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

by

Daniela Mardare, Scott Gaynor, Krzysztof Matyjaszewski

Published in the

Carnegie Mellon University
Department of Chemistry
4400 Fifth Avenue
Pittsburgh, PA 15213

June 30, 1994

Reproduction in whole or in part is permitted for any purpose of the United States Government

This document has been approved for public release and sale; its distribution is unlimited.
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.
RADICAL POLYMERIZATION OF VINYL ACETATE AND METHYL METHACRYLATE USING ORGANOCHROMIUM INITIATORS COMPLEXED WITH MACROCYCLIC POLYAMINES

Daniela Mandare, Scott Gaynor and Krysztof Maciejewski
Carnegie Mellon University
Department of Chemistry
4400 Fifth Avenue
Pittsburgh, PA 15213

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. Growing radicals can react reversibly with scavenging radicals to form covalent stable species.5, 6, 7, 8, 9, 10 Growing radicals can also react reversibly with monomer species (usually organic monomers) in order to produce persistent radicals. Growing radicals can also participate in the radical transfer reactions in which the same type of radicals are regenerated. The first approach employs usually the homolytic cleavage of C-Heteroatom bond. The second case is the result of the propagation 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 Co3+/Co2+, Cr3+/Cr2+ due to their positive redox potentials and to β-hydrogen abstraction by the formation of metal hydrides. Indeed, Co derivatives have been used as very efficient chain transfer agents, in order to regulate molecular weights of various polymers synthesized by radical processes.4, 5, 6, 7, 8, 9, 10 Initiating systems based on chromium aceto 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 (12ane-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 redox potentials for the metal3+/metal2+ 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&H*, and hexamethyl 18-ane-6, N&CH3).

Results and Discussion
Effect of Macrocyclic Ligands on the Electron Transfer Processes
The chemistry of metal ions complexed by macrocyclic and macrocyclopolyamidic ligands has developed rapidly over recent years. Macrocyclic complexes generally exhibit greater stability than acyclic analogues, therefore one of the most important application is related to stabilization of transition metal ions in inaccessible oxidation states of metals involved in radical transfer reactions with positive E° values. The size of metal ion varies with its oxidation state and the extent of transfer depends on the metal ion itself. The fact that electron transfer processes for redox couples Mn(II)-Mn(III) were found for the lowest negative values suggests that the electron transfer processes for redox couples Mn(II)-Mn(III) were found for the lowest negative values. Since the redox potential of the couple Cr3+/Cr2+ 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)3 and benzoyl peroxide (BPO), in THF, at room temperature. Fig. 1 shows the 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&H* as ligand. In the presence of ligands known to stabilize the lower oxidation state (e.g. Dpy, N&CH3), polymerization rates were reduced and lower conversions were obtained. 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)3/BPO, THF, 20°C. [VAc]0 = 5.0 M, [Cr(III)]0 = [BPO]0 = 0.25 M, [Lig]0 = [Cr(II)]0

Fig. 2 shows kinetic plots in semi-logarithmic 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&H*.

Fig. 2. First-order time-conversion plots in polymerization of VAc with Cr(OAc)3/BPO, THF, 20°C. [VAc]0 = 5.0 M, [Cr(III)]0 = [BPO]0 = 0.25 M, [Lig]0 = [Cr(II)]0

Fig. 3 shows evolution of molecular weights as a function of conversion for the same three systems. In the case of macrocyclic ligand (d) a monotonous increase of Mn 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%.

<table>
<thead>
<tr>
<th>Availability</th>
<th>Codes</th>
<th>Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dist</td>
<td>Avai and/or</td>
<td>Special</td>
</tr>
<tr>
<td>A-5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
In the absence of any ligands, a curvature in $M_n$-conversion dependence suggests 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, molecular weights were the lowest ($M_{w}/M_{n}$ = 1.54 to 1.60). In the presence of any ligands, 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 [Cr(µ-OAc)]$_2$/BPO. During oxidation of Cr(II) to Cr(III), chromium complexed by two molecules of Dpy loses an electron by an "inner-sphere" electron transfer process. Dpy preferentially stabilizes the lowest oxidation state (Cr(II)). The non-complexed Cr(III) atoms might be reductively reactive and may rapidly abstract β-hydrogen atoms from growing radicals.

The macrocyclic terthiopen (hexa)amine ligands the best stabilizers for Cr(III) (the smaller ion radius, the shorter N-metal bonding). This leads to a faster initiation by the "inner-sphere" electron transfer process:

$$\text{Ph-C-O-C-Ph} + \text{Cr}^{2+}(\text{OAc})_2 \rightarrow \text{Ph} + \text{Cr}^{3+}(\text{OAc})_2(\text{OBz})$$

(1)

Macroyclic ligand is protonated by the sulfonic acid. The benzoate ion 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(µ-OAc)]$_2$/BPO/N-ligands, in THF at ambient temperature. 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.

References
1. Greszta, D., Mardare, D., Matyjaszewski, K., Macromolecules, in press.

Acknowledgments
Acknowledgment is made to the Office of Naval Research and to the National Science Foundation, via the support within Presidential Young Investigator Award to K.M., as well as to Du Pont, Eastman Kodak, PPG Industries and Xerox Corporation for the matching funds.