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Catalytic chain transfer copolymerization of methyl methacrylate and methyl acrylate

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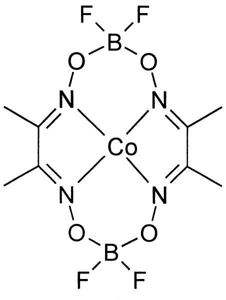
SUMMARY: Bis(aqua)bis((difluoroboryl)dimethylglyoximate)cobalt(II) (COBF) has proven to be a very effective catalytic chain transfer agent in the copolymerization of MA and MMA. The chain transfer activity depends on the fraction of MMA in the monomer feed and the total radical concentration. The polymerization can be described by a model that combines features of catalytic chain transfer for MMA homopolymerization and cobalt mediated controlled radical polymerization of MA. According to the model part of the COBF is covalently bonded to MA-ended polymeric radicals and cannot take part in the chain transfer step. The model can also account for the observed inhibition time that occurs at high chain transfer agent concentration and low fraction of MMA in the monomer feed.

Introduction

The use of certain low spin Co(II)-complexes, such as COBF (**1**), is a very effective means of controlling molar mass in the free radical polymerization of methacrylates and styrenes[1,2]. For acrylates it has been reported that these Co(II)-complexes show a much smaller activity[3] or inhibit the polymerization reaction[1]. This led to the idea that they can participate in controlled radical polymerizations[4,5].



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For industrial applications it is important that these catalytic chain transfer agents can be applied in copolymerizations. There have been a few reports on thier use in the copolymerization of styrene – methyl methacrylate[6,7,8], styrene-α-methylstyrene[9] and methyl methacrylate–n-butyl methacrylate[10,11]. This is the first paper to report on the copolymerization of methyl acrylate (MA) and methyl methacrylate (MMA) using COBF as catalytic chain transfer agent.

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Theoretical background

Mechanism of catalytic chain transfer

The generally accepted mechanism for catalytic chain transfer[12] in the polymerization of MMA is shown in Fig. 1. In the chain transfer step a hydrogen atom is abstracted from the ∀-methyl group of the growing radical chain resulting in the formation of a cobalt hydride and a dead polymer chain. The cobalt hydride can then react with monomer to reinitiate a new polymer chain. Chain transfer coefficients C_T (= k_{tr}/k_p) for COBF in a bulk polymerization of MMA up to 40.000 have been measured[13].

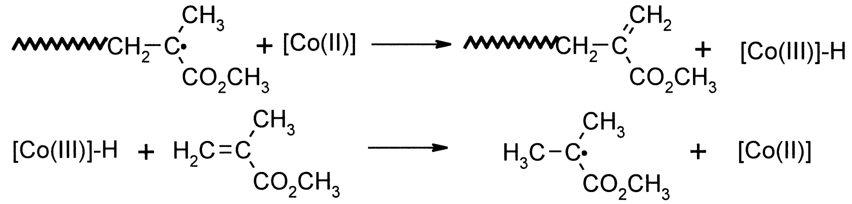


Fig. 1: Mechanism for catalytic chain transfer in the polymerization of MMA.

Mechanism of cobalt-mediated controlled radical polymerization of MA

The cobalt-mediated controlled radical polymerization of MA is based on reversible deactivation of the growing polymeric radical by a Co(II)-species[4,5]. The covalent bond formed upon combination can dissociate either thermally or photochemically. This is shown in Figure 2.

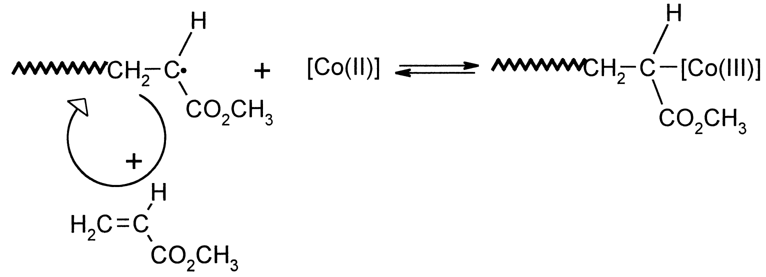


Fig. 2: Mechanism of cobalt-mediated controlled radical polymerization of methyl acrylate.

