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Mechanism of "Autoacceleration" in the Thermal Oxidative Polymerization of α-Methylstyrene

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ABSTRACT: Thermal oxidative polymerization of α-methylstyrene (AMS) has been studied at various temperatures (45−70 °C) and pressures (50−400 psi). Due to its high electron dense double bond, it undergoes thermal oxidative polymerization even at low temperatures fairly easily. The major products are poly(α-methylstyrene peroxide) (PMSP), and its decomposition products are acetophenone and formaldehyde. Above 45 °C the rate of polymerization increases sharply at a particular instant showing an "autoacceleration" with the formation of a knee point. The "autoacceleration" is supported from the fact that the plot of R_p vs T shows a rapid rise, and the plot of ln R_p vs $1/T$ is non-Arrhenius. The occurrence of autoacceleration is explained on the basis of acetophenone-induced cleavage of PMSP during polymerization, generating more initiating alkoxy radicals, which subsequently leads to the rapid rise in the rate of polymerization. The mechanism of autoacceleration is supported by the change in order, activation energy, and activation volume before and after the knee point.

Introduction

The "vinyl polyperoxides" are a narrow, but important, class of polymers[1,2] and are gaining considerable importance due to their potential applications as fuels,[3,4] initiators,[5−7] and curatives in coating and molding.[8] They are usually prepared by oxidative polymerization of vinyl monomers in the presence of a free radical initiator.[6] Available reports on thermal oxidative polymerization of vinyl monomers, which is done in the absence of an added initiator, are scarce in the literature.[9] This is because thermal oxidative polymerization of vinyl monomers generally occurs at a slower rate and hence requires higher polymerization temperatures.[9−12] It would be advantageous if thermal oxidative polymerization could be carried out at higher rates but at low temperatures to minimize the degradation of polyperoxides during polymerization.[13] To see whether this objective is fulfilled, thermal oxidative polymerization was studied in a few common vinyl monomers such as styrene, methyl methacrylate (MMA), and α-methylstyrene (AMS). Interestingly, only AMS was found to undergo thermal oxidative polymerization fairly rapidly even at low temperatures. We present here the first comprehensive study on the thermal oxidative polymerization of AMS with an emphasis on kinetics and mechanism of polymerization.

Recently, from our laboratory, detailed studies have gotten underway to carry out AIBN-initiated polymerization of styrene and AMS at high oxygen pressures so that the polymerization rate could be augmented.[14] Related to this, it is also of interest to see the effect of oxygen pressure on the thermal oxidative polymerization of AMS because unlike other common vinyl monomers, such as styrene and MMA, the AMS does not show any pressure saturation effect until 4 atm of oxygen.[15]

Experimental Section

Materials. AMS, MMA, and styrene were freed from the inhibitor and distilled under reduced pressure. Azobis(isobutyronitrile) (AIBN) (Koch Light Laboratories, England) was recrystallized three times from methanol. Methanol, acetophenone, and tetrahydrofuran (THF) were purified before use. 2,4-Dinitrophenylhydrazine (DNPH) was used as received.

Kinetic Studies. AMS was oxidatively polymerized, in the absence of an added initiator, in a Parr high pressure reactor in the temperature range 45−70 °C and pressure range 50−400 psi, as described elsewhere.[14] The polymerization time was kept at 3 h to effect low conversion for reliable kinetic analysis. The rates were reproducible to within 5% error. After completion of the reaction, the poly(α-methylstyrene peroxide) (PMSP) was precipitated in methanol. The methanol filtrate was used to estimate acetophenone as its hydrazone derivative.[10] The melting point of the hydrazone crystal was 240 °C.

Measurements. Oxidations were carried out in a 300 mL Parr reactor (Parr Instrument Company) equipped with a digital pressure transducer, temperature controller, and mechanical stirrer. The intrinsic viscosities were measured at 25 °C (in THF) using an automated Ubbelohde SCHOTT-GERATE viscometer. The 200 MHz ^{1}H NMR spectra were recorded on a Bruker AC-F 200 FT NMR spectrometer in $CDCl_3$. The chemical shifts are reported in ppm with reference to tetramethylsilane. The IR spectra were recorded on a Perkin-Elmer spectrometer, Model 781. DSC experiments were conducted on a Dupont instrument, Model 910, calibrated using indium. Samples of 1−10 mg were heated at a rate of 1−25 K/min in open aluminum pans under nitrogen atmosphere. The isothermal thermogravimetric (sample weight 5 mg) study was carried out on a Dupont 951 thermogravimetric analyzer.

