Biomimetic Aerobic Polymerization of Vinyl Monomers

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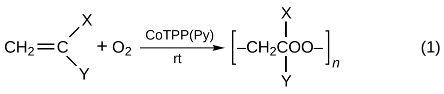
Received April 28, 1997

This is the first report of biomimetic aerobic polymerization of vinyl monomers, which has been achieved under mild conditions. When a homogeneous solution of a vinyl monomer containing a reversible oxygen carrier, namely 5,10,15,20-tetraphenyl-21*H*, 23*H*-porphinecobalt(II) pyridine complex [CoTPP(Py)], is exposed to air at room temperature, an alternating copolyperoxide is obtained (eq 1).



$$CH_2{=}C(X)(Y) + O_2 \xrightarrow[\text{rt}]{\text{CoTPP(Py)}} \left[-CH_2C(X)(Y)OO-\right]_n \qquad (1)$$

The details concerning the mechanism of this novel polymerization reaction is reported here.

Vinyl polyperoxides are gaining considerable importance for their applications as a special fuel,[1] as free radical initiators,[2] and as curatives in coating and molding.[3] They provide perhaps the only example where molecular oxygen acts as a monomer and is incorporated in the polymer backbone. Activation of molecular oxygen by a metal center for the selective oxidation of substrates is a major goal of research in chemistry and biology.[4] Cobalt(II) Schiff base complexes activate molecular oxygen and are well-known oxidizers for olefins producing carbonyl compounds and epoxides.[5] This is the first report where a reversible oxygen carrier, CoTPP(Py), has been used for the oxidative polymerization of vinyl monomers under mild conditions normally encountered in biogenetic oxygenation processes.[6]

CoTPP(Py) catalyses the oxidation of vinyl monomers {e.g., styrene (ST), α-methylstyrene (AMS), and methyl methacrylate (MMA)} to their corresponding polyperoxides {i.e., polystyrene peroxide (PSP), polymethylstyrene peroxide (PMSP), and poly(methyl methacrylate) peroxide (PMMAP)}, respectively. Polymerization was found to be instantaneous without any induction period both in air and O_2[7] (Figure 1a). All of the polyperoxides, synthesized in air as well as O_2, were found to be strictly alternating copolymers[8] of the vinyl monomer and O_2.

In the presence of O_2, the CoTPP(Py) complex exists as a 1:1 oxygen adduct.[9] Since polymerization does not occur in the absence of the catalyst, the initiaton involves addition reaction of the O_2 adduct to the alkene producing free radicals. To prove the free radical mechanism, hydroquinone (0.5 mmol) was added in the reaction mixture, and it was found to induce induction period and retard the rate of polymerization (R_p). The R_p, both in air and O_2, increases in the sequence AMS > ST > MMA, similar to that observed in the presence of the common free radical initiator 2,2′-azobisisobutyronitrile (AIBN). This is also the sequence of increasing π electron density at the double bond of the monomers and the electron accepting properties of the corresponding peroxy radicals.[10]

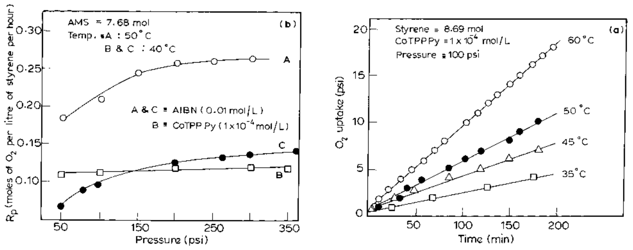


Figure 1. (a) CoTPP(Py)-catalyzed polymerization of styrene at different temperatures. (b) Dependence of R_p on pressure in the presence of CoTPP(Py) and AIBN. It may be noted that when AIBN concentration is taken as equivalent to CoTPP(Py), i.e., 1 × 10^{-4} mol/L, the rate of polymerization is negligible at 40 °C.

Unlike styrene and MMA, the AIBN-initiated AMS oxidative polymerization shows a significant pressure effect and the rate becomes independent of O_2 pressure only after 300 psi.[7] Interestingly, the oxidative polymerization of AMS, in the presence of CoTPP(Py), is independent of O_2 pressure (Figure 1b). At low O_2 concentration, the conventionally prepared polyperoxide chains contain homopolymer segments.[11] However, in the presence of CoTPP(Py) even at a low O_2 concentration, like in air, we obtain polyperoxide chains without any homopolymer segments. This observation suggests that CoTPP(Py), in addition to acting as an initiator, may also increase the dissolved O_2 concentration in the reaction mixture due to its high affinity toward O_2. At higher O_2 pressures, the dissolved O_2 in the monomer will be higher, and hence, one would observe an increase in R_p. However, O_2 pressure has no effect on R_p (Figure 1b), suggesting that the dissolved oxygen concept is not applicable here.