Measurement of chain transfer coefficients

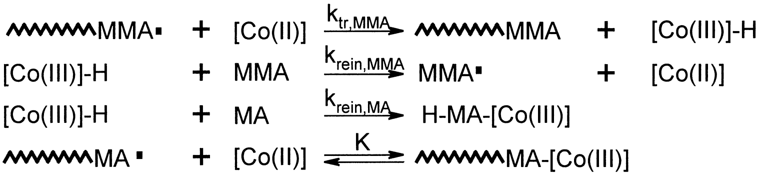
Chain transfer coefficients are mostly determined using either the Mayo method or the chain length distribution (CLD) method, which are in principle identical[14]. The former is based on a relationship between the number average degree of polymerization DP_n and the ratio of the concentration of chain transfer agent [T] and monomer [M], as given in equation (1)

$$\frac{1}{DP_n} = \frac{1}{DP_{n0}} + C_T \frac{[T]}{[M]} \qquad \textbf{(1)}$$

in which DP_{n0} is the number average degree of polymerization without added chain transfer agent. The CLD method relates the slope of the natural logarithm of the chain length distribution P(N) to the ratio of chain transfer agent and monomer concentration in a similar way.

Model for catalytic chain transfer copolymerization of MA and MMA

The copolymerization of MA and MMA in the presence of the cobalt complex is assumed to obey free-radical copolymerization kinetics according to the penultimate model. In addition to this the following reactions can occur.



Here $k_{tr,MMA}$ is the chain transfer rate constant of the cobalt species in the MMA hompolymerization and K is the equilibrium constant for reversible deactivation. The cobalt hydride formed in the chain transfer step can reinitiate either MMA, resulting in a new growing chain, or MA, resulting in an organocobalt(III) adduct. The reinitiation constants $k_{rein,MA}$ and $k_{rein,MMA}$ are assumed to be equal. MA-ended polymeric radicals can recombine with the cobalt species to a cobalt end-capped polymer. It is assumed that MA ended radicals do not give chain transfer to the cobalt complex.

In this model part of the initially added cobalt(II) will be present as organocobalt(III) species, which are inactive towards chain transfer. Equation (1) can then be rewritten as

$$\frac{1}{DP_n} = \frac{1}{DP_{n0}} + \langle C_T \rangle f_{Co} \frac{[T]_o}{[M]} \qquad \textbf{(2)}$$

in which f_{Co} is the fraction of cobalt species present as Co(II), $<C_T>$ is the average chain transfer coefficient for copolymerization and $[T]_0$ is the initial concentration of Co(II). This results in an expression for the experimentally accessible chain transfer coefficient $<C_T>'$

$$<C_T>' = <C_T> f_{Co} = \frac{<k_{tr}>}{<k_p>} f_{Co} \qquad (3)$$

in which $<k_{tr}>$ is the average chain transfer rate constant and $<k_p>$ is the average propagation rate constant. Assuming there is no transfer from MA-ended radicals $<k_{tr}>$ can be written as[9]

$$< k_{tr} > = \Phi_{MMA} k_{tr,MMA} \qquad (4)$$

In this equation M_{MMA} is the fraction of MMA-ended polymeric radicals. Both $<k_p>$ and M_{MMA} can be calculated using known copolymerization equations. M_{MMA} is described as[15] in which k_{pMAMA} and $k_{pMMAMMA}$ are the respective homopropagation rate constants and r_{MA}

$$\Phi_{MMA} = \frac{\bar{k}_{pMAMA} r_{MMA} f_{MMA}}{\bar{k}_{pMMAMMA} r_{MA} f_{MA} + \bar{k}_{pMAMA} r_{MMA} f_{MMA}} \qquad (5)$$

and r_{MMA} the respective reactivity ratios. If one assumes a steady state in organocobalt(III) species an expression for f_{Co} can be derived

$$f_{Co} = \frac{1}{1 + K[M\bullet](1 - \Phi_{MMA} + f_{MA}\Phi_{MMA})} \qquad (6)$$

where $[M\bullet]$ is the total radical concentration. So according to the model f_{Co} and therefore $<C_T>'$ are dependent on the total radical concentration and thus on initiator concentration.
In Figure 3 f_{Co} is shown as a function of the fraction of MMA in the feed for different values of $K[M\bullet]$. The parameters used for the calculation of Φ_{MMA} are shown in Table 1.

Table 1. Homopropagation rate constants and reactivity ratios for the system MA-MMA used throughout this paper.

	MMA	MA
k_p[16] ($l.mol^{-1}s^{-1}$)	843	24000
r[17]	2.49	0.26
s[18]	1.98	0.43

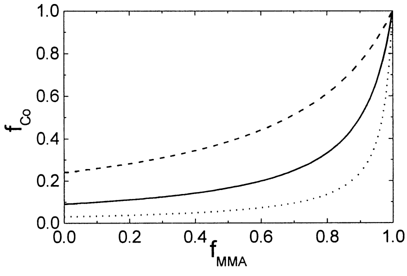


Fig. 3: The fraction of free COBF as a function of the fraction of MMA for the penultimate model. (- - -) K[M•]=3.16; (—) K[M•]=10; (•••)K[M•]=31.6.

