Macromolecules

Volume 29, Number 22 October 21, 1996

High-Pressure Kinetics of Vinyl Polyperoxides

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Received November 28, 1995; Revised Manuscript Received July 11, 1996[⊗]

ABSTRACT: This is the first report on studies carried out in detail on high-pressure oxygen copolymerization (>50 psi) of the vinyl monomers styrene and α-methylstyrene (AMS). The saturation pressure of oxygen for AMS oxidation, hitherto obscure, is found to be 300 psi. Whereas the ease of oxidation is more favorable for styrene, the rate and yield of polyperoxide formation are higher for AMS. This is explained on the basis of the reactivity of the corresponding alkyl and peroxy radicals. Below 50 °C, degradation of the poly(styrene peroxide) formed is about 2.5 times less than that observed above 50 °C, so much so that it gives a break in the rate curve, and thereafter the rate is lowered. Normal free radical kinetics is followed before the break point, after which the monomer and initiator exponents become unusually high. This is interpreted on the basis of chain transfer to the degradation products. The low molecular weight of polyperoxides has been attributed to the (i) low reactivity of $RO_2^\bullet$ toward the monomer, (ii) chain transfer to degradation products, (iii) facile cleavage of O−O bond, followed by unzipping to nonradical products, and (iv) higher stability of the reinitiating radicals. At lower temperatures, (i) predominates, whereas at higher temperatures, chiefly (ii)−(iv) are the case.

Introduction

Vinyl polyperoxides are alternating copolymers of vinyl monomers and oxygen. Vinyl polyperoxides, due to their current resurgence in various potential applications such as special fuels,[1,2] initiators,[3,4] and curatives in coating and moulding,[4] have been established as an important class of polymers.[5] For commercial applications, it is desirable that polyperoxides should be made easily and in large quantities, which cannot be achieved using a conventional glass apparatus.[6,7] For this reason, it is desirable to use a high-pressure reactor, where the rate of polymerization could be considerably enhanced, reducing the longer reaction time commonly encountered in a flushing system under static pressure,[7] besides preventing monomer losses. We report here the first systematic study on the formation of vinyl polyperoxides, namely poly(styrene peroxide) (PSP) and poly(α-methylstyrene peroxide) (PMSP), under different oxygen pressures (ambient to 400 psi) using a Parr reactor. While examining the effects of pressure, temperature, and monomer and initiator concentrations on the kinetics of polymerization, we have also attempted to understand the nature of the side reactions which may lead to the low yield and low molecular weight of polyperoxides.

Experimental Section

Styrene was purified by washing with 10% NaOH several times and passing over silica gel column and dried. A 25 mL volume of styrene and recrystallized AIBN (0.01 M) were placed in a Parr reactor and pressurized with O_2. The reaction was carried out (i) at different temperatures (45, 50, 55, 57.5, and 60 °C), maintaining the pressure constant (100 psi), and (ii) at different pressures (50−250 psi at intervals of 50 psi), keeping the temperature constant (50 °C). Oxidation of freshly distilled α-methylstyrene (AMS) was carried out at different O_2 pressures (50−400 psi at intervals of 50 psi), keeping the temperature constant (50 °C). The reaction was carried out with constant stirring, and polymerization time was kept at 3 h to effect low conversion for reliable kinetic analysis. The O_2 consumption was measured as a function of time using a pressure transducer. Blank experiments, in the absence of AIBN, were carried out for each run to determine accurately the O_2 consumption in the polymerization process. Experiments with different monomer and initiator concentrations were performed under an O_2 pressure of 100 psi at 50 °C. At the end of the reaction, PSP and PMSP were precipitated from the reaction mixture using methanol and dried at ambient temperature in vacuum and weighed.

The PSP and PMSP were characterized by ^{1}H NMR.[8,9] ^{1}H NMR spectra were recorded on a Bruker AC-F 200 MHz spectrometer in $CDCl_3$ and the chemical shifts reported in ppm with reference to tetramethyl silane. The number-average molecular weight ($\bar{M}_n$) was obtained using a Waters ALC/GPC 244 instrument with THF as a mobile phase at 25 °C, using polystyrene standards.

[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1996.

