Polymerization of Methyl Methacrylate Using Dimanganese Decacarbonyl in the Presence of Organohalides

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ABSTRACT: Dimanganese decacarbonyl ($Mn_2(CO)_{10}$) initiates the radical polymerization of methyl methacrylate (MMA) in the presence of a variety of organic halides including $C_6H_5CH_2Br$, $Me_2C(Br)$-CO_2Et, $BrCH_2C(Br)=CH_2$, and $ClCH_2C(Cl)=CH_2$ in toluene at 60−90 °C. When using allylic halides (e.g., $BrCH_2C(Br)=CH_2$ or $BrCH_2C(CO_2Me)=CH_2$), the number-average molecular weights and molecular weight distributions of the PMMA were both low and relatively narrow. The production of relatively low molecular weight polymers when using allylic halides could be explained by an addition-fragmentation chain-transfer mechanism and this is supported by end-group analysis.

Introduction

Transition-metal-mediated atom transfer radical polymerization (ATRP) has emerged as an important method of controlled or living polymerization, capable of producing (meth)acrylic polymers with predictable molecular weights and low polydispersities.[1] The majority of ATRP uses copper(I) complexes with a variety of ligands, although these are principally either alkyl substituted bipyridine derivatives developed by Matyjaszewski[2] or *N*-alkyl-2-pyridylmethanimine Schiff base ligands pioneered by Haddleton.[3] In addition to Cu(I) based systems, other transition-metal-catalyzed ATRP systems are actively being explored, including those based on Ru(II),[4] Fe(II),[5] Ni(II),[6] Rh(I),[7] or Pd(II)[8] metal halides. Living radical polymerizations proceed via the reversible cleavage of the carbon−halide bond from the dormant ω-polymer end, followed by addition of monomer to the growing polymer chain. The fascination with these systems is due to the ability to yield specific polymers relatively easily, with predictable molecular weights and molecular architecture.[9] Additionally, the halide-terminated polymers can be further employed as the starting point for block copolymerization.[10]

There are however, significant difficulties still associated with these systems, primarily because they require relatively high concentrations of the metal catalyst, which can be difficult to extract from the polymer. The use of insoluble supports has tried to circumnavigate this issue, by attaching either the metal halide or alkyl halide initiator to an insoluble functionalized resin bead.[11,12] On completion of the polymerization, the beads can be removed by filtration.

Work within our group has recently involved developing alternative and more versatile free-radical initiator systems for organic synthesis.[13] We have shown, for example, that dimanganese decacarbonyl ($Mn_2(CO)_{10}$) can be used to generate organic carbon-centered radicals from organohalides, which can partake in dimerization or cyclization reactions.[14] The manganese pentacarbonyl radical ($\bullet Mn(CO)_5$), generated by either thermolysis or photolysis of the relatively weak Mn−Mn bond, can abstract a halogen atom from a variety of organohalides (RX) bearing weak C−X bonds, forming carbon-centered radicals (R•). This method provides an efficient and mild procedure for radical generation and the ensuing propagation reactions.

The use of dimanganese decacarbonyl in radical-initiated polymerizations is relatively unexplored. In 1974, Bamford showed that the photolysis of $Mn_2(CO)_{10}$ in the presence of CCl_4 led to polymerization of methyl methacrylate (MMA), to high conversion (90%), but gave no indication of molecular weight analysis.[15] More recently, Yagci reported the cationic polymerization of cyclohexene oxide on photolysis of $Mn_2(CO)_{10}$ in halogenated solvents, in combination with an onium salt, which resulted in a new method for initiating cationic polymerization.[16] This photoinitiated cationic polymerization yielded low molecular weight polymer (M_n ∼4 100) and relatively narrow polydispersity (M_n/M_w = 1.26−1.48) but this was coupled with low conversion (0−13%, after 2 h). Hudson and co-workers have also recently investigated a heterogeneous graft copolymerization using $Mn_2(CO)_{10}$ as the initiator.[17]

Our studies have concentrated on the use of carbon-centered radicals produced by thermolysis of $Mn_2(CO)_{10}$, in conjunction with an alkyl or allylic halide in toluene, as shown in Scheme 1. It was envisaged that this could provide a mild and efficient approach to a variety of radicals that could initiate polymerization of MMA to form poly(methyl methacrylate) (PMMA) bearing several different end groups.

