SHORT PAPER

J. Chem. Research (S),
2001, 380–383

Radical polymerisation of vinyl monomers initiated by the thermolysis of alkene ozonates[†]

J.E. Lockley[a,b], J.R. Ebdon[a] and S. Rimmer[a]*

[a]*The Department of Chemistry, The Dainton Building, University of Sheffield, Brook Hill, Sheffield, South Yorkshire S3 7HF, UK*
[b]*Present address: Victrex Technology Centre, Hillhouse International, Thornton Cleveleys, Lancashire FY5 4QD, UK*

Radicals, derived from the ozonates of alkenes, have been shown to be capable of initiating polymerisations of methyl methacrylate, styrene and vinyl acetate: in the case of styrene polymerisations the molar masses obtained at low conversion did not follow the expected trend with temperature.

Keywords: radicals, vinyl monomers, alkene ozonates

Introduction

Recently, we reported that the crude ozonates of tetramethylethene (TME) can be used as radical sources, following thermolysis, and that the radicals are produced at a rate that is suitable for the initiation of the polymerisation of vinyl monomers.[1,2] Thermolysis of ozonates also has utility in the synthesis of block coplymers.[3] The ozonolysis of TME has been well documented[4–6] and the product mixture includes acetone diperoxide, acetone cyclic-triperoxide and open-chain oligomeric peroxides. Whilst all of these species are capable of forming radicals,[7–9] our previous work has shown that below 100°C it is mainly the triperoxide and oligomeric peroxides that are the initiating species.[2,10] We now report further extension to a variety of alkene ozonates and the polymerisation of two other vinyl monomers, styrene and vinyl acetate, with the ozonate of TME.

Polymerisation of MMA with ozonates of alkenes other than TME

In our earlier studies we showed that solutions of ozonised TME, could be used as initiators for the radical polymerisation of methyl methacrylate (MMA). Table 1 shows that several alkenes with diverse structural features can also be used in a similar way. The results are restricted to ozonolysis at 0 °C and to the polymerisation of MMA and serve to illustrate the scope of the technique. All of these alkene ozonates are apparently capable of producing radicals, following thermolysis between 60 and 100 °C. As expected, in all cases yields of polymer, after 1 h reaction time, increase as the temperature is increased. The polymerisations were deliberately stopped at low conversion (after 1 h). However, a few preliminary experiments using TME ozonide showed that high conversions of MMA could easily be obtained at longer reaction times. Also, the number average molar masses decrease with increasing temperature and no significant differences are observed in the polydispersities of the polymers obtained. The production of polymer at temperatures as low as 60 °C strongly suggests that the main initiating species are oligomeric peroxides rather than the more stable ozonide and cyclic diperoxides that are also products of the ozonolysis. It has not as yet been possible to identify fully the full range of structures obtained during the ozonolysis of these alkenes, owing to the very complex nature of the product distributions. Polymerisations initiated by the ozonates of 1-phenyl-prop-1-ene and *trans*-oct-4-ene appear to be subject to a considerable degree of chain transfer, in that the number average molar masses are significantly reduced when compared to the polymers produced in the other polymerisations, whilst the nominal rates of polymerisation in

Table 1 Mn = number average molar mass, PD = polydispersity. Results of polymerisations of MMA initiated by ozonates of various alkenes.

Alkene	Temp./C	Conversion after 1 hour (%)	M_n/kg mol^{-1}	PD
2,3,4-trimethyl-pent-2-ene	60	7.1	236	3.1
	80	9.8	203	2.4
	100	13.2	154	2.3
2,4,4-trimethyl-pent-2-ene	60	4.8	201	2.6
	80	8.0	163	2.5
	100	17.7	130	2.3
trans-oct-4-ene	60	3.6	197	2.5
	80	8.9	65	2.9
	100	13.8	50	2.9
oct-1-ene	60	2.6	301	3.1
	80	5.4	209	2.8
	100	13.0	167	2.7
cyclopentene	60	4.7	195	2.6
	80	7.1	175	2.2
	100	15.9	107	2.2
trans-1-phenyl-prop-1-ene	60	3.5	27	2.0
	80	6.5	22	2.1
	100	13.5	14	1.9

---

* To receive any correspondence. E-mail S.Rimmer@Sheffield.ac.uk

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

these cases were not significantly different from those of the other polymerisations. Transfer presumably occurs to a component, as yet unidentified, of the ozonate mixture. However, it is not possible to identify products that are not present in the other ozonates but are common to the ozonate mixtures obtained from these alkenes.

