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Effect of Water and Oxygen on the Polymerization of Vinyl Acetate Initiated by Aluminum Alkyls, Bipyridyls, and Nitroxyl Radicals

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**EFFECT OF WATER AND OXYGEN ON
THE POLYMERIZATION OF VINYL ACETATE
INITIATED BY ALUMINUM ALKYLs, BIPYRIDYLs,
AND NITROXYL RADICALS**

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Abstract: Effect of water and oxygen on the polymerization of vinyl acetate initiated by aluminum alkyls, bipyridyls and TEMPO is reported. Reactions with nearly complete exclusion of water and oxygen is very slow and provides a mixture of oligomers in a few hours. With small amounts of oxygen (0.01 to 0.05 mol %) and water (0.05 to 0.08 mol %), reactions were significantly accelerated, however, at higher concentrations of water and oxygen, the polymerization rates decreased and polydispersities were higher.

We have previously reported the polymerization of vinyl acetate and methyl methacrylate using a tri-component system consisting of aluminum alkyls, R_3Al ($R = \text{ethyl, isobutyl}$), a bidentate ligand such as 2,2'-bipyridyl and a nitroxyl radical such as TEMPO [1-3]. Our initial investigations indicated good control of molecular weights and polydispersities of the obtained polymers and copolymers. Some of the kinetic and mechanistic studies suggested that the polymerization proceeded by radical intermediates. The observed control was ascribed to rapid equilibration between growing radicals and dormant species, hypothetically, hypervalent organoaluminum species [3].

However, we were not able to identify the structure of these species spectroscopically and some additional studies indicate possibility of a side reaction with a dipyridyl ring [4]. A more detailed investigation showed that

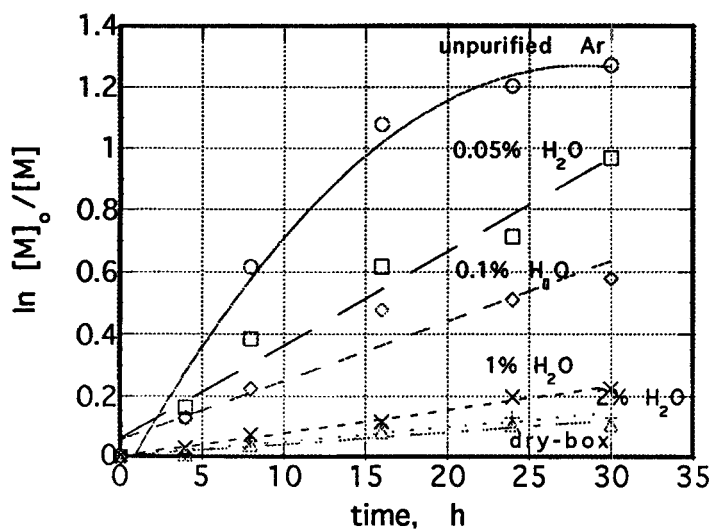


Figure 1. Kinetics of VAc polymerization in benzene at 60 °C with different amounts of water; $[M]_0=2.5M$, $[I]_0=0.025M$; $Al(iBu)_3/BPY/TEMPO=1:1:2$.

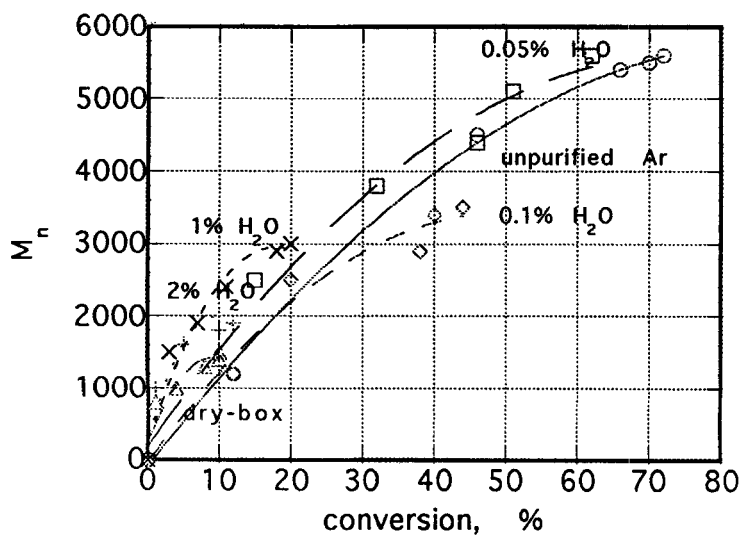


Figure 2. Evolution of molecular weights with conversion in VAc polymerization in the presence of different amounts of water

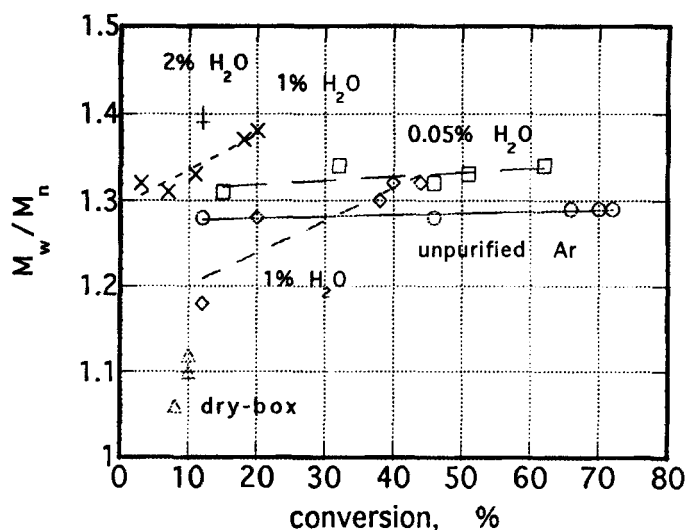


Figure 3. Evolution of polydispersities with conversion in VAc polymerization in the presence of different amounts of water

the polymerization rates and molecular weights were dependent on various impurities and were strongly affected by even small amounts of water and oxygen in the reaction mixture.

It seems that the reaction with nearly complete exclusion of water and oxygen (dry-box with < 1 ppm O₂ and < 1 ppm H₂O) is very slow and provides a mixture of oligomers in a few hours. By using either unpurified argon as an inert gas or adding controlled amounts of oxygen (0.01 to 0.05 mol %) and water (0.05 to 0.08 mol %), reactions were significantly accelerated (Figure 1). Molecular weights increased with conversion and polydispersities decreased below $M_w/M_n = 1.3$ (Figures 2, 3). However, at higher concentrations of water and oxygen, the polymerization rates decreased, whereas molecular weights and polydispersities increased ($M_w/M_n > 1.5$).

It is not clear what is the precise mechanism of polymerization under such conditions, as well as the structures of the active species in the above discussed systems. It is possible that small amounts of oxygen catalyze formation of aluminum peroxides and water leads to alumoxanes. Nevertheless, polymerization kinetics and structures of the obtained products are very sensitive to even minute amounts of impurities such as water and

oxygen. Additional problems are related to the aging of the initiating system. It seems that other controlled radical polymerization systems, such as TEMPO mediated [3, 5, 6] or atom transfer radical polymerization (ATRP), [7-10] have much lower sensitivity to impurities and do not require catalytic activation by water/oxygen.

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