Polym. Bull. (2012) 69:149–161
DOI 10.1007/s00289-011-0697-3

ORIGINAL PAPER

Kinetic and thermochemical study of the oxidative polymerization of α-substituted styrenes

Sunirmal Pal · Pradip Kr. Ghorai · Priyadarsi De

Received: 23 July 2011 / Revised: 1 December 2011 / Accepted: 28 December 2011 /

Abstract This article reports a systematic kinetic study on the oxidative polymerization of α-substituted styrene monomers such as styrene (St), α-methylstyrene (AMS), 4-chloro α-methylstyrene (CAMS), and α-phenylstyrene (APS) in the presence of 2,2′-azobisisobutyronitrile as a free radical initiator at 100 psi oxygen pressure and 40-50 °C in toluene. The rate of oxidative polymerization follows the order: APS $>$ CAMS $>$ AMS $>$ St. Theoretical calculations have been performed using density functional theory to support the order of oxidative polymerization rates. In addition, the synthesis and characterization of poly(4-chloro α-methylstyrene peroxide) (PCAMSP) is reported here for the first time. Elemental analysis and nuclear magnetic resonance spectroscopy confirm the alternating copolymer structure of PCAMSP with –O–O– bonds in the main chain. Thermal degradation studies using differential scanning calorimeter and thermogravimetric analysis reveal that PCAMSP degrades highly exothermically and the average enthalpy of degradation at various heating rates is found to be 48.7 ± 0.6 kcal/mol, which is of the same order reported for other vinyl polyperoxides.

Keywords Oxidative polymerization · Polyperoxide · Kinetics · Activation energy

Introduction

Radical polymerization of vinyl monomers in the presence of high oxygen pressure is known as oxidative polymerization. The main product of oxidative polymerization is polyperoxide, an alternating copolymer of vinyl monomer and molecular

---

S. Pal · P. Kr. Ghorai · P. De (✉)
Department of Chemical Sciences, Indian Institute of Science Education and Research-Kolkata,
Nadia, Mohanpur 741252, West Bengal, India
e-mail: p_de@iiserkol.ac.in

oxygen [1–3]. Polyperoxide finds importance as polymeric radical initiators [4–6] for vinyl monomers in the synthesis of homopolymers, block copolymers, etc. Their importance as curators in coating and molding applications has been established [7]. Polyperoxides degrade highly exothermically in contrast to common polymers, and exhibit unusual phenomenon of auto-pyrolysis indicating its potential use as an autocombustible fuel [8]. Recently, degradable polyperoxides by the radical alternating copolymerization of 1,3-diene monomers with molecular oxygen at an atmospheric pressure are reported [9–14]. Application of polyperoxides from 1,3-diene monomers for dismantlable adhesion has been established [15]. For industrial and commercial applications, it is desirable that polyperoxides should be made easily and in large quantities, which cannot be achieved unless and until we know the reaction kinetics (i.e., the rate of polymerization, activation energy, etc.) of the oxidative polymerization process. So, we have decided to develop a reactivity scale for the various vinyl monomers toward oxidative polymerization by studying reaction kinetics.

In the literature, the effect of oxygen pressure on the oxidation of styrene (St) [16], α-methyl styrene (AMS) [17], and oxidative copolymerization [18] of St with AMS has been studied in detail. However, there is no systematic study for the kinetics of oxidative polymerization of styrenic monomers to understand the effect of α-substitution. The rates of oxidative polymerization reaction should depend on substitution group present in the monomer. The electronic nature of the α-substituent in the vinyl monomer determines the stability of propagating radicals in the propagation step. In this study, we report the first systematic study on the kinetics of oxidative polymerization of α-substituted styrene monomers such as St, AMS, 4-chloro α-methylstyrene (CAMS), and α-phenylstyrene (APS) in the presence of a free radical initiator 2,2′-azobisisobutyronitrile (AIBN) at 40–50 °C and 100 psi oxygen pressure. From kinetic studies, we have determined rate of polymerization, activation energy (E_a), and various thermodynamic parameters such as enthalpy of activation ($\Delta H^{\#}$), entropy of activation ($\Delta S^{\#}$), and Gibbs free energy of activation ($\Delta G^{\#}$). Experimental rates of oxidative polymerizations have been supported by density functional theory (DFT) calculations.

Experimental

Materials

St (Sigma, 99+%), α-methylstyrene (AMS, Sigma, 98%), CAMS (Sigma, 98%), and APS (Sigma, 97%) were passed through a column of basic alumina prior to polymerization to remove the antioxidant/inhibitor. The AIBN (Sigma, 98%) was recrystallized twice using methanol. Anhydrous toluene (Sigma, 99+%), and $CDCl_3$ (Cambridge Isotope, 99% D) were used as received. The oxygen used was of high purity (BOC, 99.9%). The solvents, petroleum ether (boiling range, 60–80 °C), chloroform, etc., were purified by standard procedures.