S0024-9297(95)01769-4 CCC: $12.00

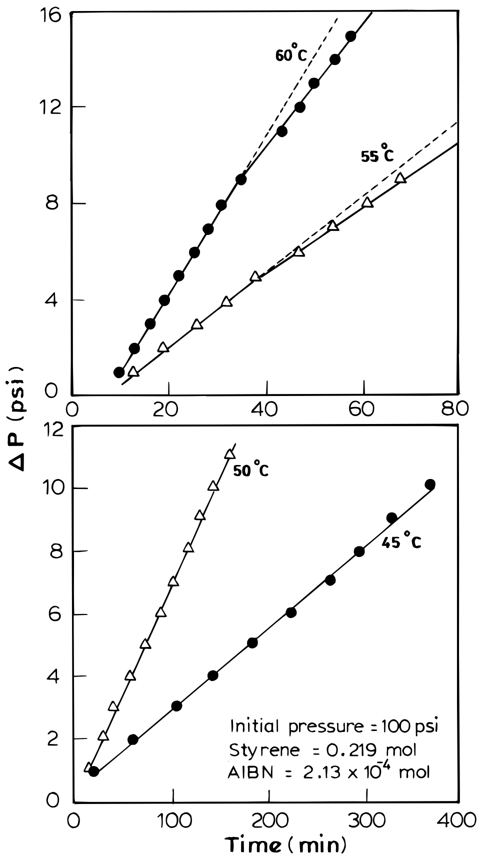


Figure 1. Fall in O_2 pressure (ΔP) due to O_2 consumption as a function of time for styrene oxidative polymerization at different temperatures; total reaction time was 3 h.

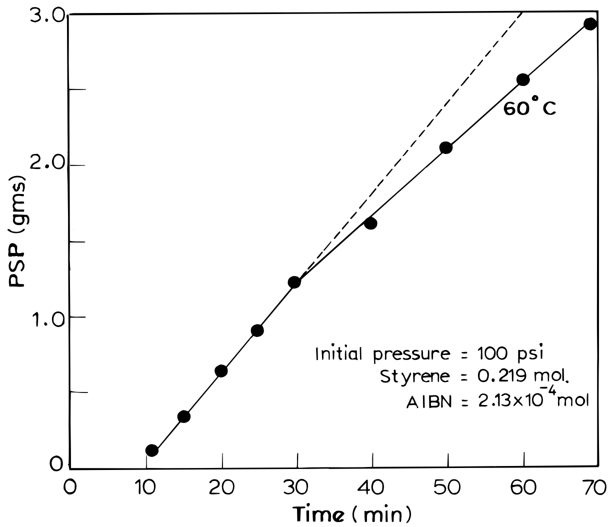


Figure 2. Yield of PSP as a function of time at 60 °C.

Benzaldehyde, which is one of the major products of thermal decomposition of PSP, was determined by precipitating it as the dinitrophenylhydrazone derivative using a solution of 2,4-dinitrophenylhydrazine (DNPH) (5 g) in 100 mL of methanol and 5 mL of concentrated HCl as a reagent. It may be noted that vinyl polyperoxides, unlike acid polyperoxides, are quite safe to handle. Unlike simple organic peroxides like benzoyl peroxide, the vinyl polyperoxides are not shock sensitive, but they should be stored in the dark and in a refrigerator to minimize degradation.

Results and Discussion

The ^1H NMR spectrum of PSP in $CDCl_3$ showed resonance signals at 4.0, 5.3, and 7.2 ppm, which were assigned to methylene, methine, and aromatic protons, respectively.[8] For PMSP, the signals were at 1.46, 4.16, and 7.2 ppm for methyl, methylene, and aromatic protons, respectively.[9] The $\bar{M}_n$ values for PSP and PMSP were found to be 5000 and 5300, respectively.[9]

