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Autocatalytic Oxidative Polymerization of Indene by Cobalt Porphyrin Complex and Kinetic Investigation of the Polymerization of Styrene

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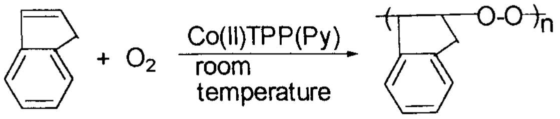
ABSTRACT: This is the first report on the oxidative polymerization of indene using cobalt(II) tetraphenyl porphyrin pyridine [Co(II)TPP(Py)] complex, which led to the formation of poly(indene peroxide), PINDP, having narrow polydispersity. The polymerization was carried out at room temperature and low oxygen pressure. The dual behavior of Co(II)TPP(Py) as a dioxygen carrier as well as an initiator was investigated. The mechanism of polymerization is described and supported from the kinetic analysis, UV−visible, ESR, and ^{1}H NMR studies. The rate of formation of PINDP is higher for Co(II)TPP(Py) catalyzed polymerization compared to the usual free radical, AIBN, initiated polymerization. The stability of PINDP was estimated from its rate of degradation and compared with other related vinyl polyperoxides. The PINDP was further used as a peroxide macroinitiator for the polymerization of styrene. The polymerization obeys classical kinetics. The K^2 values of the peroxide macroinitiator was determined, which reveals that it can also be used at higher temperature for the polymerization. An "active" polystyrene was also synthesized, containing peroxy segments at the chain ends.

Introduction

Free radical polymerization remains one of the most widely used industrial processes to design new polymers with novel physical properties. Unlike other vinyl polymerizations, radical polymerization can be used with a broad variety of monomers because it tolerates many functional groups. It is also synthetically much less demanding than anionic and cationic processes because it tolerates a wide variety of reaction media and occurs at convenient temperatures. Transition-metal catalyzed free radical polymerization has been reported, which produced polymers with narrow polydispersities.[1−10]

Vinyl polyperoxides[11−13] are a narrow but unique class of polymers in the sense that they degrade highly exothermically,[14−16] in contrast to common polymers which degrade endothermically. They are receiving increased attention due to their physicochemical behavior such as autopyrolyzability[17] and autocombustibiliy,[18] and for their roles as specials fuels,[17] in coating and molding applications,[19] and finally as base-catalyzed initiators.[20−22] They provide perhaps the only example where molecular oxygen acts as a monomer and is incorporated in the polymer backbone. Although vinyl polyperoxides can be synthesized from vinyl monomers and O_2 at 50 °C using a free radical initiator (AIBN), their yields are very low and they have broad polydispersities (~2.0) due to their facile degradation and chain transfer reactions.[23,24] We are continuing to develop a low-temperature polymerization in order to curtail their degradation.

This is the first report of a synthesis of the stable vinyl polyperoxide, namely, poly(indene peroxide) (PINDP), which has been achieved at room temperature and with low oxygen pressure. When a homogeneous solution of indene containing a reversible oxygen carrier, namely, cobalt(II) tetraphenyl porphyrin pyridine complex [Co(II)TPP(Py)], is exposed to O_2, an alternate copolyperoxide, PINDP, is obtained (eq 1).



(1)

Important features of Co(II)TPP(Py) as a catalyst will be compared with a conventional free radical initiator, AIBN, in the polymerization process. The stability of PINDP will be estimated and compared with similar vinyl polyperoxides. In addition, the synthesis and kinetics of the polymerization of styrene, which is the most industrially used polymer, have been carried out using the new initiating system. The formation of the "active" polystyrene will be discussed.

Experimental Section

Materials. Indene (97%, Aldrich) and styrene (98%, Ranbaxy) were freed from inhibitor by washing with 10% aq NaOH and then with distilled water several times. After being dried over anhydrous Na_2SO_4, they were distilled under reduced pressure. Co(II)TPP (99%, Aldrich) was used as received. 2,2′-Azobis(isobutyronitrile) (AIBN) (98%, Koch Light) was recrystallized thrice from methanol. Chloroform (98%, Ranbaxy) was purified by passing through a column of activated alumina (4-ft long by 1.75-in diameter at a flow rate of 3 mL/min), refluxed with P_2O_5 for 12 h and then distilled. The distilled $CHCl_3$ was stored in the dark before use. Methanol (98%, Ranbaxy) was purified by warming 100 mL with clean dry magnesium turnings (5 g) and iodine (0.5 g) in a flask until the iodine disappears. Then 1 L of methanol was added and, after refluxing for 3 h, it was distilled off, excluding moisture from the system. Petroleum ether (98%, Ranbaxy) was purified by shaking several times with conc H_2SO_4, then 10% H_2SO_4 and conc KM_nO_4 until the permanganate color persists. The mixture was washed with water, aq Na_2CO_3, and again with water, dried with $CaCl_2$, refluxed with sodium wire for 4 h, and distilled. Pyridine (98%, Ranbaxy) was purified by stirring 800 mL for 24 h with a mixture of ceric sulfate (20 g) and anhydrous K_2CO_3 (15 g), then filtered, and fractionally distilled.[25]

