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Notes

Demonstration of the Inhibitory Role of Oxygen during the Room-Temperature Radical Polymerization of Styrene Initiated by a Cobalt(II)-Sodium Borohydride Redox System

V. A. BHANU and K. KISHORE*

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India.

Received September 26, 1988;
Revised Manuscript Received January 10, 1989

Oxygen plays two exactly opposite roles in radical polymerization reactions: it can either initiate or retard (or even inhibit) these reactions.[1] The unique case of high-pressure radical polymerization of ethylene, in fact, illustrates both these roles.[2] Unlike its role in initiation,[3,4] the retarding or inhibitory action of oxygen in such reactions is scarcely understood, notwithstanding the well-known peroxide scheme.[5] Furthermore, the peroxide-based inhibitory action of oxygen in radical polymerization is temperature dependent, owing to the fact[5] that the peroxides could decompose at higher temperatures, generating additional radicals that may initiate polymerization. In this context, the study of polymerization reactions wherein noninitiating, stable products are obtained in the presence of oxygen would be useful for better understanding of the inhibitory role of oxygen in radical polymerization.

With this background, attention was drawn to a recent report[6] regarding mimicking of enzyme activity; the reaction involves oxidation of styrene-like substrates to corresponding 1-phenylethanol derivatives via a 1-phenylethyl radical intermediate in the presence of various cobalt complexes (mostly square-planar type) and BH_4^-. It was realized that if this redox reaction is carried out in an oxygen-free atmosphere in the presence of excess monomer, the radicals produced could initiate a polymerization. This reaction system would thus provide an illustration of the inhibitory role of oxygen in the radical polymerization reactions. Hence we decided to carry out some experiments to prove the viability of the above theme, in the case of styrene polymerization. Further, this would also involve extending the versatility of square-planar Co^{2+}–BH_4^- systems to the tetrahedral complexes (Figure 1), hitherto unused in polymerization reactions.

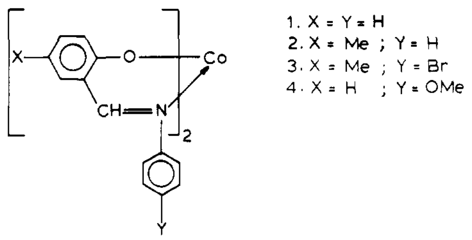

Figure 1. Tetrahedral Co complexes used as catalysts.

Styrene was washed with 10% NaOH and water and dried over anhydrous Na_2SO_4, prior to distillation under reduced pressure. Salicylaldehyde was vacuum distilled before use, and 5-methylsalicylaldehyde was prepared as described elsewhere;[7] these were subsequently used to prepare the tetrahedral cobalt complexes.[8] The new complexes (2 and 3) were characterized as follows: (a) 2: IR (KBr) 2990 (w), 1610 (s), 1570 (s), 1480 (m), 1370 (m), 1300 (s), 1190 (m), 1150 (s), 810 (m) cm^{-1}; mp 201 °C. Anal. Calcd for $C_{28}H_{24}N_2O_2Co$: C, 70.13; H, 5.04; N, 5.84; Co, 12.30. Found: C, 70.13; H, 5.06; N, 5.64; Co, 12.28. (b) 3: IR (KBr) 2990 (w), 1610 (s), 1580 (s), 1520 (s), 1480 (m), 1450 (s), 1370 (m), 1310 (s), 1200 (s), 1160 (s), 1140 (m), 1070 (m), 1000 (m), 820 (m) cm^{-1}; mp 262 °C. Anal. Calcd for $C_{28}H_{22}N_2O_2Br_2Co$: C, 52.77; H, 3.47; N, 4.39; Co, 9.26. Found: C, 52.61; H, 3.47; N, 4.33; Co, 9.25. The general procedures used for the aerial oxidation as well as the polymerization of styrene employing each of the tetrahedral complexes 1–4 are discussed below.

A mixture of freshly distilled styrene (17.5 mmol), cobalt complex (1.7 mmol), and $NaBH_4$ (1.7 mmol) in tetrahydrofuran (THF) (30 mL) was stirred magnetically for 16 h in air at room temperature (28 °C). The solvent was removed completely under reduced pressure, and the residue was extracted with chloroform (2 × 25 mL) and dried over anhydrous Na_2SO_4. The chloroform solution was concentrated to half its volume (25 mL). To this chloroform solution, acetyl chloride (3 mL) and triethylamine (3 mL) were added simultaneously. It was then left

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for 4 h. The solvent was removed under reduced pressure, and the better isolable acetyl derivative of 1-phenylethanol was purified by thin-layer chromatography (TLC, silica gel, hexane:ethyl acetate, 20:1 for **1**, **3**, and **4** and benzene alone for **2**). The yield of the acetyl derivative in all the cases was 15% (mol/mol monomer); IR (neat) $\nu_{max} = 1760$ cm^{-1} (O—C=OCH$_3$); ^{1}H NMR (CDCl$_3$) δ 1.5 (3 H, d, J = 8 Hz, -CH-CH$_3$), 1.9 (3 H, s, COCH$_3$), 5.8 (1 H, q, -CH-CH$_3$O), and 7.1–7.3 (5 H, m, Ar–H).