Experimental

Materials: MMA and MA (both from Merck) were distilled and passed over a column with inhibitor remover prior to use. Azobisisobutyronitril (AIBN, Fluka) and toluene (Biosolve) were used as received. COBF (bis(aqua)bis((difluoroboryl)dimethylglyoximate)cobalt(II)) was prepared according to a procedure of Baka□ and Espenson[19]. It was analysed using UV-Vis spectroscopy and elemental analysis (experimental C: 23.0 %, H: 3.91 %, N: 13.5 %; calculated C: 22.8 %, H: 3.83 %, N: 13.3 %). One single batch was used throughout all experiments.

Polymerizations: All monomers and solvents were purged with argon for at least one hour prior to use. COBF and AIBN were weighed into separate vials, sealed with septa and an argon stream was passed over for more than one hour. Stock solutions of COBF and AIBN in monomer were prepared. All monomer transfer was done by gastight syringe. For reactions at high initiator concentrations, AIBN was weighed directly into the reaction vials. Reaction mixtures were made of both monomers, COBF-solution and AIBN solution to a total volume of about 5 ml. Reactions were carried out at three different fractions of monomer in the feed and for each fraction at different initiator concentrations. At each set of conditions a total of eight polymerizations was done at different COBF concentrations. Before the polymerizations were started the reaction vials were immersed in an ice/water bath and purged with argon for an additional 20 minutes. Polymerizations were carried out in a water bath at a constant temperature of 60 °C (±0.5 °C). Reactions were stopped by addition of hydroquinone and cooling. Monomer was evaporated and the polymer dried under vacuum at 40 °C. Conversion was determined gravimetrically. Polymerizations to determine the inhibition time were carried out in a similar fashion. In these experiments the initiator concentration was kept constant and the COBF concentration was varied. Two sets of experiments were done at respectively $f_{MMA} = 0$ and $f_{MMA} = 0.46$. Samples were taken by a syringe and conversion was monitored.

Analyses: ^{1}H-NMR was carried out to determine the copolymer composition. Spectra were recorded with a Varian 300 MHz spectrometer at 298 K, using $CDCl_3$ as a solvent and tetramethylsilane as an internal reference. The composition was determined from the α-CH_3 and the total -O-CH_3 regions[20]. Size exclusion chromatography (SEC) was carried out using THF as an eluent at a flow rate of 1 ml.min^{-1}. Two Polymer Laboratories PLgel 5 μm Mixed-C columns (300 x 7.5 mm) and PLgel 5 μm guard column (50 x 7.5 mm) were used and calibrated with Polymer Laboratories narrow MWD polystyrene standards. The polystyrene calibration curves were converted into copolymer composition dependent calibration curves as was done before for the system styrene-MMA[21].

Results and Discussion

Homopolymerization of methyl methacrylate with COBF

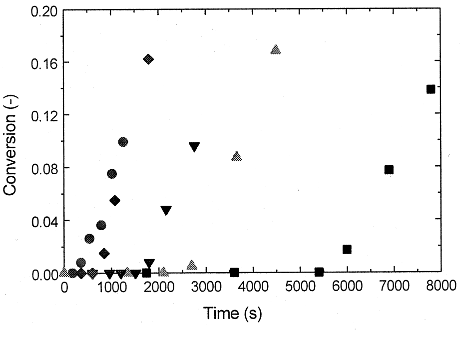
For the chain transfer coefficient of COBF at 60 °C in the homopolymerization of MMA a value of 3.88 10^4 was found. This agrees well with values reported in literature[13].

Inhibition in the homopolymerization of methyl acrylate with COBF

The conversion-time graphs for the methyl acrylate homopolymerizations in the presence of COBF are shown in Figure 4. The inhibition period increases with increasing ratio of [COBF] over [AIBN]. Assuming that each growing polymer chain that is initiated by an AIBN radical fragment is captured by COBF until COBF has reached its equilibrium concentration, one can calculate a theoretical inhibition period t_o according to

$$t_o = \frac{-\ln\left(1 - \frac{(1-f_{Co})[COBF]_o}{2f[AIBN]_o}\right)}{k_d} \approx \frac{(1-f_{Co})[COBF]_o}{2fk_d[AIBN]_o} \qquad (7)$$

where the AIBN dissociation rate constant $k_d = 9.7\ 10^{-6}\ s^{-1}$ [22] and f is the initiator efficiency.



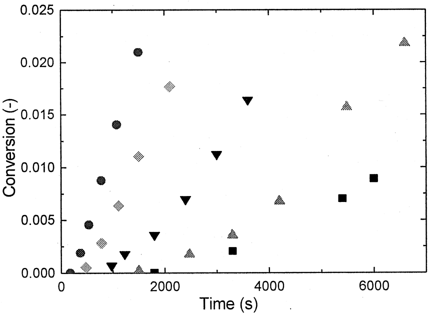


Fig. 4: Homopolymerization of MA in presence of COBF. [COBF]/[AIBN]: ● = 0; ◆ = 0.012; ▼ = 0.020; ▲ = 0.047; ■ = 0.104.