Preparation of Co(II)TPP(Py) Complex. Co(II)TPP(Py) complex was prepared by mixing solutions of equivalent

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concentrations of Co(II)TPP and Py (1:1) in indene. The formation of Co(II)TPP(Py) complex was evident from the bathochromic shift of the 413 (soret peak) and 528 nm (Q peak) of Co(II)TPP complex to 440 and 553 nm, respectively, in the UV−vis absorption spectra.

Oxidative Polymerization of Indene. A solution of Co(II)TPP(Py) (1.6 mg, 9.55×10^{-5} mol/L) in indene (25 mL, 8.57 mol/L) 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 (i) at different temperatures (27, 35, 40, 50, and 60 °C), maintaining a pressure constant (200 psi), and (ii) at different pressures (30, 50, 100, 200, 300, 400, and 500 psi) keeping the temperature constant (40 °C). The reaction was carried out at constant stirring, and polymerization time was kept at 3 h to effect low conversion (10%) for reliable kinetic analysis. The consumption of oxygen (ΔP) was measured as a function of time using a pressure transducer. The rate of polymerizations (R_p) was calculated from the slope of the oxygen uptake versus time plot. Blank experiment, in the absence of Co(II)TPP(Py), was carried out to determine the O_2 consumption in the polymerization process. Experiments with different concentrations of indene and Co(II)TPP(Py) were performed under an O_2 pressure of 200 psi at 40 °C. At the end of the reaction, the solution was precipitated by dropwise addition into petroleum ether to give PINDP as a white solid, yield 8.5%. $\bar{M}_n$ (27 °C) = 3.5×10^3 and polydispersity = 1.12; ^{1}H NMR δ 2.8−3.2 (−CH_2−), 5.1 (>CH−CH$_2$−), 5.6 (>CH−Ar), 7.0−7.5 ppm (Ar−H).

Polymerization of Styrene. Styrene (STY, 1.85 mL, 3.23 mol/L) and PINDP (14 mg, 0.02 mol eqiuv/L in chlorobenzene (3.15 mL) was freeze−thawed three times with liquid nitrogen and then heated at 80 °C. The polymerization was kept for 2 h to effect low conversion (15%) for reliable kinetic analysis. The rate of polymerization (R_p) was calculated from the slope of the conversion versus time plot. Experiments with different concentrations of STY and PINDP were performed at 80 °C. At the end of the reaction, the solution was precipitated by dropwise addition into methanol to give polystyrene (PS) as a white solid. Yield 10.2%. $\bar{M}_n = 1.2 \times 10^5$; ^{1}H NMR δ 1.42 (−CH_2−), 1.84 (>CH−), and 6.4−7.2 ppm (Ar−H).

Analytical Methods. The ^{1}H NMR spectra in CDCl$_3$ were recorded on a Bruker ACF 200 MHz spectrometer using tetramethylsilane as an internal standard. The UV−visible studies were performed at room temperature on a Hitachi instrument, model U-3400. The spectra of Co(II)TPP(Py) complex in indene was recorded before and after the polymerization reactions. The ESR spectra were recorded at 77 K on a X band Varian E109 spectrometer. For recording ESR spectra of Co(II)TPP(Py)$^-$OO$^\bullet$, the catalyst solution in CH$_2$Cl$_2$ was purged with O_2 at room temperature for 10 min and transferred into an ESR tube, and the spectra at the liquid nitrogen temperature was recorded using diphenylpicrylhydrazyl (DPPH) as an internal standard. The number average molecular weights ($\bar{M}_n$), weight average molecular weights ($\bar{M}_w$), and polydispersities ($\bar{M}_w/\bar{M}_n$) were estimated using gel permeation chromatography (GPC). The GPC was performed on a modular system comprising a Waters 590 HPLC pump, a Waters 717 autosampler, and an ERMA ERC-7515A refractive index detector (ERMA CR, Inc., Tokyo). The columns used were 60 cm PLGel mixed-B 10 μ columns (10^4, 10^3, 500, and 100 Å) (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 at 30 °C. 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.). The isothermal degradation rates were studied using a DuPont thermogravimetric (TG) analyzer model 951 under nitrogen atmosphere. The temperature was calibrated using indium. Isothermal TG thermograms were obtained with 10 mg samples at 85 °C.

