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Shining a Light on Catalytic Chain Transfer

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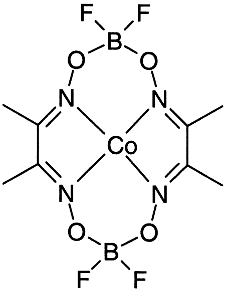
Summary: The catalytic chain transfer polymerization of styrene is only truly effective when the reaction mixture is exposed to (UV-)light. The apparent chain transfer constant depends inversely on radical concentration and can be increased up to 8000. These results can be explained by combining aspects of both catalytic chain transfer and the formation of cobalt-carbon bonds. For the catalytic chain transfer polymerization of *n*-butyl acrylate a chain transfer constant of 650 was found. The resulting transfer coefficient has the same order of magnitude as the one for *n*-butyl methacrylate. This means that the absence of an α-methyl group hardly influences the transfer step itself. Furthermore, the effect of possible impurities on the catalytic chain transfer polymerization of methyl methacrylate is investigated.

Introduction

Cobaloximes, such as CoBF (**1**) are well known to catalyze the chain transfer to monomer reaction in the free-radical polymerization of methacrylates and styrenes. This type of catalysis was first discovered by Enikolopyan et al.[1] in the late seventies and has been developed further for the production of oligomers on an industrial scale. The use of catalytic chain transfer agents has several advantages over more traditional ways of producing low molecular weight polymers as first no large amounts of initiators and transfer agents like mercaptans are required and second all polymers will have a terminal double bond suitable for post reacting.[2,3] Especially for methacrylates these catalysts are very active and only ppm quantities of the catalyst are required to obtain low molecular weight polymers. The generally accepted mechanism for catalytic chain transfer (CCT) consists of two consecutive reactions as shown for methyl methacrylate (MMA) in Figure 1. In the first step the cobalt catalyst, which has one unpaired electron, abstracts a hydrogen from the α-methyl group at the end of the growing radical chain forming a



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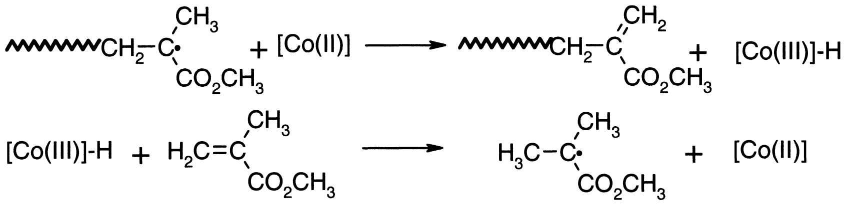

Figure 1. Mechanism for catalytic chain transfer.

cobalt hydride and a macromonomer. In the second step the cobalt hydride transfers the hydrogen to monomer thereby reinitiating a new chain and reforming the cobalt(II) species. Acrylates on the other hand are known to be able to undergo, under specific conditions, a controlled or living type of radical polymerization with some of these cobalt catalysts[4,5] as is shown in Figure 2 for methyl acrylate. It was recently shown

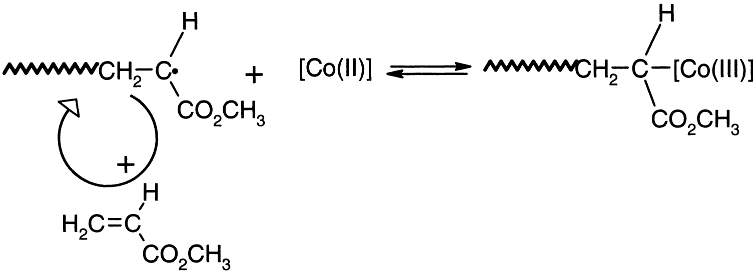

Figure 2. Mechanism of cobalt-mediated controlled radical polymerization of methyl acrylate.

