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Evaluation of acylphosphine oxide polymerization initiators using differential scanning calorimetry

**Hany F. Sobhi · John M. Masnovi ·
Alan T. Riga**

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Abstract This study examines the polymerization of dental monomers catalyzed by synthesized acylphosphine oxides in a differential scanning calorimetry (DSC) cell. This research focuses on establishing a relationship between radicals generated by the acylphosphine oxide photoinitiators and the kinetic reaction rates of methyl methacrylate (MMA) and acrylamide (ACM), a model monomer. The thermal stability of mono- and di-acylphosphine oxides was examined by DSC. Endothermic melting and exothermic polymerization reactions initiated with the two initiators were recorded. The acrylamide model system laid the ground work for the critical evaluation of the synthesized new initiators of mono (2,4,6-trimethylbenzoyl) diphenylphosphine oxide, and bis(2,4,6-trimethylbenzoyl) phenylphosphine oxide. The bis(acyl) phosphine oxide photoinitiator was more reactive than the mono-(acyl) phosphine oxide with methyl methacrylates under laboratory conditions. In exothermic reactions, temperatures rose higher and more rapidly for bis(acyl) phosphine oxide initiated reactions than mono-(acyl) phosphine oxide initiated reactions.

Keywords Differential scanning calorimetry · Methylmethacrylates · Acrylamide · Radical polymerization · Photoinitiators · Mono-acylphosphine oxide · Bis-acylphosphine oxide · Polypropylene fumarate

H. F. Sobhi (✉) · J. M. Masnovi · A. T. Riga
Department of Chemistry, Cleveland State University,
2121 Euclid Avenue, Cleveland, OH 44115-2406, USA
e-mail: h.sobhi@csuohio.edu

A. T. Riga
e-mail: a.riga@csuohio.edu

Introduction

Photochemical polymerization is an attractive strategy in the production of biopolymer materials because of the controlled initiation and termination, often short reaction times, and possibility for special controls [1]. Biomedical polymers made by the photopolymerization of multifunctional acrylates and methacrylates are of interest for use as dental biomaterials [2, 3]. For example, photopolymerized multifunctional methacrylates were prepared and used as model polymers for dental applications [4, 5]. Photochemical initiators are commonly used for crosslinking unsaturated monomers and polymers containing unsaturated functional groups. These initiators typically absorb light in the far UV region and act by homolysis to form organic radicals. The radicals initiate crosslinking of alkenes by radical addition processes. The reactivity of benzoyldiphenyl-phosphine oxides, benzoylphosphonate, and pivaloylphosphonates as photoinitiators in a radical vinyl polymerization process was studied at 347 nm, in which α-scission occurs upon irradiation to give the phosphinoyl radical and the acyl radical. The quantum yield of the reaction depends on the nature and the chemical structure of the acyl group of the initiator. Acylphosphine oxides [$C_6H_5COPO(C_6H_5)_2$] have been used as photoinitiators in the photocrosslinking of polypropylene fumarate (PPF) to form porous scaffolds for bone tissue engineering and dental applications [6]. Bis(acyl)phosphine oxides are highly efficient photoinitiators. These materials strongly absorb in the near UV to the visible region of the spectrum and have been shown to photolize in a stepwise fashion to produce up to four radicals (Fig. 1) [7].

The reaction of bis(2,4,6-trimethylbenzoyl) phenylphosphine oxide, available commercially as Irgacure 819, with methyl 2-*tert*-butylacrylate has indicated that the

