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The photoinitiated polymerisation of 4-methylene-1,3-dioxolanes

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Abstract

4-Methylene-1,3-dioxolanes can be polymerised via a cationic or free radical mechanism. In both cases there is a possibility that ring opening and elimination can occur following addition of the chemically active species to the methylene group. Use of real time infrared spectroscopy to monitor the polymerisation of these compounds using a photogenerated acid showed that ring opening occurred concurrently with disappearance of the unsaturation of the vinyl ether group. The reaction proved to be very rapid. The resultant polymers were characterised by gel permeation chromatography (GPC) analysis. When such a dioxolane is reacted with a thiol in the presence of a radical photoinitiator the vinyl group is destroyed but ring opening is not observed. Clearly, addition of a thiyl radical to the methylene generates a radical which reacts preferentially with the thiol by hydrogen abstraction rather than undergoing fragmentation. © 1997 Elsevier Science S.A.

Keywords: Cationic polymerisation; Ring opening; FTIR-RTIR spectroscopy

1. Introduction

The radiation curing industry is currently showing much interest in the use of vinyl ethers as polymerisable materials since they are potential alternatives to the commonly used acrylates and methacrylates [1]. Vinyl ethers are rapidly polymerised by acid generating photoinitiators but are relatively unreactive towards free radicals [2]. On the other hand, a 1:1 mixture of a vinyl ether and a maleate or fumarate ester can be polymerised most effectively by use of a free radical initiator [3].

The free radical initiated homopolymerisations of 2-substituted-4-methylene-1,3-dioxolanes is relatively slow, requiring long reaction times to obtain high molecular weight polymers. In principle, the radical polymerisation process can give three types of polymeric product, shown in Fig. 1.

These polymer structures arise from the following mechanisms shown in Figs. 2–4.

Product studies of the free radical polymerisation of 2-phenyl-4-methylene-1,3-dioxolane, 2-methyl-2-phenyl-4-methylene-1,3-dioxolane and 2,2′-diphenyl-4-methylene-1,3-dioxolane have shown that these first two compounds undergo vinyl, ring opening and elimination upon thermal free radical polymerisation [4,5]. The elevated temperature

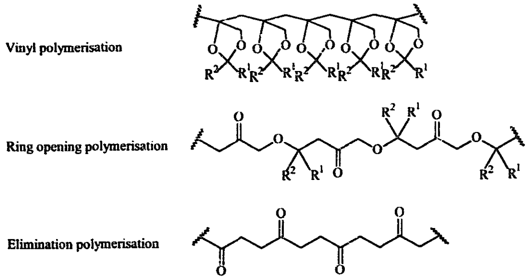

Fig. 1. The three possible extreme product structures arising from the polymerisation of 2-substituted-4-methylene-1,3-dioxolanes.

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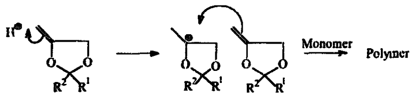

Fig. 2. The cationic vinyl polymerisation of 2-substituted-4-methylene-1,3-dioxolanes.

required to activate the initiators influences the product distribution. Lower temperature free radical photopolymerisations led only to a ring-opened polymer in the case of 2-phenyl-4-methylene-1,3-dioxolane [6]. The diphenyl compound undergoes quantitative elimination of benzophenone [7,8] (see Fig. 4).

Less research has been conducted in the area of the cationic polymerisation of simple 4-methylene-1,3-dioxolanes [9]; these compounds are vinyl ethers and have been shown to be polymerised by Brönsted, Lewis and photogenerated acids [10,11]. Analysis of the polymer produced in the reactions of appropriately substituted dioxolanes showed that polymerisation had occurred via the vinyl and ring opening mechanism analogous to the one shown in Figs. 2 and 3. Unsubstituted 4-methylene-1,3-dioxolane was found to produce the vinyl polymer, whilst 2-methyl substituents gave ring-opened polymer segments. The extent to which ring opening occurs is highly dependent on the nature and number of substituents, thus 2,2′-dimethyl-4-methylene-1,3-dioxolane exhibits a higher degree of ring opening compared with 2-methyl-4-methylene-1,3-dioxolane.