Experimental Section

General Information. Methyl methacrylate (MMA) (Aldrich, 99%) was purified by passing through a column of activated basic alumina and deoxygenated with a stream of nitrogen, for 0.5 h. Dimanganese decacarbonyl, $Mn_2(CO)_{10}$ (Strem, 98%), was purified by vacuum sublimation and stored under nitrogen prior to use. Anhydrous toluene (Aldrich, 99.8%) was deoxygenated by purging with nitrogen for 1 h prior to use. *tert*-Butyl 2-(bromomethyl)acrylate[18] was prepared using a

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Scheme 1. Dimanganese Decacarbonyl-Promoted Radical Polymerization of Methyl Methacrylate

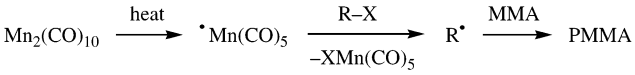

Table 1. Conversion Data for Poly(methyl methacrylate) Produced Using $Mn_2(CO)_{10}$ with Various Organohalides at 90 °C

entry	organohalide initiator (RX)	conv/%[a]	k^{app}/s^{-1} [b]
1	$C_6H_5CH_2Br$	84	8.4×10^{-5}
2	$C_6H_5CH_2Cl$	32	2.4×10^{-5}
3	$PhSO_2Cl$	84	8.0×10^{-5}
4	1,2-$(BrCH_2)C_6H_4$	77	6.8×10^{-5}
5	4-$FC_6H_4CH_2Br$	80	7.5×10^{-5}
6	4-^{t}Bu$C_6H_4CH_2Br$	86	1.9×10^{-5}
7	$PhCH(Br)CH_3$	81	9.3×10^{-5}
8	$Me_2C(Br)CO_2Et$	86	1.1×10^{-5}
9	$BrCH_2C(CO_2{}^t Bu)=CH_2$	60	4.2×10^{-4}

[a] Determined from gravimetry; time = 5 h; 25% w/w in toluene, MMA:RX:$Mn_2(CO)_{10}$ = 50:1:1. [b] This was determined from plots of $In[M_0]/[M]$ versus time.

standard literature procedure while all other reagents were used as received.

Polymerization Procedure. MMA (3.75 g, 4 mL, 37.46 mmol; 25% w/w in toluene) was added to a solution of $Mn_2(CO)_{10}$ (0.29 g, 0.75 mmol) in deoxygenated toluene (11.25 g, 13 mL) in a Schlenk tube, under a nitrogen atmosphere. The tube was immersed into a thermostated oil bath at 90 °C for 1 h, after which time *tert*-butyl 2-(bromomethyl)acrylate (0.17 g, 0.75 mmol) was added via a degassed syringe (time = 0). Samples (1−2 mL) were removed every hour for conversion and molecular weight analysis (the conversion calculations assume that the manganese impurity in the polymer is $Mn_2(CO)_{10}$, rather than a mixture of $XMn(CO)_5$ and $Mn_2(CO)_{10}$). Conversion of the polymer reached 60% after 5 h and the apparent constant of propagation (k^{app}) was 4.2×10^{-4} s^{-1} from a first-order rate plot (of $In[M]_0/[M]$ vs time, where $[M]_0$ = concentration of the MMA at t = 0 and [M] = concentration of MMA at 1−5 h). Prior to molecular weight analysis, manganese byproducts were removed by aerial oxidation—a solution of the crude polymer in THF:toluene (99:1) is left to stand for 24 h resulting in the formation of a precipitate that can be removed by filtration.

