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Vinylarenetricarbonyl complexes of chromium as chain propagation regulators for polymerization of acrylic monomers

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The polymerization of methyl methacrylate and butyl acrylate initiated by azo-bis-isobutyronitrile in the presence of metal-containing monomers (*p*-methylstyrene-, stilbene- and α-methylstyrene-chromiumtricarbonyl) was studied. Kinetic parameters (i.e. the decrease in the autoacceleration during the polymerization of acrylic monomers, its shift towards a high conversion region in the presence of α-methylstyrenechromiumtricarbonyl, a linear dependence of the molecular weight of a polymethyl methacrylate and the shift of molecular-weight distribution curves to a high molecular weight region with conversion) demonstrate the influence of vinylarenetricarbonyl complexes of chromium on basic steps of polymerization. It is important to note that the above organometallic compounds enable the controlled synthesis of polymers under temperature conditions (50–70 °C) corresponding to those of the industrial polymer production. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: vinylarene complexes; chromium; acrylic monomers; controlled polymer synthesis

INTRODUCTION

Radical polymerization in the living chain mode is a key direction in the development of synthetic polymer chemistry at the turn of the 21st century.[1–3] Its performance allows one to change the reactivity of macroradicals and, hence, to control chain propagation by modifying the kinetic parameters of polymerization and the molecular weight characteristics of the polymers produced. In order to carry out such a process, various approaches are utilized, viz. ('atom transfer radical polymerization') (ATRP), 'reversible addition–fragmentation chain transfer' (RAFT) and the application of nitroxide stable radicals 'nitroxide-mediated polymerization' (NMP)' including their generation *in situ* during polymerization.[1,3] In the latter case, active additives such as nitroso compounds, nitrones, etc. are introduced to the polymerizing medium to carry out the controlled process. These compounds, which form stable spin-adducts with a high macromolecular 'tail' when acting with growing macroradicals, are more effective regulators than their low molecular weight analogs.[4–8] This fact allows controlled polymer synthesis under rather mild temperature conditions that are close to those used in industrial production.

In this paper, to control chain propagation during the radical polymerization of methyl methacrylate (MMA) and butyl acrylate (BA), the following organometallic monomers were employed: vinylarenechromiumtricarbonyl complexes with bulk organic ligands, in particular *p*-methylstyrenechromiumtricarbonyl (PCC), stilbenechromiumtricarbonyl (STC) and α-methylstyrenechromiumtricarbonyl (MCC). These compounds, under radical initiation conditions when a growing or an initiating radical is added to them, should form stable spin-adducts capable of regulating polymer chain growth.

EXPERIMENTAL

All reactions involving tricarbonylchromium complexes were carried out under an atmosphere of argon using standard

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techniques.[9] Benzenechromiumtricarbonyl (BCC) and STC were prepared following a published procedure.[9] MCC and the related monomer PCC were synthesized according to the method[10] via the intermediate complex $(NH_3)_3Cr(CO)_3$. The synthesis of this intermediate was simplified by using atmospheric pressure conditions. The physical constants of the compounds are in agreement with literature data.[10–13] The overall yields of STC, BCC, MCC and PCC were 50%, 62%, 73% and 51% respectively. MMA and BA were purified by vacuum distillation before use. MCC (as well as BCC, PCC, STC) was added in the course of polymerization of MMA and BA, both in bulk (MCC, BCC) and in ethyl acetate (PCC, STC) using azo-bis-isobutyronitrile (AIBN) as a free radical initiator at 50 °C (BA) and 70 °C (MMA). The concentration of the monomers in ethyl acetate was 20 wt%.

The polymerizations were conducted using a previously described technique.[14] Weighed batches of STC and PCC were dissolved in ethyl acetate; measured amounts were then charged into tubes with appropriate amounts of the acrylic monomer and the initiator. The tubes were triply degassed and immersed into a constant-temperature bath for a predetermined time. After polymerization, the tubes were cooled and the mixture diluted with a small amount of ethyl acetate. 5–10 ml solution was precipitated dropwise in 200 ml of heptane bubbled with argon. The isolated polymer was washed three times with new portions of heptane. After reprecipitation the polymers were dried and then weighed.