We now report upon the application of real time FTIR to a study of the cationic photopolymerisation reaction of 2-phenyl-4-methylene-1,3-dioxolane, 2-methyl-2-phenyl-4-methylene-1,3-dioxolane and 2,2′-diphenyl-4-methylene-1,3-dioxolane. The free radical induced addition of a thiol to these compounds is also described.

2. Experimental

2.1. Materials

3-Chloro-1,2-propanediol, benzene, potassium *tert*-butoxide, acetophenone, benzaldehyde, γ-butyrolactone, 4-toluenesulphonic acid, *n*-butyl vinyl ether, 1-octanethiol and pentaerythritol tetrakis(3-mercaptopropionate) were supplied by Aldrich Chemical Co. Ltd. and used as received. THF (GPC grade) was distilled over lithium aluminium hydride, and benzophenone, 2-isopropyl thioxanthone and [4-(phenylthio)phenyl]diphenyl sulphonium hexafluorophosphate were obtained from Sericol Ltd. and used as received.

2.2. Representative dioxolane synthesis: 2,2′-diphenyl-4-methylene-1,3-dioxolane (3)

2.2.1. Ketalisation

3-Chloro-1,2-propanediol (50.0 g, 0.45 mol) was placed in a three-necked round-bottom flask (500 ml), together with benzophenone (18.2 g, 0.45 mol), benzene (300 ml) and 4-toluenesulphonic acid (0.2 g, 1.6 mmol). The mixture was heated to reflux for 24 h with the continual removal of water

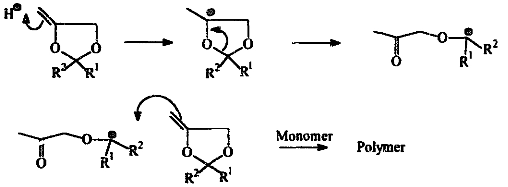

Fig. 3. The cationic ring opening polymerisation of 2-substituted-4-methylene-1,3-dioxolanes.

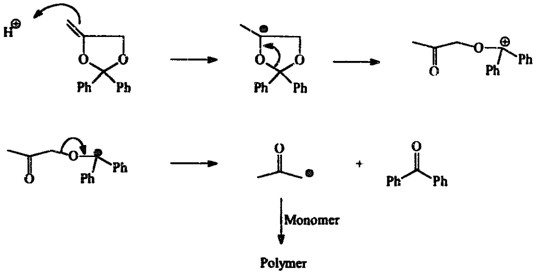

Fig. 4. The cationic elimination polymerisation of 2-substituted-4-methylene-1,3-dioxolanes.

using a Dean and Stark apparatus. After cooling, the benzene solution was extracted with a dilute aqueous sodium hydrogen carbonate solution followed by water. The organic layer was dried with anhydrous magnesium sulphate and the solvent removed in vacuo to give an oil which was distilled under reduced pressure (b.p. 150 °C at 200 mtorr) to give a clear oil (18.4 g, 67%). Found: C 69.9%, H 5.5%, $C_{16}H_{15}ClO_2$ requires C 69.9%, H 5.5%. IR (neat film): 1084, 1028 cm^{-1} (C–O–C), 754 cm^{-1} ($-C_6H_5$). ^1H NMR (100 MHz, $CDCl_3$, TMS ref.): $\delta=7.3$ ppm (multiplet, 10 H, $-C_6H_5$) 4.3 ppm (multiplet, 1 H, C–**CH**(–O)(–CH_2Cl) 4.0 ppm (multiplet, 2 H, O–**CH_2**CH) 3.5 ppm (multiplet, 2 H, –**CH_2**Cl).

2.2.2. *Elimination*

Potassium *tert*-butoxide (22.0 g, 0.2 mol) was placed in a three-necked round-bottom flask (300 ml) and dry tetrahydrofuran (50 ml), a dropping funnel and condenser were fitted. The solution was stirred magnetically and heated to 55 °C. 2,2′-diphenyl-4-chloromethyl-1,3-dioxolane (29.0 g, 0.1 mol) in dry THF (100 ml) was added dropwise over a period of 1.5 h, and then the mixture was left for 5 h. The solution was then slowly added to distilled water (500 ml) and the product was extracted with diethyl ether. The ether was removed and the 2,2′-diphenyl-4-methylene-1,3-dioxolane distilled under reduced pressure (b.p. 120 °C at 300 mtorr) (19.5 g, 82%). Found: C 80.3%, H 5.9%, $C_{16}H_{14}O$ requires C 80.6%, H 5.9%. IR (neat film): 1688 cm^{-1} (C=C) 1078, 1026 cm^{-1} (C–O–C), 748 cm^{-1} ($-C_6H_5$). ^1H NMR (270 MHz, $CDCl_3$, TMS ref.): $\delta=7.4$ ppm (multiplet, 10 H, $-C_6H_5$), 4.5 ppm (multiplet, 2 H, O–**CH_2**–C(–)=), 3.9 ppm (multiplet, 2 H, –C=**CH_2**).

