ELSEVIER

Polymer 42 (2001) 9329–9333

polymer

www.elsevier.com/locate/polymer

Emulsion polymerization of methyl methacrylate initiated by alkene ozonates

D. Cunliffe[a], J.E. Lockley[a,1], J.R. Ebdon[a], S. Rimmer[a,*], P. Palasz[b], S. Emmett[b]

[a]*The Department of Chemistry, University of Sheffield, The Dainton Building, Brook Hill, Sheffield S3 7HF, South Yorkshire, UK*
[b]*ICI Paints, Wexham Road, Slough SL2 5DS, Berkshire, UK*

Received 8 April 2001; received in revised form 22 May 2001; accepted 31 May 2001

Abstract

Ozonolysis of tetramethyl ethene, *trans*-4-octene or 1-octene in water leads to species, which after thermolysis at 60°C, generate radicals that initiate radical emulsion polymerization of methyl methacrylate (MMA). The course of the reaction is dependent on the structure of the alkene used. Tetramethyl ethene ozonates give the highest final yield of polymer, although the rates of polymerization observed from 0 to approximately 60% conversion are found to be essentially equivalent, regardless of the structure of the alkene employed. The difference in final conversion is attributed to changes in the half life of the generated peroxy species as a function of alkene structure. From these differences it is inferred that the initiating species are organo peroxides, probably hydroxy hydroperoxides, rather than hydrogen peroxide. Two latex systems, one stabilized by a cationic surfactant and the other by an anionic surfactant, were successfully prepared. Ozonolysis of water followed by heating in the presence of MMA does not produce polymer. However, ozonolysis of an aqueous sulphonate surfactant solution does produce a species that forms radicals on thermolysis and these radicals initiate radical polymerization of MMA, which proceeds to high conversion in emulsion. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Emulsion polymerization; Ozonolysis; Peroxide

1. Introduction

Conventional emulsion polymerizations can be initiated by both water-soluble and water-insoluble azo, peroxy and persulphate compounds [1]. Alternative sources of initiation have included polymerizations with both γ-radiations [2] and β-radiation [3]. A different approach would be to generate the active (radical producing species) in situ from a precursor material. With this idea in mind, we have recently shown that the products from the ozonolysis of alkenes can, on thermolysis, generate radicals that can be used to polymerize vinyl monomers [4–7]. Thus, an alkene can be considered to be a type of protected radical initiator, which is activated by reaction with ozone. These previous experiments were performed in non-participating organic solvents and the main source of the radicals was found to be cyclic and oligomeric peroxides. However, the course of ozonolysis in participating solvents, such as water, is known to involve the production of the hydroxy hydroperoxide (or alkoxy hydroperoxides in the case of alcohols) [8] intermediate rather than the tetroxanes, trioxanes and oligo-peroxides produced during ozonolysis in non-participating solvents [8–29]. The difference is usually understood to be due to fast reaction of the carbonlyl oxide with the participating solvent as shown in Scheme 1 (production of alkoxy and hydroxy hydroperoxides from the reaction of carbonyl oxides formed during ozonolysis in alcohol and water, respectively).

Other fates for the carbonyl oxide derived from terminal alkenes following interaction with water have also been proposed [30] and are shown in Scheme 2 (alternative pathways following the interaction of water with a carbonyl oxide). Alkoxy hydroperoxides derived from ozonolysis have been used in radical fragmentation organic synthesis [31]. Also polymers such as cellulose have been converted into graft copolymers via initiation of radical polymerization from peroxides produced during ozonization of cellulose [32]. However, there appear to be no reports on the behavior of the products of alkene ozonolysis, in water, as initiators of radical polymerization. This is surprising since the products of these reactions are potentially radical-generating peroxy species and also ozonolysis is a very simple, cheap and environmentally acceptable method of generating

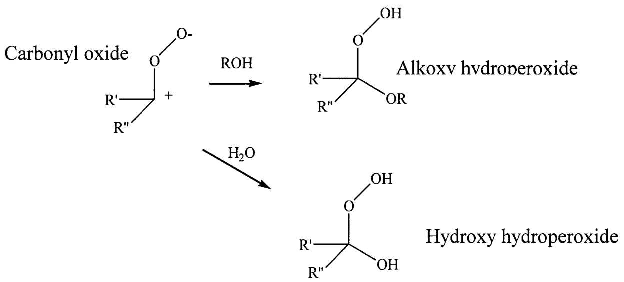
---

[*] Corresponding author. Tel.: +44-114-222-9565; fax: +44-114-273-8673.