For styrene oxidation at 45 and 50 °C, as shown in Figure 1, the O_2 consumption with respect to time, at a constant pressure of O_2 (100 psi), is a simple linear plot. Interestingly, at 55 °C and above, there is a break in the linear plot, and we get two slopes, as can be seen in Figure 1. To corroborate this observation, the rate of PSP formation at a given temperature was obtained gravimetrically by precipitation as a function of time, keeping the pressure at 100 psi. At 45 and 50 °C, a continuous rate plot was obtained, but at 60 °C (Figure 2), we got again a discontinuous plot. These results are very similar to those observed in O_2 consumption experiments as discussed before. To understand this behavior, we analyzed the reaction products. Unreacted styrene was removed from the reaction mixture, and ^1H NMR spectra were taken. At 45 and 50 °C, besides the PSP peaks, no other peaks were seen, particularly in the region of the aldehydic protons. At 55 °C and above, the reaction mixture below and above the break point was examined. Below the break point, the ^1H NMR spectrum was almost the same as those of the reaction mixture at 45 and 50 °C. After the break point, an additional peak in the aldehydic region (10.1 ppm) appeared. This may result from the degradation of PSP; benzaldehyde and formaldehyde are the degradation products of PSP.[10] Apparently, at higher temperatures (50 °C and above), the formed PSP degrades, and the rate of degradation increases with temperature. An attempt was made to quantitatively estimate the products of PSP decomposition. However, efforts to collect the total formaldehyde were in vain, since most of the formaldehyde escapes, and some may polymerize in the liquid phase; hence, the results were irreproducible. Benzaldehyde was therefore estimated by the hydrazone derivative method, from which the amount of PSP that degraded was estimated. Benzaldehyde was also estimated from the ^1H NMR spectrum of the reaction mixture. The ^1H NMR spectrum was expanded 64 times in the aldehydic region to estimate benzaldehyde. The extent of degradation was estimated by comparing the CH_2 proton signal of PSP. It was found that, at 60 °C, after 30 min (before the break point), 3.3% of PSP degrades to benzaldehyde, and after 1 h and 30 min (after the break point), almost 2.5 times (8.3%) of PSP degrades. The ^1H NMR results were consistent with the hydrazone derivatives estimation.

Due to the formation of gaseous formaldehyde on PSP degradation, the pressure in the reaction vessel will show an apparent decreased O_2 consumption. It possibly accounts for a break in the plot of O_2 consumption at 55 °C and above. It also explains a decrease in the PSP yield after the break point at 55 °C and above. Within the limitation of the NMR instrument, no other side products were detected, which suggests that side reactions other than PSP degradation are of no consequence. The effects of varying monomer and initiator concentrations ([M] and [I])at a given O_2 pressure were examined. The results are given in Table 1; from the data, initiator and monomer exponents were calculated. A general simplified mechanism for the oxidative polymerization of styrene,[5,11] applicable in excess O_2 concentration, is shown in Scheme 1. Below the break point, the monomer and initiator exponents were found

Table 1. Effect of Initiator and Monomer Concentration on the Rate of Styrene Oxidative Polymerization[a]

AIBN [I] (mol/L × 10^3)	styrene [mL (mol)]	$R_{p1} \times 10^4$ (atm/s)	$R_{p2} \times 10^4$ (atm/s)
8.5	25.0 (0.218)	4.1	2.8
10.2	25.0 (0.218)	3.7	3.4
11.6	25.0 (0.218)	5.1	4.4
12.2	25.0 (0.218)	5.1	3.7
13.4	25.0 (0.218)	5.1	4.5
16.0	25.0 (0.218)	6.4	5.8
17.9	25.0 (0.218)	5.9	5.4
10.2	20.0 (0.174)	3.8	2.4
10.2	22.5 (0.196)	4.2	3.0
10.2	25.0 (0.218)	3.7	3.4
10.2	27.5 (0.240)	4.9	3.8
10.2	30.0 (0.262)	6.6	3.9
10.2	32.5 (0.284)	5.6	5.3
10.2	35.0 (0.305)	6.2	5.7
10.2	38.0 (0.332)	6.8	6.6

[a] Conditions: temperature, 60 °C; pressure, 100 psi; reaction time, 3 h.

to be close to unity and one-half, respectively. The correlation coeffcients for monomer and initator exponent plots were found to be between 0.90 and 0.99. Hence, on the basis of Scheme 1, we can write

$$-\frac{d[O_2]}{dt} = R_{p1} = \frac{k_p''(k_i)^{0.5}}{(k_t)^{0.5}}[M][I]^{0.5} \qquad (1)$$

where R_{p1} is the rate of O_2 consumption below the break point, as shown in Figure 1; the other terms have their usual meanings. Above the break point, the monomer and initiator exponents vary significantly, and the rate of O_2 consumption is given by

