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Catalytic Oxidative Polymerization of Vinyl Monomers Using Cobalt Phthalocyanine Complex and an Exploratory Investigation on the Polymerization of Vinyl Acetate

A. K. Nanda* and K. Kishore

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

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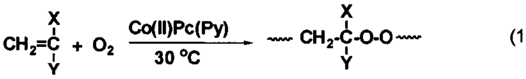
ABSTRACT: This is the first report on the oxidative polymerization of vinyl monomers using cobalt(II) phthalocyanine pyridine {$Co^{II}Pc(Py)$} complex. The mechanism of polymerization is described and it has been supported from the kinetic data, UV−vis, ESR and ^1H NMR studies. It is found that the rate of polymerizations (R_p) and number-average molecular weights ($\bar{M}_n$) of the vinyl polyperoxides are higher for $Co^{II}Pc(Py)$ catalyzed polymerization compared to the usual free radical, AIBN, initiated polymerization. This is supported by their activation energy of initiation (E_i) and total activation energy (E_a) of polymerization. The peroxide macroinitiator has been used for the polymerization of vinyl acetate. The polymerization obeys classical kinetics. The K^2 values of the peroxide macroinitiator has been determined, which reveals that it can also be used at higher temperature for the polymerization compared to monomeric peroxide initiator, benzoyl peroxide. The "active" poly(vinyl acetate) has also been synthesized, which contains peroxy segments at the chain ends.

Introduction

Recent years have witnessed rapid development of transition-metal-catalyzed free radical polymerization. A variety of transition metal catalysts of copper,[1] ruthenium,[2,3] iron[4] and nickel[5,6] have been successfully employed in the polymerization processes. However, the use of cobalt(II) phthalocyanine {$Co^{II}Pc$} catalyst in polymerization is scantly reported in the literature. Since its discovery, metal phthalocyanines have become one of the most important candidates for numerous applications such as electrophotography, optical data storage systems, chemical sensors, photovoltaic cells, fuel cells, electronic devices, photodynamic therapy of cancer, self-assembled monolayers and oxidation of organic compounds.[7−15]

This is the first report on the oxidative polymerization of vinyl monomers, which has been achieved at low temperatures. When a homogeneous solution of a vinyl monomer containing a reversible oxygen carrier, namely cobalt(II) phthalocyanine pyridine complex [$Co^{II}Pc(Py)$], is exposed to oxygen, an alternating copolyperoxide is obtained (eq 1).



$$CH_2{=}\overset{X}{\underset{Y}{C}} + O_2 \xrightarrow[30\ ^\circ C]{Co(II)Pc(Py)} \sim\sim CH_2\text{-}\overset{X}{\underset{Y}{C}}\text{-}O\text{-}O\sim\sim \qquad (1)$$

Vinyl polyperoxides[16−21] are a narrow but unique class of polymers in the sense that they degrade highly exothermically,[22−24] in contrast to common polymers which degrade endothermically. They are receiving increased attention due to their physicochemical behavior such as autopyrolyzability,[25] autocombustibiliy,[26] specials fuels,[25] and coating and molding applications[20] and finally for their role as base-catalyzed initiators.[27] Although polyperoxides can be synthesized by the vinyl monomers and O_2 at 50 °C using the free radical initiator, 2,2′-azobis(isobutyronitrile) (AIBN), their yield and molecular weight are not very high on account of their facile degradation and chain transfer reactions.[18,28,29] Hence, there have been continued efforts for a method wherein polymerization could be carried at low temperatures for curtailing their degradation.

The oxidative polymerization of vinyl monomers in the presence of $Co^{II}Pc(Py)$ complex has proved to be highly rewarding. Important features of $Co^{II}Pc(Py)$ as a catalyst is compared with conventional free radical initiator, AIBN in the polymerization processes. In addition, the synthesis and kinetics of the polymerization of vinyl acetate (VOAc) have been carried out using new initiating system and the formation of "active" poly(vinyl acetate) (PVOAc) is discussed.