that in the copolymerization of methacrylates and acrylates in the presence of a catalytic chain transfer agent both mechanisms play an important role.[6] In the catalytic chain transfer polymerization of styrene, formation of covalent bonds between polystyrene radicals and the cobalt species was shown to play a role as well.[7,8,9] In this paper the consequences of this bond formation will be discussed from a kinetic point of view. Acrylates have been considered not to undergo catalytic chain transfer as they lack an α-methyl group[10] and as the corresponding polyacrylate radicals form covalent bonds to the Co(II) species.[11,12] The chemistry of the chain transfer step is a second topic in this paper. Recently, we submitted a paper on the effect of non-coordinating solvents like toluene and *n*-butyl acetate on the determined chain transfer coefficient.[13] The effects appeared to be no solvent effects, but effects of solvent impurities. The third aspect of CCT that will be discussed in this paper is the influence of deliberately added impurities on the determined chain transfer constants (C_T). In this way we hope to clarify the nature of the contaminating species.

Experimental Section

Materials. Styrene (Aldrich, 99%), *n*-butyl acrylate (BA, Merck, 99%) and methyl methacrylate (MMA, Merck, 99 %) were all distilled under vacuum and stored at –10 °C. Prior to use, all monomers were passed over a column containing inhibitor remover and basic alumina. Toluene and tetrahydrofuran (THF) (both Biosolve, AR) were purified using a Grubbs solvent purification set-up[14], purged with argon for at least three hours and stored over molsieves in a glovebox. Methanol (Biosolve), 1-dodecanethiol (Aldrich, 98 %), benzoyl peroxide (Aldrich, 97 %), acetic acid (Merck, 99 %) were used as received. Azobis(methylisobutyrate) (AIBMe, Wako Chemicals) was recrystallized from methanol. CoBF (bis(aqua)bis((difluoroboryl)dimethylglyoximate)cobalt(II)) was prepared according to a procedure of Bakac and Espenson[15]. It was analysed using UV-Vis spectroscopy and elemental analysis (experimental C: 23.1 %, H: 3.81 %, N: 13.3 %; calculated C: 22.8 %, H: 3.83 %, N: 13.3 %). One single batch was used throughout all experiments.

General polymerization procedure. Monomers and solvents were purged with argon for at least three hours prior to transfer into a glovebox. All reaction mixtures were prepared inside a glovebox. Stock solutions of CoBF in monomer or solvent were prepared and stored for a longer period of time. AIBMe solutions in monomer were prepared immediately prior to the experiment. Reaction mixtures were made of the CoBF-solution, monomer, solvent or additive and an AIBMe solution to a total volume of about 5 mL. Reactions were carried out at different solvent or additive concentrations. At each set of conditions a total of eight polymerizations was done at different CoBF concentrations. Polymerizations were carried out in a water bath at a constant temperature of 60 °C (±0.2 °C) in the dark unless stated otherwise. Reactions were stopped by addition of hydroquinone and cooling. Monomer was evaporated and the polymer dried under vacuum at 60 °C. Conversion was determined gravimetrically.

Analyses. Size exclusion chromatography (SEC) was carried out using THF as an eluent at a flow rate of 1 mL$\cdot$ min^{-1}. Two Polymer Laboratories PLgel 5 μm Mixed-C columns (300 × 7.5 mm) and PLgel 5 μm guard column (50 × 7.5 mm) were used and calibrated with Polymer Laboratories narrow MWD polystyrene standards.

Results and Discussion

Solvent impurities. In a recent paper we discussed the effect of non-coordinating solvents on the catalytic chain transfer polymerization of MMA.[13] The solvent effects reported in literature[10,16] appeared to be effects of solvent impurities and dissappeared after thorough solvent purification. However the nature of the impurities was unclear. Therefore, we deliberately added impurities to the bulk polymerization of MMA. The effect of these impurities on low conversion polymerizations is small when these are present in low concentrations (Figure 3). From studies of CCT in emulsion polymerization[17] and on the polymerization of methacrylic acid[18] it is known that at low pH CoBF is prone to decomposition. That is why, we would have expected to see an effect of acetic acid, but even at 1 mol· L^{-1} no clear decrease in C_T can be observed. Peroxides are known to oxidize cobalt complexes from Co(II) to Co(III) and in that way reduce the rate of transfer with respect to the rate of propagation[19], but here we did not observe any effect either. As alcohols are present in alkyl esters, methanol was tested as well, but it did not change the obtained transfer coefficients and neither did 1-dodecanethiol. Only in THF C_T decreased quite drastically but only at concentrations over 1 mol· L^{-1}. This decrease may be due to the presence of peroxides despite thorough purification or due to coordination to the catalyst as THF has stronger coordinating capabilities as toluene and *n*-butyl acetate. So the exact nature of the impurities present