2-Phenyl-4-methylene-1,3-dioxolane (**1**) and 2-methyl-2-phenyl-4-methylene-1,3-dioxolane (**2**) were prepared in a similar way.

2-Phenyl-4-chloromethyl-1,3-dioxolane, 80% yield (b.p. 75 °C at 200 mtorr). Found: C 59.6%, H 5.6%, $C_{10}H_{11}ClO_2$ requires C 60.5%, H 5.6%. IR (neat film): 1090, 1070 cm^{-1} (C–O–C), 758, 698 cm^{-1} ($-C_6H_5$). ^1H NMR (100 MHz, $CDCl_3$, TMS ref.): $\delta=7.3$ ppm (s, 5 H, $-C_6H_5$) 5.8, 5.7 ppm (d, 1 H, Ar–**CH**(–O)$_2$) 4.2 pp, (multiplet, 1 H, C–**CH**(–O)(–CH_2Cl)) 4.1 ppm (multiplet, 2 H, O–**CH_2**–CH) 3.5 ppm (multiplet, 2 H, –**CH_2**Cl).

2-methyl-4-phenyl-4-methylene-1,3-dioxolane, 85% yield (b.p. 74 °C at 300 mtorr). Found: C 72.9%, H 6.6%, $C_{10}H_{10}O_2$ requires C 74.1%, H 6.7%. IR (neat film): 1685 cm^{-1} (C=C) 1090, 1070 cm^{-1} (C–O–C), 758, 698 cm^{-1} ($-C_6H_5$). ^1H NMR (100 MHz, $CDCl_3$, TMS ref.): $\delta=7.3$ ppm (s, 5 H, $-C_6H_5$), 6.0 ppm (s, 1 H, Ar–**CH**(–O)$_2$), 4.5 ppm (multiplet, 2 H, O–**CH_2**–C(–)=), 4.3 ppm (multiplet, 1 H, –C=**CH**), 3.8 ppm (multiplet, 1 H, –C=**CH**).

2-methyl-2-phenyl-4-chloromethyl-1,3-dioxolane, 85% yield. (b.p. 75 °C at 500 mtorr) Found: C 62.1%, H 6.4%, $C_{11}H_{13}ClO_2$ requires C 62.1%, H 6.2%. IR (neat film): 1070 cm^{-1} (C–O–C), 764, 700 cm^{-1} ($-C_6H_5$). ^1H NMR (100 MHz, $CDCl_3$, TMS ref.): $\delta=7.3$ ppm (s, 5 H, $-C_6H_5$), 4.2 ppm (multiplet, 1 H, C–**CH**(–O)(–CH_2Cl)) 4.1 ppm (multiplet, 2 H, O–**CH_2**–CH) 3.6 ppm (multiplet, 2 H, –**CH_2**Cl) 1.6 ppm (d, 3 H, Ar–C(–O)$_2$–**CH_3**).

2-methyl-2-phenyl-4-methylene-1,3-dioxolane, 58% yield (b.p. 60 °C at 500 mtorr). Found: C 75.1%, H 7.1%, $C_{11}H_{12}O_2$ requires C 75.0%, H 6.9%. IR (neat film): 1684 cm^{-1} (C=C), 1046 cm^{-1} (C–O–C), 764, 700 cm^{-1} ($-C_6H_5$). ^1H NMR (100 MHz, $CDCl_3$, TMS ref.): $\delta=7.3$ ppm (s, 5 H, $-C_6H_5$), 4.4 ppm (multiplet, 2 H, O–**CH_2**–C(–)=), 4.3 ppm (multiplet, 1 H, –C=**CH**), 3.8 ppm (multiplet, 1 H, –C=**CH**) 3.64 ppm (s, 3 H, Ar–C(–O)$_2$–**CH_3**).