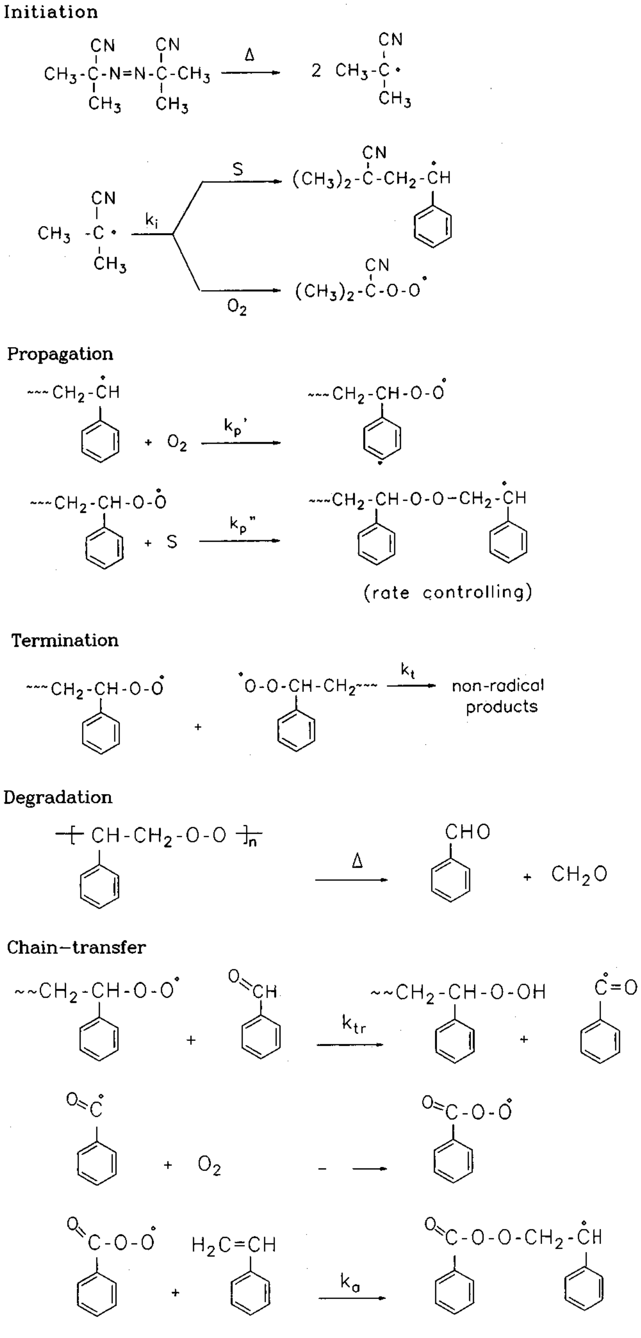
$$-\frac{d[O_2]}{dt} = R_{p2} = \frac{k_p''(k_i)^{0.5}}{(k_t)^{0.5}}[M]^{1.5}[I]^{1.0} \qquad (2)$$

It may be noted from Figure 1 that $R_{p2} < R_{p1}$.

The most important feature of the PSP is the absence of initiator-derived end groups and the presence of end groups derived from the chain-transfer process. The formation of a benzoyl end group has been proposed, resulting from the chain transfer to benzaldehyde.[8] Since the chain-transfer reaction is of great significance in polyperoxide formation, it should be considered in any discussion on kinetics. At low temperatures (<50 °C), although chain transfer takes place, the formation of degradation products is very low; hence, benzaldehyde is not detected by ^{1}H NMR. At higher temperatures (above 50 °C), however, with increased PSP degradation, a higher amount of benzaldehyde is formed; hence, there is more chain transfer compared to the normal propagation. Consequently, we observe a substantial reduction in R_p after the break point. This reduction in R_p results from the low reactivity of the reinitiating benzoyl peroxy radical due to its higher stability, which is discussed below.