Table 1. Characteristics of PINDP Prepared at Different Temperatures[a]

temperature (°C)	R_p (mol/L h)	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
27	0.033	3.53	1.12
35	0.069	2.98	1.21
40	0.085	2.85	1.24
50	0.114	2.22	1.48
60	0.212	1.46	1.87

[a] [Indene] = 8.57 mol/L, [Co(II)TPP(Py)] = 9.55×10^{-5} mol/L, and oxygen pressure = 200 psi.

Table 2. Kinetic Data of Oxidative Polymerization of Indene with Co(II)TPP(Py)[a]

[indene] (mol/L)	[catalyst] × 10^5 (mol/L)	O_2 (psi)	R_p (mol/L h)	PINDP (mol/L)	k_a (L/mol h)
8.57	0	200	0	0	0
5.23	9.55	200	0.040	0.126	0.342
6.15	9.55	200	0.052	0.186	0.348
7.00	9.55	200	0.062	0.234	0.343
7.69	9.55	200	0.072	0.251	0.342
8.57	9.55	200	0.085	0.315	0.346
8.57	4.65	200	0.058	0.186	0.340
8.57	5.77	200	0.064	0.234	0.339
8.57	9.55	200	0.085	0.316	0.346
8.57	11.38	200	0.092	0.329	0.344
8.57	13.44	200	0.100	0.344	0.346
8.57	15.53	200	0.107	0.351	0.343
8.57	18.56	200	0.117	0.366	0.343
8.57	23.22	200	0.131	0.385	0.342
8.57	9.55	30	0.083	0.314	0.343
8.57	9.55	50	0.083	0.313	0.339
8.57	9.55	100	0.085	0.317	0.346
8.57	9.55	200	0.085	0.316	0.346
8.57	9.55	300	0.084	0.315	0.343
8.57	9.55	400	0.085	0.316	0.346
8.57	9.55	500	0.084	0.316	0.344

[a] Temperature = 40 °C, reaction time = 3 h, and diluent = chlorobenzene.

Results and Discussion

Molecular Weights. The $\bar{M}_n$ and polydispersity values of PINDP obtained at various temperatures are listed in Table 1. The polymers have narrow polydispersities at lower temperatures. At higher temperatures (>50 °C), the peroxide linkages degrade, which facilitates various chain transfer reactions resulting in the formation of low-molecular-weight polymers with broader polydispersity.

Kinetics of Polymerization. The oxidative polymerization of indene by varying monomer (M), catalyst concentrations, and O_2 pressure are given in Table 2. In the presence of O_2, the Co(II)TPP(Py) complex exists as a 1:1 oxygen adduct.[26] Since the polymerization does not occur in the absence of Co(II)TPP(Py) (Tables 2, blank run), the initiation evidently involves addition of the O_2 adduct to the indene producing free radicals. To probe the free radical mechanism, hydroquinone (0. 55 mol/L) was added to the reaction mixture, which induced an induction period and retarded the polymerization (Figure 1). A plot of ln R_p versus ln[Co(II)TPP(Py)] yields a straight line (using the data of catalyst variation experiments, Table 2), and the slope indicates the order of the reaction was close to 0.5 with respect to Co(II)TPP(Py). Similarly, monomer exponent of 1.5 was obtained from the slope of ln R_p versus ln[M] (using the data of monomer variation experiments, Table 2), and there was a zero-order dependence on O_2 pressure (using the data of O_2 pressure variation experiments, Table 2). The rate of polymerization (R_p) is obtained as

