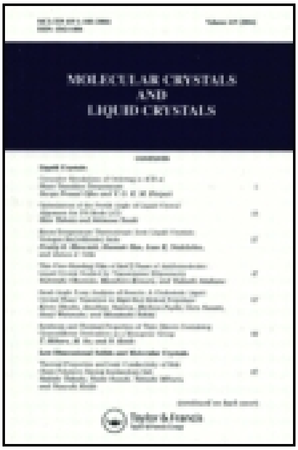

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Phosphorus Compounds as Photoinitiators for Radicalic Polymerization

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PHOSPHORUS COMPOUNDS AS PHOTOINITIATORS FOR RADICALIC POLYMERIZATION

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p-Methoxybenzoyldialkylphosphonates, where alkyl = methyl, ethyl and p-methoxy-benzoyldiphenylphosphine oxide were synthesized by Michaelis-Arbuzov reaction. These compounds were used as photoinitiators for radicalic polymerization of acrylic monomers. The photoreactivity parameters were determined by differential photocalorimetry (DPC), in isothermal conditions, using 1,6-hexandioldiacrylate (HDDA) as monomer, in the presence and absence of amine. The influence of concentration on film pendulum hardness was studied.

Keywords: acylphosphonates; acylphosphine oxides; differential photocalorimetry

INTRODUCTION

In the field of photoinitiators, phosphorus compounds of type acylphosphine oxides and acylphosphonates have been developed as a new class of UV photoinitiators. These compounds are effective as photoinitiators for various unsatured systems, especially they are reactive towards acrylates [1,2]. On UV irradiation acylphosphonates and acylphosphine oxides undergo a Norrish type I α-scission to form carbonyl and phosphonyl radicals able to initiate polymerization [3].

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The aim of this paper is to present the synthesis of *p*-metoxybenzoyldialkylphosphonates (alkyl = methyl, ethyl) and *p*-metoxybenzoyldiphenylphosphine oxide, and their applications as photoinitiators for radical polymerization of acrylic monomers.

Differential photocalorimetry was used to monitor polymerization reactions.

Their photoinitiating efficiency was compared with commercial products. The influence of concentration on pendulum hardness was determined.

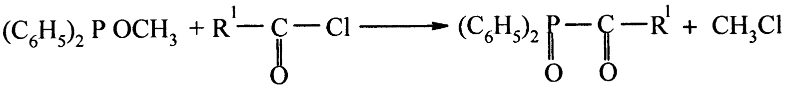
EXPERIMENTAL

Acylphosphonates were synthesized by Michaelis-Arbuzov reaction between acidic chlorides and trialkylphosphites (reaction 1) and acylphosphine oxide was synthesized by Michaelis-Arbuzov reaction between acidic chlorides and diphenylmethylphosphinite (reaction 2) [1,2]:

$$(RO)_3P + R^1-\underset{\underset{O}{\|}}{C}-Cl \longrightarrow (RO)_2\underset{\underset{O}{\|}}{P}-\underset{\underset{O}{\|}}{C}-R^1 + RCl$$

where: R = methyl, ethyl;

R^1 = *p*-methoxyphenyl.



$$(C_6H_5)_2\,P\,OCH_3 + R^1-\underset{\underset{O}{\|}}{C}-Cl \longrightarrow (C_6H_5)_2\underset{\underset{O}{\|}}{P}-\underset{\underset{O}{\|}}{C}-R^1 + CH_3Cl$$

where: R^1 = *p*-methoxyphenyl.

Reagents

Trialkylphosphites were used as received from Aldrich.

Acidic chlorides were obtained in laboratory from *p*-methoxybenzoic acid and thionyl chloride in molar ratio 1:1.5, respectively [4]. In such cases all thionyl chloride must be removed from acidic chloride before addition of the trialkylphosphite.

Diphenylmethylphosphinite was obtained from diphenylchlorphosphine and methanol in petroleum ether, in the presence of N,N-diethylaniline, as previously reported [5].

Synthesis of *p*-methoxybenzoyldialkylphosphonates

In a flask equipped with mechanical or magnetic stirrer, dropping funnel and condenser was added the acidic chloride in toluene. Trialkylphosphite (alkyl = methyl, ethyl), in stoichiometric ratio, was added drop wise over 20 min by stirring continuously. The reaction mixture was heated for 2 hours over an oil bath at 40°C when the reagent is trimethylphosphite, and for 8 hours at 80°C when the reagent is triethylphosphite, with continuous stirring. Acyldialkylphosphonate was purified by vacuum distillation (90°C/12 mmHg).

Synthesis of *p*-methoxybenzoyldiphenylphosphine Oxide

In a flask equipped with mechanical or magnetic stirrer, dropping funnel and condenser was added 0.1 mol *p*-metoxibenzoyl chloride in toluene. 0.1 mol diphenylmethylphosphinite was added to *p*-metoxibenzoyl chloride drop wise, over 20 min, with continuous stirring. The mixture was heated at 60°C for 2 hours. The obtained compound were recrystallized from cyclohexane.

The synthesized compounds were characterized by IR spectroscopy using FTIR Nicolet 710 spectrometer.