Comparison of $k_p/k_t^{1/2}$ values for the oxidation of various vinyl monomers[11] indicates that, when peroxy radical is attached to an electron-donating group, like in styrene and AMS, the rate of oxidation is high. On the contrary, when electron-withdrawing groups are attached to the peroxy radicals, like in MMA, acrylonitrile, and methyl vinyl ketone, the rate of oxidation is very low. In the present case, in the benzoyl peroxy radical, an electron-withdrawing group (>C=O) is attached to peroxy radical, which explains the experimental observation of the decrease of R_p after the break point. We have attempted to substantiate the above by considering the stability of H(CO)O−O$^\bullet$ and $H_3CO-O^\bullet$ radicals. When the AM1 (Austin Model 1) quantum mechanical molecular model was used to calculate the heat of formation ($\Delta H_f°$) of the radicals H(CO)O−O$^\bullet$ and $H_3CO-O^\bullet$, the values were −32.3 and −7.8 kcal/mol, respectively. This suggests that −(CO)O−O$^\bullet$ radical should be more stable than $-CH_2O-O^\bullet$ radical, which goes to show that benzoyl peroxy radical gets stabilized.

Scheme 1. Kinetic Scheme for the Copolymerization of Styrene and Oxygen



Let us consider the low-temperature kinetics below the break point. For AIBN-initiated polymerization, E_i = 30 kcal/mol.[13] The activation energies for the propagation (E_p) and termination (E_t) for styrene oxidation are 8.4 and 1.8 kcal/mol, respectively.[14] When these values are considered, the overall activation energy (E_a) according to eq 3 should be 22.5 kcal/mol.

$$E_a = E_{p1} + E_i/2 - E_t/2 \tag{3}$$

However, a higher E_a (29 kcal/mol) was experimentally obtained. It shows that some chain transfer is taking place. Hence, the activation energy (E_{tr}) for the chain-transfer process should be included, and eq 3 can be modified as

$$E_a = E_p + E_{tr} + E_i/2 - E_t/2 \tag{4}$$

On substituting the values of the observed E_a, E_p, E_i, and E_t, we get $E_{tr} = 6.5$ kcal/mol. The low value of E_{tr}, compared to E_p, is concordant with the view that chain transfer would be preferred over normal propagation for PSP formation.This further supports the finding that benzaldehyde is an efficient chain-transfer agent, particularly in oxygen copolymerization, due to the higher stability of the benzyl peroxy radicals.

When we consider the category of chain-transfer processes,[13] it may be noted that, in the present case, the rate of polymerization at low temperature (below 50 °C) is not affected throughout the polymerization reaction (see Figure 1). Below the break point, the amount of chain-transfer agent (benzaldehyde) formed is less than the benzaldehyde formed after the break point at 60 °C, as indicated by ^{1}H NMR spectra; hence, propagation rate constant (k_p'') is not much affected. Besides, as indicated by E_{tr} and E_p values, the chain transfer rate constant (k_{tr}) should be higher than the normal propagation rate constant (k_p''). This would result in low molecular weight of PSP, which is, indeed, the case (~5000).[15]

In the high-temperature kinetics, after the break point, the overall activation energy (E_a) was found to be 63 kcal/mol, which is substantially higher than the corresponding value below the break point. Since PSP degradation is higher in this region, apparently the polymerization process is overrun by degradation. After the break point, chain transfer to benzaldehyde is very significant, forming benzoyl peroxy radicals (Scheme 1). The rate of reinitiation, and hence the rate of PSP formation after the break point, are reduced due to the relative stability of the benzoyl peroxy radicals (Scheme 1). Due to the pressure of the formed formaldehyde, the observed decrease in O_2 pressure and the associated kinetics become complicated, as is reflected in the monomer and initiator exponents (eq 2). The unusually high initiator and monomer exponents could be attributed to the degradative chain transfer to the degradation product,[16] i.e., to benzaldehyde, which results in the lowering of R_p (i.e., $R_{p2} < R_{p1}$) and increase in the order with respect to initiator from 0.5 to 1.0, suggesting that reinitiation by benzoyl peroxy radical is significantly low. If chain-transfer agent increases the initiator exponent, it would affect the monomer exponent as well; generally, monomer exponent may increase above unity. Indeed, in the present case, the monomer exponent is 1.5.