AIBN was purified by recrystallization from methanol at 50 °C. Di-*tert*-butylperoxytriphenylantimony (DPA) was prepared according to a published method.[15] Monomer ratios present in the polymers (e.g. polymer compositions) were determined by chromium elemental analyses that were performed spectrophotometrically.[16] The molecular weight characteristics of polymers were estimated viscometrically and by gel permeation chromatography (GPC). The GPC measurements were made using a Waters instrument (USA) equipped with a set of five Styragel columns with pore diameters of 10^5, 3×10^4, 10^4, 10^3 and 250 Å and a Waters R-403 differential refractometer. Polystyrene standards with narrow molecular weight distributions were used for calibration.[17] Gel permeation chromatograms were run in tetrahydrofuran at 30 °C. Electron spin resonance (ESR) spectra were recorded on a Bruker radiospectrometer in special tubes. DPA was used as a radical source at 30 °C and nitrosodurene was employed as a spin trap. The method of ESR study was similar to that described previously.[18] The kinetic study was carried out gravimetrically and using a thermometric technique.[19]

RESULTS AND DISCUSSION

The generation of the most stable spin-adduct, of course, may be expected in the case of MCC, since it forms a tertiary radical when reacted with an initiating or a growing radical, in contrast to a secondary one for PCC and STC.

The ESR study of the initiation of MCC polymerization at room temperature with DPA as a butoxyl radical source[14,20–22] using the spin trap approach shows the generation of oxygen-centered radical spin adducts *tert*-BuO–N(O)–Bu-*tert* (a triplet with splitting constant $a_N = 27.3$ G), as well as the MCC tertiary radical adduct (a triplet with constant $a_N = 14.0$ G). The subsequent transformation of the metal-containing radical in a monomer medium was studied by way of example of MMA and BA polymerization with a low concentration of the indicated additive.

The kinetic study of the polymerization of MMA at 70 °C and BA at 50 °C initiated by AIBN showed that the introduction of 1% MCC leads to a significant retardation of the process: up to the limited conversion, the polymerization proceeds for more than 10 h. The autoacceleration of the polymerization considerably reduces and is shifted to the high conversion region in the presence of less than 1% MCC in a reaction mixture (Fig. 1a and b). It should be noted that the organometallic monomer nature influence on the kinetics of the polymerization of acrylic monomers becomes more pronounced with increasing MCC concentration.

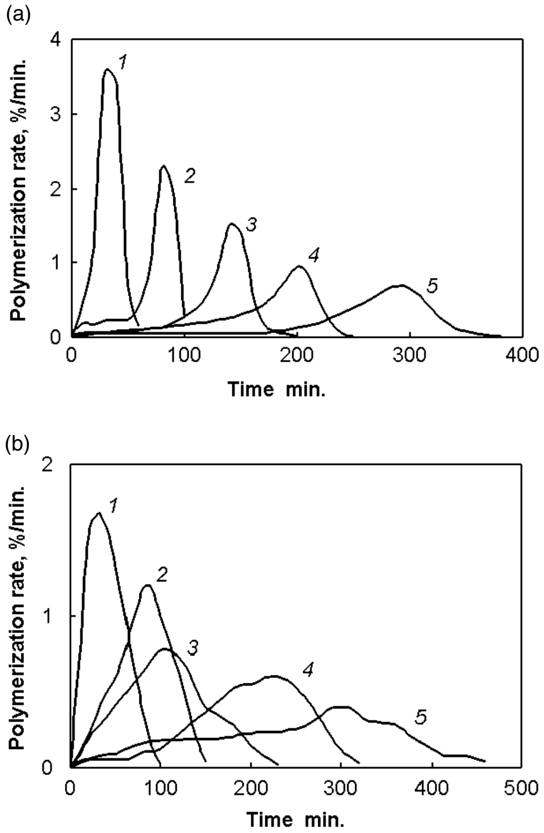
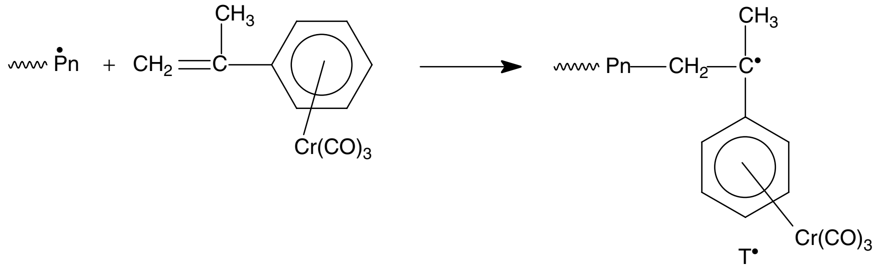


Figure 1. Differential kinetic curves for polymerization in the presence of AIBN (0.1 mol%) and MCC. (a) MMA polymerization, at 70 °C; [MCC]: (1) 0; (2) 0.1; (3) 0.3; (4) 0.5; (5) 0.7 mol%. (b) BA polymerization, at 50 °C; [MCC]: (1) 0; (2) 0.1; (3) 0.2; (4) 0.3; (5) 0.4 mol%.



