Effect of Viscosity on the Autoxidation of Emulsions

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Polymerization of olefins that takes place in emulsified mixtures rather than in homogeneous solution proceeds at a faster rate and often results in the formation of polymers with considerably higher molecular weight.[2] This emulsion effect in polymerization is of both industrial and academic interest; however, attempts to extend the effect to other free-radical reactions have not been successful. Most recently we have surveyed the oxidation of various emulsified hydrocarbons by molecular oxygen using a number of different emulsifying agents at controlled rates of initiation and have failed to find evidence that a simple emulsification has any effect on rate or products.[3]

Because viscosity of the media is important in polymerization and appears to contribute to rate enhancement, at least in the final stage of an emulsion polymerization,[4] we have sought to determine whether there is an effect of viscosity in autoxidation. Since chain-carrying species in autoxidation have a low molecular weight compared to those in polymerization, one might expect much less dependence on viscosity. The study of the effect of viscosity on the oxidation of compounds in the bulk phase is complicated by the difficulty of diffusing oxygen into a viscous medium. However, this difficulty is not important in an emulsion where the oxidizing media have a high surface-to-volume ratio. We have investigated the effect of viscosity on the oxidation of emulsified mixtures that were prepared by adding the desired monomer to freshly prepared polymer latex, and the results are reported below.

Experimental Section

Procedure. All monomers were reagent grade and freshly distilled before use. Emulsifiers were from the same source as previously described.[3]

Most of the techniques employed were as previously described.[3] The polymer latexes were synthesized by emulsifying the appropriate monomer, then exposing the emulsion to Co-60 radiation at a rate of 200 rads/min. The progress of the polymerization was followed by removing samples, breaking the emulsion with methanol, and analyzing for unreacted monomer in the supernatant by GLC. Mixtures of emulsified monomer and polymer were prepared by combining known portions of emulsified monomer and latexes where polymerization was carried to completion. Autoxidations of these mixtures under Co-60 irradiation were followed by measuring the oxygen consumption in the apparatus previously described.[3]

Results

The oxidation of methyl methacrylate (MMA), styrene, and Tetralin has been accomplished in sodium lauryl sulfate (NLS) or poly(oxyethylene palmitate) (POEP) emulsions (or both) with various amounts of either poly(methyl methacrylate) or polystyrene latex. The latexes were formed at sufficiently high emulsifier concentration to give latex particle concentrations of $10^{14.\pm 0.5}$ particles/cm^3. While the reactivity of the polymeric latexes is very low compared to the monomers, the polymeric latexes increase the viscosity of the emulsion particle significantly. Table I summarizes the effect of latex on the rate of oxidation of the monomers. The rate of oxidation is expressed in moles of O_2 consumed per mole of substrate per minute. Since under emulsion conditions bulk rate expression applies,[3] the rate expressed in this form is a constant

$$R_0 = CR_i^{1/2}[\mathrm{RH}]$$

or

$$R_0/[\mathrm{RH}] = CR_i^{1/2}$$

Small variations in rate, because of variations in the emulsifier concentration, were corrected to the rate corresponding to a concentration of 6.25 ± 0.05 g/l. by using our earlier observation that the rate depended on the one-half power of the emulsifier concentration.[3] In the styrene and Tetralin experiments, 5.55 ± 0.05 g/l. was used for the standard emulsifer concentration.

While the monomer and polymer used are totally miscible in bulk, only a limited amount of monomer will be absorbed by the latex particle. The saturation ratio results from the increased surface energy due to swelling of the particle by the monomer which compensates the free energy of mixing for methyl methacrylate. To ensure that there were no monomer droplets where oxidation could occur, the ratio of monomer to latex has been kept below the saturation ratio. This point ranges from 2 to 3 g of MMA/g of poly-MMA depending on conditions.[4]

The latex used usually corresponded to that derived from the monomer studied, except in one experiment with styrene where the latex was composed of poly-MMA. For the oxidation of Tetralin, poly-MMA was used as the latex.

Discussion

The data from Table I are presented graphically in Figure 1. The rates of oxidation of both methyl methacrylate and styrene increase as the proportion of latex is increased. The increase of the proportion of latex (a decrease in the substrate/latex ratio) causes an increase in viscosity within the swollen latex particle. The oxidation of Tetralin, in contrast, shows no dependence on substrate/latex ratio and therefore is unaffected by viscosity.