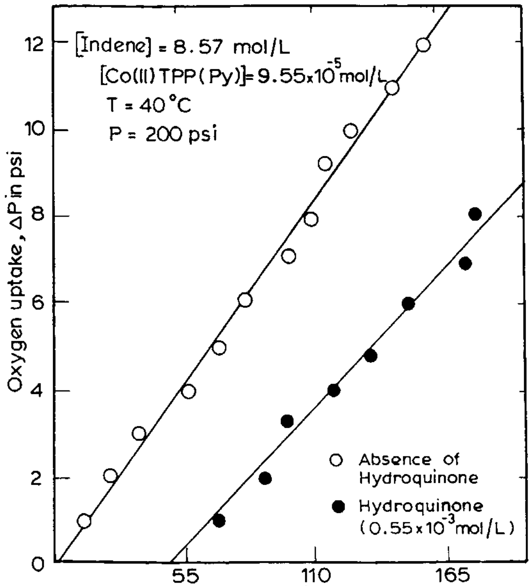


Figure 1. Effect of hydroquinone on the oxidative polymerization of indene.

$$R_p = k_a[M]^{1.5}[Co(II)TPP(Py)]^{0.5} \qquad (2)$$

where, k_a is the overall rate constant (Table 2).

The oxidative polymerization of indene in the presence of Co(II)TPP(Py) is independent of O_2 pressure (Table 2). This suggests that Co(II)TPP(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 R_p should increase. However, O_2 pressure has no effect on R_p (Table 2), suggesting that the dissolved O_2 concept is not applicable here. Hence, Co(II)TPP(Py) most likely acts as an oxygen supplier to sustain the oxidative polymerization.

UV−vis Studies. The UV−vis spectra (Figure 2) were recorded to study the nature of the cobalt complex before and after the polymerization. The UV−vis spectra of Co(II)TPP(Py) adduct in the monomer remains unaffected and has the same absorbance after the polymerization reaction. It indicates that $Co(III)TPP(Py)^{-}OO^{\bullet}$ regenerates Co(II)TPP(Py) after an electrophilic addition reaction with the monomer, and that Co(II)TPP(Py) is not consumed or undergo irreversible oxidation under the present reaction condition.

ESR Studies. The g_{av} value from ESR analysis of neat $Co(II)TPP(Py)^{-}OO^{\bullet}$ was 2.017 which is close to the reported g value (2.015) for the $ROO^{\bullet}$ radical.[27] This confirms that $Co(III)TPP(Py)^{-}OO^{\bullet}$ is formed.

Mechanism of Polymerization. The kinetic analysis and UV−vis and ESR studies support the polymerization steps shown in Scheme 1. The reaction of Co(II)TPP(Py) with O_2 generating $Co(III)TPP(Py)^{-}OO^{\bullet}$ is a fast process (Scheme 1). Hence, the rate of polymerization does not depend on the concentration of O_2 (Table 2).

Therefore,

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

The rates of initiation (R_i), propagation (R_p), and termination (R_t) were determined in the following way.

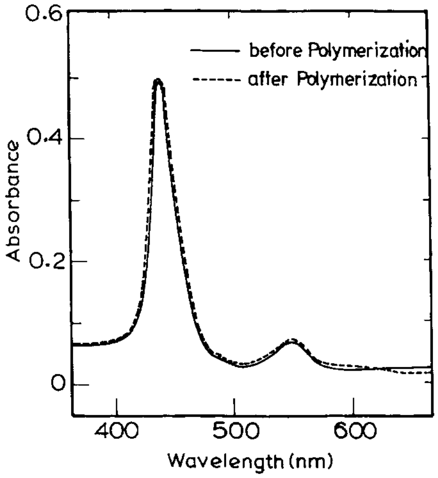


Figure 2. UV−vis spectra of Co(II)TPP(Py) before and after the polymerization: room temperature, [Co(II)TPP(Py)] = 9.55 × 10^{-5} mol/L, [indene] = 8.57 mol/L.

$$R_i = 2k_i[Co(II)TPP(Py)][M] \qquad (3)$$

$$R_p = k_{p1}[MOO^{\bullet}][M] \qquad (4)$$

$$R_t = 2k_t[MOO^{\bullet}]^2 \qquad (5)$$

Assuming steady-state approximation,

$$R_i = R_t \qquad (6)$$

Hence,

$$2k_i[Co(II)TPP(Py)][M] = 2k_t[MOO^{\bullet}]^2 \qquad (7)$$

Equation 7 can be rearranged to eq 8.