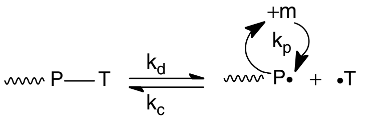
Scheme 1.

The data indicate that a stable organometallic radical (Scheme 1) results from the interaction of a growing radical with MCC and, like nitroxyl or trityl radicals, it can react with polymer radicals via the reversible inhibition mechanism (pseudoliving polymerization;[1–3] Scheme 2). Thus, this radical is capable of regulating the polymer chain propagation.

The radical $T^{\bullet}$ may also be presented as a resonance structure containing an unpaired electron at the chromium atom (Scheme 3). Such a type of radical is also able to form a labile bond with propagating radicals and can further control the polymerization process according to Scheme 2.

The kinetic data obtained gravimetrically are well consistent with the description of the principles of polymerization in the presence of MCC. For example, the dependence of the conversion on reaction time is a pronounced S-shape for MMA polymerization with autoacceleration, whereas it has a smoother form in the presence of MCC (0.1–0.7 mol%) (Fig. 2, curves 1 and 2 respectively).

The results of the molecular weight characteristics for MMA polymers are in good agreement with the kinetic data of the process. Number-average (M_n), weight-average (M_w) molecular weights and polydispersity indexes (M_w/M_n) for polymethyl methacrylate are listed in Table 1. As follows from the data presented and more clearly from Fig. 3 (curve 3), the M_n values grow linearly with conversion when MCC is used as a regulating additive. This fact is one of the general features of living polymerization. For comparison, curve 1 in Fig. 3 demonstrates the dependence on the molecular weight of polymethyl methacrylate: when AIBN acts as an initiator, a spontaneous uncontrolled propagation takes place. Unfortunately, we failed to estimate the molecular weight characteristics of polybutylacrylate because of the cross-linking of the polymer formed—it hardly dissolves in any solvent.



Scheme 2. $P^{\bullet}$: a growing radical of MMA, BA; $T^{\bullet}$: a stable radical; k_d: adduct dissociation constant; k_c: combination constant; k_p: propagation constant; m: acrylic monomer.

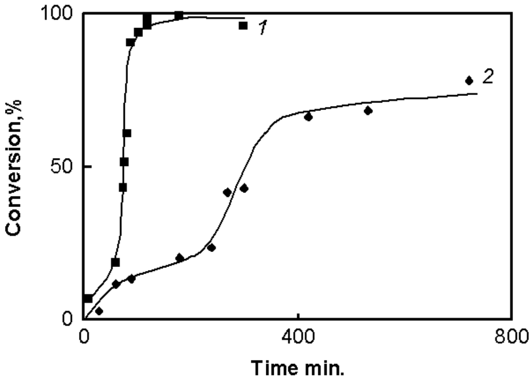
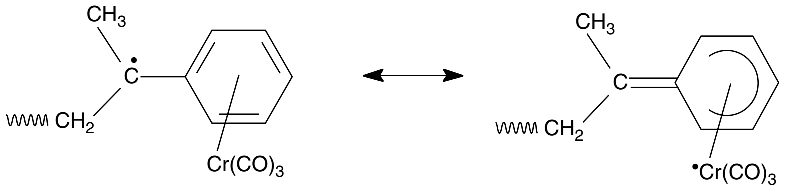


Figure 2. Integral curves of MMA polymerization in the presence of AIBN (0.1 mol%) and MCC at 70 °C. [MCC]: (1) 0; (2) 0.7 mol%.

Polydispersity indexes of the polymethyl methacrylate samples obtained in the presence of MCC were determined to be 1.5–1.8 (Table 1) and these differ slightly with conversion up to 30–40%. The molecular weight distribution (MWD)



Scheme 3.