Polymer Analysis. Molecular weight and molecular weight distribution of the polymers were measured by gel permeation chromatography (GPC), on a system equipped with a guard column and two 6 μm Shodex columns (KF-802.5, pore size 80 Å and KF-803, pore size 100 Å) at 45 °C, with a Waters 2410 differential refractive index detector using tetrahydrofuran at 1 mL min^{-1} as eluent. Molecular weight was calculated against nine narrow PMMA standards in the range 5.59×10^5 to 960 g mol^{-1}. Polymer conversions were measured by gravimetry. ^{1}H NMR spectra were recorded on either a Joel EX 270 or Bruker AMX 500 spectrometer.

Results and Discussion

Polymerization of MMA with Various Organohalides. Initially, a series of experiments were conducted to investigate the polymerization of MMA by thermolysis of a solution of $Mn_2(CO)_{10}$ in the presence of several organohalides. In contrast to the work conducted by either Bamford[15] or Yagci,[16] which concentrated on conducting polymerization studies in halogenated solvents (CCl_4, $CHCl_3$, or CH_2Cl_2), our initial studies employed only one equivalent of the organohalide in toluene at 90 °C. As shown in Table 1, a variety of organohalide initiators bearing weak C−X bonds can be used to efficiently polymerize MMA. The requirement for a weak C−X bond is illustrated by the much lower conversion observed when using benzyl chloride in place of benzyl bromide (Table 1, entries 1 and 2). Polymerization using benzenesulfonyl chloride showed no differences in conversion and reaction rate compared to benzyl bromide (Table 1, entry 3). A variety of substituted benzylic bromides can be employed (Table 1, entries 4−7) and, as predicted, these showed only slight differences in conversion and reaction rate to benzyl bromide. Tertiary bromides can also be used as illustrated by the efficient polymerization using $Me_2C(Br)CO_2Et$ (Table 1, entry 8). The reaction of the allylic bromide initiator, $BrCH_2C(CO_2{}^t Bu)=CH_2$, was particularly interesting (Table 1, entry 9). In this case, the PMMA had an M_n value of 20 855 (M_w/M_n = 1.28), while all of the polymers derived from the other organohalide initiators had significantly higher values of M_n, which exceeded the total exclusion limit of the GPC column (~25 000 for accurate molecular weight determination).

Table 2. Molecular Weight and Conversion Data for Poly(methyl methacrylate) Produced Using $Mn_2(CO)_{10}$ with Various Organohalides at 60 °C

entry	organohalide initiator (RX)	conv/%[a]	M_n	M_w/M_n	k^{app}/s^{-1} [c]
1	$C_6H_5CH_2Br$	55	[b]		8.4×10^{-5}
2	CCl_4	60	[b]		4.7×10^{-5}
3	$BrC(CH_3)_2CO_2Et$	54	[b]		4.0×10^{-5}
4	$BrCH_2CH=CH_2$	32	[b]		2.3×10^{-5}
5	$BrCH_2CH=CHPh$	10	[b]		6.2×10^{-6}
6	$BrCH_2C(CO_2{}^t Bu)=CH_2$	16	3 476	1.19	4.5×10^{-6}
7	$BrCH_2C(CO_2Me)=CH_2$	15	5 958	1.26	8.4×10^{-6}
8	$BrCH_2C(=CH_2)Br$	32	17 597	1.41	1.9×10^{-5}
9	$ClCH_2C(=CH_2)Cl$	9	22 561	1.52	6.4×10^{-6}

[a] Determined from gravimetry; time = 5 h; 25% w/w in toluene, MMA:RX:$Mn_2(CO)_{10}$ = 50:2:1. [b] The total exclusion limit of the GPC column was exceeded. [c] This was determined from plots of $In[M_0]/[M]$ versus time.

