

COMPARATIVE STUDY OF THE PHOTOINITIATING REACTIVITY OF THE ACYLPHOSPHONATES AND ACYLPHOSPHINE OXIDES

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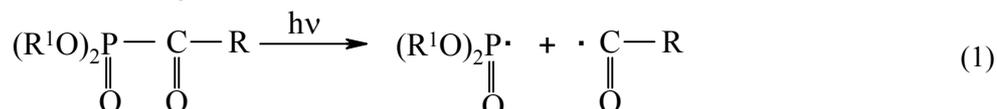
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Acylphosphonates and acylphosphine oxides compounds are known as efficient photoinitiators for radical polymerization of acrylic and vinylic monomers. This paper studies the polymerization of hexanedioldiacrylate with photoinitiators by differential scanning photocalorimetry (photo-DSC) and presents the comparative study concerning the photoinitiating efficiency of the phosphorus compounds. The efficiency of the photoinitiators depends on the structure of the compounds. The most reactive photoinitiators are the compounds with benzene rings and substituted with methoxy groups in *para* position followed by the bifunctional photoinitiators isophthaloyl and terephthaloyl derivatives.

INTRODUCTION

The UV-curing of photopolymerizable systems, containing monomer/oligomer, photoinitiator and additive, have found industrial applications, mainly in coating and printing domain, in adhesives and microelectronics. These systems undergo rapid transformation of liquid monomer/oligomer into

solid polymer simply by exposure to UV radiation in the presence of photoinitiators.¹ The photoinitiators play a key role in UV-curable systems by generating the reactive species, free radicals (reaction 1), able to initiate the polymerization of the multifunctional monomers and oligomers:



where: R = *para*-methoxybenzoyl;
R¹ = methyl, ethyl.

UV-curing coating systems have advantages such as: good cost/performance relation, low energy consumption, high chemical and mechanical strength of the final coatings, low to no volatile organic compounds (no solvent), and high speed of the process even at room temperature.

A large variety of photoinitiators has been developed to provide these requirements. The phosphorus containing photoinitiators of type acylphosphine oxides and acylphosphonates were found effective in photoinitiation of polymerization of olefin monomers.² These compounds exhibit an absorption band in the range 340–400 nm.

In this paper is reported the comparative study concerning the photoinitiating efficiency of the phosphorus compounds, acylphosphonates and acylphosphine oxides, in radical polymerization of hexanedioldiacrylate (HDDA), by differential scanning photocalorimetry (photo-DSC).

RESULTS

In Fig. 1 is shown a typical exotherm plot of HDDA polymerization using *para*-methoxybenzoyldiphenylphosphine oxide as photoinitiator (3%w/w), in the presence of triethylamine as additive (3%w/w). From the thermograms we can obtain photoreactivity parameters of photoinitiated polymerization of HDDA initiated by synthesized photoinitiators.

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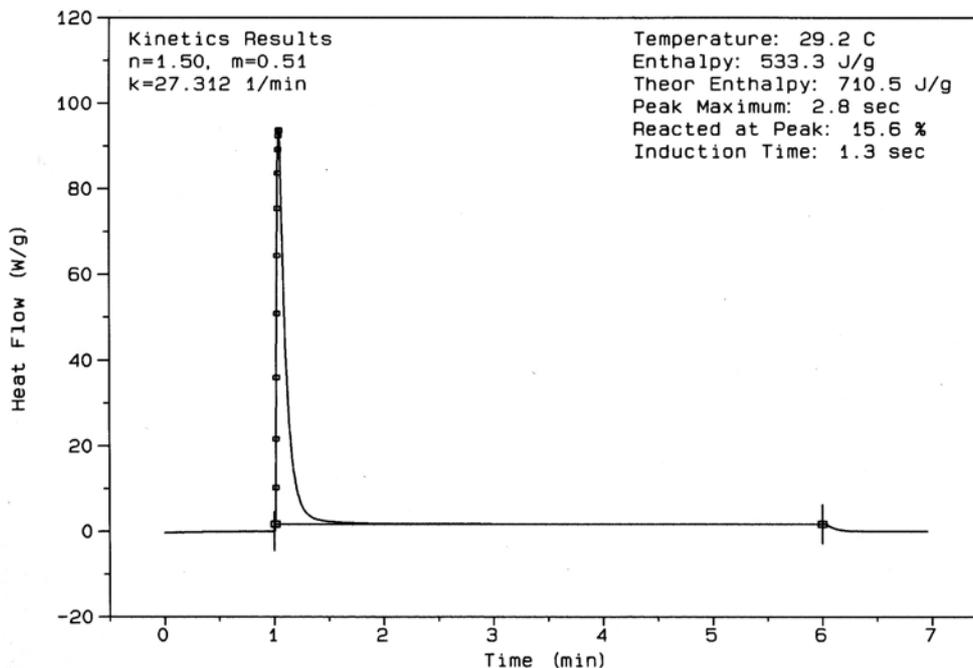


Fig. 1 – Typical exotherm plot of the photopolymerization of HDDA initiated by *para*-methoxybenzoyldiphenylphosphine oxide (3% w/w), in the presence of triethylamine as additive (3% w/w).