The following reasons may be cited for obtaining low molecular weight peroxides: (i) low reactivity of $RO_2^\bullet$ radical toward the monomer, (ii) facile cleavage of the O—O bond, (iii) chain transfer to the degradation products, and (iv) higher stability of the reinitiating radicals. At lower temperatures, reaction (i) is the most favorable. But at higher temperatures, reactions (ii)—(iv) occur more dominantly. This complicates the mechanism of polymerization, as is evident from the abnormally high E_a value, which we are unable to account for presently, and also by the abnormally high activation volume ($\Delta V^{\#}$), which will be discussed later.

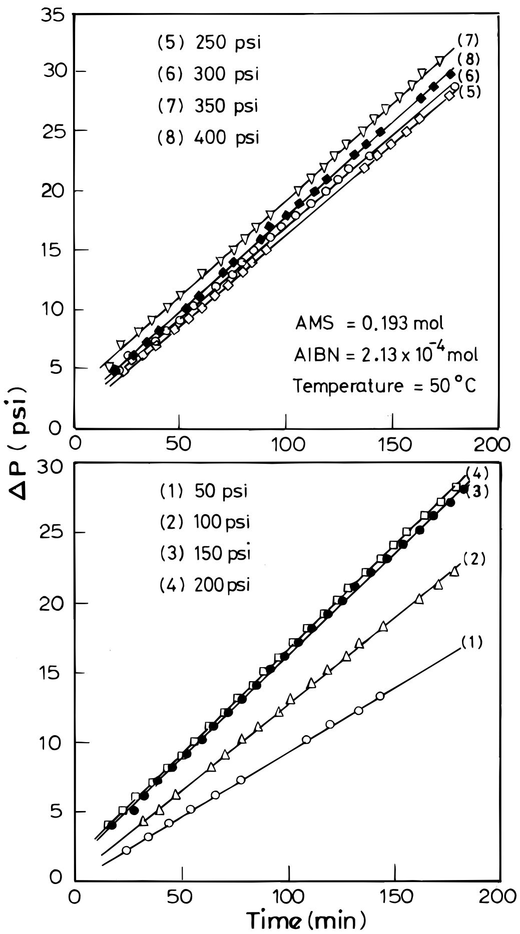


Figure 3. Fall of O_2 pressure (ΔP) due to O_2 consumption as a funtion of time for AMS oxidative polymerization at different pressures; reaction was carried out for 3 h.

It was reported earlier that styrene oxidation at 50 °C becomes independent of O_2 pressure above 2 psi[11] and the main product is PSP. Considering the errors in the measurement of R_p [(6.0 ± 0.5) × 10^{-4} atm/s] and yield (4.7 ± 0.4%), the variations in R_p and yield with respect to styrene were within experimental error in the pressure range of 50—250 psi, which is consistent with the fact that no pressure effect[11] is observed above 2 psi. However, for AMS, it has been reported that the oxidation is not independent of O_2 pressure, even up to 62 psi.[17] Hence, the intent was to examine the saturation pressure of O_2 in AMS oxidation. The AMS oxidation was carried out in the pressure range 50—400 psi at 50 °C (Figure 3). Initially, the rate increases rapidly with O_2 pressure, and then a horizontal asymptote is reached (Figure 4a).

The saturation pressure corresponding to the point of maximum bending in the plot of R_p vs pressure was determined mathematically. At the point of maximum bending, the pressure effect would be negligible, and the third derivative would become zero.[18] The R_p vs pressure data (Figure 4a) were fitted to a fourth-order polynomial, and the third derivative was obtained, as shown in Figure 4b. The third derivative becomes zero at 320 psi. A similar exercise was carried out for the yield vs pressure plot also (Figure 5). Interestingly, it also shows a behavior similar to that disscussed above for R_p. The saturation pressure of O_2 for AMS oxidation was found to be 280 psi, which is consistent with that