Polymerizations

The kinetics of oxidative polymerizations were studied at 100 psi oxygen pressure using 2 mol L^{-1} monomer solution in toluene in the presence of AIBN (0.02 mol L^{-1}) as radical source in a Parr reactor (Parr Instrument Co., USA) equipped with a digital pressure transducer, temperature controller, and mechanical stirrer. The polymerization reaction was carried out at different temperatures (40, 44, 47, and 50 °C) with mechanical stirring (220 rpm), maintaining the pressure constant (100 psi). For the reliable kinetic analysis, conversion was kept below 15%. The O_2 consumption was measured as a function of time using a digital pressure transducer. Polyperoxide was separated from the reaction mixture by precipitating it with petroleum ether. They were isolated and purified by repeated precipitation from chloroform solution followed by the removal of the solvent by vacuum drying at room temperature. Caution: The vinyl polyperoxides are not shock- or friction-sensitive, but they should be handled carefully and stored in the dark and in a refrigerator to minimize photo and thermal degradations, respectively.

Instrumentation

The 400 MHz ^1H NMR spectra were recorded on a JEOL, ECS-400 spectrometer in $CDCl_3$ solvent. The FTIR spectrum was recorded on KBr pellets using a Perkin-Elmer RXI spectrometer. Molecular weights and molecular weight distributions of polyperoxides were determined by gel permeation chromatography (GPC) using Waters 515 HPLC pump, Waters 2414 refractive index detector and two columns (Styragel HT4 and Styragel HT3). The eluent was tetrahydrofuran (THF) at 30 °C and the flow rate was 0.3 mL/min. Narrow molecular weight polystyrene standards were used to generate the calibration curve. The elemental analysis was carried out on a Perkin-Elmer Series-II, CHNO/S Analyzer-2400. The thermal analysis was carried out using a Mettler Toledo DSC1 STARe differential scanning calorimeter (DSC) at different heating rates (5, 10, 20, and 40 °C min^{-1}) with sample sizes of $\sim$2–4 mg in N_2 atmosphere. The thermogravimetric analysis (TGA) was accomplished on a Mettler Toledo TGA/SDTA 851e instrument at a heating rate of 10 °C min^{-1} with a sample weight of $\sim$5 mg in N_2 atmosphere.

Computational studies

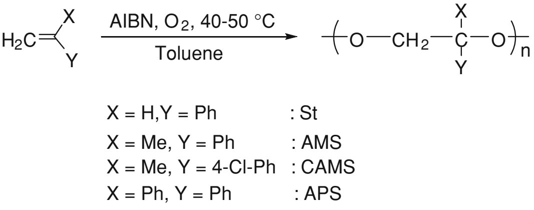
The DFT has been employed as an established and predictive means to understand the effect of α-substitution on the kinetics of oxidative polymerization of styrenic monomers. Geometry optimizations and vibrational frequency analyses were carried out at the level of DFT-based methods as implemented in the electronic structure program Gaussian 03 [19]. We have used the Becke's three parameter hybrid exchange functional [20] combined with the Lee–Yang–Parr non-local correlation function [21] abbreviated as B3LYP. The split-valence basis set with diffuse functions, namely 6-311+G(d), have been employed for all atoms. Vibrational frequencies were calculated for optimized structures to verify that no negative frequency was present for minimum energy structures and one negative frequency for the transition state (TS) structures.

Result and discussion

Synthesis and spectral characterization of the polymers

As shown in Scheme 1, the oxidative polymerizations of four α-substituted styrene monomers have been studied in toluene at different temperatures (40, 44, 47, and 50 °C) maintaining the pressure constant (100 psi). Formation of poly(styrene peroxide) (PSP) was confirmed from ^{1}H NMR spectroscopy in $CDCl_3$, which showed resonance signals at 4.0, 5.3, and 7.2 ppm due to methylene, methine, and aromatic protons, respectively [22]. For poly(α-methylstyrene peroxide) (PAMSP), the signals were at 1.46, 4.16, and 7.2 ppm for methyl, methylene, and aromatic protons, respectively [23]. For poly(α-phenylstyrene peroxide) (PAPSP), the signals were at 4.44 and 6.87–7.25 ppm for methylene and aromatic protons, respectively [24]. However, synthesis and characterization are not reported in the literature for poly(4-chloro α-methylstyrene peroxide) (PCAMSP). The ^{1}H NMR spectrum of PCAMSP in $CDCl_3$ is shown in Fig. 1, which shows signals at δ 1.4, 4.1, and 7.1–7.3 ppm corresponding to methyl protons (3H), methylene protons (2H) and aromatics protons (5H), respectively. No homopolymer impurities could be detected from the ^{1}H NMR spectrum. Elemental analysis was carried out for PCAMSP. The experimental values are C, 58.57%; H, 4.93%; O + Cl, 36.50% in agreement with the calculated values of C, 58.55%; H, 4.91%; O + Cl, 36.54% for $C_9H_9O_2Cl$. The FTIR spectrum of PCAMSP showed a weak characteristic O–O absorption at 895 cm^{-1}. The DSC studies were performed in nitrogen atmosphere at heating rates of 5, 10, 20, and 40 °C/min. The DSC studies reveal that PCAMSP undergoes a highly exothermic and complete degradation. The average enthalpy of degradation (ΔH°_D) at various heating rates was found to be 48.7 ± 0.6 kcal/mol, which is of the same order reported for other vinyl polyperoxides [25]. The activation energy for the degradation (E_d) process was determined from Kissinger's plot [26]. The value of E_d was found to be 38.5 ± 2 kcal/mol (Table 1), which is comparable with the dissociation energy of the O–O bond [27, 28]. The TGA of the PCAMSP was carried out at 10 °C/min and the weight loss occurs in a single step sharply around 122 °C (T_{max}). These studies indicate 1:1 copolymeric structure of PCAMSP.

