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NEW INITIATORS FOR CONTROLLED RADICAL POLYMERIZATION OF ACRYLIC MONOMERS

by

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13. ABSTRACT *(Maximum 200 words)*

Polymerization of acrylic monomers was redox initiated by mixtures (1:1) of transition metal derivatives (acetates, metallocenes) with arenediazonium salts. In most cases, molecular weights increase with the conversion and polydispersities are lower than in a typical radical or anionic polymerization at these temperatures. Trapping experiments and relative monomer reactivities based on copolymerization studies indicate that these polymerizations proceed via a radical mechanism. The improved polymerization control can be ascribed to an equilibrium between growing radicals and dormant persistent radicals.

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NEW INITIATORS FOR CONTROLLED RADICAL POLYMERIZATION OF ACRYLIC MONOMERS

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Introduction

The succesful design of new well defined polymers and copolymers requires the enhanced control over the structure, reactivity and chemoselectivity of the propagating species. This usually happens in living systems in which transfer and termination are below detection level. However, in some systems tranfer and termination cannot be completely avoided. Nevertheless, it is posible to convert nonliving anionic, cationic and free radical polymerizations into controlled polymerizations yielding well defined polymers and copolymers. One approach is based on the modification of the reactive chain ends with transition metal complexes. It is possible to tune the electronic and stereochemical properties of the complexes by adjustment of Lewis acidity and the oxidation state of the metal as well as the ligand sphere. Thus, the reactivity of the modified propagating chain-ends can be adjusted over a wide range, allowing the polymerization to proceed under well controlled conditions.

The enhanced control was observed in radical polymerization of vinyl acetate in the presence of transition metal derivatives such as chromium acetate ("aged" benzoyl peroxide/$Cr(OAc)_2$)[1] or chromium acetate and/or chromium alkyls coordinated by macrocyclic amines[2]. Additionally, controlled polymerization of electron-accepting monomers (methyl methacrylate, di-2-ethylhexyl itaconate) was achieved using lanthanum versatate/diazonium salts[3].

In this paper, we report the controlled radical polymerization of acrylic monomers (methyl acrylate, methyl methacrylate), using as initiating systems combinations of transition metal derivatives with arenediazonium salts (components of Sandmeyer reaction).

Experimental

Transition metal derivatives (chromium (II) acetate, rhodium (II) acetate, cobalt (II) acetate, cerium (III) acetate, dicyclopentadienylchromium, Cp_2Cr, dicyclopentadienylzirconium dichloride, Cp_2ZrCl_2, dicyclopentadienylruthenium, Cp_2Ru) were used without any purification, as received from Aldrich. p-Chlorobenzenediazonium tetrafluoroborate (DS) was prepared by diazotization of p-chloroaniline hydrochloride with sodium nitrite in aqueous acid media, at 0°C, for 15 minutes. Then, sodium tetrafluoroborate was added and the reaction mixture stirred for additional 45 minutes, at 0°C. Inhibitors were removed from acrylic monomers by washing with a 5% NaOH aqueous solution, followed by drying over $MgSO_4$ and distilling over CaH_2. Tetrahydrofuran was freshly distilled over Na-anthracene. Polymerizations were carried out in degassed and sealed tubes under Ar, in a mixed solvent THF-acetone, at 40°C. Polymers were precipitated in hexane, filtered, dried and characterized by GPC and ^{1}H-NMR. Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC), using a Waters 510 pump equipped with a 410 differential refractometer and UV detector, using THF as eluent with a flow rate of 1.0 mL·min^{-1}, and with three ULTRASTYRAGEL columns (100Å, 500 Å and Linear) in series. The molecular weight calibration curve was obtained using polystyrene standards. PMMA microstrucures were determined by ^{1}H-NMR, spectra being recorded with a Nicolet 300 MHz spectrometer in $CDCl_3$ solutions, at 25°C.

Results and Discussion

According to literature[4,5], some organometallic compounds can be oxidized in the presence of arenediazonium salts, which are reduced to phenyl-based radicals (eq. 1).

(1)

Mt = Rh^{II}, Cr^{II}, Co^{II}, Ce^{III}, Ru^{II}, Zr^{IV}
R = OAc, cyclopentadienyl

Figures 1-3 show typical behavior of polymerization of methyl methacrylate (MMA) initiated by mixtures of transition metal acetates with p-chlorobenzenediazonium tetrafluoroborate.

