Macromolecules **2002,** *35,* 6505−6510 **6505**

Catalytic Oxidative Polymerization of 1,1-Diphenylethylene at Ambient Temperature and Potential Application of Peroxide Macroinitiator[†]

Ajaya Kumar Nanda*,[‡] and Kausal Kishore

Department of Polymer Science and Engineering, University of Massachusetts,
Amherst, Massachusetts 01003-4530, and Department of Inorganic and Physical Chemistry,
Indian Institute of Science, Bangalore 560012, India

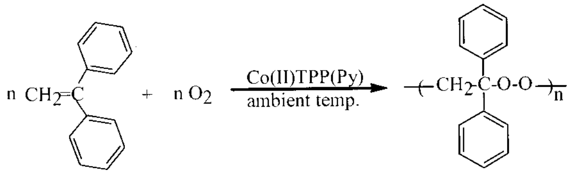
Received June 11, 2001; Revised Manuscript Received May 21, 2002

ABSTRACT: The Co(II)TPP(Py) complex was used as an efficient dioxygen carrier for the radical polymerization of 1,1-diphenylethylene (DPE), which has a low ceiling temperature, at ambient temperature and low oxygen pressure. The mechanism of polymerization is discussed on the basis of kinetic data, UV−vis, ESR, and ^{1}H NMR studies. The rate of polymerization (R_p) and number-average molecular weights (M_n) of poly(1,1-diphenylethylene peroxide) (PDPEP) are higher and the polydispersity is lower than in 2,2′-azobis(isobutyronitrile) (AIBN) initiated polymerization. PDPEP was further used as a macroinitiator for the polymerization of MMA. The polymerization obeys classical kinetics. The K^2 value of the PDPEP has been determined from the slope of R_p^2 vs $[M]^2[I]$, which reveals that it can also be used at higher temperature for the polymerization. An "active" PMMA was also synthesized, containing initiating segments in the polymer backbone.

Introduction

The transition-metal-based radical polymerization is versatile for various vinyl monomers in the synthesis of tailor-made polymers.[1−17] One can precisely control radical polymerization of such monomers by using metal complexes of Fe,[1−3] Co,[4−7] Ni,[8,9] Cu,[10−14] and Ru.[15−17] The metal-based systems are some of the most efficient techniques to generate polymers with narrow polydispersity.

Vinyl polyperoxides[18−21] degrade highly exothermically,[22−25] in contrast to common polymers, which degrade endothermically. They are receiving increased attention due to their physicochemical behavior such as autopyrolyzability,[26,27] autocombustibiliy,[28] speciality fuels,[26] coating and molding applications,[29] and their role as base-catalyzed initiators.[30−33] 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 above 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.[34,35] We are continuing to develop the polymerization at ambient temperature in order to suppress their degradation. The vinyl monomer, 1,1-diphenylethylene (DPE), does not homopolymerize thermally or by adding a free radical initiator due to its low ceiling temperature. However, we present here the first oxidative radical polymerization of DPE, which was achieved at ambient temperature and low oxygen pressure. Exposure of a homogeneous solution of DPE containing cobalt(II) tetraphenylporphyrin−pyridine complex [Co(II)TPP(Py)] as reversible oxygen carrier to O_2 produces an alternating copolyperoxide, poly(1,1-diphenylethylene peroxide) (PDPEP) (eq 1).



(1)

The kinetics and mechanism of the polymerization of DPE using Co(II)TPP(Py) will be discussed and compared with a conventional polymerization using free radical initiator, 2,2′-azobis(isobutyronitrile) (AIBN). In addition, the synthesis and kinetics of the polymerization of methyl methacrylate (MMA) were carried out using the new initiating system. The formation of the "active" poly(methyl methacrylate) (PMMA) will be discussed.

Experimental Section

Materials. DPE (97%, Aldrich) was used after distillation under reduced pressure. MMA (95%, Ranbaxy) was freed from inhibitor by washing with 5% aqueous NaOH and then with distilled water several times. After drying over anhydrous Na_2SO_4, it was distilled under reduced pressure. Co(II)TPP (99%, Aldrich) was used as received. The synthesis of Co(II)TPP has been described elsewhere.[36,37] 2,2′-Azobis(isobutyronitrile) (AIBN) (98%, Koch Light) was recrystallized thrice from methanol. Chloroform (98%, Ranbaxy) was purified by passing it through a column of activated alumina (4 ft long by 1.75 in. diameter at a flow rate of 3 mL/min), refluxed over 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 concentrated H_2SO_4, then 10% H_2SO_4, and concentrated $KMnO_4$ until the permanganate color persists. The mixture was washed with water, aqueous 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.[38]

Preparation of Co(II)TPP(Py) Complex. The Co(II)TPP(Py) complex[36,37] was prepared by mixing solutions of equiva-

---

[†] This paper is dedicated to the memory of Professor Kausal Kishore.