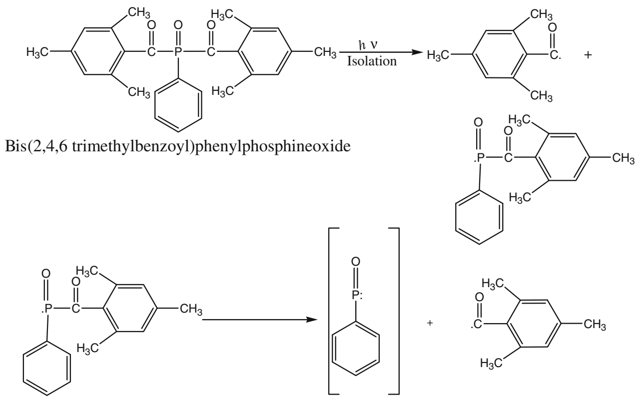

Fig. 1 α-Cleavage of bis(2,4,6-trimethylbenzoyl) phenylphosphine oxide

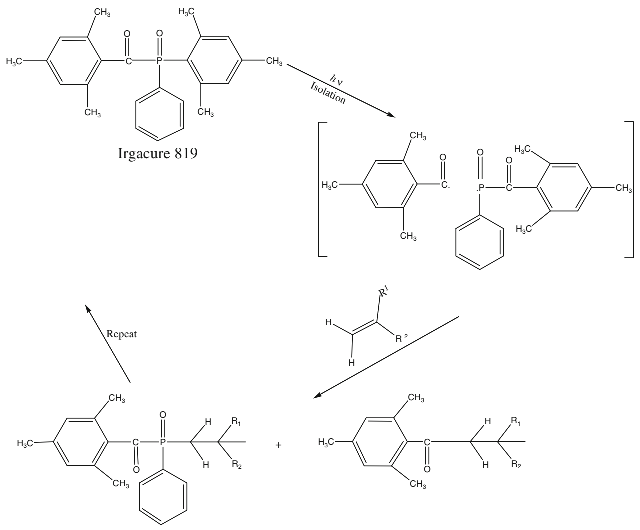

Fig. 2 Synthesis of macrophotoinitiator

cleavage produces both phosphorus- and carbon-centered radicals. Electron spin resonance (ESR) also showed that the addition of the phosphorus-centered radicals to the acrylate bond was more efficient by at least one order of magnitude than that of trimethylbenzoyl radicals (Fig. 2) [8].

DSC—fundamental properties and polymerization kinetics

Thermal and kinetic polymerization properties of new synthetic phosphine oxides were measured in the liquid state by differential scanning calorimetry (DSC). The DSC measurements used were heat (W g^{-1}) and rate (W g^{-1} min^{-1}) as a function of temperature (°C) and time (min). Each monomer, i.e., acrylamide (ACM) and methyl methacrylate (MMA), and the initiators were also examined by DSC to determine their melting, decomposition, and thermal polymerization properties.

Experimental

Methods

The DSC was temperature calibrated with a known material, i.e., indium metal. The DSC was calibrated with indium melting at 157 °C with a heat of fusion of 28.4 J g^{-1} according to ASTM E967 [9]. The standard practice for heat flow calibration of a DSC was performed according to ASTM E968 [10]. The indium, tin, and zinc metals' heats of fusion were used to accomplish these measurements. The standard test method for the enthalpy of fusion by DSC was accomplished with ASTM E793 [11]. The heat of fusion of lidocaine at 80 °C was used for this calibration. The standard test method for melting temperature by thermal analysis was implemented for the temperature calibration by ASTM E794 [12]. The melting temperatures of sulfapyridine, acetanilide, and caffeine were recorded to verify the ability to determine melt temperatures. The standard test method for heats of reaction by DSC was followed to establish a protocol for heats of polymerization in this study, see ASTM E1260 [13]. The extrapolated onset temperature, the peak heat flow temperature, and the heat of reaction (polymerization) were recorded for the catalytic polymerization. The first derivative of the polymerization heat curve yielded the heat rate of reaction in mW $°C^{-1}$ min^{-1}. An adaptation of ASTM E2009, a standard test method for oxidation onset temperature by scanning DSC, was used where the exothermic oxidation (and exothermic polymerization) in J g^{-1} or J $mole^{-1}$ of a standard motor oil was used to set the parameters. The exothermic oxidation of high density polyethylene and poly-butylene from the Society of Plastics Engineers standard Resinkit® was also used to measure the repeatability of the exothermic oxidation (implying polymerization exothermic behavior) analysis at ±10%.

TAI 2920 DSC characterized the monomers with the following conditions: heating rate 10 °C min^{-1}, nitrogen flow of 80 mL min^{-1}, heating range from 0 to 160 °C, and sample size 10 mg.