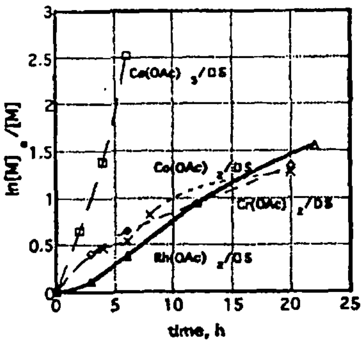

Fig. 1 Time-conversion plots in semilogarithmic coordinates for polymerization of MMA initiated by $Mt^{n+}(OAc)_n$/p-chlorobenzenediazonium tetrafluoroborate (1:1). $[MMA]_0$ = 5M, $[I]_0 = 1.25\times10^{-1}$M, THF/acetone (1:1), 40°C.

The highest polymerization rates were observed with the initiating system based on $Ce(OAc)_3$/DS (90% conversion after 6 hours). With $Rh(OAc)_2$/DS, an induction period was found during the first 2-3 hours.

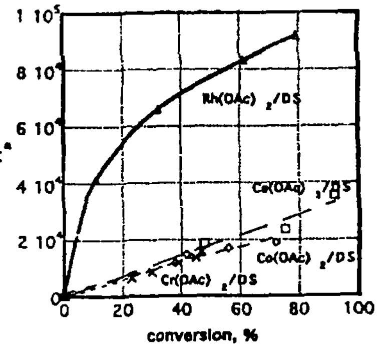

Fig. 2 M_n-conversion dependence in polymerization of MMA initiated by $Mt^{n+}(OAc)_n$/p-chlorobenzenediazonium tetrafluoroborate (1:1). $[MMA]_0$ = 5M, $[I]_0 = 1.25\times10^{-1}$M, THF/acetone (1:1), 40°C.

Molecular weights increase monotonously with conversion. The highest values were observed with $Rh(OAc)_2$/DS. It seems that the number of chains is constant for Ce, Co, and Cr-based initiating systems but it increases with $Rh(OAc)_2$/DS. This observation together with induction periods (cf. Fig. 1) suggests slow initiation for $Rh(OAc)_2$/DS. It must be noted that efficiency of initiation is very low for all of the discussed systems.

Despite slow initiation, $Rh(OAc)_2$/DS yields polymers with the lowest polydispersities (1.2-1.45). Three other systems provide polymers with higher polydispersities, although molecular weights grow linearly with conversion, indicating low contribution of transfer. On the other hand, termination for these three systems should not be very important, judging from the kinetics (Fig.1.). Thus, the broader molecular weight distribution observed in Fig. 3. might be ascribed to slow exchange between dormant and active species.

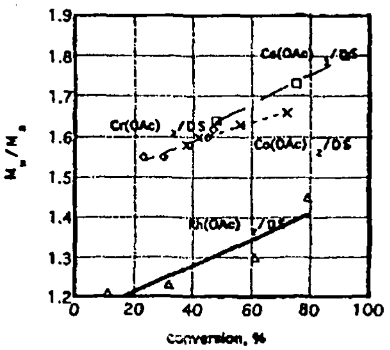

Fig. 3 M_w/M_n-conversion dependence in polymerization of MMA initiated by $Mt^{n+}(OAc)_n$/p-chlorobenzenediazonium tetrafluoroborate (1:1). $[MMA]_0 = 5M$, $[I]_0 = 1.25x10^{-1}M$, THF/acetone (1:1), 40°C.

Polymerization of MMA with initiating systems based on metallocenes/diazonium salts proceeds faster and molecular weights are lower than with initiating systems based on acetates. Figure 4 presents M_n and M_w/M_n -conversion dependences.

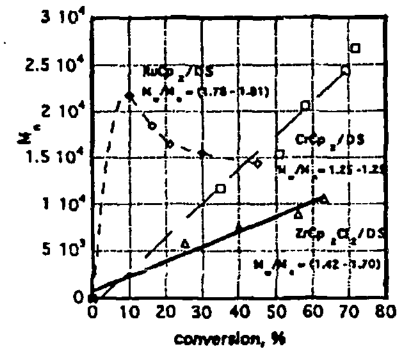

Fig. 4 M_n and M_w/M_n - conversion dependence in polymerization of MMA with metallocenes/p-chlorobenzenediazonium tetrafluoroborate (1:1). $[MMA]_0 = 5M$, $[I]_0 = 1.25x10^{-1}M$, THF/acetone (1:1), 40°C.