[‡] University of Massachusetts, Amherst.

10.1021/ma0110148 CCC: $22.00

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

Oxidative Polymerization of DPE. A solution of Co(II)TPP(Py) (1.68 mg, 2.5 μmol) in DPE (10 mL, 56 mmol) was charged in a 300 mL Parr reactor (Parr Instrument Co.) equipped with a digital pressure transducer, temperature controller, and mechanical stirrer and pressurized with O_2. The reaction was carried out (i) at different temperatures (30, 35, 40, 50, and 60 °C), maintaining a constant pressure (100 psi), and (ii) at different pressures (25, 50, 100, 150, 200, 250, 300, 350, 400, and 500 psi), keeping the temperature constant (40 °C). Also, the polymerization of DPE (2.26 mol/L) was conducted using AIBN (1.0×10^{-4} mol/L) at different pressures (25−500 psi) at constant temperature (40 °C). The reaction was carried out with constant stirring, and the polymerization time was kept at 5 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) were calculated from the slope of the oxygen uptake vs time plot. A 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 DPE and Co(II)TPP(Py) were performed under an O_2 pressure of 100 psi at 40 °C. At the end of the reaction, the solution was precipitated by dropwise addition into petroleum ether to give PDPEP as a white solid, yield 5.5%. $\bar{M}_n$(30 °C) = 5.25×10^3 and polydispersity = 1.15. ^{1}H NMR δ 4.43 (−CH_2−), 6.9−7.2 ppm (Ar−H). To analyze the effect of concentration of Py on the rate of polymerization, experiments were carried out by varying the concentration of Py (10^{-3}−10^{-5} mol/L) at constant concentration of Co(II)TPP (10^{-4} mol/L), DPE (2.26 mol/L), O_2 pressure (100 psi), and temperature (40 °C). The yield of PDPEP was calculated gravimetrically (i.e., as weight percent of expected polymer obtained after precipitation and vacuum-drying).

Polymerization of MMA. MMA (2.3 mL, 4.30 mol/L) and PDPEP (15.9 mg, 0.015 mol equiv/L in chlorobenzene (2.7 mL) was degassed by three freeze−pump−thaw cycles and then heated at 80 °C for 1 h to effect low conversion (15%) for reliable kinetic analysis The rate of polymerization (R_p) was calculated from the slope of the conversion vs time plot. Experiments with different concentrations of MMA and PDPEP were performed at 80 °C. At the end of the reaction, the solution was precipitated by dropwise addition into methanol to give poly(methyl methacrylate) (PMMA) as a white solid, yield 11.7%. $\bar{M}_n = 1.9 \times 10^5$. ^{1}H NMR δ 0.8−1.1 (−CH_3), 1.89 (−CH_2−), and 3.65 ppm (−OCH_3).

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−vis studies were performed at room temperature on a Hitachi instrument, model U-3400. The spectra of the Co(II)TPP(Py) complex in DPE was recorded before and after the polymerization reactions. The ESR spectra were recorded at 77 K on a X-band Varian E 109 spectrometer. For recording ESR spectra of Co(II)TPP(Py)$^-$OO$^\bullet$, the catalyst solution in CH_2Cl_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 were 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 comprised of 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 μm columns (10^4, 10^3, 500, and 100 Å) (Polymer Laboratories Ltd., Shropshire, UK). 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 of PDPEP and PMMA were calculated using polystyrene and poly(methyl methacrylate) standards, respectively. The software used for the calculations was PL caliber version 7.04 (Polymer Laboratories Ltd., UK).

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

temp (°C)	$R_p \times 10^1$ (mol/(L h))	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
30	0.151	5.25	1.15
35	0.253	4.81	1.18
40	0.323	4.53	1.22
50	0.515	3.67	1.38
60	0.922	2.59	1.60

[a] [DPE] = 2.26 mol/L, [Co(II)TPP(Py)] = 1.0×10^{-4} mol/L and oxygen pressure = 100 psi.