Experimental Section

Materials. α-Methylstyrene (AMS), styrene (STY), and VOAc were freed from inhibitor by washing with 10% NaOH solution and then with water several times. After drying over anhydrous Na_2SO_4, they were distilled under reduced pressure. $Co^{II}Pc$ (Aldrich) was used as received. AIBN was recrystallized thrice from methanol. The solvents used were purified by standard procedure.[30]

Preparation of $Co^{II}Pc(Py)$ Complex. $Co^{II}Pc(Py)$ complex was preapred by mixing solutions of equivalent concentrations of $Co^{II}Pc$ and Py (1:1) in vinyl monomer. The formation of $Co^{II}Pc(Py)$ complex is evident from the bathocromic shift of the 316 (B-band), 579 (vibronic band) and 645 nm (Q-band) of $Co^{II}Pc$ complex to 337, 599, and 666 nm respectively, in the UV−vis absorption spectra.

Oxidative Polymerization of Vinyl Monomers. A solution of $Co^{II}Pc(Py)$ in a vinyl monomer was charged in a 300 mL Parr reactor (Parr Instrument Co.) equipped with a digital pressure transducer, temperature controller, mechanical stirrer and pressurized with O_2. The reaction was carried out at different temperatures, pressures, catalyst and monomer concentrations. For examining the effect of monomer concentration, the experiments were carried out in benzene. All the reactions were carried out at constant stirring and the polymerization time was kept at 4 h to effect low conversion (i.e., 10%) for reliable kinetic analysis. The consumption of oxygen (ΔP) was measured as a function of time using a pressure transducer. The rate of polymerization is calculated from the slope of oxygen uptake (ΔP) vs time plot. To determine the

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yield, polyperoxide, namely, poly(α-methylstyrene peroxide) (PMSP) and poly(styrene peroxide) (PSP) were precipitated from the reaction mixture using petroleum ether as a nonsolvent and dried in a vacuum and weighed.

UV−Visible Studies. The UV−visible studies have been done at room temperature on a Hitachi instrument, model U-3400. The spectra of $Co^{II}Pc(Py)$ complex in a vinyl monomer is recorded before and after the polymerization reactions.

ESR Studies. The ESR spectra were recorded at 77 K on a X band varian E 109 spectrometer. For recording ESR spectra of $Co^{III}Pc(Py)^{-}OO^{\bullet}$, the catalyst solution in CH_2Cl_2 was purged with O_2 at room temperature for 10 min and transferred into ESR tube and the spectra at the liquid nitrogen temperature is recorded using diphenylpicrylhydrazyl (DPPH) as an internal standard.

Polymerization of Vinyl Acetate. Bulk and solution polymerizations (in benzene) of VOAc in the presence of PMSP as a peroxide macroinitiator were carried out at 60 °C in sealed evacuated ampules. The polymers were precipitated and purified from $CHCl_3$ solution using cold heptane as non solvent, kept in the freezer for several hours, filtered, and finally dried under vacuum at 50 °C to a constant weight. The rate of polymerization (R_p) was calculated from the conversion−time data.

Analytical Techniques. The ^1H and ^{13}C NMR spectra in $CDCl_3$, were recorded on a Bruker ACF 200 MHz spectrometer using tetramethylsilane as an internal standard. IR spectra were recorded on a Perkin-Elmer model 780 spectrometer. The number-average molecular weights ($\bar{M}_n$), weight-average molecular weights ($\bar{M}_w$) and polydispersity indices ($\bar{M}_w/\bar{M}_n$) were estimated using gel permeation chromatography (GPC). The GPC was performed on a modular system comprising of a Waters 590 HPLC pump, a Waters 717 autosampler (Waters Corp., Milford, MA) and an ERMA ERC-7515A refractive index detector (ERMA CR, Inc., Tokyo). The column used was a 60 cm PLGel mixed-B 10 μm column (Polymer Laboratories Ltd., Shropshire, U.K.). The mobile phase used was unstabilized THF (EM Science, Gibbstown, NJ) at a flow rate of 0.95 mL/min. The molecular weights were calculated using 13 narrow polystyrene standards from 6 300 000 to 580 (Pressure Chemical Co., Pittsburgh, PA). The software used for the calculations was PL caliber version 7.04 (Polymer Laboratories Ltd., U.K.).