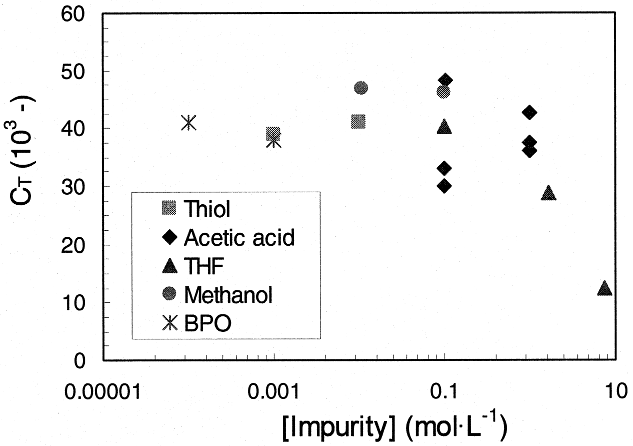

Figure 3. C_T of COBF for the bulk polymerization of MMA at 60 °C at various impurity concentrations.

in both toluene and *n*-butyl acetate that cause strong reductions in C_T remains unclear. This is an important question to be resolved for practical application of CCT in an industrial environment.

CCT of styrene. In dark, C_T for the homopolymerization of styrene was found to be around 70 which is an order of magnitude lower than in literature[20,21] where values for C_T range from 350 to 1600. The spread in these values is quite remarkable, especially when it is considered that for MMA C_T is in a much smaller range from 28.000 to 40.000. However, when the reaction vials were exposed to ordinary laboratory light C_T increased at least one order of magnitude to the range 350 to 2000 depending on initiator concentration. When the vials were exposed to a sunlamp during polymerization the obtained C_T increased even further up to a maximum of almost 7000 as shown in Figure 4. Furthermore, C_T appeared to be inversely related to the initiator concentration, which was also previously reported by Heuts et al.[9] These results can be explained when the mechanisms in Figure 1 and 2 are combined. Polystyryl radicals can form covalent bonds to the central cobalt atom, thereby reducing the amount of CoBF available for transfer. This was shown before by both UV-Vis and ESR spectroscopy.[7,8] The bond formation equilibrium depends on radical and thus initiator concentration. An increase in initiator concentration will result in an increase in radical concentration, shifting the equilibrium as shown in Figure 2 to the right. This results in a lower amount of CoBF

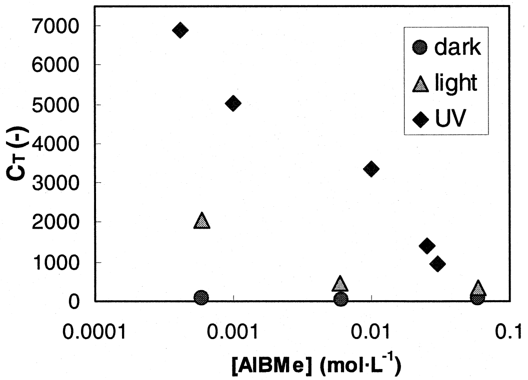

Figure 4. C_T of CoBF for the polymerization of styrene as a function of initiator concentration at 60 °C carried out in dark, laboratory light and UV-light.

available for CCT. On the other hand, the dissociation rate can be increased by (UV-) light, shifting the equilibrium to the left and thereby increasing C_T. This effect is, however, partially counteracted by an increased initiator decomposition due to the UV-light. The combination of both mechanisms may also explain the spread in the results found in literature as it is shown here that the determination of C_T is sensitive to both light intensity and initiator concentration.