$$[MOO^{\bullet}] = (k_i/k_t)^{1/2}[Co(II)TPP(Py)]^{1/2}[M]^{1/2} \qquad (8)$$

Substituting the value of $[MOO^{\bullet}]$ in eq 4 generates

$$R_p = k_{p1}(k_i/k_t)^{1/2}[Co(II)TPP(Py)]^{1/2}[M]^{3/2} \qquad (9)$$

which is further modified as eq 10.

$$R_p = k_a[Co(II)TPP(Py)]^{1/2}[M]^{3/2}$$

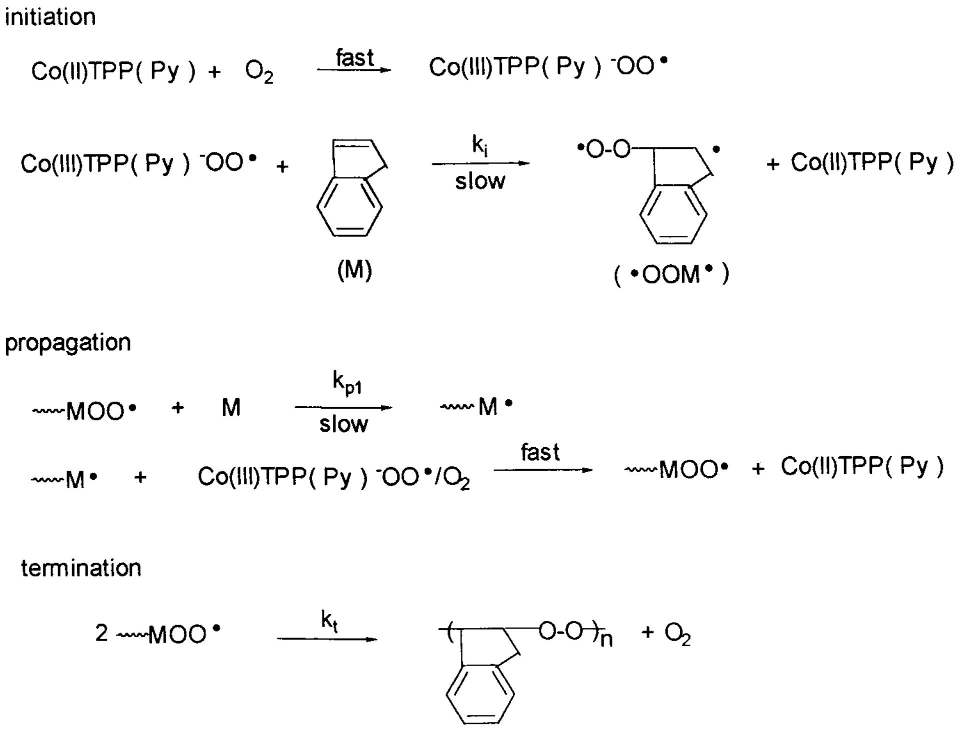
where,

$$k_a = k_{p1}(k_i/k_t)^{1/2} \qquad (10)$$

The above rate expression (eq 10) agrees well with our kinetically observed catalyst, monomer, and O_2 exponent values (eq 2). Hence, Scheme 1 adequately describes the elementary steps and kinetics of PINDP formation. UV−vis spectral studies show that Co(II)TPP(Py) is completely regenerated after the polymerization. The kinetically observed exponent value (0.5) of Co(II)TPP(Py) indicates that two radicals are generated in the initiation step.

Comparison between the R_p of Co(II)TPP(Py) and AIBN Initiated Polymerization. The overall activation energy (E_a = 9.3 kcal/mol) of the polymerization was determined from the Arrhenius equation using experimental data at different temperatures (Table 1). Figure 3 shows that the rate of polymerization using Co(II)TPP(Py) is higher than the conventional

Scheme 1. Elementary Steps of the Co(II)TPP(Py)-Catalyzed Oxidative Polymerization of Indene