Thermolysis of the Mn−Mn bond also occurred at 60 °C and polymerization of MMA using $Mn_2(CO)_{10}$ in the presence of two equivalents of benzyl bromide (25% w/w in toluene MMA:BnBr:$Mn_2(CO)_{10}$ = 50:2:1) reached a conversion of 55% after 5 h (Table 2, entry 1). The use of related organohalides (Table 1, entries 2 and 3) also gave high molecular weight polymers (with M_n values that exceeded the total exclusion limit of the GPC column) in good yield. In contrast, the use of allylic halides dramatically altered the conversion and in some cases, the molecular weight values (Table 2, entries 4−9). For example, the molecular weight distribution of the polymer prepared using 2,3-dibromopropene (Table 2, entry 8) was unimodal and relatively narrow (M_w/M_n = 1.41) and the M_n value was significantly reduced, when compared to the use of other halide initiators including benzyl bromide and carbon tetrachloride. The use of 2,3-dichloropropene (Table 2, entry 9) produced slightly higher molecular weight PMMA (than when using 2,3-dibromopropene) and the conversion was significantly lower (9 versus 32%). The lower conversion presumably reflects the stronger C−Cl (rather than C−Br) bond, which leads to a slower rate of halogen atom abstraction by the manganese pentacarbonyl radical. Substitution of the alkene double bond in the organohalide also plays an important role in the polymerization. This is illustrated by the different conversion and M_n values observed when using allyl bromide, cinnamyl bromide, and 2,3-dibromopropene (Table 2, entries 4, 5, and 8).

Mechanistic Studies. To study the effects of the allylic halide concentration, PMMA was prepared using

Table 3. Molecular Weight and Conversion Data for Poly(methyl methacrylate) Produced Using $Mn_2(CO)_{10}$ with Various Ratios of Organobromide:$Mn_2(CO)_{10}$ at 60 °C

entry	allylic or tertiary bromide initiator (RX)	RX: $Mn_2(CO)_{10}$	conv/%[a]	M_n	M_w/M_n
1	$BrCH_2C(=CH_2)Br$	1:1	40	~28 000[b]	~1.50
2	$BrCH_2C(=CH_2)Br$	2:1	32	17 597	1.41
3	$BrCH_2C(=CH_2)Br$	3:1	26	12 923	1.26
4	$BrCH_2C(=CH_2)Br$	4:1	23	8 891	1.23
5	$BrCH_2C(=CH_2)CO_2Me$	1:1	22	6 234	1.47
6	$BrCH_2C(=CH_2)CO_2Me$	2:1	15	5 958	1.26
7	$BrCH_2C(=CH_2)CO_2Me$	1:2	27	6 885	1.56
8	$BrCH_2C(=CH_2)CO_2Me$	1:3	33	7 273	1.61
9	$Me_2C(Br)CO_2Et$	1:1	48	[c]	
10	$Me_2C(Br)CO_2Et$	2:1	54	[c]	

[a] Determined from gravimetry; time = 5 h; 25% w/w in toluene, MMA:$Mn_2(CO)_{10}$ = 50:1. [b] This is only an approximate value as the total exclusion limit of the GPC column was exceeded. [c] The total exclusion limit of the GPC column was exceeded.

different molar ratios of 2,3-dibromopropene and the initiator $Mn_2(CO)_{10}$ (Table 3, entries 1−4). In each case, the polymerization was carried out in toluene (25% w/w) at 60 °C. Polymerization of MMA in the presence of a 1:1 mixture of 2,3-dibromopropene and $Mn_2(CO)_{10}$ gave PMMA in 40% yield after 5 h. Over the same time period, increasing the amount of 2,3-dibromopropene resulted in a decrease in the conversion (to 23% when using four equivalents). Similarly, the molecular weight and M_w/M_n value of the polymer were reduced when the concentration of 2,3-dibromopropene was increased. A comparable effect was observed when using $BrCH_2C(=CH_2)CO_2Me$ (Table 3, entries 5 and 6) and as predicted, when the concentration of $Mn_2(CO)_{10}$ was increased, the conversion improved (k^{app} also increased from 1.57×10^{-5} s^{-1} to 2.07×10^{-5} s^{-1} when increasing the equivalents of $Mn_2(CO)_{10}$ from 2 to 3) (Table 3, entries 7 and 8).