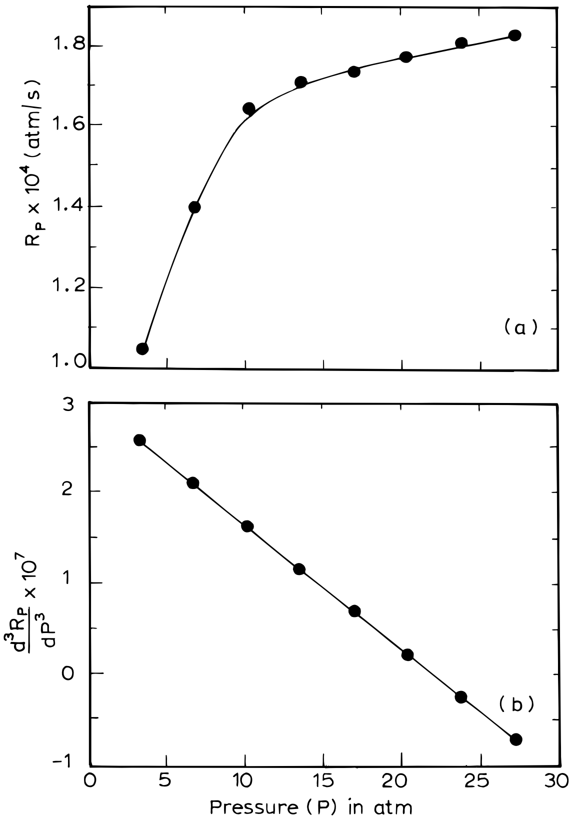


Figure 4. (a) Rate of oxidative polymerization (R_p) of AMS as a function of pressure at 50 °C. (b) Third derivative plot of (a).

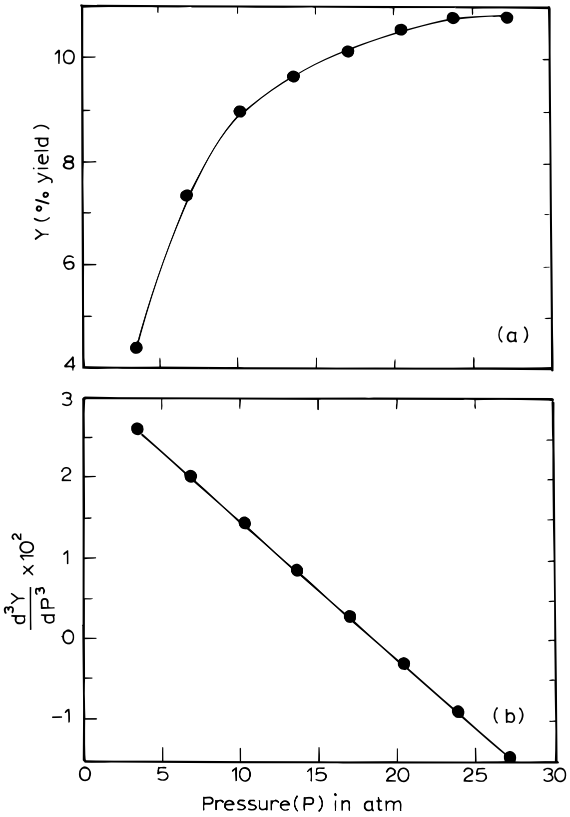


Figure 5. (a) Yield of of PMSP as a function of pressure at 50 °C; total reaction time was 3 h. (b) Third derivative plot of (a).

obtained from R_p values. Considering the above two values, the mean saturation pressure of O_2 for AMS oxidation could be taken as 300 psi, which is substantially higher than the saturation pressure of O_2 for styrene, which is 2 psi. The above results reveal that we need to maintain more controlled conditions for the oxidation of AMS compared to styrene. To substantiate this, let us consider the reactivity of the alkyl radicals toward O_2 in the first propagation step (Scheme 1); the AMS oxidation follows a similar mechanism. In the case of AMS, a tertiary radical $[-CH_2(C_6H_5)(CH_3)C^\bullet]$ is formed, and in styrene, a secondary radical $[-CH_2(C_6H_5)CH^\bullet]$ is formed. The tertiary free radical being more stable than the secondary radical, higher O_2 pressure is needed for AMS oxidation. If this were the rate-controlling step, one should observe a lower rate of polymerization and a much lesser yield of PMSP compared to PSP. On the other hand, the yield and rate for AMS are greater than those for styrene. This confirms that the first propagation step (Scheme 1) cannot be the rate-determining step in the polymerization, and it has to be the second propagation step only.

