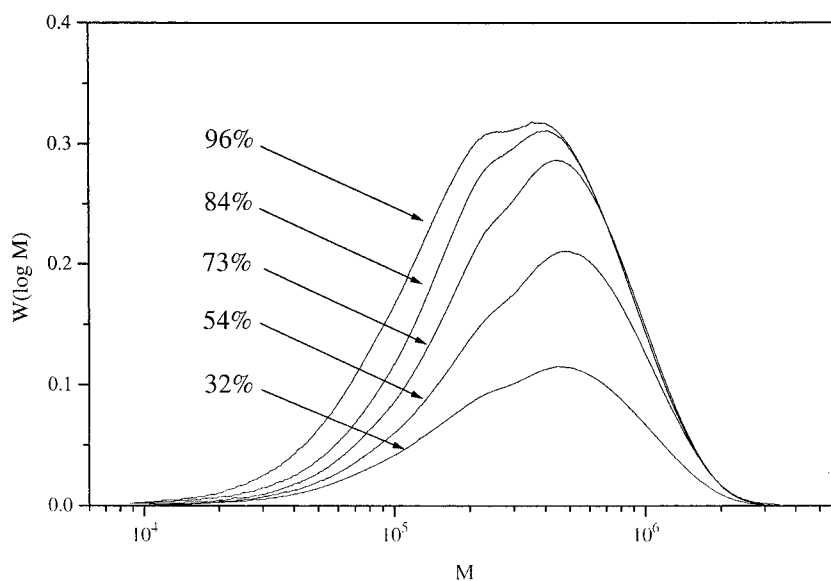


Fig. 4. Cumulative molecular weight distributions for TRIS polymerization. Samples taken at different conversion levels

of the “end-segment”, responsible for the termination reaction controlled by segmental diffusion³⁹). On the basis of this theory, the very large ester group in TRIS should induce an even lower $\langle k_t \rangle$.

The evolution of the molecular weight distribution with time is shown in Fig. 4 where the cumulative molecular weight distributions corresponding to the data points plotted in Fig. 3 are shown. It is immediately clear from this figure that the experimental molecular weights are higher than those predicted via the measured chain transfer constant ($DP_n \approx \sim C_s^{-1}[\text{TRIS}]/[\text{COBF}] = 1/(1400 \times 1.1 \cdot 10^{-4}) = 6.5 \Rightarrow \bar{M}_n \approx 2.7 \cdot 10^3$). This result,

which is reproducible, clearly indicates (again) that product control is difficult in this particular polymerization.

Despite the fact of poor molecular weight control, the molecular weight distributions are invariant with time up to high conversion. This is consistent with previous observations on catalytic chain transfer polymerizations of styrene⁴⁰), methyl methacrylate⁴⁰), and the terpolymerization of styrene, methyl methacrylate and 2-hydroxyethyl methacrylate⁴¹), suggesting that the same basic polymerization mechanism is operative for all these monomers. A noteworthy observation, however, is the occurrence of a low-molecular weight shoulder in the dis-

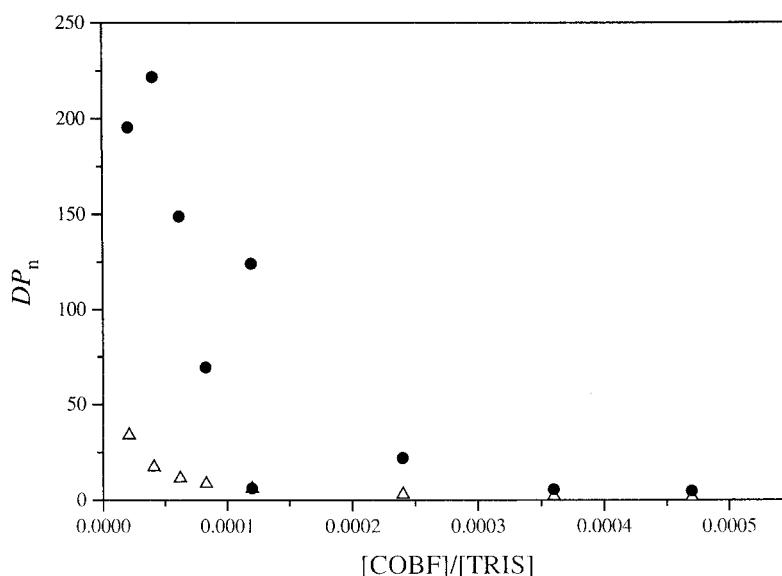


Fig. 5. Experimental DP_n values (●) and DP_n values predicted from the C_s value for TRIS catalytic chain transfer polymerization

tributions, that becomes increasingly dominant with conversion. This low-molecular weight anomaly cannot be attributed to viscosity effects, as an increasing viscosity should lead to a decreasing chain transfer constant and hence an *increasing* molecular weight.

