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RADICAL POLYMERIZATION OF VINYL ACETATE AND METHYL METHACRYLATE USING ORGANOCHROMIUM REAGENTS COMPLEXED WITH MACROCYCLIC AMINES

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Poly(vinyl)acetate and poly(methyl methacrylate) with controlled molecular weights and narrow polydispersities (1.55-1.68) were prepared by radical polymerization using initiators based on redox systems: benzoyl peroxide and $Cr(OAc)_2$ complexed by macrocyclic polyamines, in THF, at ambient temperatures. Structure of N-based ligands affects the initiation rate and propagation control. The highest degree of control was achieved by using chromium atom complexed by 1,4,7,10,13,16-hexaazacyclooctadecane trisulfate.

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RADICAL POLYMERIZATION OF VINYL ACETATE AND METHYL METHACRYLATE USING ORGANOCHROMIUM INITIATORS COMPLEXED WITH MACROCYCLIC POLYAMINES

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Introduction

Synthesis of well-defined polymers by radical polymerization requires low stationary concentration of free radicals and relatively high concentration of the growing chains. Recently, we discussed some possibilities for preparation of well-defined polymers by radical process[1]. Growing radicals can react reversibly with scavenging radicals to form covalent, stable species[2,3,4]. Growing radicals can also react reversibly with covalent species (usually organometallics) in order to produce persistent radicals[4]. Growing radicals may as well participate in the degenerative transfer reactions in which the same type of radicals are regenerated. The first approach employs usually the homolytic cleavage of C-heteroatom bonds. The third case is based on the attack of the propagating growing radicals on the labile C-heteroatom bonds in the transfer agent. The second approach utilizes the reversible formation of persistent radicals usually based on the organometallic compounds.

Metal stabilized propagating radicals based on Co and Cr were described previously. Poor control of molecular weights and the facile chain transfer processes could be attributed to the reversibility of the redox couples $Co^{3+/2+}$, $Cr^{3+/2+}$ due to their positive redox potentials and to β-hydrogen abstractions by the formation of metal hydrides. Indeed, Co derivatives have been used as very efficient chain transfer reagents, in order to regulate molecular weights of various polymers synthesized by radical processes[6]. Initiating systems based on chromium acetate and organic peroxides, in DMF as solvent, have been already reported for the radical polymerization of MMA[7]. At temperatures below 30°C, molecular weights increased monotonously with monomer conversion. These initiating systems have been unsuccessful in polymerization of other vinyl monomers such as vinyl acetate or styrene.

Macrocyclic polyamines such as 1,4,7,10-tetraazacyclododecane (12-ane-4) and 1,4,7,10,13,16-hexaazacyclooctadecane (18-ane-6)[8] and related methyl substituted derivatives are among the best complexing ligands for transition metals. The ligand sphere and the coordination geometry have a large influence on the kinetic, thermodynamic and electronic properties of transition metal complexes. In some cases the macrocyclic ligand stabilizes the highest metal oxidation state leading to exceptionally negative values for the $metal^{3+/2+}$ redox couples.

In this paper we report the controlled polymerization of vinyl acetate, VAc, and methyl methacrylate, MMA, in THF, using as the initiators some redox systems based on organic peroxides and chromium acetate in the presence of different N-based ligands (2,2'-dipyridyl, Dpy, 18-ane-6 trisulfate, N_6H^+, and hexamethyl 18-ane-6, N_6-CH_3).

Results and Discussion

Effect of Macrocyclic Ligands on the Electron Transfer Processes

The chemistry of metal ions complexed by macrocyclic and macropolycyclic ligands has developed rapidly over recent years. Macrocyclic complexes generally exhibit greater stability than acyclic analogues, therefore one of their most important application is related to stabilization of normally inaccessible oxidation states of metals involved in redox couples with positive E_{red} potentials. The size of metal ion varies with its oxidation state and therefore the steric strain enforced by the ligand backbone depends on the oxidation state of the metal. Thus, the strain energy difference for a metal ion and a set of its oxidation states is influenced by the ligand sphere. The fastest electron transfer processes for redox couples $Mt^{(n+1)+/n+}$ were found for the lowest negative E_{red} values. Since the redox potential of the couple $Cr^{3+/2+}$ is shifted to negative values in the presence of macrocyclic polyamine ligands, it was interesting to use initiators based on redox process involving oxidation of Cr(II) to Cr(III) in the presence of some organic peroxides. Furthermore, since Cr(III) atoms were stabilized in macrocyclic complexes, it was also interesting to study the influence of the complexation on stabilization of the growing radicals during propagation, by comparison with uncomplexed Cr(III) atoms, and complexed by "open" diamine ligands, such as 2,2'-dipyridyl.