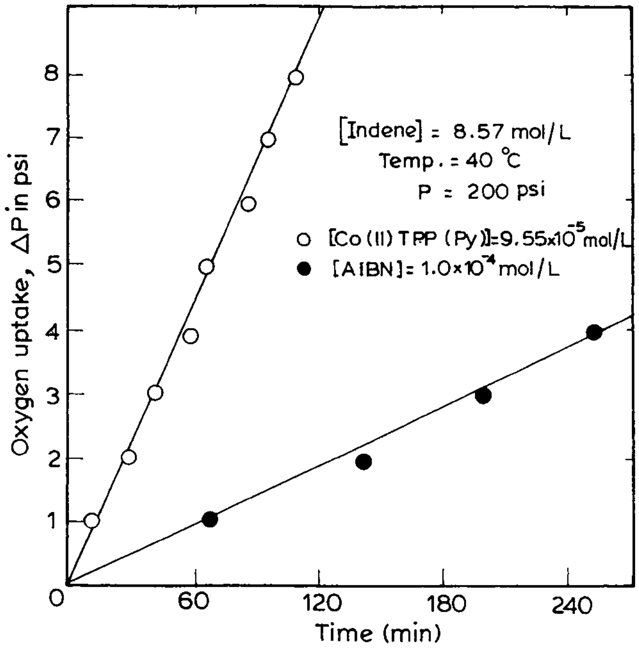


Figure 3. Oxygen consumption, ΔP, verses time for the polymerization of indene in the presence of Co(II)TPP(Py) and AIBN.

AIBN-initiated polymerization. This is because, at the temperature used, the Co(II)TPP(Py) produces radicals capable of initiating more readily than does AIBN.

Comparison of the Stability of PINDP with Other Vinyl Polyperoxides. The thermal stability of PINDP was evaluated by thermogravimetric analysis under a nitrogen atmosphere as reported earlier for poly(styrene peroxide) (PSP), poly(methyl methacrylate peroxide) (PMMAP) and poly(α-methyl styrene peroxide) (PAMSP).[15] The decomposition kinetics were studied in isothermal degradation mode at 85 °C. The polyperoxides in isothermal condition showed a continuous weight loss with time (Figure 4), suggesting a unique process without any side reactions. The rate of isothermal degradation of each polyperoxide (Table 3) was determined from the slope of weight versus time plot (Figure 4). From Table 3, PINDP is evidently the most stable vinyl polyperoxide. In addition to this, other vinyl polyperoxides (i.e., PSP, PMMAP, PAMSP, etc.)

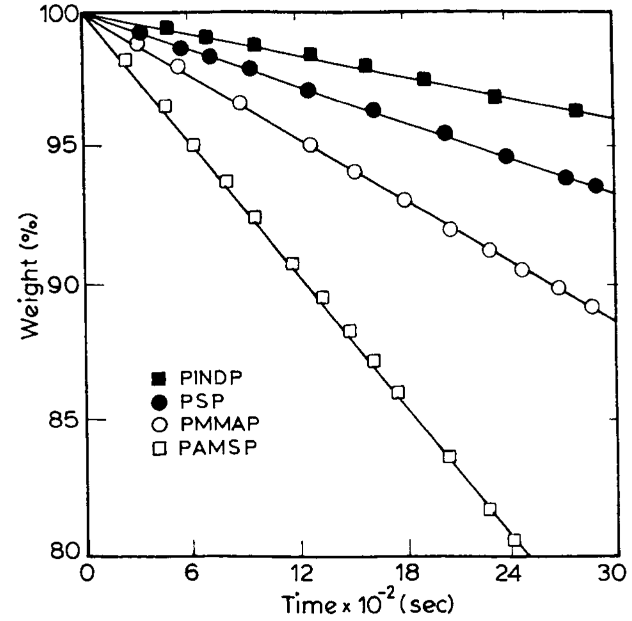


Figure 4. Isothermal TG thermograms of various polyperoxides at 85 °C: weight of each compound = 10 mg.

Table 3. Isothermal Degradation Rate of Various Polyperoxides at 85 °C

polyperoxide	degradation rate × 10^3 (wt %/s)
PINDP	1.2
PSP	2.6
PMMAP	3.3
PAMSP	8.0

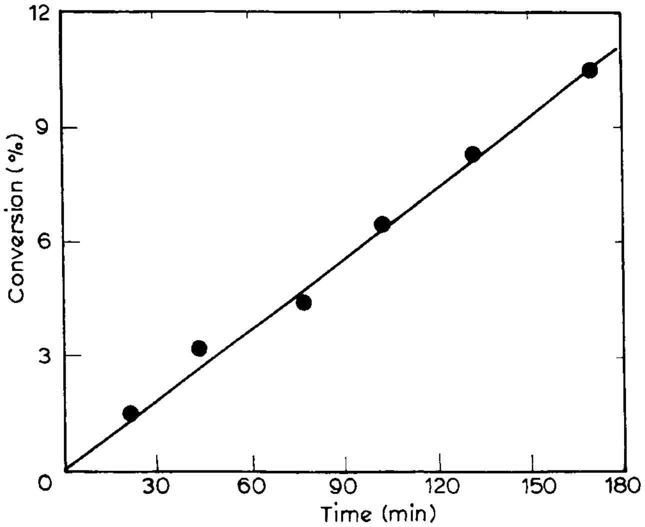


Figure 5. Conversion versus time plot for the polymerization of styrene at 80 °C initiated by PINDP: [PINDP] = 0.02 mol equiv/L, [STY] = 8.69 mol/L.