Two conceivable explanations of this observation appear tenable: (i) reversible catalyst poisoning (leading to higher molecular weights than predicted from the chain transfer constant), and (ii) the produced macromers act as chain transfer agents at higher conversions.

Reversible catalyst poisoning

Cobaloximes(II) are readily oxidized by oxygen in solution⁴², converting the active Co(II) catalyst into its inactive Co(III) derivative. Since oxygen readily dissolves in polyTRIS and TRIS, it is likely that the deoxygenation steps required for monomers such as styrene and methyl methacrylate may be insufficient for TRIS. Slight variations in the deoxygenation process in different sample preparations would then lead to significant irreproducibility. The final molecular weight parameters for a series of macromer preparations are shown in Tab. 3 indicating that lower COBF concentrations yield polymer products with a high polydispersity index and higher degrees of polymerization than those predicted from the chain transfer constant (see also Fig. 5). The low polydispersity indices for the very low molecular weight macromers originate from monomer production in the course of the CCT reaction, which is excluded from the molecular weight analysis. The results shown in Tab. 3 accord with poisoning of the catalyst by oxygen at the onset of polymerization. A fixed concentration of oxygen in the initial

Tab. 3. Summary of characteristic molecular weight parameters for a series of macromer preparations

| [COBF]/[TRIS] | \bar{M}_p | \bar{M}_n | \bar{M}_w | PDI |
|----------------------|------------------|------------------|------------------|------|
| $4.70 \cdot 10^{-4}$ | $3.9 \cdot 10^3$ | $3.6 \cdot 10^3$ | $4.0 \cdot 10^3$ | 1.12 |
| $3.60 \cdot 10^{-4}$ | $3.9 \cdot 10^3$ | $3.9 \cdot 10^3$ | $4.6 \cdot 10^3$ | 1.19 |
| $2.40 \cdot 10^{-4}$ | $16 \cdot 10^3$ | $10 \cdot 10^3$ | $19 \cdot 10^3$ | 1.86 |
| $1.20 \cdot 10^{-4}$ | $3.9 \cdot 10^3$ | $4.3 \cdot 10^3$ | $5.1 \cdot 10^3$ | 1.21 |
| $1.20 \cdot 10^{-4}$ | $74 \cdot 10^3$ | $37 \cdot 10^3$ | $105 \cdot 10^3$ | 2.87 |
| $8.30 \cdot 10^{-5}$ | $54 \cdot 10^3$ | $27 \cdot 10^3$ | $59 \cdot 10^3$ | 2.19 |
| $6.20 \cdot 10^{-5}$ | $108 \cdot 10^3$ | $53 \cdot 10^3$ | $126 \cdot 10^3$ | 2.37 |
| $4.10 \cdot 10^{-5}$ | $157 \cdot 10^3$ | $70 \cdot 10^3$ | $187 \cdot 10^3$ | 2.67 |
| $2.10 \cdot 10^{-5}$ | $161 \cdot 10^3$ | $52 \cdot 10^3$ | $167 \cdot 10^3$ | 3.18 |

solution would result in the fraction of poisoned catalyst for a high [COBF]₀ system to be very much smaller than the fraction of poisoned catalyst for a low [COBF]₀ system. Therefore the measured C_s values are dependent on experimental conditions.

Catalyst poisoning alone is an inadequate explanation for the experimental data, as it would simply result in a reduction in transfer efficiency producing an invariant molecular weight distribution with conversion. However, this is not observed. Propagating radicals can reduce the inactive Co(III) derivative of the catalyst back to its active Co(II) oxidation state⁴³. This mechanism is exploited in catalytic chain transfer using Co(III) complexes⁹. The influence of Co(III)-radical reduction was investigated in the catalytic chain transfer polymerization of methyl methacrylate with COPhBF in which a small volume of non-deoxygenated catalyst solution was added to a large volume of deoxygenated initiator solution. The molecular weight moments of polymer samples taken at different conversions are listed in Tab. 4, showing that