The thermal stability of mono- and di-acylphosphine oxides was also examined by DSC. Endothermic and exothermic reactions of the two initiators were observed. The DSC operating program for the polymerization study was 10 °C min^{-1}, nitrogen atmosphere, flow rate 80 mL min^{-1}, in an aluminum pan with crimped lid, temperature range from 25 to 300 °C, and a sample size of 20–25 mg.

Various monomers, synthetic initiators, as well as commercial inhibitors were evaluated by DSC. The benzoyl peroxide (BP) initiator was purchased from Sigma-Aldrich and was used as received, and the synthetic initiators were mono- and di-acylphosphine oxides. The monomers were MMA and ACM from Sigma-Aldrich and were used as received at concentrations of 90/10 (wt) monomer/initiator. All of the mass and thermal analysis conditions were standardized as describe above. Thermal Solutions® software was used to analyze the DSC curves.

Results and discussion

This thermal analysis study examines the polymerization of dental monomers catalyzed by synthesized acylphosphine oxides in a DSC cell. A relationship is established between the radicals generated by the initiator, and their kinetic reaction rates with the monomer, MMA, and ACM used as model monomer. BP was employed to evaluate the DSC response to exothermic polymerization heats and rates, and to compare the results with the literature [14]. The research indicates that the mono- and di-acylphosphine oxides were differentiated by the relative reaction rate (W g^{-1} min^{-1}) but not the overall heat of polymerization, ΔH_{pzn} (J g^{-1}). Auto-polymerization of ACM and decomposition of BP to form radicals were also measured. The combination of ACM/BP (90/10) wt enhanced the relative reaction rate significantly. The ACM model system laid the ground work for the critical evaluation of the synthesized (2,4,6-trimethylbenzoyl) di-phenylphosphine oxide and bis(2,4,6-trimethylbenzoyl) phenylphosphine oxide. The di-acylphosphine oxide initiator was more reactive than the mono-acylphosphine oxide initiator with MMA under laboratory conditions. The exothermic polymer reaction in the lab reactor produced temperatures that rose higher and more rapidly for the bis-acylphosphine oxide initiator. Thermal and kinetic polymerization properties of the new synthetic acylphosphine oxides were measured in the liquid state by DSC. The measurements used were polymerization heat (W g^{-1}) and rate (mW g^{-1} min^{-1}) as a function of temperature (°C) and time (min). Each monomer, ACM and MMA, as well as the synthesized initiators were examined by DSC to determine their melting, decomposition, and thermal polymerization properties (see Fig. 3).

The monomer ACM and the BP were used as model chemical substrates. They were examined separately plus in combination. ACM endothermically melted at 84 °C with a heat of fusion of 133 J g^{-1} and exothermically autopolymerized at 119 °C in nitrogen. The literature reported value for the heat of fusion for ACM is 130 J g^{-1} in air; diacetone ACM autopolymerized at 118 °C in nitrogen and 130 °C in air [15]. The average activation energy for diacetone ACM polymerization was 51.1 ± 3.0 kcal $mole^{-1}$. The latter should be approximately the same for ACM inhibitors which increased the activation energy to 64 kcal $mole^{-1}$ for *para*-methoxy phenol and 134 kcal/mol for 4-*tert*-butylpyrocatechol. Therefore, the addition of an initiator must decrease the activation energy to less than 51 kcal $mole^{-1}$. The heat of polymerization observed was 41.9 J g^{-1} and the literature was 50.0 J g^{-1} [13]. BP, the initiator, was DSC scanned and decomposed rendering radicals at 112 °C with an exothermic heat of 411 J g^{-1}. Combination of the monomer and the initiator (90/10) wt, respectively, caused the ACM monomer to polymerize at 91 °C with an exotherm of 2,100 J g^{-1}, a fivefold increase in the heat of polymerization.