are gummy liquids and difficult to handle quantitatively. They also undergo slow degradation at room temperature. These polyperoxides are very difficult to store for long periods of time. In contrast, PINDP is a solid polymer that can be stored for a longer period of time (due to its low rate of degradation) and is easy to handle.

Kinetics of Radical Polymerization of Styrene using PINDP as a Peroxide Macroinitiator. To study the polymerization of STY using PINDP as an initiator, STY was polymerized in bulk and in solution at 80 °C. The polymerization proceeds without any induction time. The conversion was kept below 15% for reliable kinetic analysis. The rate of polymerization (R_p) calculated from the slope of conversion (%) versus time plot (Figure 5) and was 1.05×10^{-4} mol L^{-1} s^{-1}. A plot of ln R_p versus ln[PINDP] (Figure 6) yields a straight line, and the slope gives the order of reaction as 0.53 with respect to PINDP. Similarly, a STY monomer exponent of 1.14 is obtained from the slope of ln R_p versus ln[STY] plot (Figure 7). The rate of polymerization of STY is given by eq 11.

$$R_p = K[M]^{1.14}[I]^{0.53} \tag{11}$$

$$\text{showing} \propto [M]^1[I]^{0.5}$$

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

The term $k_p^2(fk_d/k_t)$ is denoted as K^2 and it is a measure of the initiator reactivity;[28] f and k_d are, respectively, the initiator efficiency and decomposition rate constant of an initiator. For STY polymerization using PINDP, the value of K^2 calculated from the slope of the plot of R_p^2 versus $[M]^2[I]$ (Figure 8) is 7.10×10^{-9} L mol^{-1} s^{-2}. In the case of PINDP, 1 mol equiv is the equivalent weight in grams of the repeat unit. The value of K^2 of PINDP is comparable to the value of 2,5-dimethyl-2,5-dihydroperoxyhexane (6.00×10^{-9} L mol^{-1} s^{-2})[29] and ditertiarybutylperoxide (1.93×10^{-10} L mol^{-1} s^{-2}).[30] This suggests that PINDP may be used as a high-temperature initiator.

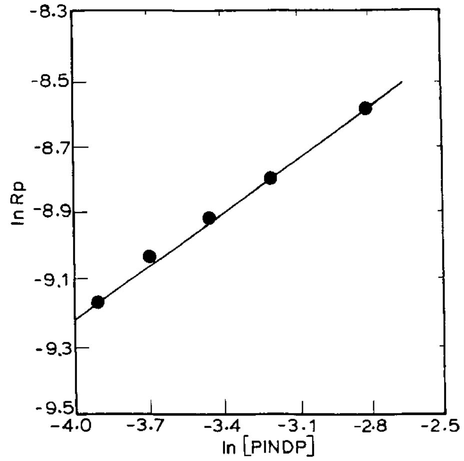


Figure 6. Dependence of R_p on PINDP concentration for styrene polymerization at 80 °C: [STY] = 8.69 mol/L.

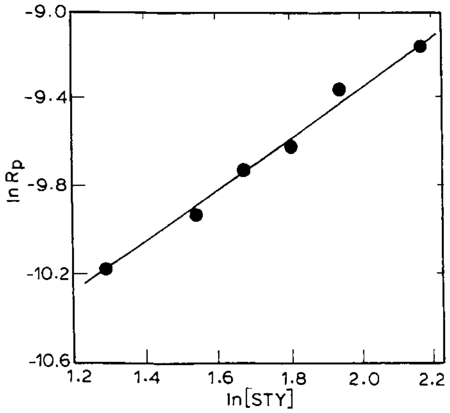


Figure 7. Dependence of R_p on styrene concentration for the polymerization at 80 °C: [PINDP] = 0.02 mol equiv/L.