Tab. 4. Summary of molecular weight characteristics obtained in a free-radical polymerization of MMA at 60 °C in the presence of oxidized COPhBF

| Conversion in % | \bar{M}_p | \bar{M}_n | \bar{M}_w | PDI |
|-----------------|-----------------|-----------------|-----------------|------|
| 43 | $87 \cdot 10^3$ | $41 \cdot 10^3$ | $86 \cdot 10^3$ | 2.10 |
| 54 | $77 \cdot 10^3$ | $36 \cdot 10^3$ | $82 \cdot 10^3$ | 2.26 |
| ~100 | $51 \cdot 10^3$ | $22 \cdot 10^3$ | $50 \cdot 10^3$ | 2.27 |

the molecular weights reduce with increasing conversion. This implies that poisoning of the catalyst is reversible^{38,42} and that the propagating radicals can regenerate the active Co(II) catalyst. The results obtained for the catalytic chain transfer polymerization of TRIS shown in Fig. 4 are consistent with this explanation as the low molecular weight shoulder seems to increase with conversion.

Macromer chain transfer agents

At high conversions an additional kinetic process may become significant. The product macromers can also act as chain transfer agents^{9,17,44} and when the concentration of macromer is high enough, then chain transfer to macromer may predominate over CCT. In such a circumstance, Eq. (1) should be modified:

$$\frac{1}{DP_n} = (1 + \lambda) \frac{\langle k_t \rangle [R^*]}{k_p [M]} + C_M + C_{\text{macromer}} \frac{[\text{macromer}]}{[\text{TRIS}]} + C_s \frac{[\text{COBF}]}{[\text{TRIS}]} \quad (11)$$

where C_{macromer} is the chain transfer constant of the macromer. The concentration of macromer is directly related to the conversion of TRIS and the average degree of polymerization:

$$[\text{macromer}] = \frac{x \cdot [\text{TRIS}]_0}{DP_n} \Rightarrow \frac{[\text{macromer}]}{[\text{TRIS}]} = \frac{x}{(1-x) \cdot DP_n} \quad (12)$$

where x is the fractional conversion and $[\text{TRIS}]_0$ is the initial TRIS concentration. Chain transfer to the macromers will become significant when the third term of the RHS of Eq. (11) is greater than the fourth term. A number of experimental studies have found that the molecular weight distribution does not change with conversion in CCT^{20,21}. This connotes that the chain transfer rate is independent of $[M]$ and thus Eq. (13) holds (provided the system is chain transfer dominated):

$$C_{\text{macromer}} \frac{x}{(1-x) \cdot DP_n} \geq C_s \frac{[\text{COBF}]_0}{[\text{TRIS}]_0} \approx \frac{1}{DP_n} \quad (13)$$

Consequently, Eq. (14) can be formulated, where x_{crit} is the fractional conversion at which chain transfer to macromer becomes the dominant chain stopping event:

$$x_{\text{crit}} \approx \frac{1}{1 + C_{\text{monomer}}} \quad (14)$$

It is noteworthy that the average degree of polymerization targeted in the catalytic chain transfer polymerization does not appear in Eq. (14). This implies that the conversion where transfer to macromer becomes dominant should be independent of the catalytic chain transfer agent concentration. Assuming that the value of C_{macromer} in this system is similar to the one found in MMA polymerization ($C_{\text{macromer}} \approx 0.2$)⁴⁴, an estimate of 0.83 for x_{crit} is obtained; for $C_{\text{macromer}} \approx 0.1$, $x_{\text{crit}} \approx 0.91$ and for $C_{\text{macromer}} \approx 0.05$, $x_{\text{crit}} \approx 0.95$. This exercise indicates that the chain transfer reaction to macromer should start to dominate at a fractional conversion between 85 and 95%, reducing the molecular weight. This result is consistent with the results shown in Fig. 4, where it is clear that the low molecular weight section of the distribution becomes more significant in the region of 84% to 96% conversion.

Conclusions

Macromers of TRIS can be readily synthesised using catalytic chain transfer. However, control over macromer production is hard to achieve utilising reaction conditions normally adopted for free radical polymerizations. The broad molecular weight distributions found experimentally are consistent with reversible oxygen poisoning of the Co(II) catalyst – a problem which may well be specific to TRIS and related compounds. In addition, a kinetic feature of CCT at high conversions may become significant; the product macromer itself may become a significant transfer agent resulting in a broadening of the molecular weight distribution at the low molecular weight end.

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