2.3. *Cationic polymerisations*

2.3.1. *Real time–Fourier transform infrared spectroscopy (RT-FTIR)*

2.3.1.1. *Representative sample preparation*

A solution was prepared in dark vials with 1 mol% of [4-(phenylthio)phenyl]diphenyl sulphonium hexafluorophosphate in several drops of γ-butyrolactone, and 99 mol% of the dioxolane.

2.3.1.2. *Spectrophotometer*

The RT-FTIR experiments were carried out on the UMA300A microscope attachment of a converted Bio-Rad Digilab FTS-60 FT-IR, fitted with an air-cooled, medium-pressure mercury xenon lamp, powered by a Kratos universal arc lamp supply (LPS 251-HR) [12]. The ultraviolet light was passed through a quartz cell containing distilled water to filter out the infrared content. The UV light was introduced through the back of the microscope attachment and focused on the sample by the internal mirror system. The UV shutter mechanism was an aluminium plate placed in the beam path which was removed by hand, the IR spectra were recorded using the Bio-Rad advanced kinetics scan software.

2.3.2. *Gel permeation chromatography (GPC)*

Samples of the monomer solution were coated onto sanitised paper (about 5 cm × 4 cm) using a K-bar which gives a 50 μm film thickness, the paper was then placed into an airtight container with a quartz top [13], and this unit was then passed under a Color Dry unit twice (one UV lamp at 40 Ft min^{-1}).

The GPC analysis was carried out on a LC2200 Bruker pump, refractive index detector and variable wavelength ultraviolet absorption detector set at 254 nM. Degassed THF (GPC grade) was used as the mobile phase at a flow rate of 1 ml min^{-1}. The GPC samples were prepared by dissolving each polymer sample in approximately 7 ml of THF, toluene was added as an internal standard. Samples of this solution were introduced onto the column via a rheodine with a 20 μl sample loop. Two PLgel 5 mM columns linked in series with a range of 2×10^2 to 2×10^6 and an efficiency of >50 000 plates. The system was calibrated with polystyrene standards over a molecular weight range of 900 to 411 000. Data processing was conducted using the Bruker ChromStar software.

2.4. Reaction of thiyl radicals with 2-phenyl-4-methylene-1,3-dioxolane

2.4.1. General reaction procedure

Equimolar solutions of thiol and methylene groups were weighed into a soda glass micro test tube, and the photoinitiator (2% by mass) added. The tube was sealed under a stream of nitrogen, shaken and placed into a light-proof box containing a Hanovia water-cooled UV lamp. Samples were taken at the times stated above for IR and ^{1}H NMR analysis.

3. Results and discussion

3.1. Real time-Fourier transform infrared spectroscopy (RT-FTIR)

The technique of real time infrared spectroscopy (RT-IR) has become well established as a method for following the progress of photoinitiated polymerisation reactions [14]. This technique has now been applied to the cationic photopolymerisation of 2-phenyl-4-methylene-1,3-dioxolane (**1**), 2-methyl-2-phenyl-4-methylene-1,3-dioxolane (**2**) and 2,2'-diphenyl-4 methylene-1,3-dioxolane (**3**). By using a modified FTIR spectrophotometer it becomes possible to monitor a change in spectra as opposed to monitoring a change in absorption intensity of one absorption band as a function of the irradiation time [15,16]. Since the dioxolanes in question lose their absorption due to the methylene group upon reaction, and ring opening generates a carbonyl group, the use of RT-FTIR enables both processes to be followed simultaneously. Spectra obtained by this way are shown in Figs. 5–12. These figures show that it is relatively easy to monitor loss of a vinyl group (1685 cm^{-1}), decrease in the absorption due to the ether link (1070 cm^{-1}) and the build up of a carbonyl group (1725 cm^{-1}). 2,2'-Diphenyl-4-methylene-1,3-dioxolane (**3**) loses its absorption due to the methylene group upon reaction and ring opening generates the dialkyl carbonyl group (1722 cm^{-1}) as is the case for **1** and **2**; for **3** the elimination reaction produces a diaryl carbonyl group