The number average molecular weight (M_n) values, shown in Table 1, for all polyperoxides were found to be between 4,400 and 5,400 g/mol. The polyperoxides



Scheme 1 General reaction conditions for the oxidative polymerization of styrenic monomers

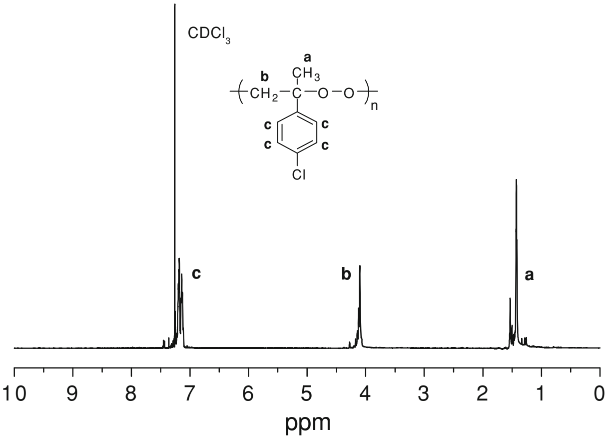


Fig. 1 The ^{1}H NMR spectrum of PCAMSP in $CDCl_3$

Table 1 Characteristics of different polyperoxides synthesized in toluene at 50 °C and 100 psi O_2 pressure

Polymer	Time (h)	Conv. (%)[a]	M_n (g/mol)[b]	PDI[b]	E_d (kcal/mol)[c]
PSP	23	18.0	5300	1.7	38.2 [31]
PAMSP	8	17.4	5100	1.8	33.0 [31]
PCAMSP	6	14.2	4400	1.7	38.5
PAPSP	3	19.5	5400	1.9	45.0 [24]

[a] Monomer conversion as determined by gravimetric analysis on the basis of the amount of monomer charged

[b] Determined by GPC in THF based on polystyrene standards

[c] Calculated from DSC studies

have low M_n due to various chain transfer reactions occurring during oxidative polymerization [29, 30]. The M_n, molecular weight distribution (PDI), and E_d values for different polyperoxides synthesized at 50 °C are shown in Table 1. Relatively broad PDI's are due to conventional free radical nature of the polymerization.

Kinetics of oxidative polymerization

Chemical kinetics, also known as reaction kinetics, includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield of product formation. A detailed examination of the mechanism of oxidative polymerization revealed that the polyperoxides formed during oxygen copolymerization undergo facile degradation above 50 °C [32]. To avoid side reactions, we have studied kinetics of oxidative polymerization at 40–50 °C. Plot of oxygen consumption (Δp) against time for the oxidative polymerization of St, AMS, CAMS, and APS at 50 °C under 100 psi oxygen pressure is shown in Fig. 2. The rate of polymerization (R_p) was calculated from the slope of the Δp against time plot. The rate of oxidative polymerizations of St, AMS, CAMS and APS with varying temperature at constant monomer (2 mol L^{-1}), AIBN (0.02 mol L^{-1}) concentrations, and oxygen pressure (100 psi) are presented in Table 2. During oxidative polymerization, the rate of O_2 consumption [32] is given by earlier reported Eq. 1;

$$-\frac{\mathrm{d}[O_2]}{\mathrm{d}t} = R_\mathrm{p} = \frac{k_\mathrm{p}(k_\mathrm{i})^{0.5}}{(k_\mathrm{t})^{0.5}}[\mathrm{M}][\mathrm{I}]^{0.5} = k_\mathrm{a}[\mathrm{M}][\mathrm{I}]^{0.5} \quad (1)$$

where R_p is the rate of polymerization, and k_p, k_i, and k_t are the propagation, initiation and termination rate constant, respectively. The [M] and [I] are monomer and initiator concentration, and k_a is the overall rate constant for the oxidative copolymerization.