Polymerisations of monomers other than MMA

In order to survey further the usefulness of alkene ozonates as initiators of polymerisation, we next examined the polymerisation of two monomers other than MMA. The % conversions of monomer (styrene or vinyl acetate) to polymer after 1 hour, at various reaction temperatures and ozonolysis temperatures, are shown in Figs 1 and 2. The dependence of the number average molar masses obtained from these polymerisations on polymerisation temperature are also plotted in Figs 3 and 4. For both monomers, the amount of polymer produced in one hour, as expected, increases with polymerisation temperature and very little difference is observed when the ozonolysis temperature is changed. This is in full agreement with our previously published work on MMA polymerisation initiated by ozonates of TME[2] and indicates that, even though large changes in product distribution of the ozonates are observed on changing the ozonolysis temperature, the mixture of oligoperoxides behaves kinetically as one species. Figure 3 shows the number average molar masses (M_n) of the polystyrene formed during these polymerisations. As with the conversion data no significant differences, arising from changing the ozonolysis temperature, were observed. However, the variations of M_n with temperature are not conventional and show maxima around 80 °C. Clearly these maxima must be the result of several processes operating at rates with differing temperature dependences. Since the maxima were not observed in our previously reported experiments, in which the ozonates of TME were used to polymerise MMA, the effect cannot be assigned to events associated with reactions of the ozonates alone. Also, maxima in the temperature dependence

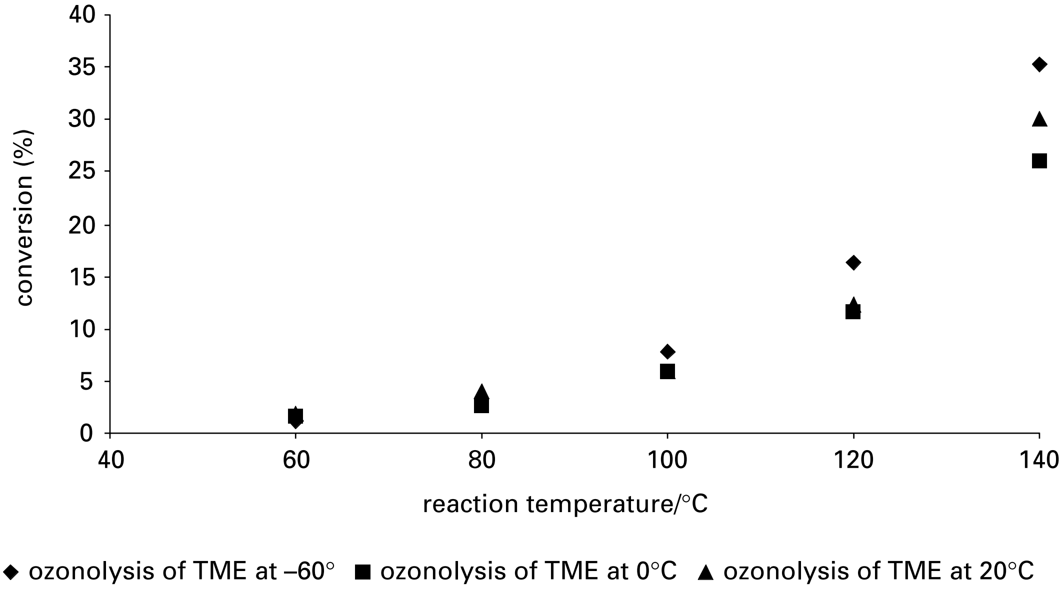

Fig. 1 Plots of conversion of styrene to polymer after one hour against polymerisation temperature for polymerisations initiated by ozonised solutions of TME.