Fig. 5: Copolymerization of MA and MMA (f_{MMA} = 0.46) in presence of COBF. [COBF]/[AIBN]: ● = 0; ◆ = 0.0080; ▼ = 0.020; ▲ = 0.048; ■ = 0.10.

For $f \approx 0.8$ and $f_{Co} \approx 0.1$ the theoretical inhibition times have the same order of magnitude as observed experimentally. After the inhibition period polymerization starts very rapidly at a nearly constant rate, which implies that the radical concentration and thus the fraction of free

COBF remain constant. So the assumption that there is a steady state in the cobalt species, made for the calculation of f_{Co}, seems to be correct for the homopolymerization of MA. The molecular weight of the polymer decreases slightly with increasing COBF-concentration resulting in $\langle C_T \rangle'$ = 8 for the MA homopolymerization, which means that transfer from MA-ended polymeric radicals can indeed be neglected. The observations of Enikolopyan et al.[1] who reported inhibition in the homopolymerization of MA using cobalt porphyrins and of Janowicz[3] who reported a limited chain transfer activity are both in agreement with the results presented here.

Inhibition in the copolymerization of methyl acrylate and methyl methacrylate with COBF

The conversion-time graphs for the MA-MMA copolymerizations in the presence of COBF are shown in Figure 5. For the copolymerization inhibition times increase with increasing [COBF]/[AIBN] ratio, but inhibition times are shorter compared to the homopolymerization of MA. This means that a smaller fraction of COBF is covalently bound to MA-ended radicals compared to the MA homopolymerization. This is in agreement with the model calculations for f_{Co} shown in Figure 4. Besides this it can be seen that the polymerization rate increases during the first percent of conversion, which means that during this stage f_{Co} will still be above the steady state value, resulting in a higher chain transfer activity in the very beginning of the reaction.

Chain transfer in methyl acrylate – methyl methacrylate copolymerization

The chain transfer coefficient was determined at three different fractions of MMA in the feed and at three different initiator concentrations. The results are shown in Figure 6. It can be seen that $\langle C_T \rangle'$ increases with increasing f_{MMA} and decreasing initiator concentration. Although $\langle C_T \rangle'$ is between 150 and 15000, which is lower than for the MMA homopolymerization, it is still substantially higher than for conventional chain transfer agents. The model predictions were calculated using equations 3 and 6, the parameters in Table 1 and an

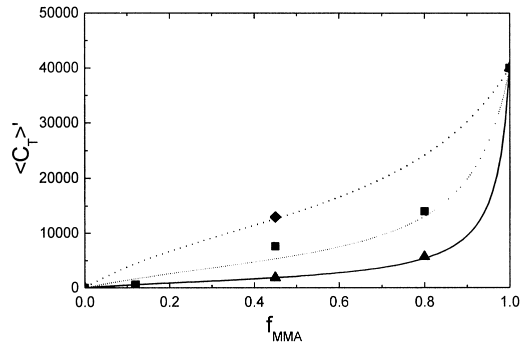


Fig. 6: Copolymerization of MA and MMA in presence of COBF. Experimentally determined $\langle C_T \rangle$ at ◆ [AIBN] = 0.0006 M; ■ [AIBN] = 0.006 M; ▲ [AIBN] = 0.06 M; Model fits (- - -) [M•] = 6.32 10^{-9} M; (—) [M•] = 2 10^{-8} M; (•••) [M•] = 6.32 10^{-8} M.

estimate of the equilibrium constant $K = 5\ 10^8$, which has the same order of magnitude as the ones reported for porphyrinatocobalt complexes[5]. The total radical concentration estimates are based on $[M\bullet] = (fk_d[I]/k_t)^{0.5}$ where the termination rate constant k_t is set to $1.5\ 10^8\ l.mol^{-1}s^{-1}$, neglecting conversion, chain length and monomer feed composition effects. The experimental data and the model predictions are in good agreement both in changing monomer feed composition and initiator concentration. So the model correctly predicts an increase of $<C_T>'$ with decreasing initiator concentration and an increase of $<C_T>'$ with increasing MMA content.

Conclusions

In this work it was shown that COBF is a very active catalytic chain transfer agent in the copolymerization of MA and MMA. The chain transfer coefficient appears to be dependent on monomer feed composition and on initiator concentration. In some cases an inhibition period is observed. A model, combining features of both catalytic chain transfer polymerization of methacrylates and cobalt-mediated controlled radical polymerization, which can describe these effects, was developed. The model predicts that part of the COBF is covalently bonded to MA-ended polymeric radicals and that therefore the apparent chain transfer coefficient is lowered compared to the chain transfer coefficient for MMA homopolymerizations.

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