The best control of molecular weights and the lowest polydispersities was observed with $CrCp_2$/DS. In the presence of $RuCp_2$/DS molecular weights decreased with conversion. This could be ascribed to transfer via β-H abstraction from the growing chains and the formation of ruthenium hydrides, capable of reinitiation.

Tacticities of PMMA prepared in systems initiated by metal acetates(metallocenes)/diazonium salts are presented in Table 1. The microstructures are similar to those obtained in radical polymerization.

Table 1

Microstructures of PMMA Prepared in Systems Initiated by Transition Metal Derivatives/DS

Initiator	(mm),%	(mr), %	(rr), %	ρ a)
$Rh(OAc)_2$/DS	2.1	26.7	71.2	1.75
$Co(OAc)_2$/DS	2.6	35	62.4	1.27
$Cr(OAc)_2$/DS	2.8	28.9	68.3	1.61
$Ce(OAc)_3$/DS	3.2	31.4	65.4	1.46
$ZrCp_2Cl_2$/DS	1.7	24.8	73.5	1.9
$RuCp_2$/DS	5.6	34	60.4	1.74
$CrCp_2$/DS	2.4	31.1	66.5	1.32

a) ρ = persistence ratio = 2 (m)(r)/(mr)

In order to have a deeper insight into the mechanism of these polymerizations we have performed model trapping experiments and copolymerization studies. It seems that water and weak acids do not affect conversions, propagation rates and molecular weights, suggesting that the chains ends have radical rather than enolate structures. In copolymerization of MMA and styrene, reactivity ratios also similar to those calculated in any radical process. Radical species have been previously directly observed by EPR in a similar initiating system, based on lanthanum derivatives[3].

Polymerization of methyl acrylate (MA) shows a behavior similar to MMA (Figs. 5, 6). The increase of molecular weights with conversion for MA is much less pronounced than for MMA polymerization. This can be ascribed to slower initiation and also to transfer reactions. The latter is most clearly noted when molecular weights decrease with conversion for $Co(OAc)_2$/DS. These side reactions lead to increase of polydispersities.

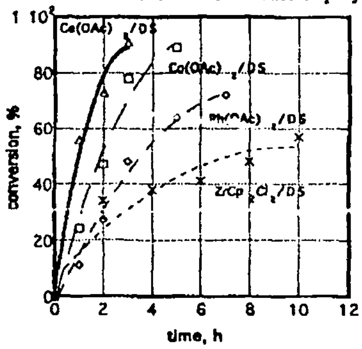

Fig. 5 Time-conversion plots in polymerization of methyl acrylate initiated by transition metal derivatives/p-chlorobenzenediazonium tetrafluoroborate (1:1). $[MA]_0 = 5M$, $[I]_0 = 1.25x10^{-1}M$, THF/acetone (1:1), 40°C.

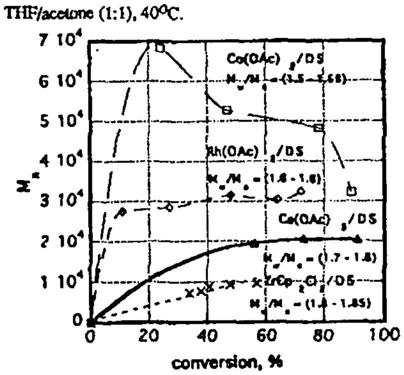

Fig. 6 M_n (M_w/M_n) - conversion dependence in polymerization of methyl acrylate initiated by transition metal derivatives/p-chlorobenzenediazonium tetrafluoroborate (1:1). $[MA]_0 = 5M$, $[I]_0 = 1.25x10^{-1}M$, THF/acetone (1:1), 40°C.

Conclusions

Polymerization of acrylic monomers was redox initiated by mixtures (1:1) of transition metal derivatives (acetates, metallocenes) with arenediazonium salts. In most cases, molecular weights increase with the conversion and polydispersities are lower than in a typical radical or anionic polymerization at these temperatures. Trapping experiments and relative monomer reactivities based on copolymerization studies indicate that these polymerizations proceed via a radical mechanism. The improved polymerization control can be ascribed to an equilibrium between growing radicals and dormant persistent radicals.

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