Results and Discussion

Polymerization of AMS and Autoacceleration. AMS cannot be homopolymerized either by thermal methods or by adding a free radical initiator due to its low ceiling temperature. However, we have observed that AMS undergoes thermal oxidative polymerization in the absence of an added initiator at 45 °C at a substantial rate in contrast to styrene and MMA, which do not polymerize even at 50 °C (3 h, 100 psi of O_2). This may be due to the high electron density of the AMS double bond which is responsible for its high reactivity toward oxygen.[15] The rate of polymerization was obtained from the slope of the linear plot of the oxygen consumption with time. At high oxygen pressure (>50 psi) the products of thermal oxidative polymerization of AMS are PMSP and its decomposition products

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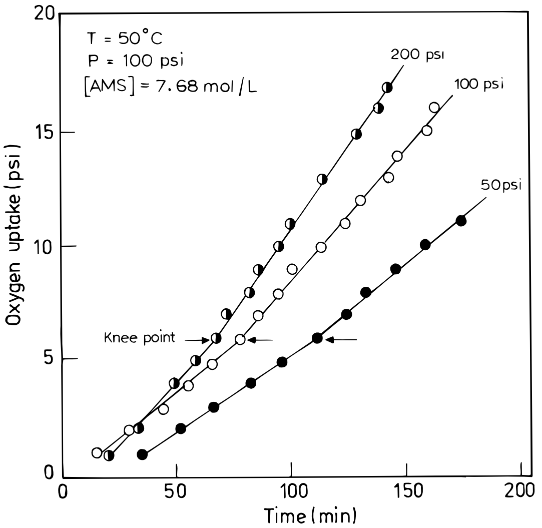


Figure 1. Oxygen consumption (ΔP) as a function of time for the thermal oxidative polymerization of AMS at 50, 100, and 200 psi.

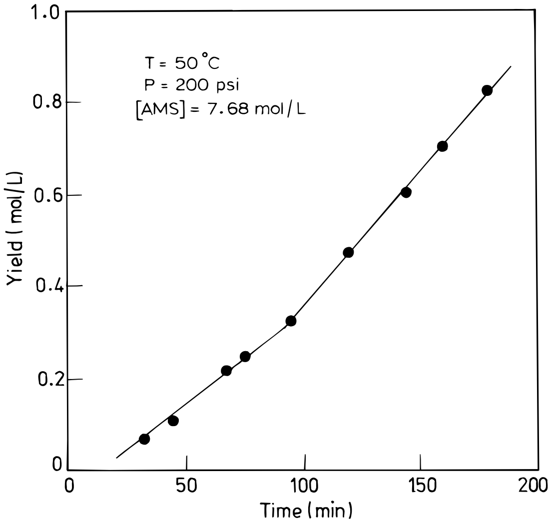


Figure 2. Yield of PMSP during thermal oxidative polymerization of AMS.

acetophenone and formaldehyde.[16] The ^{1}H NMR spectrum of product shows peaks corresponding to PMSP (1.46 ppm for $-CH_3$, 4.16 ppm for $-CH_2$), acetophone (2.6 ppm for $-CH_3$), and unreacted AMS {2.36 ppm for $-CH_3$, 5.5 ppm (doublet) for $>CH-$, and 7.5 ppm (multiplet) for aromatic protons}. Formaldehyde is deposited as a white polymeric solid on the sides of the reaction vessel, and some of it may also escape along with the unreacted oxygen. According to the degradative unzipping mechanism, formaldehyde and acetophenone are formed in equimolar quantities.[16]

The oxidative polymerizations of AMS at various temperatures (45−75 °C) have been studied at 100 and 200 psi of oxygen pressure; the conversion was kept below 10%. For all the temperatures below 60 °C, in terms of O_2 uptake, the rates of polymerization show an increase after a particular time with a knee point formation (Figure 1). As expected, a similar knee point formation is also seen in the plot of polymer (PMSP) yield as a function of time (Figure 2). In radical chain polymerization reactions, at low conversions, one would normally expect the reaction rate to fall with time (i.e., the extent of conversion), since the monomer and initiator concentrations decrease with conversion.[17] In the present case of AMS oxidative polymerization, an opposite behavior is observed; i.e., the rate of polymerization increases with time. Hence, it is indicative of the presence of an "autoacceleration".[17] However, the shape of the curve is not what is typically seen for autoacceleration. Conventionally, in autoacceleration, the rate as a function of conversion exhibits a maximum like that observed in the classic case of Trommsdorff effect.[18−22] The "autoacceleration" here is an unusual type where the polymerization rate of AMS rises at a particular instant exhibiting a knee point. R_{p1} and R_{p2}, the rates of polymerization before and after the knee point respectively, were calculated from the plots shown in Figure 1. It may also be noted from Figure 1 that $R_{p1} < R_{p2}$. Above 60 °C there is no R_{p1} because no knee point is observed above 60 °C and the rate corresponds to R_{p2} only. The R_{p2} vs temperature plot for AMS polymerization is shown in Figure 3a. R_{p2} shows a rapid rise with temperature, like that observed in explosion reactions, thus explicitly showing the existence of autoacceleration. This is further supported by the fact that R_{p2} exhibits a non-Arrhenius temperature dependence (Figure 4).