The reversibility of cobalt-polystyrene radical bond formation was shown via the production of bimodal polystyrene in a one step process. In Figure 5 the successive molecular weight distributions for the catalytic chain transfer polymerization of styrene are shown. During the first four hours the reaction vials were exposed to laboratory light, after which the light was turned off and the vials were protected from light during the next two hours of reaction. The molecular weight distributions (MWD) shown correspond to samples taken after two, four, five and six hours. It can be clearly seen that during the first two hours polymer is formed with a M_{peak} around 25×10^3 g· mol^{-1}. After the light is turned off a shift to a M_{peak} around 200×10^3 g· mol^{-1} occurs. The opposite effect is shown in Figure 6. Here the first three hours of reaction took place in

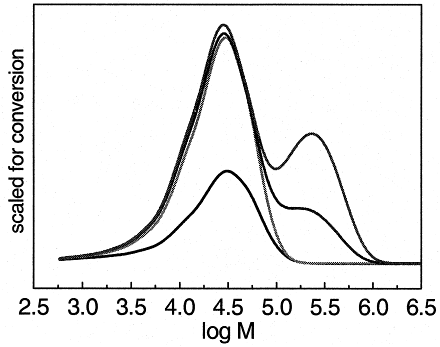

Figure 5. Molecular weight distributions for the catalytic chain transfer polymerization of styrene at 60 °C at successive conversions. The first four hours reaction vials were exposed to light, after which the light was turned off. Samples were taken after 2, 4, 5 and 6 hours.

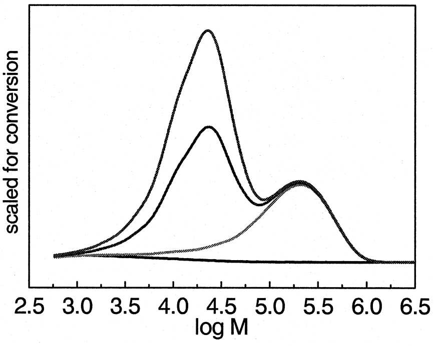

Figure 6. Molecular weight distributions for the catalytic chain transfer polymerization of styrene at 60 °C at successive conversions. The first two hours reaction vials were put in dark, after which they were exposed to light for three hours. Samples were taken after 1, 2, 3.5 and 5 hours.

dark, after which the reaction mixture was exposed to light for two hours. The first sample was taken after one hour after which conversion was only 0.16 %. The molecular weight distribution was still on the low molecular weight side with a M_{peak} around 1000 g· mol^{-1}. After two hours molecular weights had shifted to 220×10^3 g· mol^{-1}. After the light is turned on the molecular weight of the newly formed polymer decreases again. The shifts in MWD can be easily explained from the mechanisms in Figures 1 and 2. For the reaction shown in Figure 6 the concentration of CoBF available for transfer is still decreasing when the first sample is taken after one hour. Most newly initiated polystyrene radicals are covalently bonded to CoBF and therefore the conversion rate is low. The molecular weight of the polymer that is formed is rather low as a large part of the total amount of CoBF added to the reaction mixture is still available for transfer. When the second sample is taken after two hours an equilibrium between bound and unbound polystyrene radicals is reached. Conversion rates increase as not all freshly generated radicals will be trapped anymore and the average molecular weight increases as only a small amount of CoBF can take part in the transfer reactions. When the light is turned on the dissociation rate of the cobalt-polystyrene radicals bond goes up, resulting in a shift of the bound-unbound equilibrium to more free CoBF, which in turn gives lower molecular weights. This clearly shows the reversibility of the covalent bond between the polystyrene radical and the cobalt species.

The combination of the mechanisms shown in Figures 1 and 2 needed to explain the experimental observations in the catalytic chain transfer polymerization of styrene closely resembles earlier observations in the catalytic chain transfer copolymerization of methyl acrylate and methyl methacrylate.[6] The main difference is that in the case of styrene the chemistry that inhibits and enables catalytic chain transfer is captured in one single monomer.

CCT of acrylates. Acrylates are believed not to undergo CCT to a large extent, as they lack an α-methyl group[10] and as their corresponding polyacrylate radicals form covalent bonds to the cobalt catalyst.[11,12,22] For the homopolymerization of methyl acrylate (MA) in toluene at 60 °C we recently reported an apparent C_T of 8,[6] similar to another recently reported value determined by Roberts et al.[22] Janowicz[23] published results for MA in butanone at 80 °C from which a C_T of 190 can be calculated. It is also known that polyacrylate radicals can form covalent bonds to cobalt species (Figure 2).