The mechanism of a reaction between two components A and B may be expressed as follows:

$$\mathrm{A} + \mathrm{B} \rightleftharpoons (\mathrm{A} + \mathrm{B})_{\mathrm{cage}} \qquad (1)$$

$$(\mathrm{A} + \mathrm{B})_{\mathrm{cage}} \rightarrow \mathrm{product(s)} \qquad (2)$$

The rate expression is

$$\mathrm{d[product]}/\mathrm{d}t = k_1 k_2 (k_{-1} + k_2)^{-1}[\mathrm{A}][\mathrm{B}] \qquad (3)$$

Changing the viscosity of the reaction medium is anticipated to affect process 1 rather than 2 because (1) is a diffusion process requiring solvent reorganization. The rate constant for a process such as 1 may be expressed as[5]

$$k_1 = (4\pi N/1000)(r_{\mathrm{A}} + r_{\mathrm{B}})(D_{\mathrm{A}} + D_{\mathrm{B}})$$

where r_A and r_B are the reaction radii for A and B assuming a spherical shape and D_A and D_B are the diffusion constants of A and B under the conditions of the reaction. The diffusion constant may be approximated by the Stokes–Einstein equation as a function of the temperature (T) and viscosity (η) of the medium and radius of the diffusing species, although in polymeric systems it is only a rough approximation[6]

$$D = kT/6\pi\eta r \qquad (4)$$

In most cases there is little interaction between A, B, and solvent ($\Delta S_1 = 0$, $\Delta H_1 = 0$), and the rate constant for the reverse process k_{-1} is identical with k_1.

When k_2 is much smaller than k_{-1}, the reaction is not diffusion controlled and eq 3 reduces to the typical expression

$$\mathrm{d[product]}/\mathrm{d}t = k_2[\mathrm{A}][\mathrm{B}] \qquad (5)$$

Table I
Oxidation of Methyl Methacrylate (MMA), Styrene (S), and Tetralin (T) in the Presence of Latex at 50°

Substrates, mol/l. of solvent	Emulsifying agent, g/l. of solvent	Latex, mol/l. of solvent	Substrate/ latex	Rate × 10^5 Gross, mol of O_2/ l. of solvent/ min	Rate × 10^5 Specific,[a] mol of O_2/ mol of substrate/min
MMA 1.022	5.56 NLS	0	∞	1.44	1.50
	(6.25 NLS)	0		(1.53)	
MMA 2.330	6.25 NLS	0	∞	3.75	1.61
MMA 1.449	6.29 NLS	MMA 0.990	1.46	3.45	2.30
MMA 0.956	6.28 NLS	MMA 1.309	0.73	4.14	4.17
MMA 0.666	3.50 NLS	MMA 0.990	0.67	2.56	4.92
	(6.25 NLS)			(3.40)	
MMA 0.420	6.30 NLS	MMA 1.680	0.25	3.35	7.47
None	6.24 NLS	MMA 2.330	0	0.29	
S 0.969	5.52 POEP	0	∞	9.69	10.0
S 0.485	5.56 POEP	S 0.396	1.22	10.00	20.6
S 0.797	2.88 NLS	MMA 1.500	0.53	27.2	34.1
	(5.55 NLS)			(37.5)	(47.0)
T 0.810	5.56 POEP	0	∞	5.93	7.31
T 0.880	5.70 POEP 2.87 NLS	MMA 0.995	0.80	5.85	7.32

[a] Note: Specific rate of reaction is corrected for the small rate of oxidation latex.

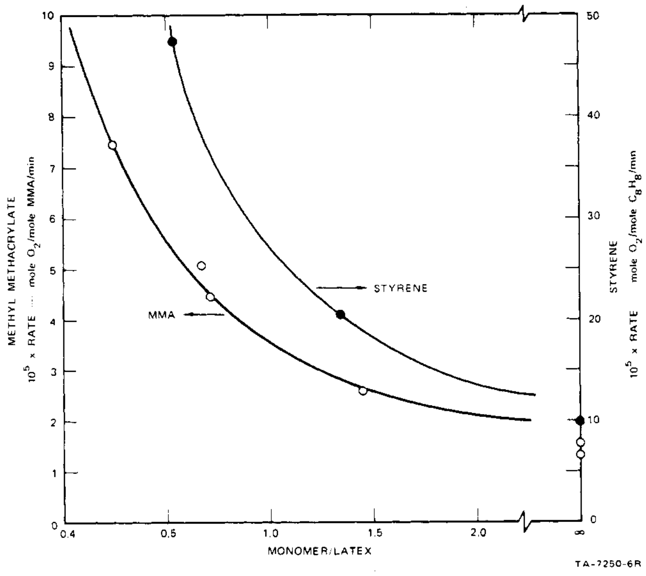

Figure 1. Oxidation of methyl methacrylate and styrene at 50° and 200 rads/min.