E-mail address: s.rimmer@sheffield.ac.uk (S. Rimmer).

[1] Present address: Victrex Technology Centre, Hillhouse International, Cleveleys FY5 4QD, Lancashire, UK.

0032-3861/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(01)00413-X



Scheme 1.

peroxides from readily available starting materials. The hydroxy hydroproxide species are generally regarded as being reactive intermediates but they are stable enough to be observed by FTIR and HPLC [30]. They are also rather polar species that are expected to be at least partially water soluble.

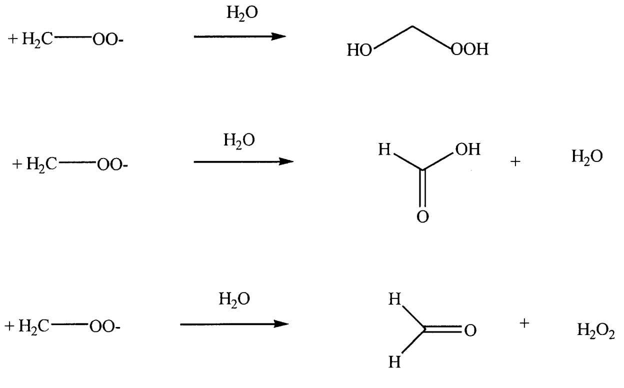
Initiation of polymerization by the hydroxy hydroperoxide species may produce polymer with chain-end functionality dictated by the structure of the starting alkene. Since the alkene precursors are far more chemically stable than the common azo, peroxy or persulphate initiators, it may be possible to add a larger range of chain-end functionalities than is possible with the latter conventional initiators. Also, the possibility of exerting a large degree of control over the water/oil solubility of functional alkenes used as initiator precursors may offer advantages in emulsion polymerization in the future. The following paper describes the aqueous ozonolysis of several alkenes and then illustrates the use of the products in the emulsion polymerization of methyl methacrylate (MMA). In the course of these experiments, we have also noticed that ozonolysis of a sulfonate surfactant produces a species that, after thermolysis, also initiates polymerization of MMA in emulsion.

2. Experimental

2.1. Emulsion polymerizations

2.1.1. Materials

Cetyl ammonium bromide (Fisher) and sodium dodecyl phenoxy benzene sulfonate (DPOS-45, Cytec, aq. 50%) were used as supplied. MMA was purified by washing with 2% NaOH aq. and then vaccum distilled.



Scheme 2.

2.1.2. Instrumentation

SEC measurements were carried out with a RI detector at ambient temperature using THF as the solvent and toluene as a flow marker. Polymer Laboratories gel mixed B; 3 × 30 cm high-molecular-weight columns were used with a flow rate of $1\ \mathrm{ml\ min^{-1}}$. Sample concentrations were $2\ \mathrm{mg\ cm^{-3}}$. Calibrations were performed with PMMA standards from Polymer Laboratories (UK) and a third order fitting routine was used. Particle sizes of all the latexes were obtained by photon correlation spectroscopy (PCS) with a Coulter N4, submicron particle size analyzer using a single angle (90°) measurement. The latex samples were diluted 100-fold prior to PCS.