Therefore, as the concentration of $BrCH_2C(=CH_2)Br$ or $BrCH_2C(=CH_2)CO_2Me$ increases, so the M_n values become lower and the conversion decreases. This is a surprising result as increasing the concentration of the organohalide should increase the rate of conversion of MMA to PMMA as illustrated by the polymerizations using the tertiary bromide initiator, $Me_2C(Br)CO_2Et$ (Table 3, entries 9 and 10).

The structure of the PMMA, obtained when using $Mn_2(CO)_{10}$/2,3-dibromopropene, was analyzed by ^1H NMR spectroscopy to determine the nature of the end groups. Hence, characteristic alkenic signals, derived from the propene, were observed between δ 5 and 6 ppm. Two sets of alkenic signals were observed (absorptions at δ 6.12 and 5.51 ppm were attributed to the alkene protons adjacent to the α-end, while the peaks at δ 6.21 and 5.28 ppm were assigned to the ω-end), which suggested the presence of two vinyl bromide units in the polymer. The presence of two vinyl bromide end groups could be explained by termination of the polymer using a radical addition-fragmentation chain-transfer mechanism, in which the growing polymer chain reacts with a second molecule of 2,3-dibromopropene (Scheme 2). This would lead to the expulsion of a bromine radical which, for example, could react with $Mn_2(CO)_{10}$ to regenerate the $\bullet Mn(CO)_5$ radical (together with $BrMn(CO)_5$). If this mechanism were operative, then changing the substituents on the alkene double bond of the allylic halide would be expected to influence the rate of radical addition-fragmentation. This is supported by the results in Table 2, which show that differently substituted

Scheme 2. Radical Addition to 2,3-Dibromopropene Followed by Fragmentation

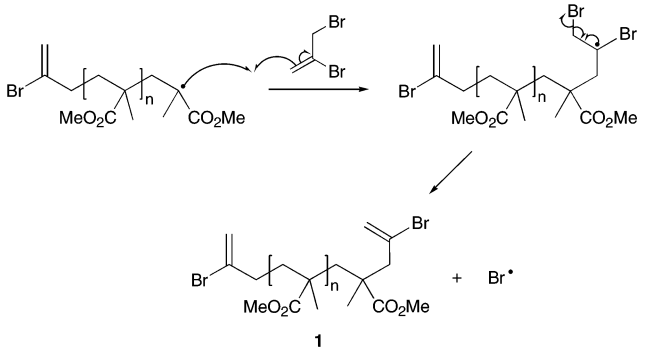

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Table 4. Molecular Weight and Conversion Data for Poly(methyl methacrylate) Produced Using CCl_4 (2 Equiv), an Organohalide (2 or 3 Equiv), and $Mn_2(CO)_{10}$ (1 Equiv) at 60 °C

entry	allylic or benzyl halide initiator (RX)	RX:CCl_4: $Mn_2(CO)_{10}$	conv/%[a]	M_n	M_w/M_n
1	$BrCH_2C(=CH_2)Br$	2:2:1	29	7 096	1.50
2	$BrCH_2C(=CH_2)Br$	3:2:1	32	6 583	1.45
3	$ClCH_2C(=CH_2)Cl$	2:2:1	39	10 570	1.66
4	$ClCH_2C(=CH_2)Cl$	3:2:1	35	11 637	1.61
5	$C_6H_5CH_2Br$	2:2:1	40	[b]	
6	$C_6H_5CH_2Br$	3:2:1	37	[b]	

[a] Determined from gravimetry; time = 5 h; 25% w/w in toluene MMA:$Mn_2(CO)_{10}$ = 50:1. [b] The total exclusion limit of the GPC column was exceeded.

allylic halides produce polymers of different molecular weight. The growing polymer chain could also abstract a hydrogen or bromine atom from the 2,3-dibromopropene, and this would also be influenced by substitution of the allylic halide. Finally, analysis of ^1H NMR spectra of polymers produced in the presence of related alkenes to 2,3-dibromopropene, including 2,3-dichloropropene, also showed the presence of vinyl end groups.