Table 1. Molecular weight determinations of polymethyl methacrylate synthesized in the presence of AIBN (0.1 mol%) as the initiator and MCC

No.	AIBN/MCC (mol%)	Monomer conversion (%)	$10^{-3}\,M_n$	$10^{-3}\,M_w$	M_w/M_n
1	1 : 0	98	667	1600	2.4
2	1 : 7	3	115	205	1.8
3	1 : 7	11	116	189	1.6
4	1 : 7	68	190	590	3.1
5	1 : 10	27	82	148	1.8
6	1 : 10	55	103	233	2.3
7	1 : 10	89	176	789	4.5

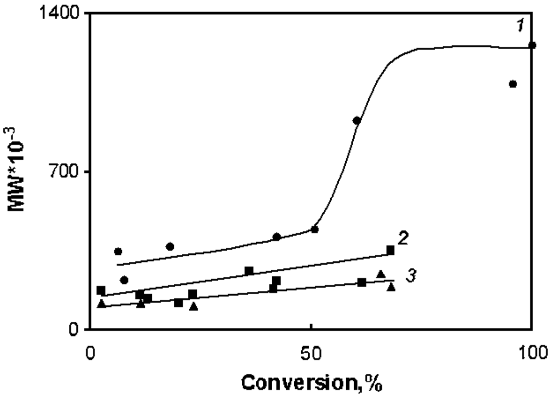


Figure 3. Molecular weight (MW) of polymethyl methacrylate *versus* conversion: (1, 2) viscosity-average MW; (3) M_n. Initiator: AIBN (0.1 mol%); $T = 70\,°C$; [MCC]: (1) 0; (2) 0.7; (3) 0.7 mol%.

analysis of the polymers discussed shows a shift in the MWD curves towards the higher molecular weight region with conversion. This phenomenon is one of the general features of pseudoliving polymerization. The growth of a high molecular-weight shoulder in the MWD curves (Fig. 4) becomes pronounced in the high conversion region (more than 50%), as well as there being a corresponding increase in the M_w/M_n values (see Table 1). This is apparently related to the fact that, together with the 'living' polymer, a non-growing polymer is also formed in the system, and this process is more active upon high conversions. Similar observations were found in the system when triphenylmethyl radical was utilized as a chain growth regulator.[1–3]

This suggests that the polymer chain growth control in the presence of organometallic compounds is connected with the known stabilization of an active radical in the coordination sphere of the metal.[23,24] If the polymer chain growth regulation by MCC is associated with such a type of coordination, then BCC, as an analog of the metal-containing monomer that has no double bond, should change the kinetic principles of polymerization as well. However, a study of the influence of BCC in concentrations up to 1% in the AIBN-initiated MMA polymerization shows that, in this case, the process proceeds similarly to that without BCC.

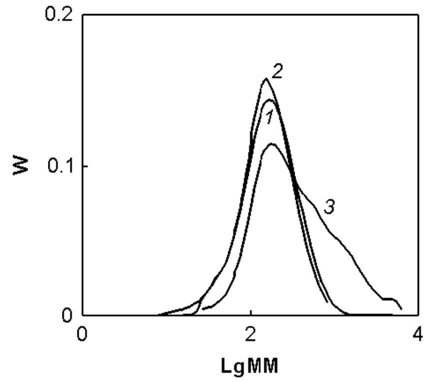


Figure 4. Molecular-weight distribution of polymethyl methacrylate samples synthesized at 70 °C in the presence of AIBN (0.1 mol%) and MCC (0.7 mol%). Conversion: (1) 3; (2) 11; (3) 68%.

The data unambiguously confirm that the polymerization of MMA in the presence of catalytic amounts of MCC occurs via a pseudoliving mechanism. As in the case of *C*-phenyl-*N*-*tert*-butylnitrone and 2-methyl-2-nitrosopropane proposed by us previously to control the polymer chain propagation in the radical initiation,[4–8] stable radicals (growing regulators) are generated *in situ* in the polymer system due to the interaction of initiating or growing radicals with MCC (Scheme 1). A stable radical $T^\bullet$ is capable of reacting with the growing macroradical of MMA to form a labile bond according to Scheme 2.

Further, chain propagation occurs due to the consecutive introduction of the monomer through a $[\sim P_n - T]$ bond. As a consequence, a linear increase in the polymer molecular weight with conversion (Fig. 3) and the reduction of a spontaneous autoacceleration during the polymerization (Fig. 1) are observed.