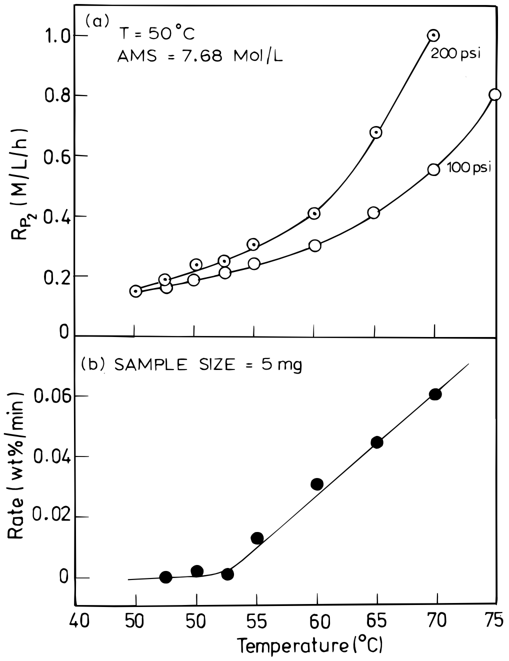


Figure 3. (a) Effect of temperature on the rate of thermal oxidative polymerization of AMS at 100 and 200 psi. (b) Effect of temperature on the rate of isothermal decomposition of PMSP in N_2 atmosphere.

The observation of autoacceleration seems to be quite interesting, and hence its mechanism and kinetics were studied. Table 1 summarizes the results of polymerization of AMS at 50 °C. The AMS concentration variation experiments were carried out using chlorobenzene as a diluent. The exponents were calculated from the slope of the plot of ln R_p vs ln [M] and ln R_p vs ln $[O_2]$. The rate of polymerization before the knee point (R_{p1}) was found to be proportional to $[AMS]^{1.7}[O_2]^{0.5}$. These exponents of AMS and oxygen are close to the theoretical exponents (1.5 and 0.5 for monomer and oxygen respectively) as outlined in the Mayo−Russell mechanism[9,12] for the thermal oxidative polymerization (see Scheme 1). According to this mechanism the thermal chain initiation involves the addition of oxygen to the double bond, forming a biradical.[12] After the knee point the monomer and oxygen exponents vary significantly; the rate of polymerization (R_{p2}) becomes $[AMS]^{2.0}[O_2]^{0.3}$.

Table 1. Effect of Oxygen Pressure and AMS Concentration on the Thermal Oxidative Polymerization of AMS[a]

[AMS] (mol/L)	O_2 (psi)	R_{p1} (psi/min)	R_{p2} (psi/min)	R_{p1} ((mol/L)/h)	R_{p2} ((mol/L)/h)	PMSP ((mol/L)/h)	acetophenone ((mol/L)/h)
4.61	200	0.045	0.051	0.076	0.086	0.135	0.036
5.53	200	0.061	0.067	0.103	0.113	0.148	0.033
6.15	200	0.074	0.087	0.125	0.147	0.186	0.036
6.76	200	0.086	0.108	0.146	0.183	0.195	0.037
7.68	50	0.058	0.086	0.098	0.146	0.105	0.037
7.68	100	0.082	0.111	0.139	0.188	0.168	0.035
7.68	150	0.100	0.126	0.169	0.213	0.210	0.034
7.68	200	0.110	0.137	0.186	0.232	0.247	0.034
7.68	300	0.135	0.162	0.229	0.274	0.264	0.033
7.68	350	0.135	0.163	0.229	0.276	0.266	0.032
7.68	400	0.135	0.163	0.229	0.276	0.267	0.032

[a] Temperature = 50 °C; reaction time = 3 h; diluent = chlorobenzene.