To provide further support for the radical addition-fragmentation mechanism and substantiate the polymer ^1H NMR data, model studies were investigated. These were designed to form small molecule adducts derived from radical initiation and chain termination of the reaction of MMA with 2,3-dibromopropene. Hence, thermolysis of $Mn_2(CO)_{10}$ (1 equiv) with 2,3-dibromopropene (2 equiv) and MMA (1 equiv) in toluene afforded the desired adduct, methyl 5-bromo-2(2-bromoprop-2-enyl)-2-methyl-hex-5-enoate, [**1**, $n = 0$] in 6% yield. Significant quantities of 2,5-dibromohexa-1,5-diene, derived from dimerization of 2,3-dibromopropene, and MMA adducts of higher M_n values were also recovered. The ^1H NMR spectrum of the hex-5-enoate [**1**, $n = 0$] exhibited the same set of alkenic peaks at identical chemical shifts to that of the polymer. Hence, 2,3-dibromopropene appears to be involved in both the initiation and chain-transfer steps of the polymerization.

Mixed Initiator Systems. MMA was also polymerized using $Mn_2(CO)_{10}$ with either 2,3-dichloro- or 2,3-dibromo-propene in the presence of CCl_4 (Table 4). The manganese pentacarbonyl radical was expected to selectively react with CCl_4 (because of the very weak C−Cl bond; BDE ~295 kJ mol^{-1}) to initiate the polymerization, while the substituted propene was expected to react with the growing polymer chain. Addition of the substituted propene was therefore expected to lower the M_n value of the polymer produced from the $Mn_2(CO)_{10}$/

Table 5. Molecular Weight and Conversion Data for Poly(methyl methacrylate) Produced Using $BrCCl_3$ (2 Equiv), an Allylic Halide (0, 2, or 3 Equiv) and $Mn_2(CO)_{10}$ (1 Equiv) at 60 °C

entry	allylic halide initiator (RX)	RX:$BrCCl_3$:$Mn_2(CO)_{10}$	conv/%[a]	M_n	M_w/M_n
1		0:2:1	47	[b]	[b]
2	$BrCH_2C(=CH_2)Br$	2:2:1	33	6 054	1.38
3	$BrCH_2C(=CH_2)Br$	3:2:1	31	5 266	1.36
4	$ClCH_2C(=CH_2)Cl$	2:2:1	43	8 506	1.69
5	$ClCH_2C(=CH_2)Cl$	3:2:1	36	7 997	1.61

[a] Determined from gravimetry; time = 5 h; 25% w/w in toluene MMA:$Mn_2(CO)_{10}$ = 50:1. [b] The total exclusion limit of the GPC column was exceeded.

CCl_4 reaction. As shown earlier, in the absence of the propene, the M_n value for the CCl_4 reaction exceeded the limit of the GPC column (Table 2, entry 2) while in the presence of 2,3-dibromopropene or 2,3-dichloropropene (under equivalent reaction conditions), the M_n value was much lower, that is, 6.5−11.6 k (Table 4, entries 1−4). When the allylic halide was replaced by benzyl bromide, the M_n values substantially increased (Table 4, entries 5 and 6), which gives further support to the addition-fragmentation chain-transfer mechanism in the presence of allylic halides. As shown in Table 5, similar results were obtained from related $BrCCl_3$-mediated polymerizations.

Summary and Conclusions

In conclusion, this work has demonstrated that thermolysis of $Mn_2(CO)_{10}$ in the presence of organohalides can efficiently yield PMMA. Of particular note are the polymerizations using allylic halides that produce low molecular weight PMMA with relatively narrow M_w/M_n values. This can be explained by a radical addition-fragmentation mechanism, which can allow the synthesis of polymers bearing a variety of end-group functionalities, by either use of single or mixed organohalide initiator systems.

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