Results and Discussion

Characterization and Molecular Weights. The ^1H NMR spectra of PMSP showed resonance signals at 1.46, 4.16, and 7.2 ppm, which were assigned to methyl, methylene, and aromatic protons, respectively.[18] For PSP, the signals are at 4.0, 5.3, and 7.2 ppm for methylene, methine, and aromatic protons, respectively.[18] The polyperoxides thus obtained were alternating copolymers (i.e., 1:1 stoichiometry) of vinyl monomers and oxygen. They contain hydroxyl and carbonyl as end groups[31,32] which were detected from their IR and ^{13}C NMR spectra, respectively. The $\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$) values for PMSP and PSP are 7155 (1.7) and 6515 (1.8), respectively. It is interesting to note that polyperoxides of high molecular weights and narrow polydispersities have been obtained using the present method compared to AIBN-initiated polymerization.[20]

Kinetics of Polymerization. The oxidative polymerization of AMS and STY by varying monomer (M), catalyst concentrations, and O_2 pressure are given in Tables 1 and 2 respectively. Since the polymerization does not occur in the absence of $Co^{II}Pc(Py)$ (Tables 1 and 2, blank run), the initiation involves addition reaction of the O_2 adduct of the complex to the alkene producing radicals. To probe the free radical mechanism, hydroquinone (0.6 mmol) was added to the reaction mixture, and it was found to induce induction period and retard the polymerization (Figure 1).

Table 1. Kinetic Data of Oxidative Polymerization of AMS with $Co^{II}Pc(Py)$ Catalyst[a]

run	[AMS] (mol/L)	[catalyst] × 10^5 (mol/L)	O_2 (psi)	$R_p \times 10^1$ (psi/min)	$R_p \times 10^1$ (mol/L/h)[b]	PMSP (mol/L)	k_a (L/mol/h)
*	7.69	0	100	0	0	0	0
A	3.48	9.303	100	0.077	0.130	0.048	0.208
A	3.69	9.303	100	0.083	0.140	0.085	0.209
A	4.61	9.303	100	0.118	0.200	0.133	0.209
A	6.15	9.303	100	0.179	0.302	0.207	0.210
A	7.69	9.303	100	0.260	0.440	0.250	0.214
B	7.69	6.299	100	0.214	0.361	0.160	0.213
B	7.69	7.069	100	0.225	0.380	0.170	0.212
B	7.69	7.979	100	0.239	0.404	0.192	0.212
B	7.69	8.750	100	0.246	0.415	0.208	0.208
B	7.69	8.920	100	0.249	0.421	0.213	0.209
B	7.69	9.300	100	0.259	0.437	0.250	0.213
B	7.69	9.480	100	0.262	0.443	0.256	0.213
B	7.69	10.000	100	0.270	0.455	0.277	0.213
C	7.69	9.303	50	0.258	0.436	0.252	0.212
C	7.69	9.303	100	0.259	0.437	0.250	0.213
C	7.69	9.303	200	0.258	0.436	0.255	0.213
C	7.69	9.303	250	0.259	0.437	0.253	0.214
C	7.69	9.303	300	0.260	0.439	0.251	0.213
C	7.69	9.303	350	0.258	0.436	0.252	0.211
C	7.69	9.303	400	0.259	0.438	0.251	0.212

[a] Temperature = 40 °C, reaction time = 3 h, diluent = benzene; A = [monomer] variation; B = [catalyst] variation; C = $[O_2]$ pressure variation; * = blank run. [b] Calculated using the relationship reported earlier (ref 19)

Table 2. Kinetic Data of Oxidative Polymerization of STY with $Co^{II}Pc(Py)$ Catalyst[a]