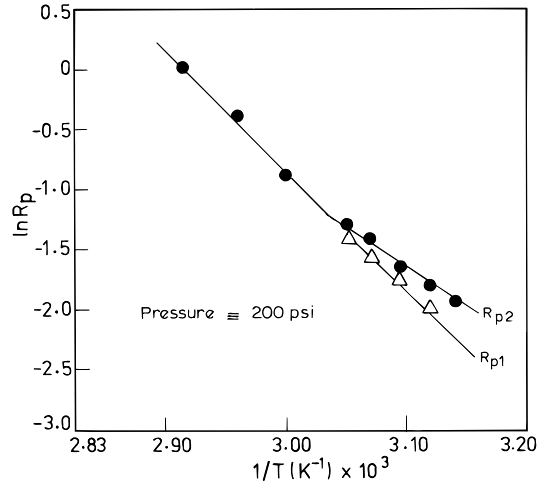
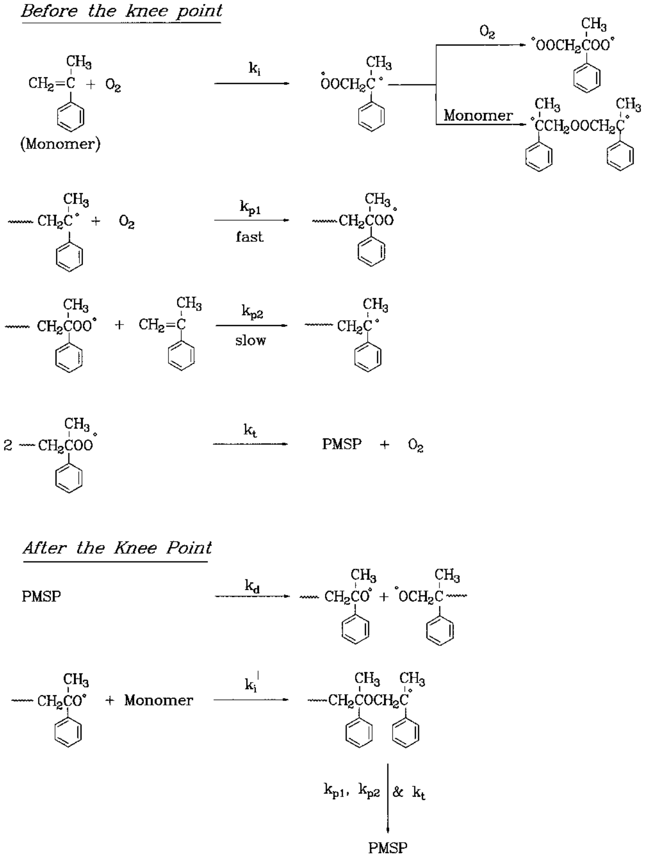


Figure 4. Arrhenius plot for the rate of thermal oxidative polymerization of AMS at 200 psi.

As the polymerization temperature increases the dissolved oxygen concentration in AMS, which functions both as a monomer and an initiator, decreases, and hence, one would expect a decrease in rate at higher temperatures.[13] Contrarily, the rate increases with temperature (PMSP formation increases with temperature, Table 2), and it shows autoacceleration of the polymerization at higher temperatures. This anomaly can be explained only on the basis that more initiating radicals are generated at higher temperatures. The most plausible reason could be the decomposition of the formed PMSP, which itself is a free radical initiator, participating in the initiation process, in addition to the usual initiating mechanism as outlined in Scheme 1. The role of PMSP as free radical initiator has been demonstrated recently.[5] If this happens, one should observe a decrease in molecular weight of PMSP with an increase in temperature. Indeed, the intrinsic viscosity was found to decrease linearly with temperature as shown in Figure 5.

The mechanism of autoacceleration can be described as follows. PMSP degrades through O–O bond cleavage to form alkoxy radicals (PO•) which may further initiate polymerization along with the usual thermal initiation as proposed before the knee point formation. Some of the alkoxy radicals would also unzip to give acetophenone and formaldehyde. Acetophenone formation was found to increase with temperature (Table 2). The highly polar acetophenone thus formed further accelerates the PMSP degradation giving more radicals for initiation. Thus, autoacceleration in the AMS oxidative polymerization sets in. The proof for catalytic effect of acetophenone on PMSP degradation is discussed in the "Kinetics of PMSP Degradation" section. It may be noted that the decomposition of peroxide is strongly solvent dependent, and the rate increases with the solvent polarity, implying a relatively polar transition state.[23] However, such reactions are generally complex and are not clearly understood. Occurrence of "autoacceleration" is further corroborated from the studies on isothermal degradation of neat PMSP at different temperatures from TGA (Figure 3b). Up to 50 °C no significant degradation of PMSP was observed. Thereafter a sudden rise in the isothermal weight-loss rate was observed because above 50 °C substantial degradation of PMSP takes place.

Scheme 1. Kinetic Scheme for the Thermal Oxidative Polymerization of AMS before and after the Knee Point



It may also be pointed out here that the temperature above which autoacceleration is seen in TGA runs (Figure 3b) and the polymerization rate in a Parr reactor are different. This is because the DSC runs were carried out with neat PMSP whereas the polymerization rates were measured in monomer solution. Being