Figure 2 shows that the rates of oxidative polymerization at 50 °C follow the order: APS > CAMS > AMS > St. This result indicates that the rates of oxidative polymerization reaction depend on the substitution group present in the vinyl monomer. Let us now discuss why the rate and yield for AMS are more than those for St. On the basis of the second propagation step (Eq. (iv) in Scheme 2, rate determining step), the reactivity of the $-\mathrm{MO}_2^\bullet$ radical (where M is the monomer) toward the monomer should be compared. The peroxy radical formed from AMS, i.e., [$-CH_2$–(Ph)(CH_3)C–O–$O^\bullet$], is more reactive than the peroxy radical formed from St, [–CH_2–(Ph)CH–O–$O^\bullet$], due to the penultimate effect [32] of the electron-donating methyl group. In addition to the reactivity of $-\mathrm{MO}_2^\bullet$ toward the monomer, we have to also consider the electron richness of the vinyl π bond in the monomer. The electron density is more in AMS than in St due to the presence of electron-donating methyl group; hence, the reactivity of AMS toward $-\mathrm{MO}_2^\bullet$ would be much higher than that of St. Therefore, the R_p for AMS is higher compared to those for St.

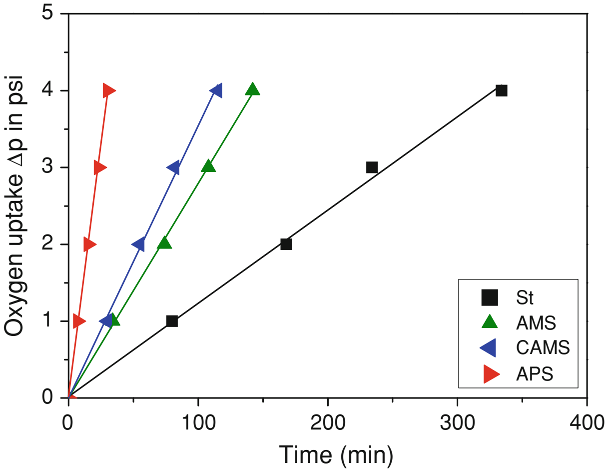


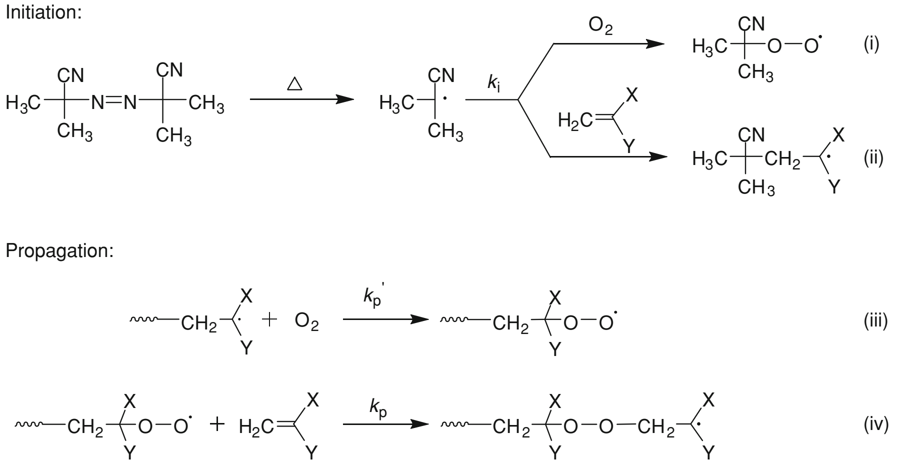
Fig. 2 Plot of oxygen consumption (Δp) against time for the oxidative polymerization of St, AMS, CAMS, and APS at 50 °C under 100 psi oxygen pressure

Table 2 Kinetic data for the oxidative polymerization of α-substituted styrene monomers in the presence of AIBN initiator

Monomer	Temperature (°C)	$R_p \times 10^4$ (psi s^{-1})	$R_p \times 10^7$ (mol L^{-1} s^{-1})	$k_a \times 10^7$ (L mol^{-1} s^{-1})
St	50	1.967	5.052	17.866
	47	1.235	3.203	11.325
	44	0.700	1.832	6.479
	40	0.472	1.251	4.422
AMS	50	5.248	13.483	47.676
	47	2.730	7.079	25.033
	44	2.265	5.929	20.965
	40	1.283	3.402	12.031
CAMS	50	5.885	15.118	53.458
	47	4.872	12.634	44.675
	44	3.160	8.272	29.250
	40	1.992	5.281	18.674
APS	50	14.849	38.149	134.900
	47	12.650	32.805	116.000
	44	9.943	26.029	92.040
	40	7.375	19.553	69.140

[a] [monomer] = 2 mol L^{-1} [AIBN] = 0.02 mol L^{-1}; in toluene at 100 psi oxygen pressure; $k_a = k_p(k_i/k_t)^{1/2}$

The APS has highest R_p due to two phenyl groups present in ethylene, which highly stabilized the $-MO_2^\bullet$ radical. Among AMS and CAMS, the rate of polymerization of CAMS is higher than that of AMS due to extra conjugation of propagating radicals with para substituted Cl group.