run	STY (mol/L)	[catalyst] × 10^5 (mol/L)	O_2 (psi)	$R_p \times 10^1$ (psi/min)	$R_p \times 10^1$ (mol/L)[b]	PSP (mol/L/h)	k_a (L/mol/h)
*	8.698	0	100	0	0	0	0
A	4.175	9.303	100	0.040	0.068	0.030	0.079
A	5.220	9.303	100	0.056	0.095	0.068	0.083
A	6.959	9.303	100	0.087	0.147	0.115	0.083
A	7.655	9.303	100	0.099	0.167	0.170	0.082
A	8.698	9.303	100	0.123	0.207	0.226	0.084
B	8.698	7.065	100	0.106	0.179	0.162	0.083
B	8.698	8.640	100	0.117	0.198	0.182	0.083
B	8.698	9.300	100	0.122	0.207	0.226	0.084
B	8.698	9.799	100	0.126	0.213	0.241	0.084
B	8.698	11.890	100	0.138	0.233	0.265	0.083
B	8.698	12.390	100	0.147	0.248	0.267	0.086
C	8.698	9.303	50	0.122	0.206	0.225	0.084
C	8.698	9.303	100	0.123	0.207	0.226	0.084
C	8.698	9.303	200	0.123	0.208	0.227	0.085
C	8.698	9.303	300	0.123	0.207	0.228	0.083
C	8.698	9.303	400	0.123	0.208	0.227	0.085

[a] Temperature = 50 °C; reaction time = 3 h, diluent = benzene; A = [monomer] variation; B = [catalyst] variation; C = $[O_2]$ pressure variation; * = blank run. [b] Calculated using the relationship reported earlier (ref 19).

A plot of $\ln[d[O_2]/dt]$ vs $\ln[Co^{II}Pc(Py)]$ yields a straight line, and the slope indicates the order of the reaction is close to 0.5 with respect to $Co^{II}Pc(Py)$ for all the monomers. Similarly, monomer exponent of 1.5 is obtained from the slope of $\ln[d[O_2]/dt]$ vs $\ln[M]$, for all the monomers and a zero order dependence on O_2 pressure (50−400 psi) was found.

The rate of polymerization (R_p) of AMS is greater than STY (Tables 1 and 2), which is similar to that observed in the presence of the common free radical initiator, AIBN. This is also the order of increasing π-electron density at the double bond of the monomers and the electron accepting property of the corresponding peroxy radicals.[33]

The AIBN-initiated AMS oxidative polymerization unlike STY shows a significant pressure effect,[19,34] and the rate becomes independent of O_2 pressure only after

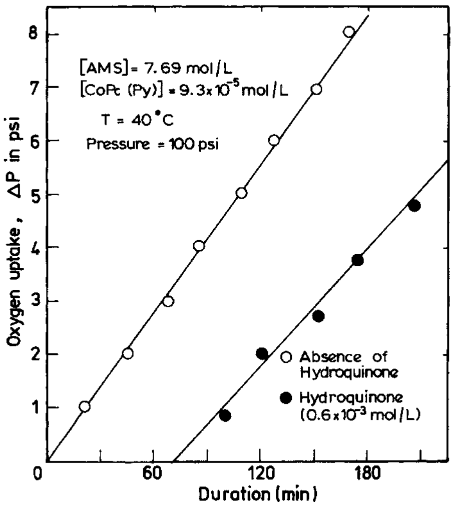


Figure 1. Effect of hydroquinone on the oxidative polymerization of AMS.

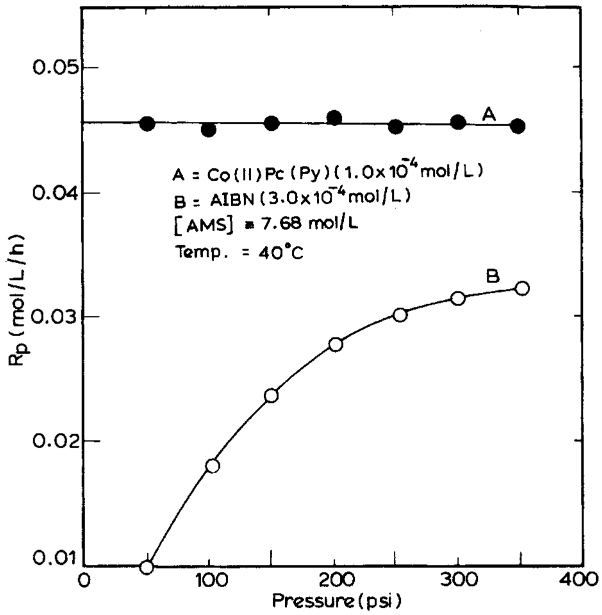
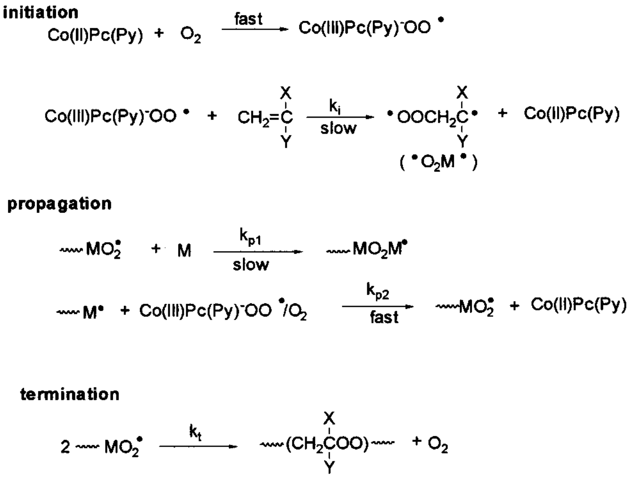