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

[DPE] (mol/L)	[CoTPP(Py)] $\times 10^4$ (mol/L)	O_2 (psi)	$R_p \times 10^1$ (mol/(L h))	[PDPEP] (mol/L)	k_a (L/(mol h))
2.26	0	100	0	0	0
0.68	10.0	100	0.049	0.021	0.923
1.13	10.0	100	0.113	0.042	0.915
1.59	10.0	100	0.181	0.112	0.896
2.26	10.0	100	0.323	0.224	0.903
3.39	10.0	100	0.587	0.449	0.938
2.26	4.45	100	0.214	0.143	0.930
2.26	5.35	100	0.235	0.159	0.912
2.26	6.72	100	0.263	0.180	0.907
2.26	8.67	100	0.299	0.202	0.911
2.26	11.22	100	0.340	0.242	0.899
2.26	13.81	100	0.377	0.251	0.943
2.26	17.25	100	0.422	0.297	0.922
2.26	21.32	100	0.469	0.335	0.936
2.26	10.0	25	0.319	0.220	0.932
2.26	10.0	50	0.322	0.226	0.929
2.26	10.0	100	0.323	0.224	0.903
2.26	10.0	150	0.320	0.219	0.897
2.26	10.0	200	0.326	0.224	0.938
2.26	10.0	250	0.324	0.222	0.925
2.26	10.0	300	0.323	0.225	0.919
2.26	10.0	350	0.322	0.221	0.917
2.26	10.0	400	0.325	0.226	0.934
2.26	10.0	500	0.324	0.226	0.933

[a] Temperature = 40 °C, reaction time = 5 h, and diluent = chlorobenzene $k_a = k_{p1}(k_i/k_t)^{1/2}$.

Results and Discussion

Molecular Weights. The $\bar{M}_n$ and polydispersity values of PDPEP 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 slowly,[25] which facilitates various chain transfer reactions,[35,39] resulting in the formation of low molecular weight polymers with broader polydispersity.

Kinetics of Polymerization. The oxidative polymerization of DPE with varying monomer (M) and catalyst concentrations and O_2 pressure is presented in Table 2. In the presence of O_2, the Co(II)TPP(Py) complex exists as a 1:1 oxygen adduct.[40] Since the polymerization does not occur in the absence of Co(II)TPP(Py) (Table 2, blank run), the initiation evidently involves addition of O_2 adduct to DPE, producing free radicals. To probe the free radical mechanism, the polymerization was conducted using a free radical inhibitor, hydroquinone (HQ) (0.62 mol/L) (Figure 1). The polymerization starts after an induction period of 60 min. However, the rate of polymerization after an induction period was similar to the rate of polymerization conducted without adding HQ. These results indicate that Co(II)TPP(Py) is not inhibited/deactivated by HQ. Hence, the chain transfer reactions of the Co

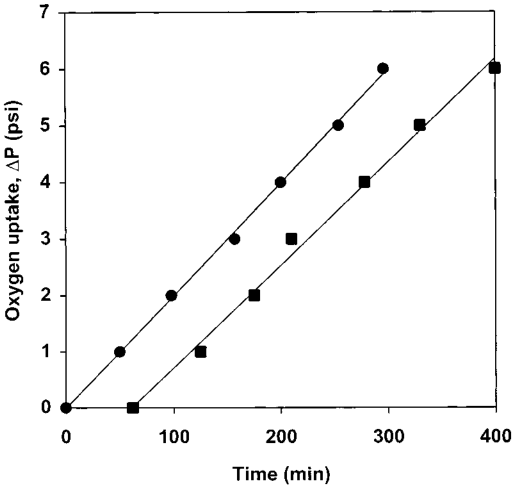


Figure 1. Effect of hydroquinone on the oxidative polymerization of DPE ([DPE] = 2.26 mol/L, [Co(II)TPP(Py)] = 1.0 × 10^{-4} mol/L, temperature = 40 °C, pressure = 100 psi): (●) in the absence of hydroquinone; (■) in the presence of hydroquinone (0.62 mol/L).