Derivative heat flow versus time/temperature from a temperature scanned DSC of the polymerization rendered interesting data. Polymerization of BP and an ACM monomer yields the relative rate of polymerization of ACM/BP which was greatly enhanced to 788 W g^{-1} min^{-1}. Figure 4 directly explains the relative rate of polymerization of 314 W g^{-1} min^{-1} for only BP, 788 W g^{-1} min^{-1} for the ACM/BP reaction, and 13 W g^{-1} min^{-1} for only ACM. The model system (ACM and the initiator) behaved appropriately and the DSC tracked the exothermic events.

The melting properties of mono- and di-acylphosphine oxides are summarized in Table 1. Triplicate DSC melting curves differentiated the two initiators, i.e., the average mono melting temperatures were 90–94 °C with a heat of fusion of 49 J g^{-1}, the average bis melting temperatures were 132–135 °C with a heat of fusion of 92 J g^{-1}, and the sharp melting over a 3–4 °C range is a measure of a pure compound. Acylphosphine oxides are known to catalyze monomer polymerization by generating multiple radicals. For example, (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (364 g $mole^{-1}$) generates two radicals and bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (416 g $mole^{-1}$) three radicals. The melting temperatures clearly and statistically differentiate the two initiators, and the differentiated initiators samplings were in triplicate.

The DSC polymerization was a two-step process and the peak temperatures were observed at 26 and 54 °C for the di-acylphosphine oxide, and 36 and 54 °C for the

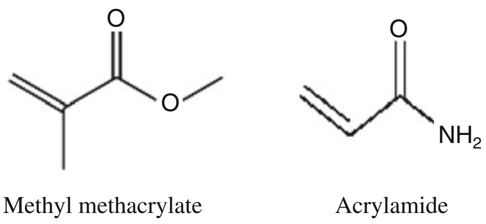

Fig. 3 Model monomers used for the polymerization with mono- and di-acylphosphine oxides

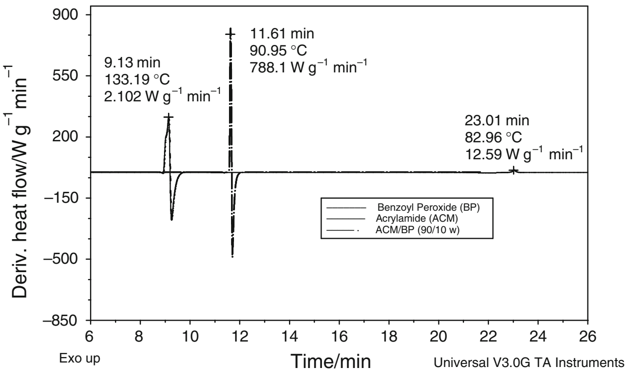

Fig. 4 Derivative heat flow versus time/temperature of benzoyl peroxide by DSC

Table 1 The average DSC melting properties of the mono- and di-acylphosphine oxide in triplicate

Initiator	Melt temperature/°C	Peak melt temperature/°C	Heat of fusion/J g^{-1}
Mono-acylphosphine oxide	92	94	49.4
Di-acylphosphine oxide	132	135	92.5

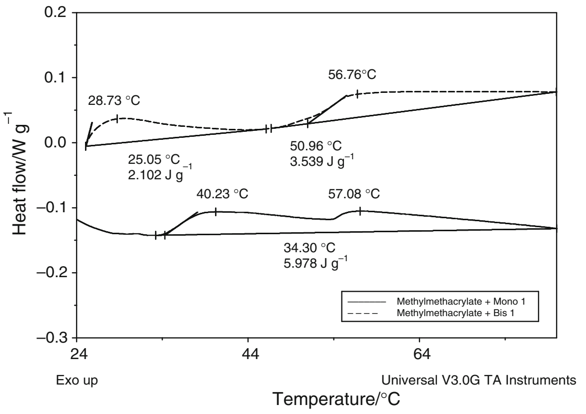

Fig. 5 Polymerization in the DSC cell of acylphosphine oxide catalysts and the monomer methyl methacrylate

Table 2 DSC heat of polymerization of the mono- and di-acylphosphine oxide with methyl methacrylate