Figure 2. Effect of O_2 pressure on $Co^{II}Pc(Py)$-catalyzed and AIBN-initiated polymerization.

350 psi. Interestingly, the oxidative polymerization of AMS, in the presence of $Co^{II}Pc(Py)$ is independent of O_2 pressure (Figure 2). This observation suggests that $Co^{II}Pc(Py)$, 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 pressure, 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 2) suggesting that the dissolved O_2 concept is not applicable here. Hence, it is most likely that $Co^{II}Pc(Py)$ acts as an oxygen supplier to sustain the oxidative polymerization.

UV–Vis Studies. The UV–vis spectra were recorded to study the nature of the cobalt complex before and after the polymerization. The UV–vis spectra of Co^{II}-Pc(Py) adduct in the monomer remains unaffected with same absorbance after the polymerization reaction. It indicates that $Co^{III}Pc(Py)^{-}OO^{\bullet}$ adduct after an electrophilic addition reaction with the monomer regenerates $Co^{II}Pc(Py)$ and does not undergo irreversible oxidation under the present reaction condition.

Scheme 1. Mechanism of $Co^{II}Pc(Py)$-Catalyzed Oxidative Polymerization



ESR Studies. The g_{av} value from the ESR analysis of neat $Co^{III}PC(Py)^{-}OO^{\bullet}$ was found to be 2.016 which is close to the reported g value (2.015) for the $ROO^{\bullet}$ radical[35] revealing the formation of $Co^{III}Pc(Py)^{-}OO^{\bullet}$ radical.

Mechanism of Polymerization. On the basis of the kinetic analysis and UV–vis and ESR studies, the mechanism of polymerization is given in Scheme 1. The reaction of $Co^{II}Pc(Py)$ with O_2 generating $Co^{III}Pc(Py)^{-}OO^{\bullet}$ radical is a fast process (Scheme 1). Hence, the rate of polymerization does not depend on the concentration of O_2 (Tables 1 and 2).

Therefore

$$[Co^{II}Pc(Py)] \cong [Co^{III}Pc(Py)^{-}OO^{\bullet}]$$

It is assumed that mainly quadratic chain termination takes place between the peroxy radicals.[31,32] The rate of initiation (R_i), rate of propagation (R_p) and the rate of termination (R_t) were determined in the following way:

$$R_i = 2\,k_i[Co^{II}Pc(Py)][M] \tag{2}$$

$$R_p = k_{p1}[MOO^{\bullet}][M] \tag{3}$$

$$R_t = 2k_t[MOO^{\bullet}]^2 \tag{4}$$

Assuming steady-state approximation

$$R_i = R_t \tag{5}$$

Hence

$$2\,k_i[Co^{II}Pc(Py)][M] = 2k_t[MOO^{\bullet}]^2 \tag{6}$$

Equation 6 could be arranged as

$$[MOO^{\bullet}] = (k_i/k_t)^{1/2}[Co^{II}Pc(Py)]^{1/2}[M]^{1/2} \tag{7}$$

Substituting the value of $[MOO^{\bullet}]$ in eq 3, we get

$$R_p = k_{p1}\,(k_i/k_t)^{1/2}[Co^{II}Pc(Py)]^{1/2}[M]^{3/2} \tag{8}$$

which is further modified as

$$R_p = k_a[\mathrm{Co^{II}Pc(Py)}]^{1/2}[\mathrm{M}]^{3/2} \quad \text{where } k_a = k_{p1}(k_i/k_t)^{1/2} \tag{9}$$

The above rate expression (eq 9) appears to be in excellent agreement 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 $\mathrm{Co^{II}Pc(Py)}$ is completely regenerated after the polymerization. Experimentally observed exponent value (0.5) of $\mathrm{Co^{II}Pc(Py)}$ indicates that two radicals (i.e., diradical for the present system) are generated in the initiation step.