To probe further into the mechanism, the polymerization experiment was carried out in a tube.[12] The top liquid column of about 5 cm produced pure PMMAP, whereas in the rest of the tube mostly homopolymer PMMA was formed. This shows that in the top layer a continuous supply of O_2 is maintained to form the polyperoxide. The CoTPP(Py)$^{-}$OO$^{\bullet}$ reacts with the alkyl radical (R$^{\bullet}$) and converts it into a peroxy radical (ROO$^{\bullet}$). The R$^{\bullet}$ can also be converted to ROO$^{\bullet}$ by its direct reaction with O_2. However, the radical−radical reaction between CoTPP(Py)$^{-}$OO$^{\bullet}$ and R$^{\bullet}$ would be much faster compared to the reaction of the R$^{\bullet}$ with the O_2. The deoxygenated CoTPP(Py), thus produced in the process, moves at the top of the liquid surface and absorbs O_2 from air to regenerate CoTPP(Py)$^{-}$OO$^{\bullet}$, and the reaction with the R$^{\bullet}$ continues. As the polyperoxide chains grow, the mobility of the R$^{\bullet}$, compared to that of CoTPP(Py), is curtailed for its reaction with O_2. Hence, it is most likely that CoTPP(Py) acts as an oxygen supplier for the oxidative polymerization to sustain. Thus, the present investigation provides a new method of oxidative polymerization of vinyl monomers which could be christened as "oxygen transfer polymerization". Formation of the homopolymer at the bottom of the tube suggests that CoTPP(Py)$^{-}$OO$^{\bullet}$ acts as an exclusive initiator because of its inability to move to the remote top surface at a rapid rate. As a result, O_2 concentration is

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(7) (a) Kishore, K.; Paramasivam, S.; Sandhya, T. E. *Macromolecules* **1996**, *29*, 6973. (b) All polymerizations were carried out in neat monomer. Only for examining the monomer concentration effect were the experiments carried out in chlorobenzene. Polymerization was also carried out in air, at atmospheric pressure by using air balloon, in a 250 mL round-bottom flask with stirring at 27 °C.

(8) (a) Jayanthi, S.; Kishore, K. *Macromolecules* **1996**, *29*, 4846. (b) The GPC number average (M_n = 7920) and weight average (M_n = 1390) molecular weights were determined with respect to polystyrene standard.

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(12) MMA solution of CoTPP(Py) (5 × 10^{-5} mol/L) was taken in a long tube of 50 cm length and 1 cm diameter. It was exposed to air at room temperature without stirring for 16 days.

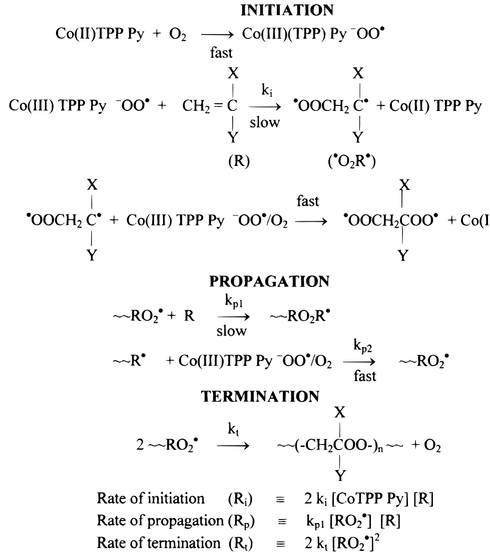
S0002-7863(97)01335-8 CCC: $15.00

Table 1. Kinetic Data on the CoTPP(Py)-Catalyzed Oxidative Polymerization

				av rate constant k_a (mol^{-1} L h^{-1})		
		exponent values		air^a	O_2 (100 psi)	
monomer	T (°C)	monomer	CoTPP(Py)	(25 °C)	40 °C	50 °C
AMS	40	1.6	0.4	0.040	0.42	0.65
ST	50	1.5	0.5	0.020	0.23	0.31
MMA	50	1.5	0.5	0.002	0.01	0.02

[a] Atmospheric pressure (14.7 psi).

Scheme 1



depleted as we go down the tube and the alkyl radicals are compelled to react with the monomer to form the homopolymer.

A plot of ln[CoTPP(Py)] vs ln[d[O_2]/dt] yields a straight line, and the slope indicates the reaction order is close to 0.5 with respect to CoTPP(Py) for all of the monomers. Similarly, monomer exponent of 1.5 and a zero-order dependence on O_2 pressure (50−350 psi) was found for all of the vinyl monomers (see Table 1).

The mechanism of polymerization and the rate of initiation (R_i), propagation (R_p), and termination (R_t) are shown in Scheme 1. Assuming a steady state between R_i and R_t, R_p could be given as The above rate expression appears to be in excellent agreement

$$R_p = k_a[\mathrm{R}]^{1.5}[\mathrm{CoTPP(Py)}]^{0.5}; \quad k_a = k_{p1}(k_1{}^{0.5}/k_t{}^{0.5}) \qquad (2)$$

in terms of experimentally observed catalyst, monomer, and O_2 exponent values. Hence, Scheme 1 adequately describes the mechanism and kinetics of polyperoxide formation. UV−vis spectral studies show that CoTPP(Py) is completely regenerated after the polymerization. Experimentally observed exponent value (0.5) of CoTPP(Py) indicates that two radicals are generated in the initiation step.