Table 2. Effect of Temperature on the Thermal Oxidative Polymerization of AMS

O_2 (psi)	T (°C)	R_{p1} (psi/min)	R_{p2} (psi/min)	R_{p1} ((mol/L)/h)	R_{p2} ((mol/L)/h)	PMSP ((mol/L)/h)	acetophenone ((mol/L)/h)
200	45.0	0.060	0.092	0.103	0.158	0.117	0.030
200	47.5	0.080	0.097	0.135	0.165	0.155	0.032
200	50.0	0.103	0.113	0.174	0.192	0.248	0.034
200	52.5	0.125	0.137	0.210	0.230	0.260	0.036
200	55.0	0.156	0.182	0.260	0.304	0.320	0.037
200	60.0[b]		0.246		0.405	0.467	0.039
200	65.0[b]		0.417		0.675	0.750	0.072
200	70.0[b]		0.651		1.040	1.120	0.110
100	47.5	0.070	0.092	0.120	0.157	0.150	0.018
100	50.0	0.082	0.111	0.139	0.188	0.170	0.020
100	52.5	0.115	0.131	0.193	0.220	0.220	0.028
100	55.0	0.128	0.147	0.214	0.245	0.250	0.032
100	60.0[b]		0.232		0.300	0.290	0.043
100	65.0[b]		0.309		0.510	0.510	0.055
100	70.0[b]		0.488		0.780	0.740	0.074
100	75.0[b]		0.760		1.20	1.250	0.137

[a] Reaction time = 3 h. [b] Knee point is not clearly distinguishable at higher temperatures.

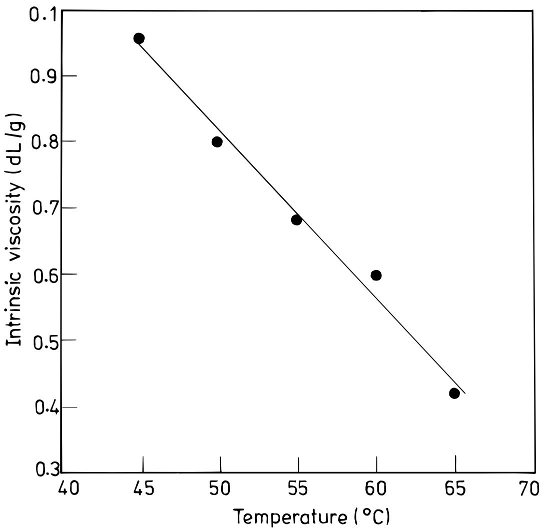


Figure 5. Dependence of intrinsic viscosity on temperature for thermal oxidative polymerization of AMS at 200 psi of oxygen.

highly exothermic, the bulk degradation of PMSP occurs at a lower temperature than in solution due to self-heating. Hence, in the present case the autoacceleration involves a feedback mechanism because acetophenone, one of the products of PMSP degradation, catalyzes the decomposition of PMSP, producing more alkoxy radicals for initiation and thereby promoting autoacceleration.

Kinetics of AMS Polymerization. In order to calculate the activation energies before and after the knee point, polymerizations were carried out at different temperatures but at a constant pressures of 100 and 200 psi, respectively (Table 2). The overall activation energies (E_a) of the polymerization were calculated by using Arrhenius equation[24] the E_a values were found to be 18 and 14 kcal/mol before and after the knee point, respectively (Figure 4), which suggests that different polymerization mechanisms are operative in the two regimes.

The knee point is indicative of the shift in the mechanism as shown by the change in the energy of activation. It may be noted that knee formation is observed only at low temperatures, for example below 60 °C, above which no knee formation is seen. Above 60 °C the degradation of PMSP is very fast, and hence, formation of acetophenone occurs right from the beginning itself and the mechanism is similar to that observed above the knee point for the polymerization rate measured below 60 °C. Above the knee point, acetophenone catalyzes the PMSP degradation, producing more alkoxy radicals, which in turn initiate the polymerization, and this results in the rapid rise in the rate of polymerization. This catalytic effect being more pronounced at higher temperatures (above 60 °C) due to the facile degradation of peroxy bonds, the "auto-acceleration" is observed at higher temperatures.

The E_a for thermal oxidative polymerization of AMS, based on Scheme 1, is given by

$$E_a = E_{p2} + E_i/2 - E_t/2. \tag{1}$$

where E_{p2}, E_i, and E_t are the activation energies for propagation, initiation, and termination respectively. The E_{p2} and E_t values for AMS polymerization are 8.1 and 3.7 kcal/mol, respectively.[25] Using the experimentally obtained E_a value (18 kcal/mol), before the knee point, the E_i value calculated from eq 1 was found to be 24 kcal/mol. This is close to the E_i value for the thermal oxidative polymerization of styrene (27 kcal/mol), calculated in a similar fashion.[10,26] Hence, the mechanism of thermal oxidative polymerization of AMS before knee point can be assumed to be similar to that of styrene, reported previously,[9] as outlined in Scheme 1.