Radical Polymerization of VAc and MMA

Radical polymerization of VAc and MMA was initiated by a redox system based on $Cr(OAc)_2$ and benzoyl peroxide (BPO), in THF, at room temperature. Fig. 1 shows time conversion plots obtained in polymerization of VAc in the presence of different ligands, or without ligands, as well as in methanol as solvent. The highest conversion (up to 90%) obtained in the shortest time (30 hours), was found in the presence of N_6H^+ as ligand. In the presence of ligands known to stabilize the lower oxidation states (e.g. Dpy, N_6-CH_3), polymerization rates were reduced and lower conversions were observed. The presence of methanol as solvent enhanced the redox initiation rate as noticed by rapid change of the color, but only 10% conversion was found after 48 hours.

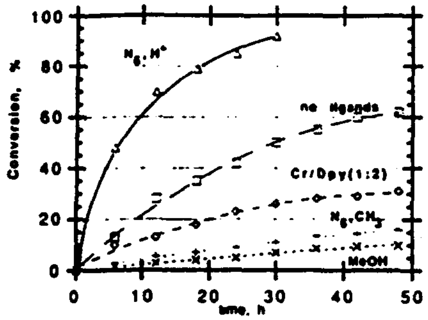


Fig. 1 Time-conversion plots in polymerization of VAc with $Cr(OAc)_2$/BPO, THF, 20°C, $[VAc]_0$ = 5M, $[Cr^{2+}]_0$ = $[BPO]_0$ = 0.25M, $[Lig]_0$ = $[Cr^{2+}]_0$

Fig. 2 shows kinetic plots in semilogarithmic coordinates calculated for three of the systems shown in Fig. 1. The absence of any curvatures indicates constant concentrations of the active species during the entire polymerization process, especially in the presence of N_6H^+.

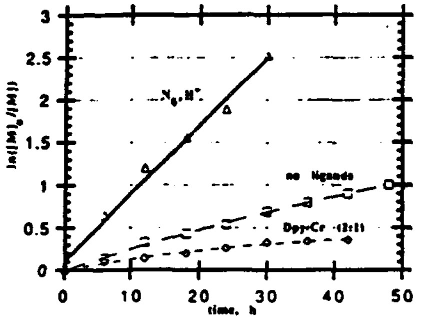


Fig. 2 First-order time-conversion plots in polymerization of VAc with $Cr(OAc)_2$/BPO, THF, 20°C, $[VAc]_0$ = 5M, $[Cr^{2+}]_0$ = $[BPO]_0$ = 0.25M, $[Lig]_0$ = $[Cr^{2+}]_0$

Fig. 3 shows evolution of molecular weights as a function of conversion for the same three systems. In the case of macrocyclic ligand (Δ) a monotonous increase of M_n with conversion was observed, although initially, up to 20% conversion, the increase was faster than at later stages. The efficiency of initiation calculated per chromium atom was about 16%.

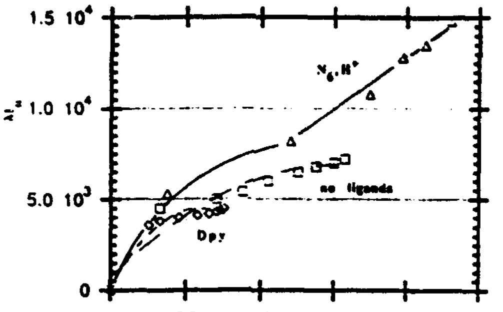


Fig. 3 M_n-conversion dependence in polymerization of VAc with $Cr(OAc)_2$/BPO, THF, 20°C, $[VAc]_o$ = 5M, $[Cr^{2+}]_o$ = $[BPO]_o$= 0.25M, $[Lig]_o$ = $[Cr^{2+}]_o$

In the absence of any ligands, a curvature in M_n-conversion dependence (□) indicates poor control of molecular weights. However, molecular weights were significantly lower than those obtained by initiation with benzoyl peroxide alone (in the absence of chromium acetate), suggesting the efficient chain transfer reactions. In the presence of Dpy as ligand for Cr(II), molecular weights are the lowest and do not vary with conversion. Probably a combination of slow initiation, fast propagation and fast chain transfer reactions might operate in this system.