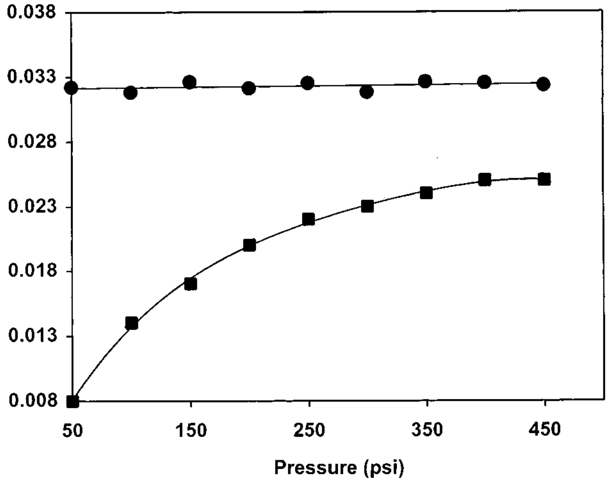
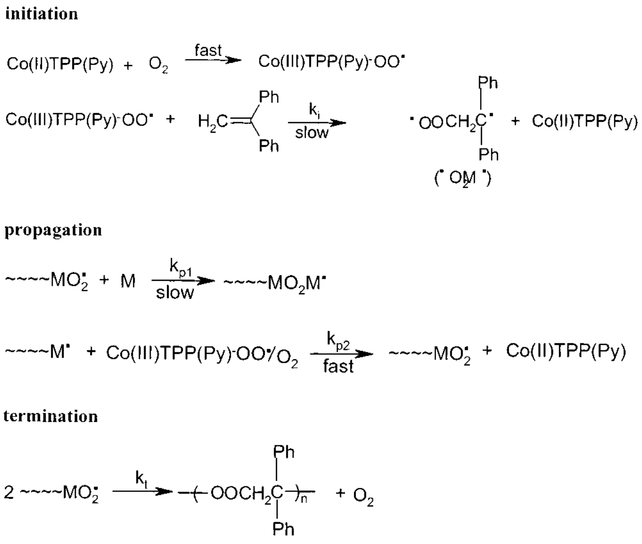


Figure 2. Dependence of R_p on Co(II)TPP(Py)-catalyzed and AIBN-initiated polymerization at different pressures ([DPE] = 2.26 mol/L, temperature = 40 °C): (●) [Co(II)TPP(Py)] = 1.0 × 10^{-4} mol/L; (■) [AIBN] = 5.0 × 10^{-4} mol/L.

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



complex to HQ do not take place under these experimental conditions. However, chain transfer reactions presumably take place from the propagating peroxy radicals to HQ.

A plot of ln R_p vs ln[Co(II)TPP(Py)] yields a straight line (using the data of catalyst variation experiments, Table 2), and the slope indicates that the order of the reaction was close to 0.5 with respect to Co(II)TPP(Py). Similarly, a monomer exponent of 1.5 was obtained from the slope of ln R_p vs 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

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

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

The AIBN-initiated oxidative polymerization of DPE shows a significant pressure effect (Figure 2), and the rate becomes independent of O_2 pressure only after 350 psi. Similar behavior has been observed during oxidative polymerization of α-methylstyrene (AMS) in the presence of AIBN at 40 °C.[39] Interestingly, the oxidative polymerization of DPE in the presence of Co(II)TPP(Py) is independent of O_2 pressure (Figure 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.[40] 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 (Figure 2), suggesting that the dissolved O_2 concept is not applicable here. Hence, it is most likely that Co(II)TPP(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 the Co(II)TPP(Py) adduct in the monomer remains unaffected and has the same absorbance after the polymerization reaction. This indicates that Co(III)TPP(Py)$^-$OO• regenerates Co(II)TPP(Py) after an electrophilic addition reaction with the monomer and that Co(II)TPP(Py) is not consumed or undergoes irreversible oxidation under the present reaction condition.

ESR Studies. The g_{av} value[41] from ESR analysis of neat Co(II)TPP(Py)$^-$OO• was 2.017, which is close to the reported g value (2.015) for the ROO• radical.[42] This indicates that Co(III)TPP(Py)$^-$OO• is formed.

Mechanism of Polymerization. The kinetic analysis, 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• is a fast process (Scheme 1). Hence, the rate of polymerization does not depend on the concentration of O_2 (Figure 2 and Table 2). Therefore, [Co(II)TPP(Py)] ≅ [Co(III)TPP(Py)$^-$OO•].

The generation of the high-spin Co complex in the reaction mixture has been reported earlier.[43–47] Again, we assume that mainly quadratic chain termination taking place between the peroxy radicals.[48–50] The rate of initiation (R_i), rate of propagation (R_p) and the rate of termination (R_t) were determined in the following way.

$$R_i = 2k_i[\mathrm{Co(II)TPP(Py)}][\mathrm{M}] \tag{3}$$

$$R_p = k_{p1}[\mathrm{MOO^\bullet}][\mathrm{M}] \tag{4}$$

$$R_t = 2k_t[\mathrm{MOO^\bullet}]^2 \tag{5}$$

Assuming steady-state approximation

$$R_i = R_t \tag{6}$$

Hence

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

Equation 7 can be rearranged to eq 8.