Kinetics of PMSP Degradation. The mechanism of decomposition of PMSP is a free radical chain reaction.[27] DSC studies show that PMSP decomposes exothermally. It was also found from DSC study that the presence of a catalytic amount of paraformaldehyde does not affect the decomposition of PMSP. However, the presence of a catalytic amount of acetophenone accelerates the decomposition of PMSP causing the peak maximum (T_m) and the initial onset decomposition temperature (T_i) to shift to lower temperatures (Figure 7). The peak in the presence of acetophenone was found to be broadened which renders it difficult to accurately determine the peak temperature (T_m). The decompositions of the neat PMSP and PMSP + acetophenone (7 wt %) were studied at different heating rates ($\phi = dT/dt$) (Table 3). In order to calculate the activation energy (E_d) for PMSP decomposition from the T_i and ϕ data, the kinetic equation which relates ϕ with T_i, was derived as follows. Let us consider the following general rate expression

$$d\alpha/dt = k(1 - \alpha)^n \tag{2}$$

where α is the fraction of PMSP decomposed at time t, k is the rate constant and n is the order of reaction.

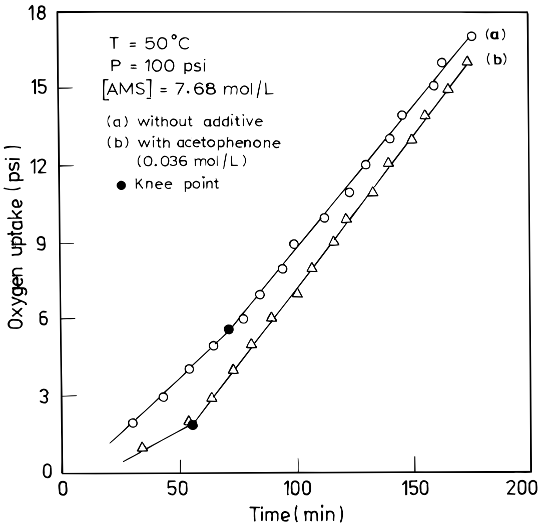


Figure 6. Oxygen consumption as a function of time: (a) without additive; (b) with acetophenone.

Table 3. Thermal and Kinetic Data on PMSP Degradation without and with Added Acetophenone[a]

scan rate (K/min)	PMSP + acetophenone (7 wt %) T_i (°C)	T_m (°C)	PMSP T_i (°C)	T_m (°C)
5	73.39	100.00	88.04	113.90
10	82.76	108.00	93.70	119.90
15	88.48	115.00	96.00	123.50
20	92.11	116.00	99.00	125.70
25	93.50	117.00	102.00	129.00
E_a(kcal/mol)	18 ± 2	23 ± 5*[a]	32 ± 2	33 ± 2

[a] T_i = initial onset decomposition temperature; T_m = peak temperature. [b] Due to a broad peak the error in E_a is greater.

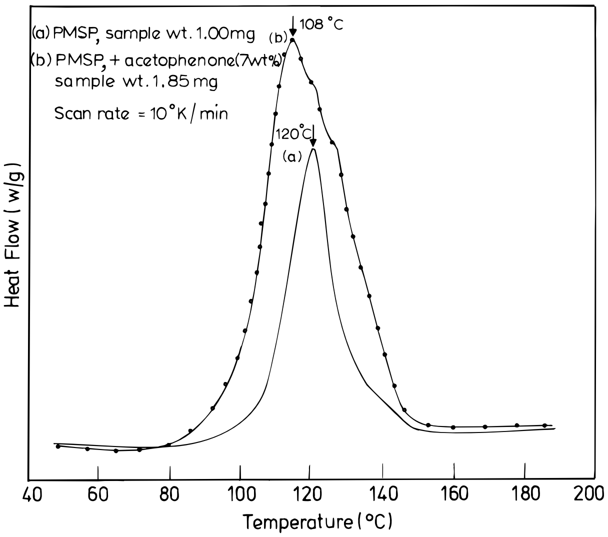


Figure 7. DSC thermograms of (a) PMSP and (b) PMSP + acetophenone (7 wt %).

Table 4. PMSP and Acetophenone Concentrations at the Knee Point in the Thermal Oxidative Polymerization of AMS at 100 psi

T (°C)	knee formation time (min)	[PMSP] (mol/L)	[acetophenone] (mol/L)
47.5	90	0.226	0.035
50.0	78	0.213	0.036
52.5	68	0.192	0.037
55.0	40	0.146	0.039

Substituting the Arrhenius equation ($k = Ae^{-E_d/RT}$) and ϕ into eq 2, we get

$$(d\alpha/dT)\phi = Ae^{-E_d/RT}(1 - \alpha)^n \tag{3}$$

At T_i the fraction of PMSP decomposed (α) is zero; $d\alpha/dT$ is generally a constant during initial decomposition conditions, and it does not vary much with the heating rate. Hence $d\alpha/dT$ may be assumed to be constant. Substituting these boundary conditions into the logarithmic form of eq 3, we get

$$\ln \phi = \ln A' - E_d/RT_i \tag{4}$$

where $A' = A/(d\alpha/dT)$.