2.1.3. Preparation of latexes stabilized by sodium dodecyl phenoxy benzene sulfonate

The alkene, either tetramethyl ethene (TME) (0.72 g, 86 mmol), *trans*-4-octene (0.72 g, 64 mmol) or 1-octene (0.72 g, 64 mmol), was dispersed in deionized water ($100\ \mathrm{cm^3}$) along with sodium dodecyl phenoxy benzene sulfonate (SDPBS) (1.00 g) in a reaction kettle equipped with nitrogen and ozone inlets, mechanical stirrer and a condenser. The assembled apparatus was placed in a water bath at room temperature (20°C) and ozone was bubbled through the mixture with vigorous stirring for 20 min. After this time nitrogen was bubbled through the mixture for 20 min to remove excess ozone. MMA (18.00 g, 0.18 mol) was added with vigorous stirring and the temperature of the bath was raized to 60°C. Heating was then continued for 4 h at 60°C under a blanket of nitrogen. Samples were taken every 15 min until, after 4 h, the reaction was quenched by placing the whole vessel into an ice bath. A sample of the final emulsion ($10\ \mathrm{cm^3}$) was precipitated into methanol ($250\ \mathrm{cm^3}$), filtered and dried overnight in a vacuum oven. The solids contents of the latex samples were measured gravimetrically by heating at atmospheric pressure in order to drive off the water. A control reaction in which SDPBS (1.00 g) was ozonized in water but in the absence of an alkene was also carried out. MMA was then polymerized using this mixture. Time vs. conversion plots were then constructed for each polymerization.

2.1.4. Preparation of latexes stabilized by cetyl trimethyl ammonium bromide

The above procedure was repeated but cetyl trimethyl ammonium bromide (CTAB) (1.00 g) was used as surfactant in place of SDPBS. A control reaction in which CTAB alone was ozonized and thermolyzed in the presence of MMA was also carried out.

A further control reaction involved the ozonolysis of water alone followed by addition of MMA and heating, at 60°C.

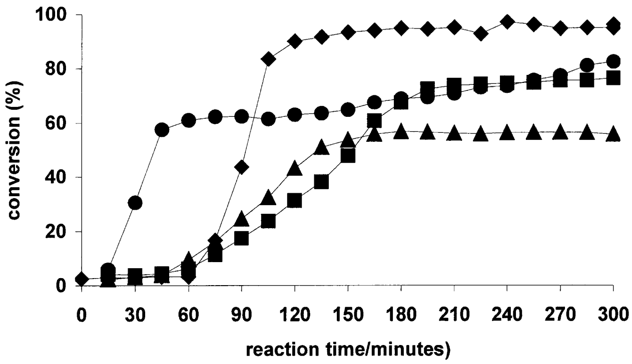
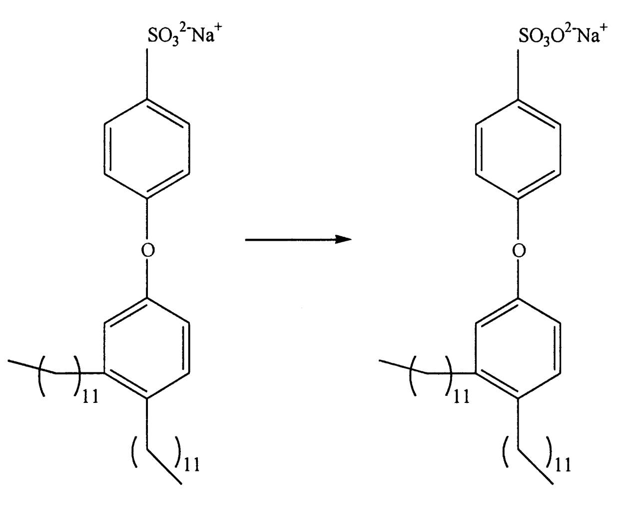


Fig. 1. Conversion/time plots for emulsion polymerizations (surfactant SDPBS) initiated by the products of ozonolysis of: TME, ◆; *trans*-4-octene, ■; 1-octene, ▲; SDPBS alone, ●.