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

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

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

which is further modified as eq 10.

$$R_p = k_a[\mathrm{Co(II)TPP(Py)}]^{1/2}[\mathrm{M}]^{3/2} \quad \text{where } k_a = k_{p1}(k_i/k_t)^{1/2} \tag{10}$$

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 PDPEP formation. UV–vis spectral studies showed 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.

Effect of Axial Base, Py. The effect of the concentration of axial base, Py, on the polymerization rate is presented in Figure 3. The elementary reactions for the effect of Py concentration on the polymerization are given in Scheme 2 (eqs 11–14).

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

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

$$\mathrm{Co(II)TPP(Py)} + \mathrm{Py} \longrightarrow \mathrm{Co(II)TPP(Py)_2} \tag{12}$$

$$\mathrm{Co(II)TPP(Py)} + \mathrm{O_2} \longrightarrow \mathrm{Co(III)TPP(Py)\text{-}OO^\bullet} \tag{13}$$

$$\mathrm{Co(II)TPP} + \mathrm{O_2} \longrightarrow \mathrm{Co(III)TPP\text{-}OO^\bullet} \tag{14}$$

Case I: When the concentration of Py equals that of Co(II)TPP, reactions represented by eqs 11 and 13 are favored, and hence the rate of polymerization reaches a maximum.

Case II: When the concentration of Py is greater than the concentration of Co(II)TPP, reactions described by eqs 11–13 occur. According to eq 12, some of the catalysts will have Py at both axial sites 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 Co(II)TPP, the O_2 absorption takes place predominately according to reactions represented by eqs 13 and 14. It may appeared that, in the absence of Py (eq 14), the complex is less effective at absorbing O_2. Consequently, the overall rate of polymerization is lower.

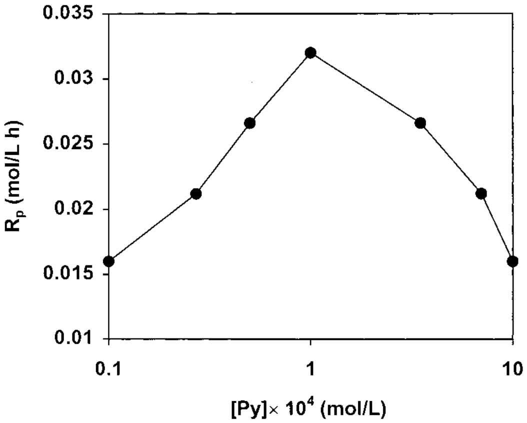


Figure 3. Dependence of R_p on the concentration of Py for the polymerization of DPE in the presence of Co(II)TPP. [DPE] = 2.26 mol/L, [Co(II)TPP] = 1.0×10^{-4} mol/L, temperature = 40 °C, pressure = 100 psi.

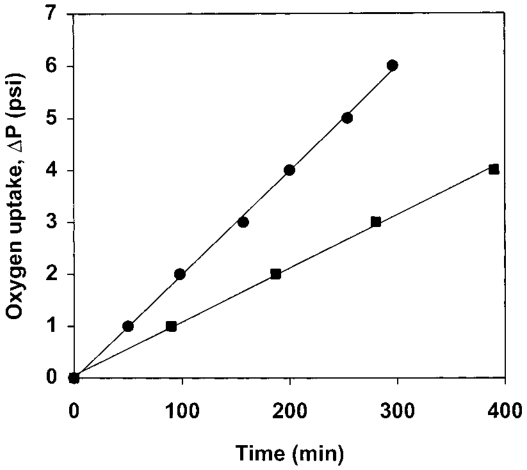


Figure 4. Oxygen consumption, ΔP, vs time for the polymerization of DPE in the presence of Co(II)TPP(Py) and AIBN ([DPE] = 2.26 mol/L, temperature = 40 °C, pressure = 100 psi): (●) [Co(II)TPP(Py)] = 1.0×10^{-4} mol/L; (■) [AIBN] = 1.0×10^{-4} mol/L.

Comparison of the R_p of Co(II)TPP(Py) and AIBN-Initiated Polymerization. The overall activation energy (E_a = 10.1 kcal/mol) of the polymerization was determined from the Arrhenius equation using experimental data at different temperatures (Table 1). Figure 4 shows that the rate of polymerization using Co(II)TPP(Py) is higher than the conventional 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.

Physical Nature of Vinyl Polyperoxides. Other vinyl polyperoxides, namely, poly(styrene peroxide) (PSP), poly(methyl methacrylate peroxide) (PMMAP), and poly(α-methylstyrene peroxide) (PAMSP) (i.e., PSP, PMMAP, PAMSP, etc.), are slightly yellow, gummy liquids that are difficult to handle quantitatively. The yellow coloration is due to degradation products produced slowly at room temperature. These polyperoxides are very difficult to store for long periods of time. In contrast, PDPEP is a white solid powder polymer that can be stored for a longer period of time and is easy to handle.