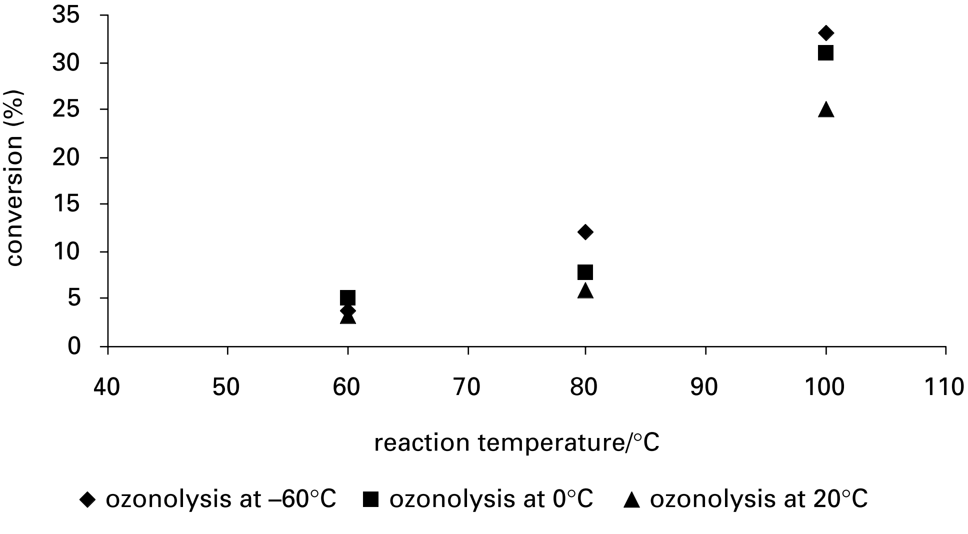

Fig. 2 Plots of conversion to polymer in 1 h against polymerisation temperature for vinyl acetate polymerisations initiated by ozonised solutions of TME.

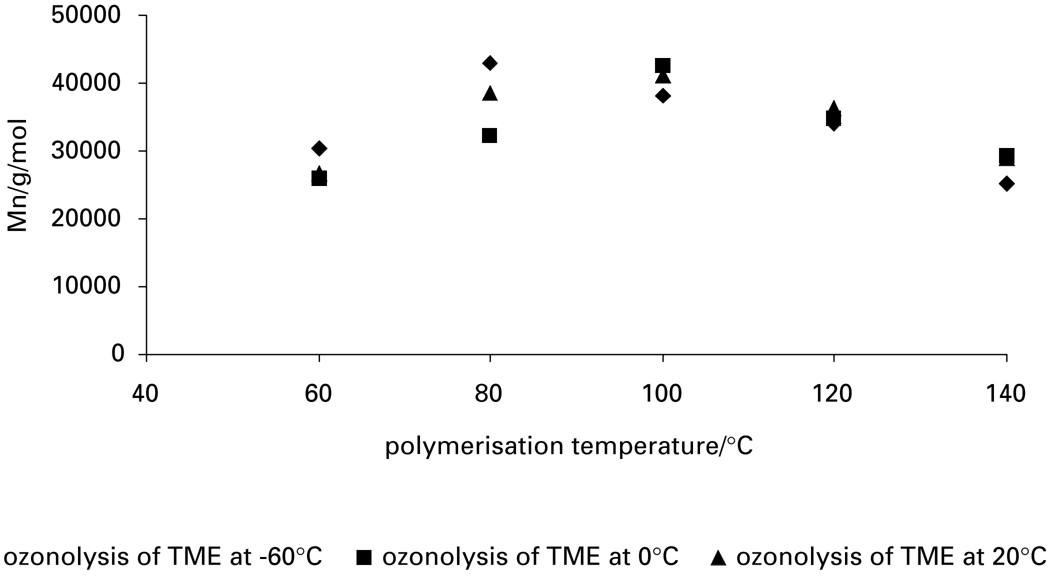

Fig. 3 Plot of molar mass of polystyrene against polymerisation temperature for polymerisations initiated by ozonised solutions of TME.

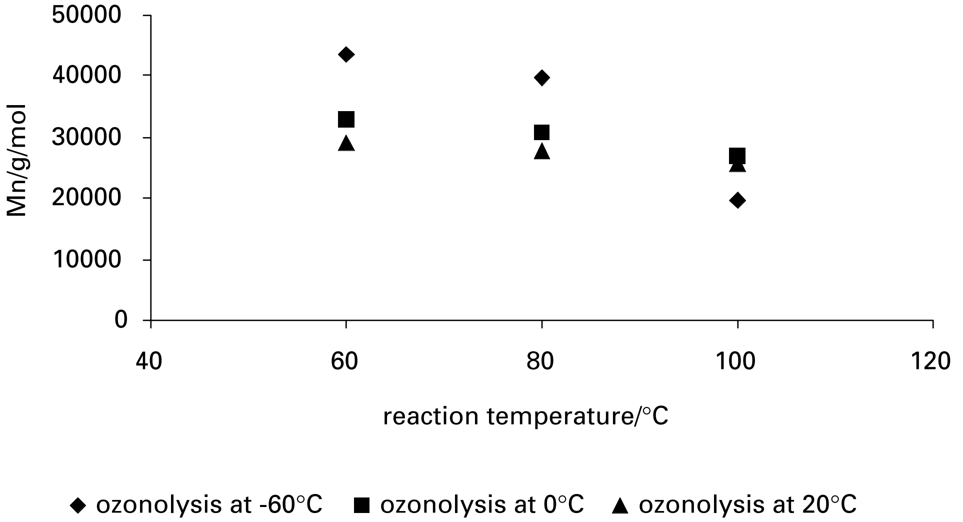

Fig. 4 Plot of molecular weight of poly(vinyl acetate) against polymerisation temperature for polymerisations initiated by ozonised solutions of TME.

of M_n are not usually observed in conventional polymerisations of styrene. Therefore, the maxima are possibly a result of changes in the rates of the termination and transfer reactions and may reflect the growing significance of the thermal polymerisation of styrene with increasing temperature. Figure 4 shows that the polymerisations of vinyl acetate follow the expected trend, that is as polymerisation temperature increases M_n decreases. Therefore, the maxima in these plots for styrene polymerisation appear to be unique features.