3. Results and discussion

3.1. Sulphonate-stabilized emulsion polymerizations

Fig. 1 shows the increase in conversion of MMA with time in emulsion polymerizations in which either TME, *trans*-4-octene or 1-octene along with sulphonate surfactant (SDPBS) were ozonized and then thermolyzed, after addition of MMA to the reaction vessel. Also shown is the time/conversion data for a polymerization in which SDPBS was ozonized alone and then monomer added. Ozonization of water alone followed by heating of the products produced negligible conversion of MMA to polymer. On the other hand, ozonization of aqueous mixture of the alkenes and SDPBS or SDPBS alone generated species, which were sources of radicals for the polymerization of MMA. Thus, in each of these cases, addition of monomer and heating produced rates of polymerization similar to those in conventional emulsion polymerizations. The initial rates of conversion for the reaction in which SDPBS only was ozonized were significantly higher than those in the other polymerizations. Therefore, these data indicate that the species produced by the ozonolysis of SDPBS is a more effective radical initiator than the products of ozonolysis of the alkenes in water. However, the final conversion was less than 100% and thus was lower than that in the polymerization initiated by TME ozonate. It is assumed that, in the system in which both alkene and SDPBS were ozonized, the alkene is more reactive to ozone than SDPBS so that, over the same ozonolysis reaction-time period, reaction of ozone with alkene is favored over reaction with SDPBS. This assumption is supported by the work of Uppo and Pryor [36]. Thus, the concentration of the more effective initiator (i.e. the species derived from the ozonization of SDPBS) is lower in these cases than in the polymerization initiated via ozonization of SDPBS alone. The reaction of SDPBS and ozone presumably produces a persulphonate, as shown in Scheme 3 (proposed synthesis of persulphate surfactant via ozonization of sulphonate surfactant).



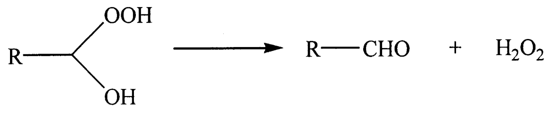
Scheme 3.

The main differences observed in the kinetic behavior of the polymerizations are in the final conversions of monomer reached in the later stages of the polymerizations.

TME > *trans*-4-octene > 1-octene

These differences strongly suggest that species of different structures are responsible for initiation of the polymerizations, since these ozonization-generated initiators clearly have differing half lives. Thus, the ozonization in water of the three different alkenes probably generates organic peroxide species rather than hydrogen peroxide Scheme 4 (possible decomposition of hydroxy hydroperoxide to yield hydrogen peroxide). That is the more substituted alkenes generate more stable ozonates, which have longer half lives.

Also, of interest is the observation that the MMA polymerizations initiated by alkene ozonates display sigmoidal time/conversation curves, similar to the form expected of Smith-Ewart kinetics. Stage I typically lasts for approximately 40 min and presumably involves particle nucleation following coagulation of oligo MMA radicals, as proposed for conventional emulsion polymerizations of this monomer [33]. Interestingly, the polymerization initiated by ozonized surfactant progressed with a stage I of much shorter duration than those initiated by the ozonized alkenes. In contrast to emulsion polymerizations of other less water soluble monomers, stage II in MMA emulsion polymerization does not normally exhibit steady-state kinetics [34,35]. The time/conversion plots derived from polymerizations initiated by ozonates of the three alkenes also show a non-steady state in stage II, i.e. curvature is seen in the time/conversion plots during the period of maximum rate (from approximately 60–180 min). The non-steady-state nature of stage II was further illustrated in the plots of the first derivative against time (not shown). This non-steady-state nature of stage II makes meaningful further analysis difficult. Therefore, calculation of parameters such as the number of radicals per particle were not attempted. The plateaux in the time/conversion plots for the polymerizations initiated by the octene ozonates occurred at conversions between 50 and



Scheme 4.

80%. It is unlikely that these low levels of conversion represent true stage III (as defined by Smith-Ewart) periods in the polymerizations because it is unlikely that all the monomer exists within polymer/monomer particles at these conversions. Rather, it is likely that the plateaux in the rate curves occur because the half-life of the peroxy initiating ozonates is less than that required to maintain a radical flux sufficient to support initiation at these later times. The polymerization initiated by the ozonate of TME proceeded to high conversion and did not appear to be subject to a decrease in radical flux during the later stages of the polymerization. These data then suggest that a different species is responsible for initiation in this system than in the previous polymerization initiated by octene ozonates. Table 1 gives the molecular weight and particle size data for these polymerizations. The data are typical for emulsion polymerizations of this monomer. However, of note is the high molecular weight attained in the polymerization initiated by the ozonized surfactant. Work is continuing on this particular aspect and will be reported in due course.