Kinetics of Radical Polymerization of MMA Using PDPEP as a Peroxide Macroinitiator. To study the polymerization of MMA using PDPEP as a

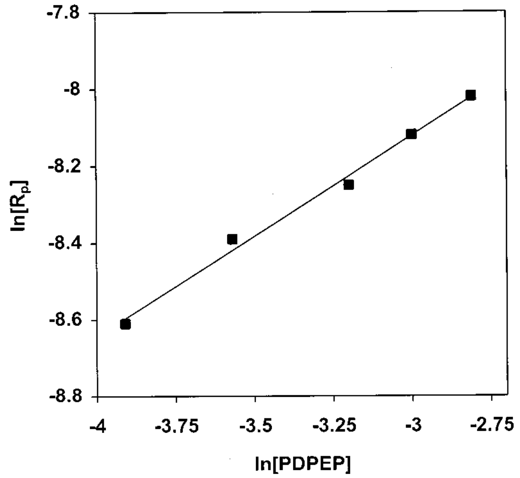


Figure 5. Dependence of R_p on PDPEP concentration for MMA polymerization at 80 °C. [MMA] = 9.35 mol/L.

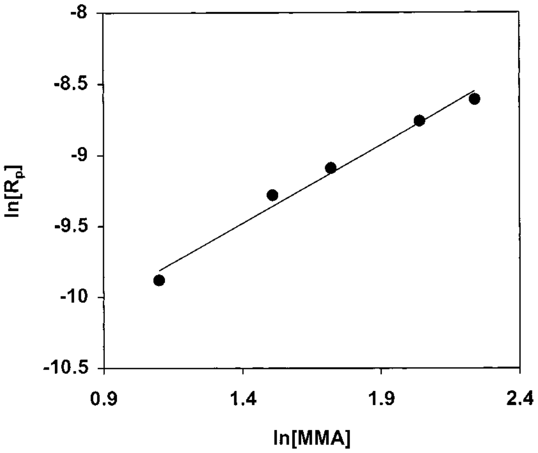


Figure 6. Dependence of R_p on MMA concentration for the polymerization at 80 °C. [PDPEP] = 0.015 mol-equiv/L.

macroinitiator, MMA was polymerized in bulk and in solution at 80 °C. The polymerization proceeds without an induction time. The conversion was kept below 15% for reliable kinetic analysis. The rate of polymerization (R_p) calculated from the slope of the conversion (%) vs time plot was 1.82×10^{-4} mol L^{-1} s^{-1}. A plot of ln R_p vs ln[PDPEP] (Figure 5) yields a straight line, and the slope gives the order of reaction as 0.48 with respect to PDPEP. Similarly, the MMA monomer exponent of 1.07 is obtained from the slope of ln R_p vs ln[MMA] plot (Figure 6). The rate of polymerization of MMA is given by eq 15

$$R_p = K[M]^{1.07}[I]^{0.48} \qquad (15)$$

showing $\propto [M]^1[I]^{0.5}$, where K, [M], and [I] respectively are the overall rate constant, monomer, and initiator concentrations.

The term $k_p^2(fk_d/k_t)$ is denoted as K^2 and is a measure of the initiator reactivity;[51] f and k_d are respectively the initiator efficiency and decmposition rate constant of an initiator. For MMA polymerization using PDPEP, the value of K^2 calculated from the slope of the plot of R_p^2 vs $[M]^2[I]$ (Figure 7) is 9.2×10^{-9} L mol^{-1} s^{-2}. In the case of PDPEP, 1 mol equiv is the equivalent weight in grams of the repeat unit. The value of K^2 of PDPEP is comparable to the value of 2,5-dimethyl-2,5-dihydroperoxyhexane (6.00×10^{-9} L mol^{-1} s^{-2})[54] and di-*tert*-butyl peroxide (1.93×10^{-10} L mol^{-1} s^{-2}).[55] This suggests that PDPEP may be used as a high-temperature initiator.