The compounds synthesized in our laboratory: *para*-methoxybenzoyldimethyl phosphonate, *para*-methoxybenzoyldiethyl phosphonate, *para*-methoxybenzoyldiphenyl phosphine oxide,³ terephthaloylbis(dimethylphosphonate), terephthaloylbis (diethylphosphonate), terephthaloylbis- (diphenylphosphine oxide),⁴ *iso*-phtaloylbis(dimethylphosphonate), *iso*-phtaloylbis (diethyl-phosphonate), *iso*-phtaloylbis

(diphenylphosphine oxide)⁵ and 2,4-dichlorophenylacetyldiethyl-phosphonate were successfully used as photoinitiators for radical polymerization of HDDA. The photopolymerization system contains triethylamine as synergist additive.⁶

The photoinitiating efficiency is expressed by the variation of polymerization rate function of conversion (Fig. 2).

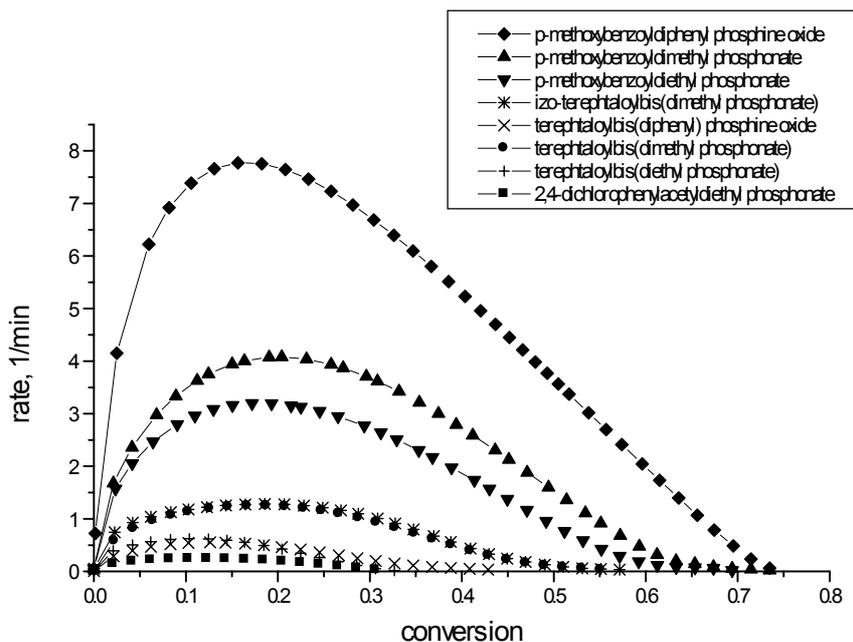


Fig. 2 – Comparative photoinitiating efficiency of synthesized acylphosphonates and acylphosphine oxides.

DISCUSSION

Fig. 2 shows that the photoinitiators derived from *para*-methoxybenzoyl are most reactive, followed by *iso*-phtaloyl- and terephtaloyl-derivatives, and 2,4-dichlorophenylacetyldiethyl phosphonate.

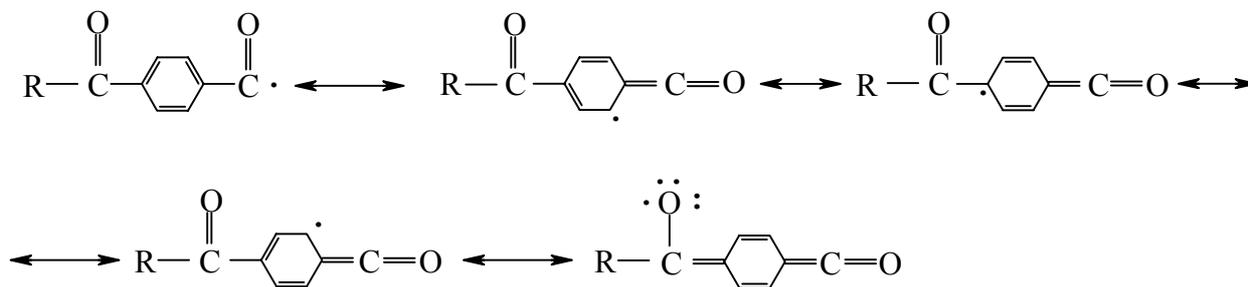
Compounds of type acylphosphine oxide (such as *para*-methoxybenzoyldiphenyl phosphine oxide, terephtaloylbis(diphenylphosphine oxide) and *iso*-phtaloylbis(diphenylphosphine oxide) are more reactive than corresponding acylphosphonates. Also, in the case of acylphosphonates is noticed that the dimethylphosphonates are more reactive than diethylphosphonates. It was proposed⁷ that the reactivity of the phosphorus centered radicals can be explained in term of the pyramidal structure of the phosphinoyl radicals which permits the site of unpaired electron to be approach easily by the reactants. Reactivity of phosphinoyl radicals depends on the substituents bulk: alcoxy in acylphosphonate and phenyl in acylphosphine oxide. Compared to the first, the latter have a