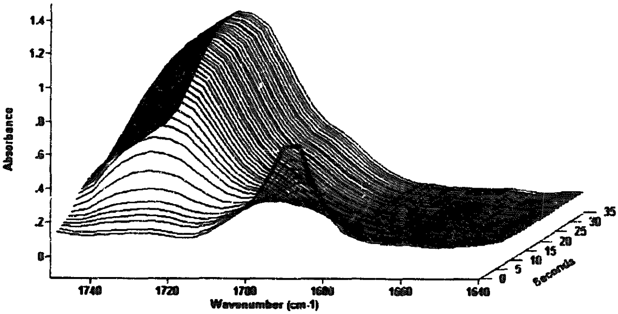

Fig. 5. The disappearance of the vinyl and appearance of the carbonyl peaks during the cationic photopolymerisation of 2-phenyl-4-methylene-1,3-dioxolane (1).

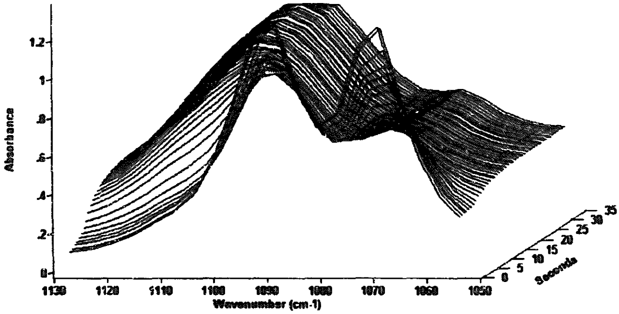

Fig. 6. The disappearance of the ether peak during the cationic photopolymerisation of 2-phenyl-4-methylene-1,3-dioxolane (1).

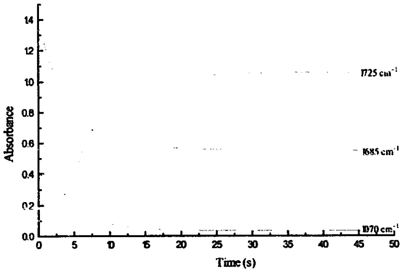

Fig. 7. The change of absorbance at 1725 cm^{-1} (polymer carbonyl group), 1685 cm^{-1} (vinyl group) and 1070 cm^{-1} (ether group) with time during the cationic photopolymerisation of 2-phenyl-4-methylene-1,3-dioxolane (**1**).

(1660 cm^{-1}), namely benzophenone. The technique of RT-FTIR spectroscopy enables all three processes to be followed simultaneously provided that the peaks do not overlap. From the spectra it is also evident that the polymerisation goes almost to completion, i.e. there are very few residual vinyl ether groups after approximately 20 s of UV irradiation; this in part reflects the fact that the cured material is a liquid rather than a solid.

It is easy to see from Figs. 7 and 10 that the growth in carbonyl group absorption is matched by a disappearance in the absorbance of the methylene group as monitored at 1685 cm^{-1}. Given that the changes in absorption intensity for the 1685 and 1725 cm^{-1} peaks cease after approximately 20 s, this suggests that the formation of the carbonyl group occurs concurrently with the destruction of the methylene group, i.e. the polymerisation occurs predominantly via the ring opening mechanism in Fig. 3.

The reduction of the methylene absorption during the cationic photopolymerisation of 2-methyl-2-phenyl-4-methylene-1,3-dioxolane (**2**) appears not to have gone to completion (see Figs. 8 and 10). The residual unsaturation at 1685s cm^{-1} may be due to unreacted monomer, or an elimination reaction giving acetophenone which has a car-

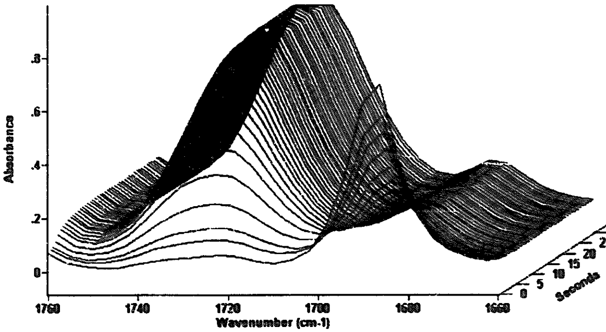

Fig. 8. The disappearance of the vinyl and appearance of the carbonyl peaks during the cationic photopolymerisation of 2-methyl-2-phenyl-4-methylene-1,3-dioxolane (**2**).