However, as the viscosity increases, k_1 will decrease, and the rate of a reaction will begin to decrease once the diffusion rate constant (k_1 and k_{-1}) approximately equals k_2. When k_{-1} is significantly smaller than k_2, the reaction becomes totally diffusion controlled as seen in the reduced form of eq 3

$$\mathrm{d[product]/d}t = k_1[\mathrm{A}][\mathrm{B}] \qquad (6)$$

In low-viscosity solutions the termination rate constants for the types of peroxy radicals that are involved range from 10^4 to 10^7 l./mol/sec.[7] These values are below that observed for diffusion-controlled reactions, which range from 10^7 to 10^{10} l./mol/sec depending on the size and shape of the diffusing species,[8,9] and therefore eq 5 applies to these termination reactions. However, as the viscosity is increased and the rate of diffusion approaches that for termination in the low viscosity medium, the reaction begins to depend on the viscosity. This is the result we see with both the oxidation of MMA and styrene. Both of these monomers form polymeric copolymers with oxygen by a peroxy radical-addition mechanism.[10,11] Since the rate of reaction depends inversely on the termination, retarding termination by increasing the viscosity accelerates the rate of oxidation. The effect is similar to the polymerization results for *n*-butyl acrylate in this regard. In this system, the termination reaction is not diffusion controlled in low-viscosity solutions ($k_t = 5 \times 10^4$ l./mol/sec),[8] but at viscosities of 10 cP or greater it shows a direct inverse dependence of the viscosity (eq 6). Again the overall polymerization process increases with the increase in viscosity.

The oxidation of Tetralin, in contrast to methyl methacrylate and styrene, showed no dependence on the change in viscosity. This undoubtedly is because the peroxy radicals are of low molecular weight and encounter less difficulty in diffusing through the Tetralin–polymer solutions. In general, smaller radicals diffuse faster and their reaction rates become sensitive to viscosity at much higher viscosities than larger radicals.

The propagation reactions for the peroxy radicals in these reactions have rate constants in the range of 1 to 100 l./mol/sec,[7] which is sufficiently below the diffusion rate even at high viscosities to not show any viscosity dependence (eq 3). Therefore, the effects of viscosity observed must be totally due to the effect on the termination reactions. Assuming the bulk reaction kinetic model where the rate of reaction depends on the one-half power of the termination constant, one may estimate the difference in k_t at high viscosity (hv) and low viscosity (lv) accordingly

$$R_0^{\mathrm{hv}}/R_0^{\mathrm{lv}} = (k_t^{\mathrm{lv}}/k_t^{\mathrm{hv}})^{1/2}$$

or

$$k_t^{\mathrm{lv}}/k_t^{\mathrm{hv}} = (R_0^{\mathrm{hv}}/R_0^{\mathrm{lv}})^2$$

Since, over the ranges studied, the rate varied by a factor of about 5 in the MMA and styrene systems, the termination constant ranges over a factor of 5^2 or 25. Furthermore, since the rate of oxidation appears to be increasing sharply at the lowest monomer/latex ratios measured, the value of k_t must be changing rapidly so that near to 100% latex the value of k_t must be at least a factor of 100 smaller than the low-viscosity value in the MMA system and even smaller in the styrene system.

The contribution of the emulsifiers to the overall consumption of oxygen in these experiments is anticipated to be small. In the previously reported study[3] a solution of emulsifier absorbed oxygen at about one-tenth the rate of the styrene emulsions. The styrene concentrations were comparable to those in the present study and no polymer latex particles were present.

The degree of rate enhancement due to increased viscosity for oxidation of both MMA and styrene is less than observed in bulk polymerization under similar conditions. At 35% conversion, approximately a 14-fold increase is observed in the polymerization rate of MMA.[12] However, the *rate of oxidation of the same mixture of polymer/monomer* is less than twice as fast as that of pure MMA. Similarly, for polymerization of styrene at 35% conversion, the rate is enhanced 2.4 times, while the oxidation rate of the same polymer/monomer mixture is 1.5 times faster than neat styrene. This difference between polymerization and oxidation is related to two factors. First, the rates of reaction of the much larger radicals in the polymerization reactions are more sensitive to viscosity than are the rates of the smaller oxidation radicals. In polymerization, the molecular weight of the chain-carrying radical ranges up to 10^5–10^6, while for oxidation the molecular weight of the chain-carrying peroxy radical is limited to 10^2–10^3 by a rapid chain-transfer reaction.[10,11]

Second, in the oxidation of pure MMA or styrene, less change in viscosity occurs with conversion than observed in polymerization because of the much lower molecular weight of oxidation products. Even at relatively high conversions in the oxidation of MMA or styrene there is little viscosity increase in the medium and a concomitantly small rate enhancement. Thus to the extent that the emulsion rate enhancement phenomenon is dependent on a rapidly increasing viscosity of the growing particle, rate enhancement in emulsion oxidation would not be expected.