Experimental

Materials: All chemicals were obtained from Aldrich. MMA, styrene and vinyl acetate were dried by stirring over calcium hydride and purified by distillation under reduced pressure. Butyl acetate and all other solvents were distilled prior to use. *Trans*-oct-4-ene (tech grade) was also distilled prior to use. Other chemicals were used as supplied.

Ozonolysis: Tetramethylethene, 2,3,4-trimethyl-pent-2-ene, 2,4,4-trimethyl-pent-2-ene, *trans*-oct-4-ene, oct-1-ene and cyclopentene were each ozonised at –60, 0 or 20 °C. In a typical procedure the alkene (2.2 mmol) was added to butyl acetate (25 cm^3) and cooled to 0 °C. Ozone generated by passing an oxygen stream through an electric discharge type ozone generator was then bubbled through the solution at a rate of 0.3 g/h for 8 minutes, at which point the solution turned blue, indicating the presence of an excess of ozone. Nitrogen was then bubbled through the solution for 20 minutes to remove the excess of ozone.

Polymerisation of MMA with alkene ozonates other than TME ozonate: MMA (18.00 g, 0.18 mol) was dissolved in butyl acetate (10 cm^3) and added to an ozonised alkene solution (15.00 cm^3) in an ampoule. This procedure was repeated with two more ampoules. The ampoules were then sealed under vacuum following the usual freeze–pump–thaw technique to remove dissolved air, which was repeated three times for each ampoule. The ampoules were then heated at 60, 80 or 100 °C for 1 h after which time they were cooled in ice. The polymers produced were precipitated into petroleum spirit, filtered through sinters, dried overnight in a vacuum oven and weighed.

Polymerisations of styrene and vinyl acetate with TME ozonates: Solutions of ozonised TME (15.00 cm^3), prepared at either –60, 0 or 20 °C, were used to initiate the polymerisation of styrene (18.00 g, 0.17 mol) or vinyl acetate (18.00 g, 0.21 mol). Solutions of TME, ozonised at –60, 0 and 20 °C, were heated with each monomer at polymerisation temperatures of 60, 80 or 100 °C in ampoules degassed using the usual freeze–pump–thaw procedure. Polymerisations were also carried out at 120 and 140 °C in three necked flasks under a blanket of nitrogen. The products obtained were precipitated into petroleum spirit, filtered through sinters, dried overnight in a vacuum oven and weighed.

Analysis: Average molar masses and molar mass distributions of the oligomers were measured by size exclusion chromatography (SEC), (calibrated against polystyrene or poly(methyl methacrylate) standards) with Styragel 5 µm mixed gel columns (Polymer Laboratories) and a refractive index detector. THF was used as the eluent at a flow rate of 1.0 cm^3/min. Sample concentrations were approximately 2.0 mg/cm^3.

Received 8 December 2000; accepted 1 July 2001
Paper 00/639

References

1 S. Rimmer and J.R. Ebdon, *J. Macromol. Sci.–Pure App. Chem.*, 1995, **A32**, 831.
2 J.E. Lockley, J.R. Ebdon, S. Rimmer and B.J. Tabner, *Polymer,* 2001, **42**, 1797
3 D. Cunliffe, J.E. Lockley, J.R. Ebdon, S. Rimmer and B.J. Tabner, *Macromol.* 2001, 34, 3882.
4 V.R. Criegee, *Just. Lieb. Ann. Chem.*, 1953**, 583**, 1
5 N.C. Bauld, J.A. Thompson, C.E. Hudson and P.S. Bailey, *J. Am. Chem. Soc.*, 1968, **90**, 1822.
6 R.W. Murray, *Acc. Chem. Res.* 1968**, 1**, 313.
7 W.A. Pryor, J.-T. Gu and D.F. Church, *J. Org. Chem.*, 1985, **50,** 185.
8 W.A. Pryor, N. Ohto and D.F. Church, *J. Am. Chem. Soc.*, 1983, **105,** 3614.
9 B. Qi, Y.H. Zhang, K.S. Shao, X.Y. Tang and M. Hu, *Chemosphere*, 1999, **38,** 1213.
10 J.E. Lockley, J.R. Ebdon, S. Rimmer and B.J. Tabner, *Macromol. Rap. Comm.* 2000, **21,** 795.