3.2. Quaternary ammonium stabilized emulsion polymerizations

Following these observations, we considered that it would be useful to examine also the preparation of latexes stabilized by cationic surfactants. Therefore, polymerizations using CTAB as the surfactant were carried out. Once again, ozonolyses of TME, *trans*-4-octene or 1-octene in water and in the presence of CTAB led to species that generated radicals on thermolysis. Thermolysis in aqueous emulsions of MMA led to the production of high molecular weight PMMA in latex form. Table 1 gives the characterization data for these polymerizations. As can be seen from these data, the CTAB-stabilized polymerizations generate PMMA with higher molecular weights and lower polydispersities than do the equivalent SDPBS-stabilized polymerizations. In order to further investigate the use of surfactant ozonates as radical initiators, CTAB was ozonized alone and then thermolyzed in the presence of MMA. However, in contrast to the previous SDPBS-containing system, polymer was not formed in this case. Therefore, it is clear that CTAB (and presumably other quaternary ammonium surfactants) does not produce radical-producing species on reaction with ozone. Fig. 2 shows the conversion vs. time plots observed for each of the CTAB-containing polymerizations. Of immediate note from this figure is the increase in rate and final conversion when TME is used as the alkene. As in the previous system, this polymerization is by far the most successful and the clear difference in the rates between this polymerization and those in which octene is used is a strong indication that the nature of the initiating species is a function of the structure of the starting alkene and is not a common product such as hydrogen peroxide. As in the SDPBS-stabilized system, thermolysis of the ozonate of neither octene yields radical fluxes that are sufficient to maintain polymerization to high conversion.

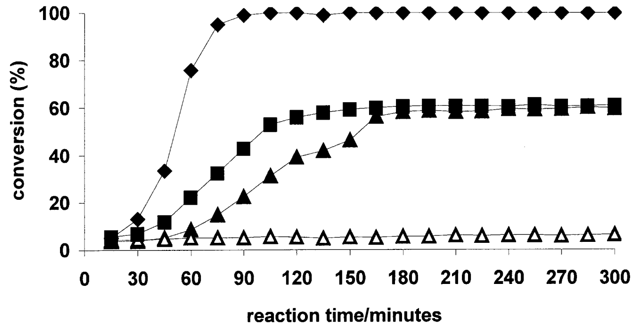


Fig. 2. Conversion/time plots for emulsion polymerizations (surfactant CTAB) initiated by the products of ozonolysis of: TME, ◆; *trans*-4-octene, ■; 1-octene, ▲; CTAB alone, △.

4. Conclusions

While much remains to studied on the these systems, we

Table 1

Final particle sizes, number average molecular weights and molecular weight distributions for the latexes

Alkene	Surfactant	Particle size (nm)	M_n (kg mol^{-1})	M_w/M_n
TME	SDPBS	280	349	4.3
trans-4-octene	SDPBS	54 (3%) 449 (97%)	268	4.4
1-octene	SDPBS	304	296	4.9
–	SDPBS	120	781	1.7
TME	CTAB	226 (51%) 527 (41%)	790	1.8
trans-4-octene	CTAB	256	703	1.8
1-octene	CTAB	228	640	1.8
–	CTAB	No polymer	No polymer	No polymer

have shown that the ozonolysis in water of alkenes generate species, which on thermolysis give radicals that initiate emulsion polymerization of MMA. The exact nature of the ozonates remains to be determined. However, it is clear from the differing kinetic behavior of these systems that the initiating species do not have a common structure. Therefore, it is unlikely that hydrogen peroxide is a significant initiator in these systems. Following on from previous studies concerned with ozonolysis of alkenes in the presence of water vapor [8], it is highly probable that the main initiators in these systems are hydroxy hydroperoxides. The latter hypothesis is supported by the fact that both of the octenes produced initiators that had half lives that were insufficient to maintain a radical flux for high conversion of monomer at 60°C. The two octenes studied here are expected to produce hydroxy hydroperoxides of lower stability, and thus also lower half life, than the hydroxy hydroperoxide generated by TME. On the other hand, the more stable ozonates of TME did generate radical fluxes that were sufficient to produce high conversion of monomer at 60°C.