Further support of the proposed mechanism of polymerization (Scheme 1) was obtained from ESR studies.[13] The ESR spectrum of neat CoTPP(Py)$^-$OO$^•$ shows hyperfine structure of eight lines,[14] the g_{av} value CoTPP(Py)$^-$OO$^•$ was found to be 2.017 which is close to the reported g value (2.015) for the ROO$^•$ radical.[15] Hence, ESR signal at a g_{av} value of 2.017 is due to the overlap of CoTPP(Py)$^-$OO$^•$ and ROO$^•$ signals. To examine how the ESR signal of CoTPP(Py)$^-$OO$^•$ is affected by addition of the monomer, ESR spectra were recorded with addition of an increasing amount of the monomer into a CH_2Cl_2 solution of the cobalt catalyst. From the peak area measurements, the spin concentration of the catalyst was calculated (Table 2) as a function of the monomer (AMS) concentration. It is clearly evident that even on dilution of the CoTPP(Py)$^-$OO$^•$ solution with the monomer, contrary to the expectations, the spin concentration increases. However, when the catalyst solution is diluted with nonmonomeric solvents such as CH_2Cl_2, the spin concentration does decrease. The ESR spectra for different monomer concentrations were taken. While ESR intensity increases, the line shape and peak-to-peak line width do not change on addition of the monomer. At higher temperature and at higher concentration of the monomer, the ESR signal at 2.017 was found to vanish completely, suggesting that it chiefly arises from ROO$^•$. The increase in the spin concentration with increase in the monomer concentration is quite intriguing. The most plausible explanation is that a single CoTPP(Py)$^-$OO$^•$ radical produces more than one ROO$^•$ radical on reaction with the monomer. If it forms only a single ROO$^•$, we would expect the spin concentration to decrease on dilution with the monomer. The proposed mechanism (Scheme 1) of polymerization involves a biradical formation. Indeed, on dilution with the monomer the spin concentration increases (Table 2).

Table 2. Spin Concentration of CoTPP(Py)$^-$OO$^•$ in AMS

10^{-17} (spin/mol)	vol ratio [monomer/catalyst(1.8mmol/L)]
1.28	0
3.83	0.10
12.14	0.78
17.85	1.50

The overall activiation energy (E_a) of the polymerization was determined from Arrhenius equation using experimental k_a data at different temperatures. In the presence of AIBN, the PSP formation gives an E_a of 25 kcal/mol.[11] By taking the reported activation energies of propogation (E_p), and termination (E_t) as 8.4 and 1.8 kcal/mol, respectively,[16] E_i was calculated ($E_i = 2E_a + E_t - 2E_p$) as 35 kcal/mol, which is comparable with the E_i values for the AIBN-initiated polymerization of vinyl monomers. In the presence of CoTPP(Py), E_a was found to be 9 kcal/mol. The corresponding E_i value was found to be only 3 kcal/mol, suggesting that R_p in the presence of CoTPP(Py) is extremely fast, which is not the case. The low E_i value may be attributed to the complexity of the mechanism. While the stability of the CoTPP(Py)$^-$OO$^•$ adduct decreases, the R_p on the other hand increases, with increase in the temperature. Hence, no meaningful conclusions could be drawn from the observed low E_i values.

The present investigation provides an elegant, hitherto new, method of oxidative polymerization at low temperatures, this could be christened as O_2 transfer polymerization. The unique multifaceted role of the CoTPP(Py) complex as an initiator and O_2 supplier in the oxidative polymerization of vinyl monomers has been established. Since CoTPP(Py) mimics the role of haemoglobin or haemocyanin for transporting molecular O_2 from the air to the polymerization site, we think such polymerization reactions could serve as a model for biological oxygenation processes.

Acknowledgment. The authors thank Prof. T. R. N. Kutty, Chairman Materials Research Centre (MRC), for allowing us to use ESR Instrument facility and Mrs. Prathima Srinivasan (MRC) for carrying out the ESR experiments. The authors also thank Prof. S. V. Bhat, Chairman of the Physics Department, for fruitful discussions on ESR studies.

Supporting Information Available: Kinetic data, ESR spectra, and one figure (3 pages). See any current masthead page for ordering information and Web access instructions.

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(13) ESR spectra were recorded at 77 K on an X band Varian E 109 spectrometer. For recording the ESR spectra of CoTPP(Py)$^-$OO$^•$, the catalyst solution in CH_2Cl_2 was purged with O_2 at room temperature for 10 min and transferred into the ESR tube, and the spectra at liquid nitrogen temperature were recorded. In a similar fashion, the ESR spectra of CoTPP(Py)$^-$OO$^•$ + monomer were also recorded. In all experiments, the volume of the solution in the ESR tube was kept constant.

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