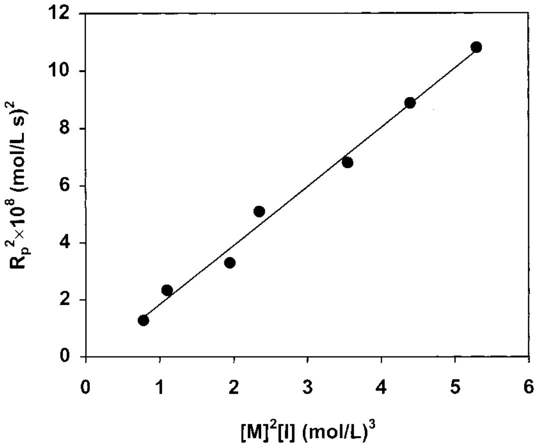


Figure 7. Plot of R_p^2 vs $[M]^2[I]$ for MMA polymerization initiated by peroxide macroinitiator, PDPEP. [PDPEP] = 0.012–0.2 mol equiv/L, [MMA] = 1.5–9.35 mol/L, temperature = 80 °C, and time = 1 h.

Characterization of PMMA. ^{1}H NMR of PMMA prepared using 0.015 mol equiv L^{-1} of PDPEP did not exhibit the signals corresponding to the PDPEP segments. To introduce peroxy segments into the chain, we have prepared PMMA using 0.13 mol equiv L^{-1} PDPEP. 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 the signals at 0.8–1.1 ($-CH_3$), 1.89–2.1 ($-CH_2-$), and 3.65 ppm ($-OCH_3$) correspond to PMMA blocks, and the peaks at 4.43 ($-CH_2-$) and 6.9–7.2 ppm (Ar–H) accorded to PDPEP segments. This "active" PMMA (i.e., PMMA containing PDPEP segments) was decomposed in chlorobenzene at 125 °C for 20 h. The $\bar{M}_n$ values before and after decomposition were 1.9×10^5 and 1.3×10^5, respectively, confirming the incorporation of peroxy segments in the backbone of PMMA.

Conclusion

DPE was radically copolymerized with oxygen using Co(II)TPP(Py) as an ambient temperature initiator. Polymeric peroxide with 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 low ceiling temperature and inherent thermal instability. An extensive look into the biological literature[54–58] could have an impact in the field of polymer science.

Unlike other vinyl polyperoxides, which are gummy liquids that are difficult to handle quantitatively and generally stored in cold, PDPEP, which is a white solid polymer and therefore easy to handle, can be safely stored at room temperature. PDPEP can be used for polymerizing MMA at higher temperatures. "Active" PMMA containing peroxy segments in the chain ends was also synthesized.