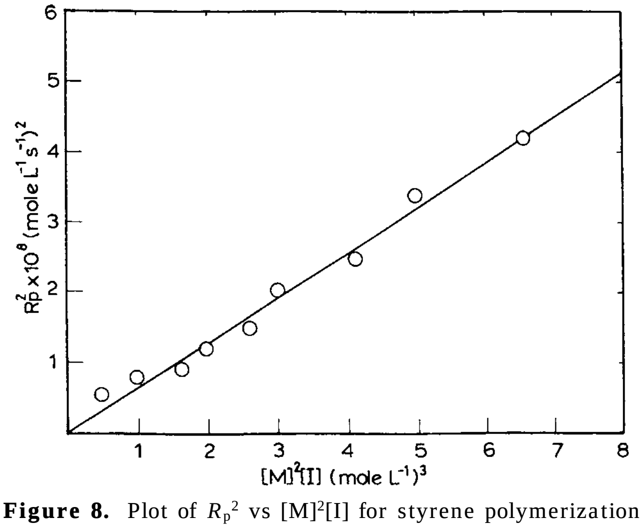


Figure 8. Plot of R_p^2 vs $[M]^2[I]$ for styrene polymerization initiated by peroxide macroinitiator, PINDP: [PINDP] = 0.01–0.15 mol equiv/L, [STY] = 1.52–8.69 mol/L, temperature = 80 °C, time = 2 h.

Characterization of Polystyrene (PS). ^{1}H NMR of PS prepared using 0.02 mol equiv L^{-1} of PINDP did not exhibit the signals corresponding to the PINDP segments. To introduce peroxy segments in the chain, we have prepared PS using 0.1 mol equiv L^{-1} PINDP. The polymer product was purified by repeated precipitation from methanol. The presence of peroxy segments in the resultant polymer chain was confirmed by ^{1}H NMR studies. In the ^{1}H NMR spectrum (Figure 9), the signals at 1.42, 1.84, and 6.4–7.2 ppm correspond to the $-CH_2-$, $>CH-$, and Ar$-H$ of PS, respectively, and the peaks at 2.8–3.2, 5.1, 5.6, and 7.0–7.5 ppm are assigned

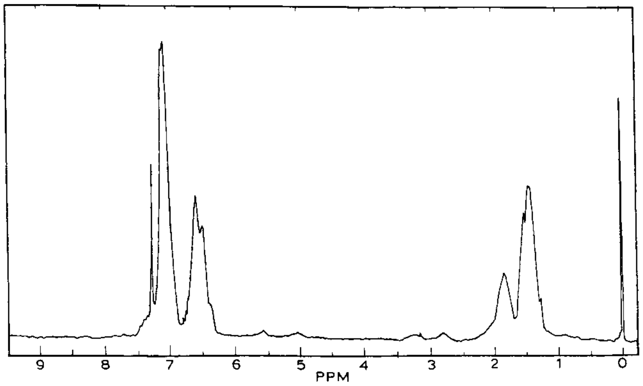


Figure 9. ^{1}H NMR spectrum of styrene prepared using 0.1 mol equiv/L of PINDP.

to $-\mathrm{C}H_2-$, $>\mathrm{C}H-\mathrm{CH}_2-$, $>\mathrm{C}H-\mathrm{Ar}$, and $\mathrm{Ar}-H$ of the PINDP segments, respectively. This active PS (i.e., PS containing PINDP segments) was decomposed in chlorobenzene at 125 °C for 20 h. The $\bar{M}_n$ values before and after decomposition were 1.2×10^5 and 1.1×10^5, respectively, confirming the incorporation of peroxy segments in the chain ends of PS. Otherwise, the molecular weight would have significantly decreased.

Conclusion

Co(II)TPP(Py) is an efficient dioxygen carrier as well as an initiator for the polymerization of indene compared to the conventional free radical initiator AIBN. Polymeric peroxide having narrow polydispersity was conveniently prepared at lower temperature. This technique may be exploited for new vinyl polyperoxides, which are otherwise difficult to synthesize due to their inherent thermal instability. Since Co(II)TPP(Py) mimics the role of hemoglobin or hemocyanin, it could have impact in the field of biology.[31,32]

PINDP is highly stable thermally compared to other vinyl polyperoxides. Unlike other vinyl polyperoxides, which are gummy liquids that are difficult to handle quantitatively and generally stored in cold, PINDP, which is a solid polymer and therefore easy to handle, can be safely stored at room temperature. PINDP can be used for polymerizing STY at higher temperatures. Active PS containing peroxy segments in the chain ends was also synthesized.

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