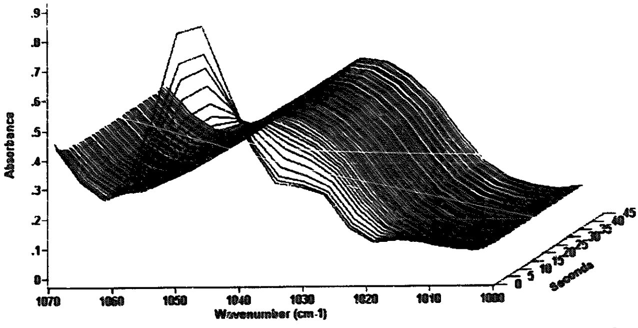

Fig. 9. The disappearance of the ether peak during the cationic photopolymerisation of 2-methyl-2-phenyl-4-methylene-1,3-dioxolane (**2**).

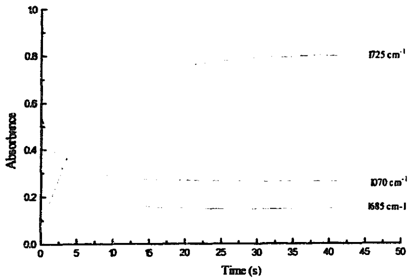

Fig. 10. The change of absorbance at 1725 cm^{-1} (polymer carbonyl group), 1685 cm^{-1} (vinyl group) and 1070 cm^{-1} (ether group) with time during the cationic photopolymerisation of 2-methyl-2-phenyl-4-methylene-1,3-dioxolane (**2**).

bonyl absorption at 1683 cm^{-1} overlapping with the methylene peak may have occurred. The 1046 cm^{-1} ether stretch also does not disappear completely. 2-Methyl-2-phenyl-4-methylene-1,3-dioxolane (**2**) is known to give a mixed vinyl and elimination structure upon thermally induced radical polymerisation [15].

Fig. 11 which relates to 2,2′-diphenyl-4-methylene-1,3-dioxolane (**3**) shows the disappearance of the methylene absorbance and the growth of the polymer carbonyl peak 1722 cm^{-1}. As with the above examples, the poly(ketone) carbonyl peak formed decreases in intensity with time, and this may be due to furan formation and subsequent polymerisation of the substituted 1,4-diketones in the acidic solution, or via photochemical reaction. The additional benzophenone carbonyl absorption at 1660 cm^{-1} appears at a similar rate to the polymer carbonyl peak as would be expected from the mechanism shown in Fig. 4.

3.2. Gel permeation chromatography (GPC)

The cationically induced photopolymerisation of the 4-methylene-1,3-dioxolanes was further studied by the irradiation of a thin film of the material. Since crosslinking was

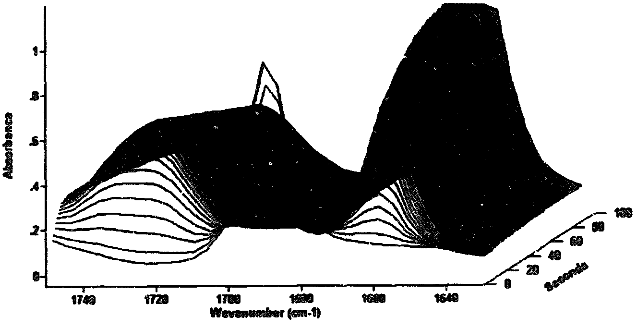

Fig. 11. The disappearance of the vinyl and appearance of the two carbonyl peaks during the cationic photopolymerisation of 2,2′-diphenyl-4-methylene-1,3-dioxolane (**3**).

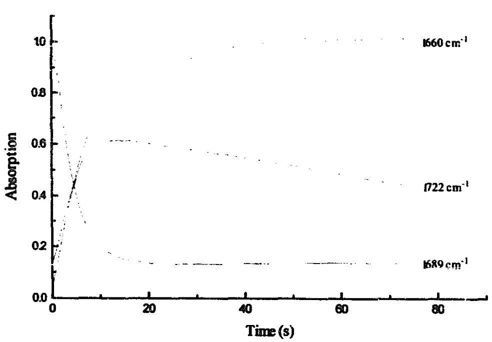

Fig. 12. The change in absorbance of the peaks at 1722 cm^{-1} (polymer carbonyl group), 1689 cm^{-1} (vinyl group) and 1660 cm^{-1} (benzophenone carbonyl group) with time during the cationic photopolymerisation of 2,2′-diphenyl-4-methylene-1,3-dioxolane (**3**).