Initiator	Temperature/°C (Step 1)	Temperature/°C (Step 2)	Heat of polymerization/J g^{-1}/J mole^{-1}
Mono-acylphosphine oxide	40	57	*5.98* 2,200
Di-acylphosphine oxide	29	57	*5.64* 2,400

The significance of the italic and underlining is to differentiate between J g^{-1} and J mole^{-1} (two calculations for the same material presented together in the table)

Table 3 DSC relative polymerization rate of mono- and di-acylphosphine oxide with methyl methacrylate from the derivative heat flow versus temperature curve

Initiator	Polymerization rate/mW g^{-1} min^{-1} (Step 1)	Polymerization rate/mW g^{-1} min^{-1} (Step 2)	Relative polymerization rate
Mono-acylphosphine oxide	90	76	100
Di-acylphosphine oxide	107	89	118

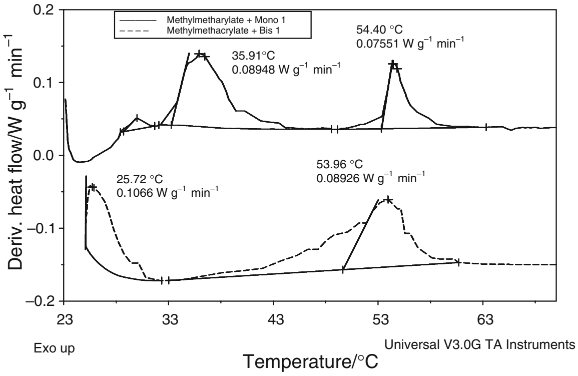

Fig. 6 The two-step DSC relative polymerization rate as the derivative heat flow of the two acylphosphine oxide catalysts and the monomer methyl methacrylate

mono-acylphosphine oxide (see Fig. 5; Table 2). There was a two-step DSC relative polymerization rate of the two acylphosphine oxide initiators and the monomer MMA. The relative polymerization rate is the ratio of the di-acylphosphine oxide rate divided by the mono-acylphosphine oxide rate, see Table 3. This rate indicates that the di-acylphosphine oxide is 18% faster than the mono-acylphosphine oxide. The relative reaction rates for both initiators for a two-step process were 107 and 89 mW g^{-1} min^{-1}, and 90 and 76 mW g^{-1} min^{-1}, respectively. The ratio of radicals formed for the two phosphine oxides is 1.5 or 3.0 [14]. The total DSC energy (mW g^{-1}) associated with the two-step polymerization process was 1.55 or 3.10. The structure–property relationship of the synthetic initiators, the number of radicals formed from each initiator, and the DSC thermal rate property are repeatable and related to the polymerization mechanism (see Fig. 6; Tables 3, 4). The relative polymerization rate is the ratio of the di-rate divided by the mono-rate.

Table 4 DSC polymerization heat rate of mono-and di-acylphosphine oxide with methyl methacrylate

Initiator	Heat/rate curve/mW g^{-1} (Step 1)	Heat/rate curve/mW g^{-1} (Step 2)	Heat ratio (di/mono) ratio radicals
Mono-acylphosphine oxide	51	24	75
Di-acylphosphine oxide	41	75	116

Conclusions

Understanding the chemical and the physical properties of existing initiators (the model system) increased the knowledge based on the model monomer reaction with the prepared initiators. The study of the polymerization process using the two model photoinitiators, i.e. mono- and di-acylphosphine oxides with model monomer ACM and MMA, was carried out in the DSC cell, which served as a polymerization reactor. These measurements revealed that the MMA monomer polymerizes in a two-step reaction with either synthesized phosphine oxide. Di-acylphosphine oxide is more reactive than the mono-acylphosphine oxide by 18% as measured by DSC. The ratio of the derivative heat flow measurement from the DSC reactivity study was 1.55 or 3.10 and the ratio of the number of known radicals from the di-acylphosphine oxide/Mono-acylphosphine oxide = 3/2 = 1.5 or 3.00. A repeatable structure (ratio of known radicals) and property (DSC measurement of total heat in the derivative heat flow reactivity study) relationship was established for the acylphosphine oxides. There was no apparent difference in the heat of polymerization when the two initiators were used with the monomer MMA.

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