From the plot of ln ϕ vs $1/T_i$ (eq 4), which was found to be a straight line, the slope gave E_d (32 ± 2 kcal/mol) for the neat PMSP decomposition. The E_d value was also calculated from the peak temperature (T_m) at various heating rates using Kissinger's method,[28] and it was consistent with that obtained from eq 4. The experimentally observed E_d value of PMSP decomposition corresponds to the thermal rupture of the peroxide bond.[16] In a similar fashion the activation energy was also determined for the decomposition of PMSP in the presence of acetophenone; the E_d value was found to be 18 ± 2 kcal/mol. The E_d value, thus obtained, could be taken as the experimentally derived E_i value for AMS polymerization in the presence of acetophenone. From the observed E_a (14 kcal/mol) for AMS polymerization, in the presence of acetophenone after the break point, together with the reported E_{p2} and E_t values,[25] the calculated value of E_i from eq 1 was found to be 16 kcal/mol, which is consistent with the experimentally observed E_i (18 ± 2 kcal/mol) from DSC experiments as discussed above. This strongly suggests that the mechanism proposed in Scheme 1 is operative even after the knee point formation, provided E_i has to be modified for the catalytic effect of acetophenone on the cleavage of PMSP. Substantial reduction of the E_i value for AMS polymerization from 32 to 18 kcal/mol in the presence of the generated catalyst acetophenone, during polymerization, seems to be responsible for the observed “autoacceleration”.

Polymerization Rate Equations. The rate of polymerization, based on Scheme 1, before the knee point can be written as

$$R_{p1} = -d[O_2]/dt = \frac{f_1 k_{p2} k_i^{0.5}}{k_t^{0.5}}[M]^{1.5}[O_2]^{0.5} \tag{5}$$

where k_t, k_{p2} and k_i are the rates of termination, propagation, and initiation respectively and f_1 is the efficiency of the initiator. In order to examine whether autoacceleration is due to the products, the change in rate was examined in the presence of added formaldehyde and acetophenone. The rate is not changed in the presence of formaldehyde. In the presence of acetophenone the time of knee point formation is reduced as shown in Figure 6. Hence, it is clear that the cause of autoacceleration is due to the products formed in the polymerization. The product analysis at the knee point shows that the amount of acetophenone increases while that of PMSP decreases, with the increase in the temperature of polymerization (Table 4). This shows that as the temperature increases even a smaller amount of the PMSP formed is sufficient to cause the autoacceleration. That is why, the time of knee point formation decreases with temperature. Because of this reason, above 55 °C, no knee formation was observed but the rate increases significantly.

Kinetics of polymerization, after the knee point is given in Scheme 1, the R_{p2} is given by

$$R_{p2} = k_{p2}[\sim\sim MOO^\bullet][M] \qquad (6)$$

Under steady state conditions

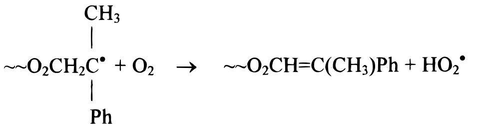
$$2f_2k_d[PMSP] + 2k_if_1[O_2][M] = 2k_t[\sim\sim MOO^\bullet]^2 \qquad (7)$$

where k_d is the rate constant for PMSP decomposition ($k_2 \ll k_{p2}$), and f_2 is the initiator (PMSP) efficiency. Equation 7 is solved for $[\sim\sim MOO^\bullet]$ and substituted in eq 6 to get the R_{p2}

$$R_{p2} = k_{p2}/k_t^{0.5}[M]\{f_2k_d[PMSP] + f_1k_i[M][O_2]\}^{0.5} \qquad (8)$$

From eq 8 it is clear that R_{p2} is not a linear function of oxygen pressure. So, the deviation from the monomer and initiator exponents, after the knee point, is inevitable, and hence, the exponents calculated from the ln−ln plot may not represent the true value. Experimentally it is difficult to study the kinetics of PMSP-initiated polymerization of AMS because the concentration of PMSP continuously increases during polymerization. Besides, acetophenone formed due to the PMSP degradation autocatalyzes the PMSP degradation.

Chain Transfer Reactions and Molecular Weight of PMSP. The molecular weight of PMSP is low[5] ($\bar{M}_n = 5300$). The molecular weight and end groups of PMSP are governed by various chain transfer reactions, which are taking place in the oxidative polymerization.[10] IR spectrum of PMSP shows bands corresponding to the end groups such as $O{=}CHC(CH_3)(C_6H_5)-$, $-CH{=}C(CH_3)C_6H_5$, and $HO_2CH_2C(CH_3)C_6H_5-$ at 1740, 1600, and 3400−3500 cm^{-1}, respectively. Out of these, the unsaturated end groups appear to be more pronounced, which was further confirmed by ^1H NMR spectrum of PMSP. The resonance signals at 1.5, 4.2, 7.2, and 4.9 ppm were assigned to the $-CH_3$, $-CH_2-$, aromatic protons and $>CH-$ proton of the unsaturated end group of PMSP respectively.[29] The presence of unsaturated chain end can be explained on the basis of chain transfer to oxygen, as follows:



$$\sim\sim O_2CH_2\overset{CH_3}{\underset{Ph}{C^\bullet}} + O_2 \rightarrow \sim\sim O_2CH{=}C(CH_3)Ph + HO_2^\bullet \qquad (9)$$