Effect of Axial Base, Py. The effect of the concentration of axial base, Py, on the polymerization rate is given in Figure 3. The general mechanism for the effect of Py concentration on the polymerization is given in Scheme 2 (eqs 10−13).

Scheme 2. Mechanism of the Effect of Py on the Rate of Polymerization

$$\mathrm{Co(II)Pc + Py \longrightarrow Co(II)Pc(Py)} \tag{10}$$

$$\mathrm{Co(II)Pc(Py) + Py \longrightarrow Co(II)Pc(Py)_2} \tag{11}$$

$$\mathrm{Co(II)Pc(Py) + O_2 \longrightarrow Co(III)Pc(Py)OO^{\bullet}} \tag{12}$$

$$\mathrm{Co(II)Pc + O_2 \longrightarrow Co(III)PcOO^{\bullet}} \tag{13}$$

Case I: When the concentration of Py equals that of $\mathrm{Co^{II}Pc}$, reactions represented by eqs 10 and 12 are favored, and hence the rate of polymerization reaches a maximum.

Case II: When the concentration of Py is greater than the concentration of $\mathrm{Co^{II}Pc}$, reactions described by eqs 10−12 occur. According to eq 11, some of the catalyst will have both axial sides Py and hence will not be able to absorb O_2. Consequently, the polymerization becomes lower.

Case III: When the concentration of Py is less than the concentration of $\mathrm{Co^{II}Pc}$, the O_2 absorption takes place predominately according to reactions represented by eqs 12 and 13. It may be appeared that in the absence of Py (eq 13), the complex is less effective to absorb O_2. Consequently, the over all rate of polymerization is lower.

Activation Energy of Polymerization. The overall activation energy (E_a) of the polymerization was determined from the Arrhenius equation using experimental k_a data at different temperatures. Figure 4 displays the R_p for STY determined at different temperatures. In the presence of AIBN, the PSP formation yields an E_a of 25 kcal/mol.[28] By taking the reported activation energies for propagation (E_p), and termination (E_t), as 8.4 and 1.8 kcal/mol, respectively,[36] the activation energy for the initiation (E_i) was

$$E_i = 2E_a + E_t - 2E_p \tag{14}$$

calculated using eq 14 as 35.0 kcal/mol, which is comparable to the E_i values for the AIBN-initiated polymerization of vinyl monomers. In the presence of $\mathrm{Co^{II}Pc(Py)}$, the E_a was found to be 13.4 kcal/mol. The corresponding E_i values using eq 14 was measured as 11.8 kcal/mol.

Comparison between the R_p of $\mathrm{Co^{II}Pc(Py)}$ and AIBN-Initiated Polymerization. From Figure 5, it is clearly seen that the rate of polymerization using $\mathrm{Co^{II}Pc(Py)}$ is higher than the conventional AIBN-initiated polymerization. This is attributed to the lower E_i and E_a values of $\mathrm{Co^{II}Pc(Py)}$ catalyzed polymerization compared to AIBN-initiated polymerization.

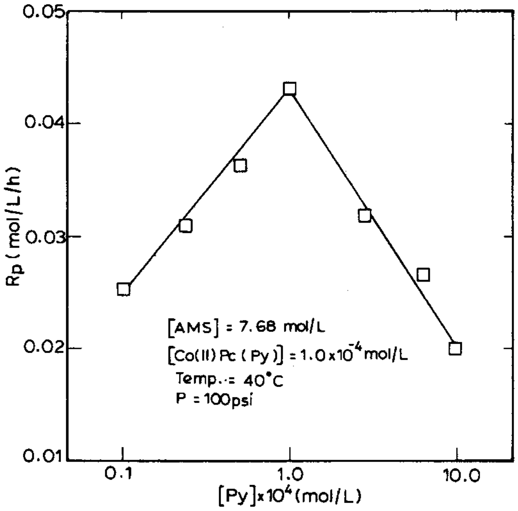


Figure 3. Oxygen consumption, ΔP, vs time for the polymerization of AMS in the presence of $\mathrm{Co^{II}Pc(Py)}$ by varying the concentration of Py.