Thus, a significant decrease in the autoacceleration during MMA and BA polymerization, its shift towards the higher conversions in the presence of MCC, and a linear dependence of the molecular weight of polymethyl methacrylate on conversion indicate that, in this system, a controlled radical polymerization takes place. Triphenylmethyl radicals, and especially nitroxyl spin-adducts such as 2,2,6,6-tetramethyl-1-piperidinoxyl (a well-known chain growing regulator),[1–3] act only at a temperature of 100–140 °C. On the contrary, the active additive proposed by us enables the controlled synthesis of polymethyl methacrylate at a lower temperature (50–70 °C), which corresponds to industrial polymer production conditions.

In addition, the kinetic study was extended to the application of other chromium-containing monomers (PCC and STC) in MMA and BA polymerization. It was established that these compounds, when added in a polymerizing mixture in amounts up to 1%, practically do not exert the kinetics of

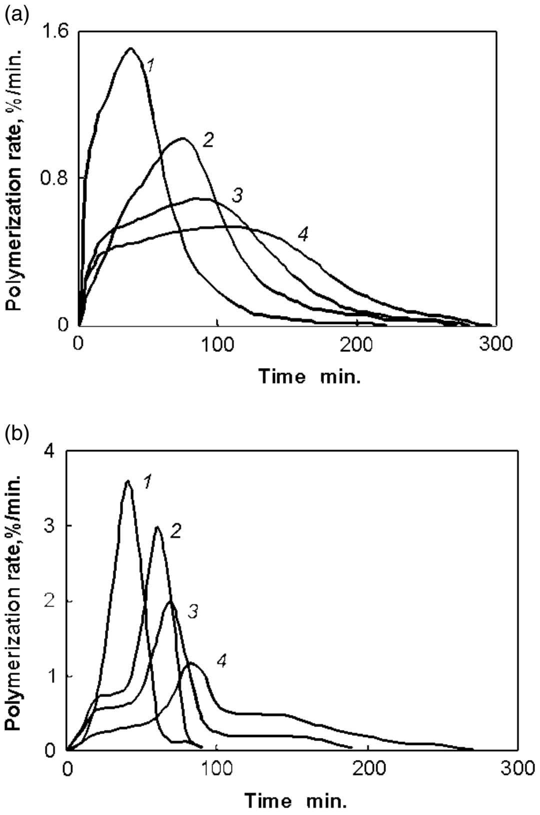


Figure 5. Differential kinetic curves for polymerization with additives. (a) BA polymerization; initiator: AIBN (0.3 mol%); $T = 50\,^{\circ}\mathrm{C}$; [PCC]: (1) 0; (2) 1; (3) 3; (4) 5 mol%. (b) MMA polymerization; initiator: AIBN (0.1 mol%); $T = 70\,^{\circ}\mathrm{C}$; [STC]: (1) 0, 0.1; (2) 1; (3) 3; (4) 5 mol%.

the polymerization of organic monomers. The subsequent increase in the organometallic compound content results in a reduction in polymerization autoacceleration. So, in the case of the polymerization of BA in the presence of PCC (Fig. 5a) and MMA in the presence of STC (Fig. 5b) as an illustration, it was shown that the initial and total rates decrease compared with the rates of the homopolymerization of BA and MMA.[25] The common features for the polymerization in the presence of these organometallic compounds were prolongation of the reaction time and a decrease in the autoacceleration with increasing additive concentration, as reported earlier for styrenechromium-tricarbonyl (SCC).[14] A near complete disappearance of the gel effect is observed in these cases with 5 mol% PCC and STC with respect to the acrylic monomers (Fig. 5a and b respectively). At these concentrations of the initial compounds the polymerizations proceed almost at the same rate from the beginning of the reaction till high conversions. The influence of PCC (which forms a copolymer in the reaction with the acrylic monomers[14]) on the kinetics is probably due to the familiar change in the copolymerization rate compared with simple homopolymerization, since, in the former case, radicals with a large difference in activity appear. The reduction of the polymerization rate and suppression of the gel effect in MMA polymerization when STC is introduced into the monomer mixture may be explained by either its participation in the chain transfer[26] or complex formation between monomers. (There is some evidence for the formation of such complexes in the case of the MMA–SCC system.[14]) As a result, no copolymer is formed. In addition, the introduction of various quantities of STC (from 5 to 40 mol%) results only in traces of chromium, independent of the initial amount of STC added.

The complete disappearance of the autoacceleration in the presence of vinylarenetricarbonyl complexes of chromium is of interest from a practical point of view, since a uniform course in the polymerization of acrylic monomers provides the synthesis of macromolecules of homogeneous composition, which is a promising target in the synthetic polymer chemistry.

Acknowledgements

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