To a magnetically stirred mixture of freshly distilled styrene (0.044 mol) and cobalt complex (0.44 mmol) in THF (15 mL), a solution of NaBH$_4$ (0.44 mmol) in distilled water (5 mL) was added in one lot under an argon atmosphere. The mixture was stirred at room temperature (28 °C) for 4 h, and it was poured into methanol (150 mL) containing 10 N HCl (5 mL). Precipitated polystyrene was filtered off and was further purified by successive precipitation from benzene solution. The polystyrene was dried under vacuum at 60 °C to a constant weight (2% conversion). The molecular weight ($\bar{M}_v$) of the polymer was determined viscometrically at 30 °C in toluene,[9] by using the intrinsic viscosity [η] relation $[\eta] = 1.1 \times 10^{-4} (\bar{M}_v)^{0.73}$. The values of $\bar{M}_v$ so obtained in the different cases being A ($\bar{M}_v$ = 6100), B ($\bar{M}_v$ = 4400), C ($\bar{M}_v$ = 5900), and D ($\bar{M}_v$ = 7700).

The aerial oxidation experiment proves that the radical CH$_3\dot{\text{C}}$H(C$_6$H$_5$) is formed in the intermediate step. On the basis of this observation, the most plausible mechanism[6] of the polymerization may be given as

$$\underset{1-4}{\mathrm{Co^{2+}L}_n} \xrightarrow{\mathrm{NaBH_4}} \underset{\mathrm{Co^{+}\ species}}{\mathrm{HCoL}_n}$$

$$\mathrm{HCoL}_n + \mathrm{C_6H_5CH{=}CH_2} \rightleftharpoons \mathrm{CH_3(C_6H_5)CHCo^{3+}L}_n$$

$$\mathrm{CH_3(C_6H_5)CHCo^{3+}L}_n \rightleftharpoons \mathrm{CH_3(C_6H_5)\dot{C}H} + \mathrm{Co^{2+}L}_n$$

$$\mathrm{CH_3(C_6H_5)\dot{C}H} + \mathrm{C_6H_5CH{=}CH_2} \rightarrow \mathrm{poly(styrene)}$$

The formation of Co$^+$ species (HCoL$_n$) is confirmed by quenching of polymerization reaction upon addition of methyl iodide.[6] Addition of *p-tert*-butylcatechol in the polymerization mixture significantly inhibits the polymerization, confirming the radical mechanism of the reaction. Mun et al.[10] in their ESR study of the polymerization of methyl methacrylate using ethyl acetylacetonate copper complex and sodium tetraphenyl borate binary redox system have also proved the transfer of the phenyl radical to the monomer as an intermediate step.

Thus, the above experiments demonstrate that the inhibitory role of oxygen during the radical polymerization of styrene initiated by Co^{2+}–BH$_4^-$ redox system is due to the formation of 1-phenylethanol. And since the 1-phenylethanol formed is a stable molecule, we believe that inhibitory action of oxygen in the present case is rather permanent. Besides, this study also provides a new redox system for the room-temperature radical polymerization, though it seems to be less efficient than the known initiators[3] of this type.

Acknowledgment. Thanks to Dr. M. S. Shashidhar for his help in the oxidative reduction experiment and to T. Mukundan for many helpful discussions. Thanks are also due to the Department of Science and Technology, New-Delhi, for financial support.

Registry No. **1**, 37981-00-3; **2**, 36423-23-1; **3**, 120173-03-7; **4**, 14566-16-6; NaBH$_4$, 16940-66-2; styrene, 100-42-5; polystyrene, 9003-53-6; oxygen, 7782-44-7; 1-phenylethanol, 98-85-1.

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Diffusion of Linear Polystyrene in Controlled Pore Glasses. Comparison of Experimental Data with a Theoretical Model of Entropic Barriers

N. EASWAR

Department of Physics, Smith College, Northampton, Massachusetts 01063. *Received October 4, 1988; Revised Manuscript Received January 24, 1989*

Diffusion of dissolved macromolecules in porous materials is central to many phenomena of scientific and technological interest. Extensive literature exists[1–4] on the experimental results on porous media, membrane separations, and polymer solutions. Recent experiments have used quasielastic light scattering as a convenient probe to measure directly the translational diffusion coefficient of polymers in porous glasses in the absence of convection, chemical reaction, and adsorption.[5–7] The measurements are made at equilibrium, without macroscopic concentration gradients, and further, since the measurements are made directly within the porous material, the equilibrium partitioning[1–3] between the unbounded solution and the pore space does not have to be known. In this note, we compare the data on the diffusion of linear polystyrene in controlled pore glasses (CPGs) reported by Bishop et al.[5,6] and Easwar et al.[7] to the predictions of the theoretical model by Muthukumar and Baumgartner.[8] This theoretical model focuses on the effects of entropic barriers on the dynamics of a polymer chain in an infinite periodic array of cavities separated by short bottlenecks. The problem has been investigated by Monte Carlo simulations and by scaling arguments, and the results demonstrate that the polymer dynamics in random media is dominantly controlled by the entropic barriers.

The CPGs used in the light-scattering measurements mentioned above are made by the phase separation upon heat treatment of sodium borosilicates followed by the selective etching of the Na$_2$O–B$_2$O$_3$ rich phase. The glasses were characterized by mercury intrusion porosimetry to have nominal pore sizes of 703, 893, and 1866 Å and are labeled as R703, R893, and R1866, respectively. The scanning electron micrograph shows the highly connected structure of R893.[6] Characterization by mercury intrusion porosimetry is shown in Figure 1. Although the distribution of pore sizes obtained from porosimetry appears narrow, the presence of constrictions such as bottlenecks is not inconsistent with the characterization data, as discussed by Bishop et al.[6,9] A recent analysis of the pore size

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