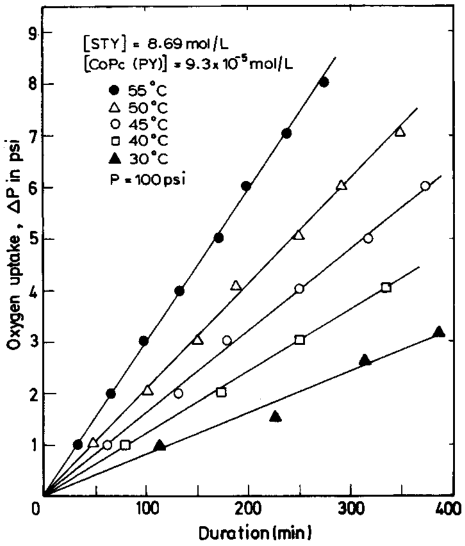


Figure 4. $\mathrm{Co^{II}Pc(Py)}$-catalyzed polymerization of STY at different temperatures.

Kinetics of Radical Polymerization of Vinyl Acetate using PMSP as a Peroxide Macroinitiator. To study the polymerization of VOAc using PMSP as an initiator, bulk, and solution polymerization of VOAc were carried out at 60 °C. The polymerization proceeds without any induction time. Conversion was kept below 10% for reliable kinetic analysis. The rate of polymerization (R_p) was calculated from the slope of conversion (%) vs time, and it was found to be 3.5×10^{-4} mol L^{-1} s^{-1}. The polymerization reactions were carried out at different initiator and monomer concentrations. A plot of ln R_p vs ln[PMSP] yields a straight line and the slope gives the order of reaction as 0.52 with respect to PMSP. Similarly, the VOAc monomer exponent of 1.12 is obtained from the slope of ln R_p vs ln[VOAc]. The rate of polymerization of VOAc is given by eq 15, showing

$$R_p = K[\mathrm{M}]^{1.12}[\mathrm{I}]^{0.52} \propto [\mathrm{M}]^{1}[\mathrm{I}]^{0.5} \tag{15}$$

where K, [M], and [I] respectively are the overall rate constant, monomer, and initiator concentrations.

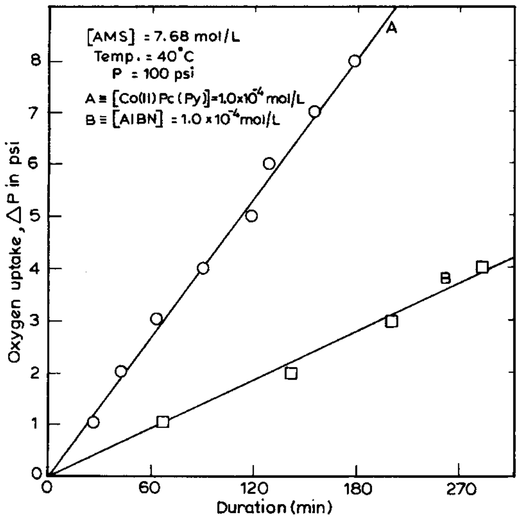


Figure 5. Oxygen consumption, ΔP, vs time for the polymerization of AMS in the presence of $Co^{II}Pc(Py)$ and AIBN.

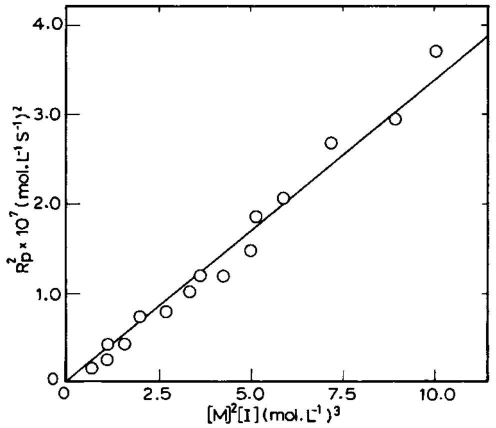


Figure 6. Plot of R_p^2 vs $[M]^2[I]$ for VOAc polymerization at 60 °C, initiated by peroxide macroinitiator, PMSP.