References

[1] Klein A, Daniels ES. In: Lovell PA, EI-Asserm, editors. Emulsion polymerization and emulsion polymers. New York: Wiley, 1997. p. 207, chapter 6.
[2] Xu XL, Zhang ZC, Ge XW, Zhang MW. J Polym Sci, Part A: Polym Chem 1998;36:257.
[3] Lukhovitskii VI, Polikarpov VV, Pozdeeva RM, Krylova LA. High Energy Chem 1993;27:19.
[4] Rimmer S, Ebdon JR. J Macromol Sci, Pure Appl Chem 1995;A32:831.
[5] Lockley JE, Ebdon JR, Rimmer S, Tabner BJ. Macromol Rapid Commun 2000;21:795.
[6] Lockley JE, Ebdon JR, Rimmer S, Tabner BJ. Polymer 2001;42:1797.
[7] Cunliffe D, Lockley JE, Ebdon JR, Rimmer S, Tabner BJ. Macromolecules 2001;34:3882.
[8] Bailey PS. Ozonation in organic chemistry, vol. 1. New York: Academic Press, 1978.
[9] Bauld NC, Thompson JA, Hudson CE, Bailey PS. J Am Chem Soc 1968;90:1822.
[10] Murray RW. Acc Chem Res 1968;1:313.
[11] Lattimer RP, Kuczkowski RL, Gilles CW. J Am Chem Soc 1974;96:348.
[12] Ramachandran V, Murray RW. J Am Chem Soc 1978;100:2197.
[13] Bailey PS, Ferrell TMJ. Am Chem Soc 1978;100:899.
[14] Criegee vR. Just Lieb Ann Chem 1953;583:1.
[15] Su J-S, Murray RW. J Org Chem 1980;45:678.
[16] Aronovitch C, Tal D, Mazur Y. Tetrahedron Lett 1982;23:3623.
[17] Murray RW, Ramachandran VJ. Org Chem 1983;48:813.
[18] Murray RW, Su J-S. J Org Chem 1983;48:817.
[19] Kuczowski RL. Acc Chem Res 1983;16:42.
[20] Griesbaum K, Zwick G, Agarwal S, Keul H, Pfeffer B, Murray RWJ. Org Chem 1985;50:4194.
[21] Murray RW, Agarwal SK. J Org Chem 1985;50:4698.
[22] Murray RW, Kong W, Radjadhyakjsha SNJ. Org Chem 1993;58:315.
[23] Ponec R, Yuzhakov G, Haas Y, Samuni UJ. Org Chem 1997;62:2757.
[24] Zhang X-M, Zhu QJ. Org Chem 1997;62:5934.
[25] Neeb P, Sauer F, Horie O, Moortgat GK. Atmos Environ 1997;31:1417.
[26] Olzman M, Kraka E, Cremer D, Gutbrod R, Andersson S. J Phys Chem A 1997;101:9421.
[27] Tsuji K, Ishikawa H. Synth Commun 1997;27:595.
[28] Samuni U, Haas Y, Fajgar R, Pola R. J Mol Struct 1998;449:177.
[29] McGill CD, Rickard AR, Johnson D, Marston G. Chemosphere 1999;38:1205.
[30] Neeb P, Sauer F, Horie O, Moortgat GK. Atmos Environ 1997;31:1417.
[31] Cardinale G, Grimmelikhuysen JC, Laan JAM, Ward JP. Tetrahedron 1984;40:1881.
[32] Karlsson JO, Gatenholm P. Polymer 1997;38:4727.
[33] Napper DH, Gilbert RG. In: Allen G, Bevington JC, editors. Comprehensive polymer science, vol. 4. Oxford: Pergamon Press, 1989. p. 171.
[34] Baxendale JH, Evans MG, Kilham SK. Trans Faraday Soc 1942;42:668.
[35] Ballard MJ, Napper DH, Gilbert RG. J Polym Sci, Part A: Polym Chem 1984;22:3225.
[36] Uppo RM, Pryor WA. Biochem Biophys Res Commun 1992;187:473.