Table 1
The weight average molecular weight values obtained for the three poly(2-substituted-4-methylene-1,3-dioxolanes)

2-Substituent	RI (MW)	UV (MW)
Ph,H (**1**)	8.1×10^3	7.3×10^3
Ph,Me (**2**)	4.3×10^3	1.8×10^3
Ph,Ph (**3**)	750	628

not expected to occur, the irradiated film was dissolved in THF and analysed by GPC (see Table 1).

The GPC trace obtained using the RI detector is similar to that obtained with the UV detector for the products obtained from **1** (Fig. 13). However, the corresponding traces for the products obtained from **2** are very different (Fig. 14). Use of the RI detector reveals a preponderance of high molecular weight material whereas the UV detector shows a much higher proportion of lower molecular weight material. This would suggest that some of the reaction is occurring via the mechanism shown in Fig. 4 since the polymer obtained by this route does not contain the UV active aryl groups. Polymerisation of **3** gives very little high molecular weight material with the RI detector indicating that there is a little material of higher molecular weight than that shown by the UV detector (Fig. 15). Presumably, with this material reaction is occurring predominantly via the mechanism shown in Fig. 4. Since benzophenone represents 76.5% of the mass of **3**, there is little material left for polymer formation if elimination of the ketone is efficient.

3.3. The reaction of thiyl radicals with 2-phenyl-4-methylene-1,3-dioxolane

The reaction of photogenerated thiyl radicals with vinyl ethers has been reported previously [17] whereas their reaction with 2-substituted-4-methylene-1,3-dioxolanes has not. As was described in Section 1 radical initiated polymerisation may lead to vinyl, ring opening and elimination processes occurring. Unfortunately, these reactions were found to be too slow to be monitored reliably by RT-FTIR and so the reactions were followed by IR and ^{1}H NMR. The bulk reaction of 2-phenyl-4-methylene-1,3-dioxolane (**1**) with 1-octanethiol and with pentaerythritol tetrakis(3-mercaptopropionate) photoinitiated by benzophenone and 2-isopropyl thioxanthone was examined. The photoreaction of *n*-butyl vinyl ether with 1-octanethiol photoinitiated by benzophenone was run as a blank. Before and after irradiation with UV, an infrared spectrum was taken, and it was found that the vinyl peaks of the vinyl ether at 1610 and 812 cm^{-1} had disappeared indicating that the addition of the thiol to the vinyl ether had taken place under these experimental conditions. The experiment was then repeated substituting the *n*-butyl vinyl ether with 2-phenyl-4-methylene-1,3-dioxolane (**1**). It was found that after 5 min UV irradiation there was

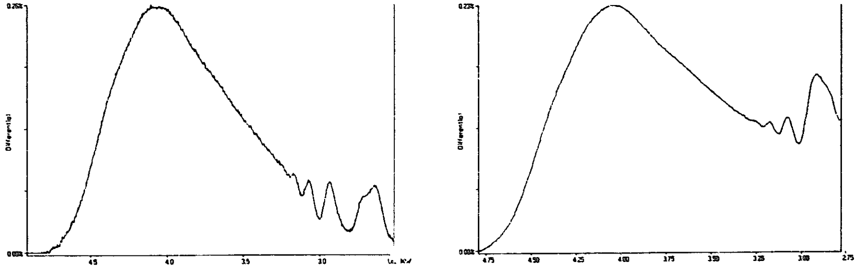

Fig. 13. The refractive index (RI) and ultraviolet (UV) detector GPC traces of poly(2-phenyl-4-methylene-1,3-dioxolane).

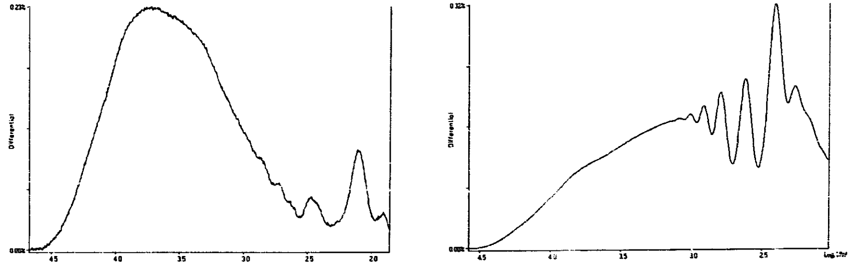

Fig. 14. The RI and UV detector GPC traces of poly(2-methyl-2-phenyl-4-methylene-1,3-dioxolane).