Generally the chain transfer reactions either do not affect or decrease the rate of polymerization.[17] Instead, not only is an increase in the rate observed but also the reaction shows an autoacceleration. This can be explained on the basis of substantial acetophenone-induced decomposition of PMSP, giving alkoxy radicals for initiating the polymerization. The intrinsic viscosity of the isolated PMSP was found to be independent of oxygen pressure and extent of conversion. However, it linearly decreases with increase in the temperature of polymerization. Hence, in addition to the chain transfer reactions, the temperature of the polymerization also controls the molecular weight of PMSP.

Effect of O_2 Pressure on the Kinetics of Polymerization. The effect of oxygen pressure on AMS polymerization, at 50 °C, is shown in Figure 1. The amount of dissolved oxygen in AMS will be greater with an increase in the oxygen pressure, which in turn will increase the rate of polymerization. The saturation pressure of oxygen, that is the pressure at which the rate of polymerization is independent of oxygen pressure, was calculated mathematically as reported recently.[14] It was found to be 300 psi for the present thermal oxidative polymerization of AMS. This value is close to the saturation pressure of oxygen for the AIBN-initiated oxidative polymerization of AMS.[14] The degradation product formation is more in the case of AMS oxidative polymerization than the styrene oxidative polymerization. This is because the activation energy for the degradative unzipping of alkoxy radicals of PMSP is lower than the alkoxy radicals of poly(styrene peroxide).[16]

The effect of pressure (p), at constant temperature, on the rate constant is given by[30]

$$(d \ln k/dp)_T = -\Delta V_o^{\ddagger}/RT \qquad (10)$$

where $\Delta V_o^{\ddagger}$ and k are the overall volume of activation and rate constant of polymerization, respectively. In general $\Delta V_o^{\ddagger}$ for oxidative vinyl polymerization is always higher than the normal free radical vinyl polymerization.[14] The values of $\Delta V_o^{\ddagger}$, in the pressure range of 50−300 psi, before and after the knee point, was found to be −1200 and −920 cm^3/mol, respectively, suggesting that the effect of pressure on the rate of polymerization before the knee point is more than that after the knee point. This can be explained from the $\Delta V_o^{\ddagger}$ of the polymerization, based on Scheme 1 after the knee point, as follows:

$$\Delta V_o^{\ddagger} = \Delta V_{p2}^{\ddagger} - {}^1/_2\Delta V_t^{\ddagger} + {}^1/_2\Delta V_i^{\ddagger} + {}^1/_2\Delta V_d^{\ddagger} \qquad (11)$$

Here, $\Delta V_{p2}^{\ddagger}$, $\Delta V_t^{\ddagger}$, $\Delta V_i^{\ddagger}$, and $\Delta V_d^{\ddagger}$ are the volumes of activation for propagation, termination, thermal initiation, and initiation by the PMSP, respectively. Usually $\Delta V_{p2}^{\ddagger}$ and $\Delta V_i^{\ddagger}$ (two molecules are coming together to form a biradical and volume decreases) are negative and $\Delta V_t^{\ddagger}$ and $\Delta V_d^{\ddagger}$ are positive.[17] $\Delta V_d^{\ddagger}$ is negligible before the knee point but prominent after the knee point. Hence, $\Delta V_o^{\ddagger}$ will always be negative before knee point, but its magnitude will be less after the knee point due to the positive value of $\Delta V_d^{\ddagger}$, which is significant only after the knee point. The negative $\Delta V_o^{\ddagger}$ indicates that increase in pressure leads to an increase in the reaction rate. The unusually higher values of the $\Delta V_o^{\ddagger}$ may be because the pressurizing gas oxygen itself is a reactant in the polymerization.

Conclusions

PMSP was synthesized by thermal oxidative polymerization of AMS at relatively lower temperatures with high yield. Thermal oxidative polymerization of AMS has been studied at different temperatures and pressures and the kinetics of the process analyzed. The unique feature of AMS thermal oxidative polymerization is its exhibition of "autoacceleration" during polymerization. Decomposition of the formed polyperoxide (PMSP) to alkoxy radicals, which is further catalyzed by its own decomposition product namely acetophenone, appears to be the main cause of autoacceleration. This behavior can be used to our advantage for using them as low temperature initiators and curatives. Besides, polyperoxides are cheap materials containing 20−50% of oxygen which could be obtained readily from air.

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