Supporting Information Available: Plots of ln R_p vs ln[Co(II)TPP(Py)] and ln R_p vs ln[M], ESR spectrum of Co(III)-TPP(Py)$^-$OO$^\bullet$ for the oxidative polymerization of DPE, conversion (%) vs time plot for the polymerization of MMA, ^{1}H NMR spectrum of "active" PMMA, and GPC traces of "active" PMMA before and after decomposition. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Matyjaszewski, K.; Wei, M.; Xie, J.; McDermott, N. E. *Macromolecules* **1997**, *30*, 8161.
(2) Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2000**, *33*, 3543.
(3) Louie, J.; Grubbs, R. H. *Chem. Commun.* **2000**, 1479.
(4) Wayland, B. B.; Basickes, L.; Mukerjee, S.; Wei, M.; Fryd, M. *Macromolecules* **1997**, *30*, 8109.
(5) Wayland, B. B.; Poszmik, G.; Mukerjee, S.; Wei, M.; Fryd, M. *J. Am. Chem. Soc.* **1994**, *116*, 7493.
(6) Sadjadi, A. S.; Walter, R. I.; Horwood, J. S. *J. Phys. Chem. A* **1997**, *101*, 9948.
(7) Gridnev, A. A.; Ittel, S. D,; Fryd, M.; Wayland, B. B. *Organometallics* **1996**, *15*, 222.
(8) Granel, C.; Dubois, Ph.; Jerome, R.; Teyssie, Ph. *Macromolecules* **1996**, *29*, 8576.
(9) Uegaki, H.; Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1997**, *30*, 2249.
(10) Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.
(11) Wang, J.-S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7901.
(12) Patten, T. E.; Xia, J.; Abernathy, T.; Matyjaszewski, K. *Science* **1996**, *272*, 866.
(13) Percec, V.; Barboiu, B. *Macromolecules* **1995**, *28*, 7970.
(14) Haddleton, D. M.; Jasieczek, C. B.; Hannon, M. J.; Shooter, A. J. *Macromolecules* **1997**, *30*, 2190.
(15) Takahashi, H.; Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1999**, *32*, 6461.
(16) Simal, F.; Demonceau, A.; Noels, A. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 538.
(17) Wu, X.; Collins, J. E.; McAlvin, J. E.; Cutts, R. W.; Fraser, C. L. *Macromolecules* **2001**, *34*, 2812.
(18) Bhanu, V. A.; Kishore, K. *Chem. Rev.* **1991**, *91*, 99.
(19) Jayaseheran, J.; Kishore, K. *J. Am. Chem. Soc.* **1998**, *120*, 825.
(20) Nanda, A. K.; Kishore, K. *Macromolecules* **2001**, *34*, 1558.
(21) Nanda, A. K.; Kishore, K. *Macromolecules* **2001**, *34*, 1600.
(22) Kishore, K.; Ravindran, K. *Macromolecules* **1982**, *15*, 1638.
(23) Nanda, A. K.; Kishore, K. *Macromol. Chem. Phys.* **2001**, *202*, 2155.
(24) Nanda, A. K.; Kishore, K. *Eur. Polym. J.* **2001**, *37*, 671.
(25) Jayaseheran, J.; Nanda, A. K.; Kishore, K. *Polymer* **2000**, *41*, 5721.
(26) Kishore, K.; Mukundan, T. *Nature (London)* **1986**, *324*, 130.
(27) Nanda, A. K.; Kishore, K. *Indian J. Chem.* **2000**, *39A*, 624.
(28) Mukundan, T.; Annakutty, K. S.; Kishore, K. *Fuel* **1993**, *72*, 688.
(29) Subramanian, K.; Kishore, K. *Eur. Polym. J.* **1997**, *33*, 1365.
(30) Mukundan, T.; Bhanu, V. A.; Kishore. *J. Chem. Soc., Chem. Commun.* **1989**, *12*, 780.
(31) Nanda, A. K.; Kishore, K. *Polymer* **2001**, *42*, 2365.
(32) Nanda, A. K.; Kishore. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3665.
(33) Nanda, A. K.; Kishore. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 546.
(34) Miller, A. A.; Mayo, F. R. *J. Am. Chem. Soc.* **1956**, *78*, 1017.
(35) Nanda, A. K.; Ganesh, K.; Kishore, K.; Surinarayan, M. *Polymer* **2000**, *41*, 9063.
(36) Rothemund, P.; Menotti, A. R. *J. Am. Chem. Soc.* **1948**, *70*, 1808.
(37) Tezuka, M.; Sekiguchi, O.; Ohnatsu, Y.; Osa, T. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2765.
(38) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; Pergamon Press: New York, 1988.
(39) Kishore, K.; Paramasivam, S.; Sandhya, T. E. *Macromolecules* **1982**, *15*, 1638.
(40) Hamilton, D. E.; Drago, R. S.; Zombeck, A. *J. Am. Chem. Soc.* **1987**, *109*, 374.
(41) Walker, F. A. *J. Magn. Reson.* **1974**, *15*, 201.
(42) Surynarayana, D.; Kevan, L. *J. Phys. Chem.* **1982**, *86*, 2092.
(43) Khenkin, A. M.; Weiner, L.; Wang, Y.; Neumann, R. *J. Am. Chem. Soc.* **2001**, *123*, 8531.
(44) Emanuel, N. M.; Denisov, E. T.; Maizus, Z. K. *Liquid-Phase Oxidation of Hydrocarbons*; Plenum: New York, 1967.
(45) Mayo, F. R. *Acc. Chem. Res.* **1968**, *1*, 193.
(46) Howard, J. A. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2, p 3.
(47) Betts, J. Q. *Rev. Chem. Soc.* **1971**, *25*, 265.
(48) Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1965**, *43*, 2737.
(49) Kishore, K.; Murthy, K. S. *Proc. Indian Natl. Sci. Acad.* **1996**, *62A* (2), 163.
(50) Nanda, A. K. *Macromol. Chem. Phys.*, submitted.
(51) Tobolsky, A. V.; Baysal, B. M. *J. Polym. Sci.* **1953**, *11*, 471.
(52) Baysal, B. M.; Bayramli, E.; Yuruk, H.; Hazar, B. *Makromol. Chem.* **1985**, *186*, 1269.
(53) Offenbach, J. A.; Tobolsky, A. V. *J. Am. Chem. Soc.* **1957**, *79*, 258.
(54) Davis, M. B. *Coord. Chem. Rev.* **1996**, *1*, 152.
(55) Neumann, R.; Dahan, M. *Nature (London)* **1997**, *388*, 353.
(56) Ortiz de Montanello, P. *Cytochrome P-450;* Marcel Dekker: New York, 1986.
(57) Meunier, B. *Chem. Rev.* **1992**, *92*, 1411.
(58) Nanda, A. K. *Biomacromolecules*, submitted.

MA0110148