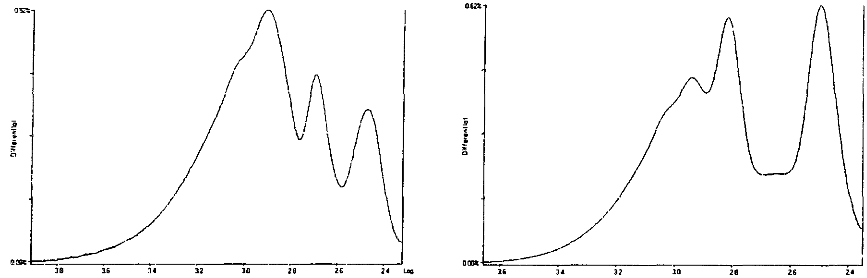

Fig. 15. The RI and UV detector GPC traces of poly(2,2′-diphenyl-4-methylene-1,3-dioxolane).

an approximate 50% reduction in the vinyl peak at 808 cm^{-1} and after 10 min the peak had reduced by approximately 60% from its former value. There was no evidence for the formation of a carbonyl compound or the destruction of ether bonds. It would therefore appear that either simple vinyl polymerisation is occurring or that there is a simple 1,2-addition of the thiol group to the double bond. Changing the photoinitiator from benzophenone to 2-isopropyl thioxanthone gave similar results.

The ^1H NMR spectrum of the reaction mixture after 1 h irradiation showed three peaks arising from the benzylic protons at $\delta = 6.0$, 5.9 and 5.7 ppm. The 6.0 ppm peak arises from the 2-phenyl-4-methylene-1,3-dioxolane, unreacted starting material, whilst the 5.9 and 5.7 ppm peaks are found in saturated 2-phenyl-4-chloromethyl-1,3-dioxolane isomers (the synthetic precursor) and we therefore suggest that the resonances at these positions in the reaction mixture are due to the formation of 2-phenyl-4-octothiomethyl-1,3-dioxolane. From the integration of the peaks it was calculated that the reaction had gone to 80% completion. That most of the reaction had occurred via predominantly 1,2-addition was indicated by the absence of resonance peaks in the $\delta = 6.0$ to 5.7 ppm region. If any reaction had taken place by ring opening, benzylic groups of the type Ph–CH_2–O– would have been produced and these resonate in the 6.0 to 5.7 ppm region. Furthermore, the ratio of the integration of the aromatic to benzylic protons remains at 5:1 throughout the reaction.

When pentaerythritol tetrakis(3-mercaptopropionate) was used in place of 1-octanethiol infrared spectra taken during the course of the reaction showed a disappearance of the vinyl peak at 808 cm^{-1} and the S–H peak (which was clearer in this thiol) at 2572 cm^{-1}. Changes in the ^1H NMR spectrum of the reaction mixture were similar to those recorded for the reaction with 1-octanethiol. Chemical shifts of the benzylic protons of the dioxolane are the same as the above 1-octanethiol/dioxolane reaction product.

4. Conclusions

The technique of RT-FTIR proves to be ideal for the monitoring of fast cationic photopolymerisations of 2-substituted-4-methylene-1,3-dioxolanes. The destruction and creation of bonds can be followed in real time as the reaction progresses. RT-FTIR in conjunction with GPC provides strong evidence for the view that the cationic polymerisation of 2-phenyl-4-methylene-1,3-dioxolane gives exclusively ring-opened polymer, whilst 2-methyl-2-phenyl-4-methylene-1,3-dioxolane also produces ring-opened polymer in addition to polymer produced by elimination of acetophenone. 2,2′-Diphenyl-4-methylene-1,3-dioxolane undergoes elimination exclusively to form a poly(ketone) and benzophenone. The photoinitiated free radical reaction of 2-phenyl-4-methylene-1,3-dioxolane with thiols leads to a 1,2-addition product with little or no ring opening occurring as was reported for some other radical initiated reactions.

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