Scheme 2 Kinetic scheme (only initiation and propagation reactions) for the oxidative polymerization of vinyl monomers

Activation energy of polymerization

The Δp as a function of time for CAMS oxidation at different temperatures under 100 psi oxygen pressure is shown in Fig. 3. The rate of polymerization of CAMS with O_2 in presence of AIBN initiator at constant pressure increases with increasing temperature. We have determined overall activation energy (E_a) of oxidative polymerization of St, AMS, CAMS, and APS from the Arrhenius plots of ln k_a against $1/T$, which were straight lines (Fig. 4). In presence of AIBN, the PCAMSP formation yields an E_a of 22 kcal/mol. For AIBN-initiated polymerization, $E_i = 30$ kcal/mol is reported [32, 33]. The activation energies for the termination (E_t) for St oxidation is 1.8 kcal/mol [34]. Side reactions during oxidative polymerizations such as chain transfer and termination are minimum since we have studied kinetics below 15% conversion at temperature range 40–50 °C, where degradation of polyperoxide is negligible. When these values are considered, the activation energies for the propagation (E_p) according to Eq. 2 should be 7.9 kcal/mol. Similarly, the E_a values were determined for St, AMS, and APS as 29, 26, and 15 kcal/mol, respectively. The E_p values were calculated as 14.9, 11.9, and 0.9 kcal/mol for St, AMS, and APS, respectively. These results indicate rate of oxidative polymerization is in the order of St < AMS < CAMS < APS.

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

Applying Eyring–Polanyi equation, we determined enthalpy of activation ($\Delta H^{\#}$) and entropy of activation ($\Delta S^{\#}$) for the oxidative polymerization of St, AMS, CAMS, and APS. The general form of Eyring–Polanyi equation;

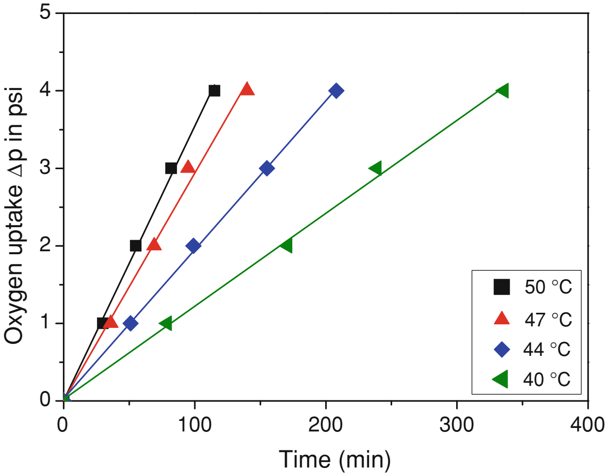


Fig. 3 Oxygen uptake (Δp) as a function of time for CAMS oxidative polymerization at 40–50 °C under 100 psi oxygen pressure

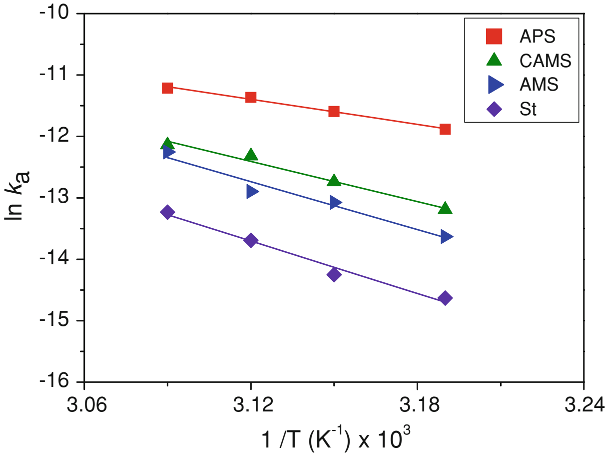


Fig. 4 Plot of ln k_a against 1/T for oxidative polymerizations of St, AMS, CAMS, and APS using AIBN initiator at 100 psi oxygen pressure

$$k_a = \frac{k_B T}{h} \exp\left(\frac{\Delta S^{\#}}{R}\right) \exp\left(-\frac{\Delta H^{\#}}{RT}\right) \tag{3}$$

where k_a is the overall rate constant, k_B is the Boltzmann constant, h is the Plank constant, R is the universal gas constant, and T is the absolute temperature. From the rearranged equation, the plot of ln (k_a/T) against (1/T) should yield a straight line with slope = ($-\Delta H^{\#}$/R) and intercept = ln (k_B/h) + ($\Delta S^{\#}/R$). As shown in Fig. 5, the plot of ln (k_a/T) against (1/T) gives straight line for the oxidative polymerizations of St, AMS, CAMS, and APS. From this plot, $\Delta H^{\#}$ and $\Delta S^{\#}$ were determined and Gibbs free energy of activation ($\Delta G^{\#}$) was calculated at 50 °C from