When the polymerization is started an inhibition time is observed in which first this bond formation takes place after which the polymerization proceeds as in an ordinary free-radical polymerization.[6] During the inhibition period small amounts of polymer are formed. In an attempt to apply UV-light assisted catalytic chain transfer to the polymerization of *n*-butyl acrylate in a similar way as to styrene we unfortunately still observed an inhibition time. However, the polymer formed during inhibition was used in the determination of C_T. The Mayo-plot is shown in Figure 7. In the calculations of the CoBF concentrations it was assumed that all CoBF was available for transfer, which will mean that the obtained value $C_T = 650$ is an underestimation. This results in a transfer coefficient (k_{tr}) that is less than 20 % smaller than for *n*-BMA (Table 1).

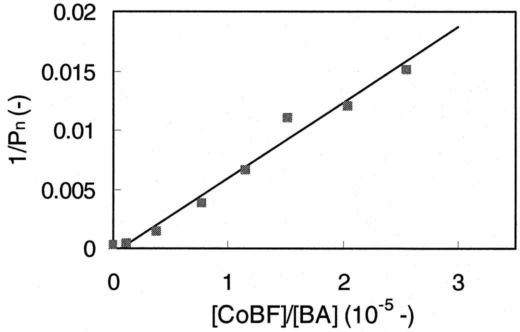

Figure 7. Mayo-plot of the polymer formed during the inhibition period of an attempted UV-light assisted catalytic chain transfer polymerization of *n*-butyl acrylate in toluene at 60 °C.

Table 1. Chain transfer constants, propagation and transfer rate coefficients for n-BMA, BA, styrene at 60 °C and α-methyl styrene at 50 °C.

Monomer	C_T (average)	k_p[a]	k_{tr}
n-BMA[b]	28.0×10^3	976	2.7×10^7
BA	0.65×10^3	33700	2.2×10^7
styrene	8.0×10^3	341	2.7×10^6
α-methyl styrene[c]	8.9×10^5	1.73	1.5×10^6

[a] All k_p-data are taken from van Herk.[24]
[b] C_T for *n*-BMA was taken from Pierik et al.[13]
[c] Data for α-methyl styrene are taken from Kukulj et al.[25]

So the absence of an α-methyl group in acrylates has hardly any influence on the transfer step itself. The reduction of free cobalt by cobalt-carbon bond formation is the cause of the absence of CCT behaviour in acrylate polymerizations. A similar comparison can be made for styrene and α-methyl styrene. Using the higher values for C_T obtained from the UV-light assisted catalytic chain transfer polymerization of styrene, one calculates similar values of k_{tr} for both styrene and α-methyl styrene. This means that in this case as well the predominant effect of the α-methyl group is the prevention of cobalt-carbon bond formation and not directly facilitating hydrogen abstraction.

If in the catalytic chain transfer polymerization of acrylates the formation of cobalt-carbon bonds can be partially prevented by an increase in temperature, which may be the case in Janowicz data[23], by using UV-light of a specific wave-length or by any other means than acrylates can be applied more easily in catalytic chain transfer polymerizations. This would result in wider scope for application in industry.

Conclusion

In this paper three aspects of catalytic chain transfer polymerization were dealt with. The first issue on what impurities cause a sharp decrease in chain transfer coefficients in low conversion solution polymerizations remained unresolved. Surprisingly, both acetic acid and benzoyl peroxide did not affect the obtained chain transfer coefficients to a measurable extent. From the catalytic chain transfer polymerization of styrene it appeared that it is only truely effective when the polymerization is exposed to light or even better UV-light. The obtained chain transfer coefficients have an inverse dependence on initiator concentration. This can be explained using a combination of both the catalytic chain transfer and the living polymerization mechanisms. For both *n*-butyl acrylate and styrene it was shown that their intrinsic chain transfer constants differ only to a small extent from the transfer constants of their counterparts *n*-butyl methacrylate and α-methyl styrene. The absence of an α-methyl group in acrylates and styrene has hardly any influence on the transfer step itself.

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