Let us now discuss why the rate and yield for AMS are more than those for styrene. On the basis of the second propagation step (Scheme 1), the reactivity of the $RO_2^\bullet$ radical toward the monomer should be compared. The peroxy radical formed from AMS, i.e., $[-CH_2(C_6H_5)(CH_3)CO-O^\bullet]$, is more reactive than the peroxy radical formed from styrene, $[-CH_2(C_6H_5)CHO-O^\bullet]$, due to the penultimate effect[5] of the electron-donating methyl group. In addition to the reactivity of $RO_2^\bullet$ toward the monomer, we have to consider the electron richness of the π bond in the monomer also. The electron density is more in AMS than in styrene; hence, the reactivity of AMS toward $RO_2^\bullet$ would be much higher than that of styrene. Hence, the rate and yield for PMSP are higher compared to those for PSP.

We have already discussed the chain-transfer reaction in PSP. In the case of AMS oxidation, too, the PMSP formed degrades to give formaldehyde and acetophenone.[9] In PSP, though, formaldehyde is not a better chain-transfer agent than benzaldehyde;[19] in the case of PMSP, formaldehyde is a relatively good chain-transfer agent compared to a ketone[20] (acetophenone). Indeed, a formyl end group has been proposed in PMSP.[17] The activation energy for the unzipping of PSP is 5 kcal/mole,[6] whereas for PMSP this activation energy is almost negligible.[6] Hence, the rate of degradation is much higher for PMSP than for PSP. The chain transfer as well as faster unzipping in PMSP limits its molecular weight, even though the rate of propagation and hence polymerization is greatly favorable in PMSP over PSP.

The effect of pressure on the oxidation of AMS was studied, and the activation volume ($\Delta V^{\#}$) was calculated using the following equation:

$$\frac{d \ln k}{dp} = -\frac{\Delta V^{\#}}{RT}$$

Normally, the value of $\Delta V^{\#}$ for vinyl polymerization is from −10 to −15 cm^3/mol,[13,21] but for AMS oxidative polymerization, $\Delta V^{\#}$ was found to be −1.8 L/mol, in the pressure range 3−30 atm, which is nearly 100 times higher than the usual effect of pressure one encounters in gaseous or other polymerization reactions. Here the pressurizing fluid is O_2, which is also one of the reactants. This may be the reason for the unusually high value of $\Delta V^{\#}$.

We have also compared the present $\Delta V^{\#}$ value with that of AMS calculated from Mayo's data[17] in the low-pressure region (0.2−1 atm). The $\Delta V^{\#}$ calculated from Mayo's data[17] was found to be −40 L/mol, which is significantly higher than our value. At still lower pressures, Mayo's data[17] yield an even higher value of $\Delta V^{\#}$ (−217 L/mol). This suggests that the mechanism of polymerization changes with pressure. It is most likely that, in the low O_2 pressure region, many side reactions affect the kinetics of polymerization; hence, the mechanism is changed.[5,11] The $\Delta V^{\#}$ was also calculated for PSP using Mayo's data[22] in the low-pressure range (0.032−0.131 atm), and it was found to be very high (−204 L/mol). It shows that $\Delta V^{\#}$ for styrene oxidation is much higher than that for AMS. This seems consistent with the higher rate and yield for PMSP compared to those for PSP. In addition to the pressurizing fluid O_2 itself acting as a reactant, the occurrence of side reactions, particularly at low pressures, and the chain-transfer reactions may also account for the abnormally high values of $\Delta V^{\#}$ in the oxidative polymerization of vinyl monomers.

Conclusions

The rate of oxidation, the saturation pressure of O_2, and the yield of polyperoxide are controlled by the reactivity of the propagating radicals. The main side reaction has been found to be the degradation of the polyperoxide. The chain transfer to the degradation products appears to be the key inhibiting factor for obtaining the low molecular weight as well as the liquidation of the initiator-derived end groups and subsequent replenishment with the chain-transfer species. These chain-transfer reactions grow rapidly at higher temperatures, leading to unusual kinetics by increasing both the monomer and initiator exponents.

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