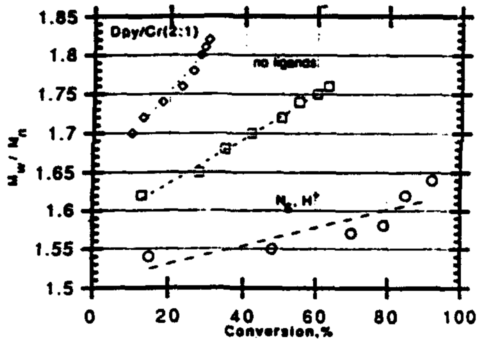


Fig.4 Dependence of polydispersities on conversion in polymerization of VAc with $Cr(OAc)_2$/BPO, THF, 20°C, $[VAc]_o$ = 5M, $[Cr^{2+}]_o$ = $[BPO]_o$= 0.25M, $[Lig]_o$ = $[Cr^{2+}]_o$

Fig.4 shows the variation of polydispersities for the same three systems. In the presence of macrocyclic ligand $N_6.H^+$ polydispersities were the lowest (M_w/M_n=1.54 to 1.63), an increase was noticed at higher conversions and higher molecular weights. In the absence of any ligand, polydispersities were higher, with an increase at the end of the reaction (M_w/M_n=1.62 to 1.76). In the presence of Dpy as ligand, the highest polydispersities (M_w/M_n=1.7 to 1.84), increasing with conversion at constant molecular weights confirm the major contribution of chain transfer reactions. It is possible that chromium hydrides are formed by elimination of β-H atoms from the growing radicals.

Fig. 5 presents M_n-conversion dependence in polymerization of MMA, with the initiating system based on $Cr(II)/BPO/N_6.H^+$. A monotonous increase of M_n with conversion is observed. Slow redox initiation process may be responsible for the initial nonlinear evolution of molecular weights. Efficiency of initiation was about 50% (at 100% conversion $M_{n,calc} = 100x[MMA]_o/[Cr^{2+}]_o=10,000$). Also, polydispersities were narrower than in a "classic" radical polymerization (M_w/M_n=1.4 to 1.7).

In the absence of any ligands, radicals are slowly generated by the electron transfer from Cr(II) to the peroxide.

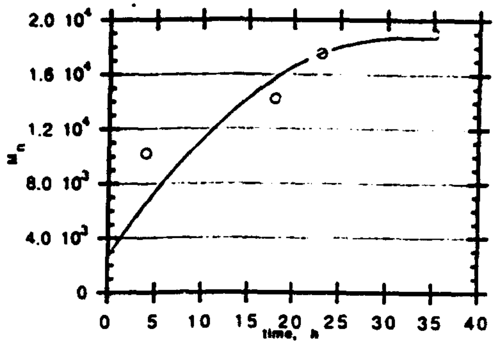
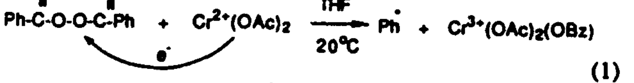


Fig. 5 M_n-conversion dependence in polymerization of MMA with $Cr(OAc)_2$/BPO, THF, 20°C, $[MMA]_o$ = 5M, $[Cr^{2+}]_o$ = $[BPO]_o$= 0.25M, $[Lig]_o$ = $[Cr^{2+}]_o$

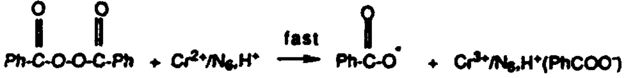


$$\mathrm{Ph\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}Ph} + \mathrm{Cr^{2+}(OAc)_2} \xrightarrow[20^\circ C]{THF} \mathrm{Ph^{\bullet}} + \mathrm{Cr^{3+}(OAc)_2(OBz)} \quad e^-$$

(1)

During oxidation of Cr^{2+} to Cr^{3+}, chromium complexed by two molecules of Dpy loses an electron by an "outer-sphere" electron transfer process. Dpy preferentially stabilizes the lowest oxidation state (Cr^{2+}). The non-complexed Cr(III) atoms might be therefore more reactive and may rapidly abstract β-hydrogen atoms from growing radicals.

The macrocyclic tetra(hexa)amine ligands the best stabilizers for Cr(III) (the smaller ion radius, the shortest N-metal bonds). This may lead to a faster initiation by the "inner-sphere" electron transfer process:



$$\mathrm{Ph\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}Ph} + \mathrm{Cr^{2+}/N_6.H^+} \xrightarrow{fast} \mathrm{Ph\text{-}\overset{O}{\overset{\|}{C}}\text{-}O^{\bullet}} + \mathrm{Cr^{3+}/N_6.H^+(PhCOO^-)}$$

(2)

Macrocyclic ligand is protonated by the sulfuric acid. The benzoate anion is therefore probably converted to benzoic acid and replaced by sulfonate anion. It is also possible that complexed chromium reacts reversibly with growing radicals. These equilibria could explain enhanced control of molecular weights and polydispersities.

Conclusions

Poly(vinyl acetate) and poly(methyl methacrylate) with controlled molecular weights were prepared by radical polymerization using the initiators based on redox systems $Cr(OAc)_2$ / BPO / N-ligands, in THF at ambient temperanures. Structure of N-ligands affects the initiation rate and propagation control. The highest degree of control was achieved by using macrocyclic polyamines 12-ane-4 and 18-ane-6.

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