The term $k_p^2(fk_d/k_t)$ is denoted as K^2, and it is a measure of the initiator reactivity;[37] the terms have their usual meanings. The value of K^2 was evaluated from the slope of the plot of R_p^2 vs $[M]^2[I]$ (Figure 6). For VOAc polymerization using PMSP, the value of K^2 was estimated as 4.2×10^{-8} L mol^{-1} s^{-2}. In the case of PMSP, 1 mol equiv is the equivalent weight in grams of the repeat unit. The value of K^2 of PMSP when compared to that of the monomeric benzoyl peroxide initiator[37,38] suggests that PMSP may be used as a high-temperature initiator.

Characterization of PVOAc. The ^{1}H NMR spectra of PVOAc prepared using 0.03 mol equiv L^{-1} of PMSP did not exhibit the signals corresponding to the PMSP segments. To introduce peroxy segments in the chain, the PVOAc have been prepared using PMSP of concentration 0.1 mol equiv L^{-1}. The polymer product was purified by repeated precipitation from cold heptane. The presence of peroxy segments in the resultant polymer chain was confirmed by ^{1}H NMR studies. In the ^{1}H NMR spectrum (Figure 7), the signals at 4.7–5.0, 2.0, and 1.5–2.0 ppm correspond to the >CH–, –C(O)CH_3, and –CH_2– protons of PVOAc, respectively[39] and the peaks at 7.2, 4.16, and 1.46 ppm are assigned to the aromatic, –CH_2–, and –CH_3 protons of the PMSP segments, respectively.[18] The $\bar{M}_n$ and polydispersity values of active PVOAc were 35 824 and 3.8, respectively. The wide polydispersity could be due to various recombination and chain transfer reactions.[40,41] Decomposition of this "active" PVOAc was carried out in chlorobenzene at 110 °C for 25 h, and the $\bar{M}_n$ values before and after the decomposition were found to be 35 824 and 31 015, respectively, confirming the incorporation of peroxy segments in the chain ends of PVOAc; otherwise, a significant reduction in the molecular weight would have been observed.

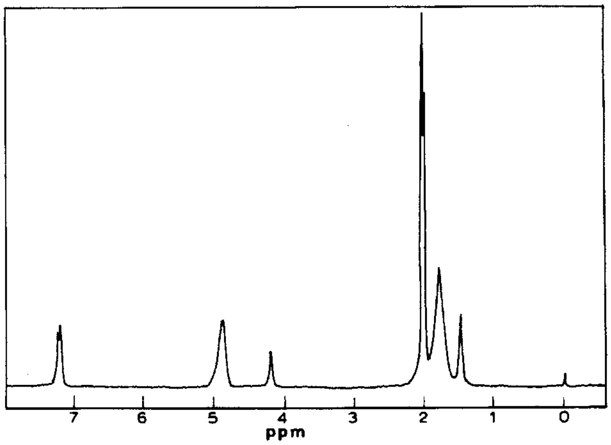


Figure 7. ^{1}H NMR spectrum of PVOAc prepared using 0.1 mol equiv L^{-1} of PMSP.

Conclusion

The present investigation provides a new method of oxidative polymerization at low temperatures. The unique dual role of the $Co^{II}Pc(Py)$ complex as an initiator and a oxygen supplier in the oxidative polymerization of vinyl monomers has been established. This technique can be utilized for the synthesis of other polymers, which are otherwise rather difficult to synthesize due to their inherent thermal instability. These polymerization reactions could serve as a model for biological oxygenation processes.

The polymerization of VOAc using peroxide macroinitiator is discussed and the results reveal that the present initiating system can be used for polymerizing other vinyl monomers at higher temperatures. "Active" PVOAc containing peroxy segments in the main chain was also synthesized.

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