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Superacids and Their Derivatives. VIII.[1] Cationic Ring-Opening Polymerization of Oxepane by Superacids and Their Derivatives

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We have hitherto reported kinetic and mechanistic studies on the ring-opening polymerizations of five-[1-5] and four-membered[6] cyclic ethers by superacid esters[1-4,6] and anhydrides[5] and related reactions of six-membered ones.[7] In the present study, this series of reactions has been extended to the polymerization of a seven-membered cyclic ether of oxepane. Superacids used were trifluoromethanesulfonic (CF_3SO_3H), fluorosulfonic (FSO_3H), and chlorosulfonic ($ClSO_3H$) acids.[4]

The polymerization of oxepane was first reported by Saegusa et al.[8,9] and by Gehm[10] with typical Lewis acid catalysts such as BF_3,[8-10] $SbCl_5$,[8] $SnCl_4$,[8] $AlCl_3$,[10] and PF_5.[10] The present study has shown that superacids (No. 1–4), their esters (No. 5–9), and an anhydride (No. 10) are effective catalysts for the ring-opening polymerization of oxepane (Table I).

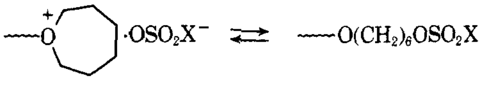
A typical run (No. 5) was as follows. To a mixture of oxepane (1.00 g, 10 mmol) and nitrobenzene (1.14 ml) in a glass tube, ethyl trifluoromethanesulfonate ($EtOSO_2CF_3$) (0.48 mmol) was added at room temperature under nitrogen. *The tube was sealed and kept at 25°. After 93 hr the* reaction mixture was poured into 20 ml of methanol containing 0.05 g of NaOH. White powder precipitated and the mixture was stirred for 20 hr at room temperature. After neutralization of the methanol solution with an aqueous HCl the powdery material was separated by filtration, dissolved in 3 ml of CH_2Cl_2, and reprecipitated again in 30 ml of methanol. The polymer was separated by filtration and dried in vacuo (0.86 g, 86% yield). Anal. Calcd for $(C_6H_{12}O)_n$: C, 71.45; H, 12.10. Found: C, 71.16; H, 11.93. The melting point of the polymer was 57°. The molecular weight was 1940 (vapor pressure osmometry in CH_2Cl_2 at 30°). This value is very close to the calculated value of 1840 (100 × 86/4.8 + 46) on the assumption that 1 mol of initiator produced 1 mol of polymer having structure **1** (n = 17.9). These findings indicate the absence of chain transfer.

$$C_2H_5{-}\!\!\left[O(CH_2)_6\right]_n\!\!{-}OH$$

1

The highest molecular weight obtained was 6200 (No. 10 in Table I) measured by vapor pressure osmometry (vpo) in CH_2Cl_2. The sample polymer was subjected to gel permeation chromatography (GPC) using tetrahydrofuran solvent. A ratio of M_w/M_n = 1.36 was obtained, indicating that a molecular weight distribution is relatively narrow. The M_n value by GPC was 6370 which is close to that obtained by vpo. The melting point of polymer became higher with an increase of the molecular weight. The rate of polymerization was faster in polar solvents such as nitrobenzene and nitromethane than in less polar ones, e.g., CH_2Cl_2 or bulk (vide infra).

A preliminary study has been carried out to examine the polymerization mechanism by means of ^1H and ^{19}F NMR spectroscopy. The oxonium (**2**)–ester (**3**) equilibrium (eq 1) of the propagating chain end was observed as in the tetrahydrofuran polymerization initiated by superacid esters.[1,2,11,12]



(1)

2a, X = CF₃
b, X = F

3a, X = CF₃
b, X = F

Figure 1 shows a ^1H NMR spectrum of the oxepane polymerization initiated by $EtOSO_2CF_3$ in nitrobenzene at 35° after 97 min, in which the initiator has already been consumed. A multiplet peak A at δ 5.3–5.0 is due to α-methylene protons (6 H) of the oxonium center **2a** and a triplet peak B at δ 4.65 is assigned to α-methylene protons (2 H) of