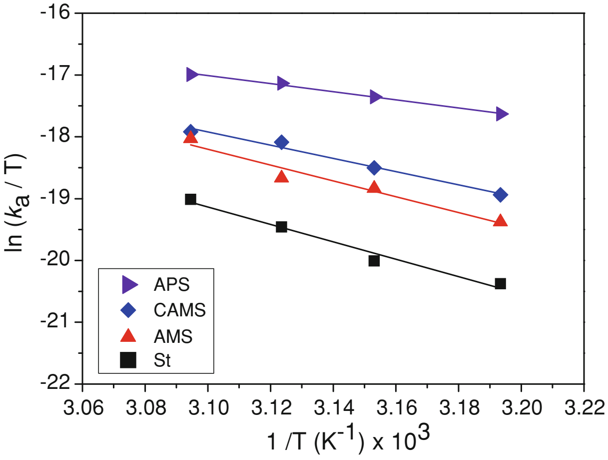


Fig. 5 Plot of ln(k_a/T) against (1/T) for oxidative polymerization of St, AMS, CAMS, and APS

the relation; $\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$, listed in Table 3 for the oxidative polymerizations of St, AMS, CAMS, and APS.

Thermodynamic parameters obtained from Eyring–Polanyi equation are apparent values due the complex nature of the overall rate constant, k_a, which is used to calculate $\Delta H^{\#}$, $\Delta G^{\#}$, and $\Delta S^{\#}$. Although it is difficult to compare, we observed decreasing trend in $\Delta H^{\#}$ and $\Delta G^{\#}$ from St to AMS, AMS to CAMS, and CAMS to APS (Table 3). Chemical reactions depend on Gibbs free energy of activation, and in Table 3 $\Delta G^{\#}$ for AMS (26.9 kcal mol^{-1}) is less than that of St (27.5 kcal mol^{-1}) once again indicates rate of oxidative polymerization of AMS is faster than St. The large negative value of entropy of activation means a slow reaction and decreased degree of freedom for the TS to the monomer. The $\Delta H^{\#}$ is maximum for St monomer followed by AMS, CAMS and APS indicates that thermodynamically the rate of polymerization follows the order: APS > CAMS > AMS > St.

Computational study

In Scheme 2, we mentioned two possible pathways for the initiation of the oxidative polymerization of vinyl monomers. Our DFT studies showed that in the initiation step, the activation energy ($E_{a,ini}$) for the reaction of $(CH_3)(CN)(CH_3)C^{\bullet}$ radical with St monomer is much higher than the reaction with O_2. The $E_{a,ini}$ for the former reaction was 9.81 kcal/mol whereas we observed negative $E_{a,ini}$ of −48.91 kcal/mol for the reaction of O_2 with $(CH_3)(CN)(CH_3)C^{\bullet}$ radical. There are a number of bimolecular reactions (a radical + O_2) that are expected to have negative activation energies [35]. These reactions fall into the general category of reactions that proceed over a potential well [36]. We further observed that in the propagation step, activation energy of propagation, $E_{a,prop} = 6.76$ kcal/mol of Eq. (iv) is much higher than the $E_{a,prop} = -50.62$ kcal/mol of Eq. (iii). Hence Eq. (iv) is the rate-determining step for the oxidative polymerization reaction. Therefore, we have considered only Eq. (iv) for further calculations to study oxidative polymerization of different styrenic monomers.

Experimentally, the rate of polymerization follows the order: APS > CAMS > AMS > St. We have computed different thermodynamic quantities which are listed in Table 4 for the polymerization reaction of St, AMS, CAMS, and APS monomers. It is observed that the activation energy of propagation $E_{a,prop}$ follow the order APS < CAMS < AMS < St. The enthalpy of product formation (ΔH) in Eq. (iv) is maximum for St monomer followed by AMS, CAMS, and APS. These results

Table 3 The E_a, $\Delta H^{\#}$, $\Delta S^{\#}$, and $\Delta G^{\#}$ values for the oxidative polymerization of St, AMS, CAMS, and APS

Monomer	E_a (kcal mol^{-1})	$\Delta H^{\#}$ (kcal mol^{-1})	$\Delta S^{\#}$ (cal K^{-1} mol^{-1})	$\Delta G^{\#}$ (kcal mol^{-1})
St	29.0	28.0	1.5	27.5
AMS	26.0	25.5	−4.3	26.9
CAMS	22.0	21.2	−16.9	26.7
APS	15.0	13.1	−40.5	26.1

Table 4 Thermodynamic parameters for the oxidative copolymerization of St, AMS, CAMS, and APS