flattened tetrahedral structure, hence it should react slower with double bonds. Also, the methoxy group is less bulky than ethoxy group; hence, the dimethoxyphosphonates are more reactive than ethoxyphosphonates.

However, in practice, acylphosphine oxides are always more reactive than the corresponding acylphosphonates,⁸ that which was noticed in the case of synthesized compounds.

It was expected that bifunctional photoinitiators derived from terephtaloyl and *iso*-phtaloyl to be more effective than monofunctional photoinitiators derived from *para*-methoxybenzoyl, because by α -scission result two phosphinoyl radicals, which are more reactive than carbonyl radicals.⁹

This lower reactivity could be explained by conjugation effects which appear in the case of terephtaloyl derivatives, due to their symmetrical structure. It may be possible an extended conjugation between both carbonyl groups (Scheme 1), which has as consequence the stabilization of the radical and, therefore, the increase of the induction time.



Scheme 1.

where: $R = (\text{CH}_3\text{O})_2\text{P}(\text{O})$

It was observed that the *iso*-phtaloyl derivatives are more reactive than terephtaloyl derivatives, because in the case of *iso*-phtaloyl the conjugation does not appear.

However, in these experimental conditions, although terephtaloyl derivatives are less reactive than *p*-methoxybenzoyl and *iso*-phtaloyl derivatives, they are effective for radical polymerization in the presence of amine.

The photoinitiator 2,4-dichlorophenylacetyldiethyl phosphonate is less reactive than *para*-methoxybenzoyldiethyl phosphonate, due to low electronic effects manifested by the groups attached on phenyl ring, which influence the α -scission of C-P bond (reaction 1).

EXPERIMENTAL

Photoinitiating activity

Materials

1,6-hexanedioldiacrylate (HDDA) (Aldrich) was used without further purification. The photoinitiators were the synthesized compounds: *p*-methoxybenzoyldialkylphosphonates and terephtaloylbis(dialkylphosphonates), alkyl=methyl, ethyl, *p*-methoxybenzoyldiphenylphosphine oxide, terephtaloylbis(dialkylphosphonates), alkyl=methyl, ethyl, terephtaloylbis(diphenylphosphine oxide), and *iso*phtaloylbis(dialkylphosphonates), alkyl=methyl, ethyl, *iso*-phtaloylbis(diphenylphosphine oxide) and 2,4-dichlorophenylacetyldiethyl phosphonate. Tertiary amines: triethylamine (TEA) (Aldrich) was used as synergist additives.

Technique

Differential scanning photocalorimetry (photo-DSC) was performed using a DuPont 930 irradiation unit with a double

head differential calorimeter 912 calibrated with indium metal standard. A standard high pressure Hg lamp with 8 mW/cm² light intensity was used for sample UV exposure.

Sample preparation

About 1.5±0.5 mg sample containing monomer HDDA, photoinitiator in a concentration of 3% weight versus monomer, and amine 3% versus monomer, were added in an aluminum DPC pan, and than covered with a PET film in order to minimize oxygen inhibition effect. Another sample is the reference which contains only HDDA. The reference was exposed before, on UV light, to achieve a complete reticulation.

Measurement

Photo-DSC experiments were carried out using computer controlled isothermal methods. Before irradiation, the sample and the reference were placed in the photo-DSC furnace for 5 min under nitrogen to remove residual oxygen and to allow temperature stabilization. Then the sample and the reference were irradiated for 5 min in an inert atmosphere. The heat flow (W/g) versus exposure time (min) was recorded for each sample to obtain photoreactivity parameters: polymerization enthalpy, time to reach peak maximum, percentage reacted at peak maximum, induction time (time to reach 1% conversion) and rate constant. The photoinitiating efficiency was obtained by plotting rate versus conversion.

CONCLUSIONS

The previously synthesized compounds acylphosphonates and acylphosphine oxides were successfully used as photoinitiators for radical polymerization of 1,6-hexandiol diacrylate. Comparative study of their photoinitiating

efficiency was carried out by differential scanning photocalorimetry (photo-DSC). The most reactive photoinitiators, not mentioned in the literature as photoinitiators, are *para*-methoxybenzoyldiphenyl phosphine oxide, *para*-methoxybenzoyldimethyl phosphonate and *para*-methoxybenzoyldiethyl phosphonate.

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