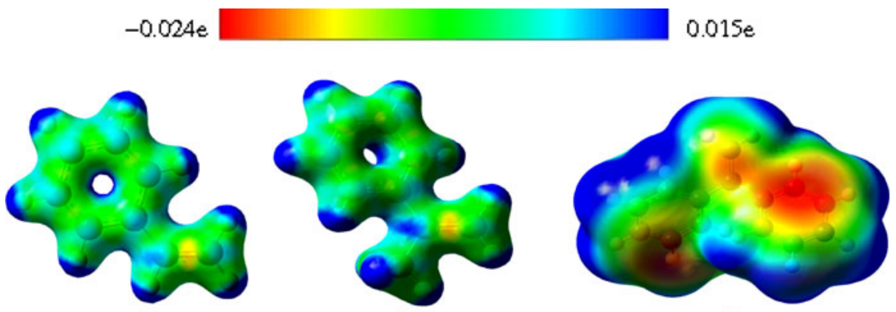
Monomer	$E_{a,prop}$ (kcal mol^{-1})	ΔH (kcal mol^{-1})
St	7.26	−8.82
AMS	6.28	−9.07
CAMS	6.14	−9.24
APS	5.84	−9.90

clearly show that thermodynamically and energetically the rate of polymerization will follow the order APS > CAMS > AMS > St, which matches well with our experimental observations discussed before. However, experimental activation energy of propagation (E_p) does not match with the calculated activation energy of propagation ($E_{a,prop}$). This could be due to the estimation we have made during the experimental evaluation of E_p. Also, approximations during DFT calculations may affect the computation of various kinetic and thermodynamic parameters.

Figures 6a, b, and c show the electron density plot for St, AMS and APS, respectively. Careful observation shows that the electron density for vinyl C=C bond of AMS (Fig. 6b) is more than St (Fig. 6a). For APS, the electron density is maximum. The electron richness of the vinyl π bond in the monomer favors to react with the $-\mathrm{MO}_2^\bullet$ radical. The R_p increases in the sequence APS > CAMS > AMS > St, is also the sequence of increasing π electron density at the double bond of the styrenic monomers.

Conclusions

The 1:1 copolymeric structure of PCAMSP was confirmed by using spectroscopy and elemental analysis. Like other vinyl polyperoxides, the PCAMSP shows a highly exothermic heat of degradation, and degradation is controlled by the dissociation of the peroxide (–O–O–) bond in the polymer main chain. The kinetics of oxidative polymerization of α-substituted styrene monomers such as St, AMS, CAMS, APS at 40–50 °C and 100 psi oxygen pressure indicated that the rates of oxidative polymerization reaction depend on α-substitution group in the monomer.



(a) (b) (c)

Fig. 6 Electron density plot of **a** St, **b** AMS, and **c** APS

For all the monomers, R_p increases with increasing temperature and follows the order: APS > CAMS > AMS > St. This was supported by the observed reverse order of activation energies of propagation during oxidative polymerization. Theoretical calculations supported the order of oxidative polymerization rates and activation energies of propagation. The experimental R_p trend was further corroborated by calculating the heats of propagating radical formation, which is maximum for St monomer followed by AMS, CAMS, and APS.

Acknowledgment The authors gratefully acknowledge the partial financial support from Indian Institute of Science Education and Research-Kolkata and Council of Scientific and Industrial Research (CSIR), New Delhi [01(2474)/11/EMR-II]. Sunirmal Pal acknowledges CSIR, Government of India for his fellowship. PKG would like to thank Department of Science and Technology, India (Project No. SR/FT/CS86/2009) for financial support.

References

1. Subramanian K (2003) Formation, degradation, and applications of polyperoxides. Polym Rev 43:323–383
2. Mogilevich MM (1979) Oxidative polymerisation of vinyl monomers. Russ Chem Rev 48:199–211
3. Mukundan T, Kishore K (1990) Synthesis, characterization and reactivity of polymeric peroxides. Prog Polym Sci 15:475–505
4. Nanda AK, Kishore K (2001) Catalytic oxidative polymerization of vinyl monomers using cobalt phthalocyanine complex and an exploratory investigation on the polymerization of vinyl acetate. Macromolecules 34:1558–1563
5. Mukundan T, Bhanu VA, Kishore K (1989) First report of a polymeric peroxide initiated room temperature radical polymerization of vinyl monomers. J Chem Soc Chem Commun 12:780–781
6. Subramanian K, Kishore K (1997) Kinetics of poly(styrene peroxide) initiated photopolymerization of methyl methacrylate. Polymer 38:527–533
7. Subramanian K, Kishore K (1997) Application of polystyrene peroxide as a curative in coating and molding compositions. Eur Polym J 33:1365–1367
8. Kishore K, Mukundan T (1986) Poly(styrene peroxide): an auto-combustible polymer fuel. Nature 324:130–131
9. Matsumoto A, Higashi H (2000) Convenient synthesis of polymers containing labile bonds in the main chain by radical alternating copolymerization of alkyl sorbates with oxygen. Macromolecules 33:1651–1655
10. Fujioka T, Taketani S, Nagasaki T, Matsumoto A (2009) Self-assembly and cellular uptake of degradable and water-soluble polyperoxides. Bioconjugate Chem 20:1879–1887
11. Sugimoto Y, Taketani S, Kitamura T, Uda D, Matsumoto A (2006) Regiospecific structure, degradation, and functionalization of polyperoxides prepared from sorbic acid derivatives with oxygen. Macromolecules 39:9112–9119
12. Matsumoto A, Taketani S (2006) Regiospecific radical polymerization of a tetrasubstituted ethylene monomer with molecular oxygen for the synthesis of a new degradable polymer. J Am Chem Soc 128:4566–4567
13. Matsumoto A, Taketani S (2004) Fabrication and degradation of polyperoxides by a radical chain process under mild conditions. Chem Lett 33:732
14. Hatakenaka H, Takahashi Y, Matsumoto A (2003) Degradable polymers prepared from alkyl sorbates and oxygen under atmospheric conditions and precise evaluation of their thermal properties. Polym J 35:640–651
15. Sato E, Tamura H, Matsumoto A (2010) Cohesive force change induced by polyperoxide degradation for application to dismantlable adhesion. Appl Mater Interfaces 2:2594–2601
16. Mayo FR (1957) The oxidation of unsaturated compounds. V. the effect of oxygen pressure on the oxidation of styrene. J Am Chem Soc 80:2465–2480
17. Mayo FR, Miller AA (1957) The oxidation of unsaturated compounds. VI. The effect of oxygen pressure on the oxidation of α-methylstyrene. J Am Chem Soc 80:2480–2493

18. De P, Sathyanarayana DN (2002) High-pressure kinetics of oxidative copolymerization of styrene with α-methylstyrene. Macromol Chem Phys 203:2218–2224
19. Frish MJ, Trucks GW, Schlegel HB et al (2004) GAUSSION 03. Gaussian, Inc., Wallingford, CT
20. Becke AD (1993) Density-functional thermochemistry. III. The role of exact exchange. J Chem Phys 98:5648–5652
21. Lee C, Yang W, Parr RG (1998) Development of the Colic–Salvetti correlation-energy formula into a functional of the electron density. Phys Rev B 37:785–789
22. Cais RE, Bovey FA (1977) Carbon-13 nuclear magnetic resonance study of the microstructure and molecular dynamics of poly(styrene peroxide). Macromolecules 10:169–178
23. Murthy KS, Kishore K, Krishnamohan V (1994) Vinyl monomer based polyperoxides as potential initiators for radical polymerization: an exploratory investigation with poly(alpha-methylstyrene peroxide). Macromolecules 27:7109–7114
24. Nanda AK, Kishore K (2001) Stable vinyl polyperoxide: synthesis, characteristics and thermal initiation potentials of poly(α-phenylstyrene peroxide). Macromol Chem Phys 202:2155–2160
25. De P, Sathyanarayana DN, Sadasivamurthy P, Sridhar S (2003) Synthesis, spectral characterization, and thermochemical studies of poly(phenyl methacrylate peroxide). J Appl Polym Sci 88:2364–2368
26. Kissinger HE (1957) Reaction kinetics in differential thermal analysis. Anal Chem 29:1702–1706
27. De P, Chattopadhyay S, Giridhar M, Sathyanarayana DN (2002) Thermal degradation studies of *para*-substituted poly(styrene peroxide)s. Polym Degrad Stab 76:511–514
28. De P, Sathyanarayana DN, Sadasivamurthy P, Sridhar S (2001) Synthesis, structural characterization, thermal studies and chain dynamics of poly(methacrylonitrile peroxide) by NMR spectroscopy. Polymer 42:8587–8593
29. De P, Sathyanarayana DN (2002) Synthesis and characterization of copolyperoxides of indene with styrene, α-methylstyrene, and α-phenylstyrene. J Polym Sci Part B 40:2004–2017
30. Latha R, Kannan S (2009) Synthesis, characterization, thermal degradation, and comparative chain dynamics studies of weak-link polysulfide polymers. J Polym Res 16:623–635
31. Nanda AK, Kishore K (2001) Catalytic radical polymerization of vinyl monomers by cobalt porphyrin complex and metamorphosis of block-into-block copolymer. Polymer 42:2365–2372
32. Kishore K, Paramasivam S, Sandhya TE (1996) High-pressure kinetics of vinyl polyperoxides. Macromolecules 29:6973–6978
33. Odian G (2004) Principles of polymerization, 4th edn. Wiley, New Delhi, p 273
34. Howard JA, Ingold KU (1965) Absolute rate constant for hydrocarbon autoxidation. Can J Chem 43:2737–2743
35. Benson SW, Dobis O (1998) Existence of negative activation energies in simple bimolecular metathesis reactions and some observations on too-fast reactions. J Phys Chem A 102:5175–5181
36. Dobis O, Benson SW (1993) Reaction of the ethyl radical with oxygen at millitorr pressures at 243–368 K and a study of the Cl + HO_2, ethyl + HO_2, and HO_2 + HO_2 reactions. J Am Chem Soc 115:8798–8809