Photoinitiating Activity

Materials

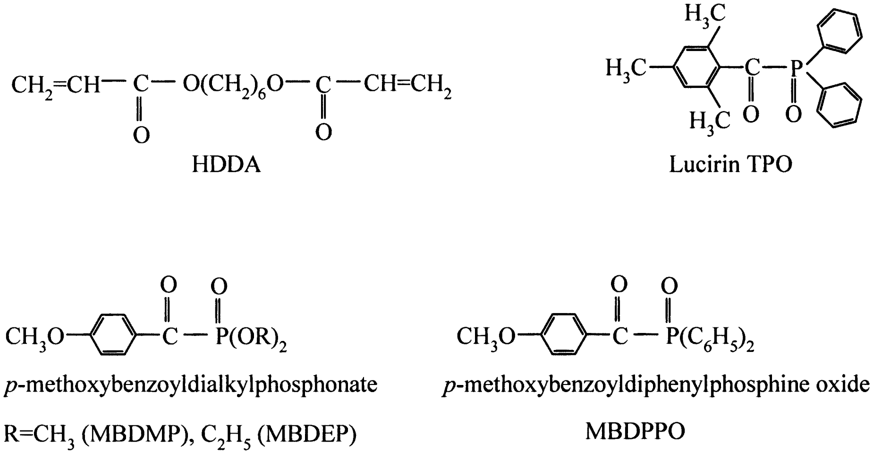
1,6-hexanedioldiacrylate (HDDA) (Aldrich) was used without further purification. The photoinitiators were the synthesized compounds: *p*-methoxybenzoyldialkylphosphonates alkyl = methyl, ethyl and *p*-methoxy benzoyldiphenylphosphine oxide (Scheme 1). Commercial photoinitiator Lucirin TPO (2,4,6-trimethylbenzoyldiphenylphosphine oxide) (BASF) was used as received (Scheme 1). Secondary and tertiary amines: diethylamine (DEA), triethylamine (TEA) and N,N-dimethylbenzylamine (BDMA) (Aldrich) were used as synergist additives.

Technique

Differential scanning photocalorimetry 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 3 mW/cm^2 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



SCHEME 1 Monomer and photoinitiators.

monomer, were added in an aluminium 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, crosslinked before, to became inert.

Measurement

DPC experiments were carried out using computer controlled isothermal methods. Before irradiation, the sample and the reference were placed in the DPC 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 maximum, percentage reacted at peak maximum, induction time (time to reach 1% conversion) and rate constant. Induction time is shorter when the photoinitiator is more reactive.

RESULTS AND DISCUSSION

In Table 1 are presented data concerning synthesis and characterization of acyldialkylphosphonates and acylphosphine oxide.

The synthesized compounds were characterized by IR spectroscopy. The P=O and P–O–C(phosphonate) are the functional groups which is most

TABLE 1 Synthesis of Acylphosphonates and Acylphosphine Oxide

Nr. crt.	Compound	Aspect	Yields, %	Phosphorus contain	
				exp.	teor.
1.	*p*-methoxybenzoyldimethyl-phosphonate MBDMP	liquid p.f.$_{2.5}$ 170°C	83	12.12	12.70
2.	*p*-methoxybenzoyldiethyl phosphonate MBDEP	liquid p.f.$_{0.4}$ 158°C	71	11.4	10.91
3.	*p*-methoxybenzoyl diphenyl phosphineoxide MBDPPO	white crystals m.p. 180–182°C	77	8.98	9.22

readily recognized from its IR strong absorption bands in the region 1320–1200 cm^{-1} and 1088–950 cm^{-1}, respectively [6]. The absorption band of P−C(alkyl) bond can be identified in the region 785–680 cm^{-1}, which have weak intensity. In the case of acylphosphine oxides, a strong absorption band can be identified at 1440 cm^{-1} (Table 2).

In Figure 1 is shown a typical thermogram with photoreactivity parameters for the photoinitiated polymerization of HDDA using MBDPPO as photoinitiator in a concentration of 3%, in the presence of 3% TEA.

From the thermograms it can obtain photoreactivity parameters of photoinitiated polymerization of HDDA with synthesized photoinitiators.

Photoreactivity parameters for synthesized compounds, recorded by differential photocalorimetry, are shown in Table 3. Theoretical polymerization enthalpy for HDDA is 710.5 J/g [7].

From Table 3 it can observe that MBDPPO shows the better values of photoreactivity parameters (in the presence of TEA), especially the induction time ($t_i = 1.3$ s) and the enthalpy of polymerization ($\Delta H = 533.3$ J/g). That means that MBDPPO is an effective photoinitiator, as effective as commercial product Lucirin TPO($t_i = 1.3$ s, $\Delta H = 517.37$ J/g). MBDMP

TABLE 2 Characteristic IR Absorption Bands of Synthesized Compounds

Nr. crt.	Compound	P=O cm^{-1}	P−C (aliphatic) cm^{-1}	P−C (aromatic) cm^{-1}	P−O−C (phosphonate) cm^{-1}
1.	MBDMP	1262	697	–	1028
2.	MBDEP	1257	696	–	1023
3.	MBDPPO	1252	650	1440	–

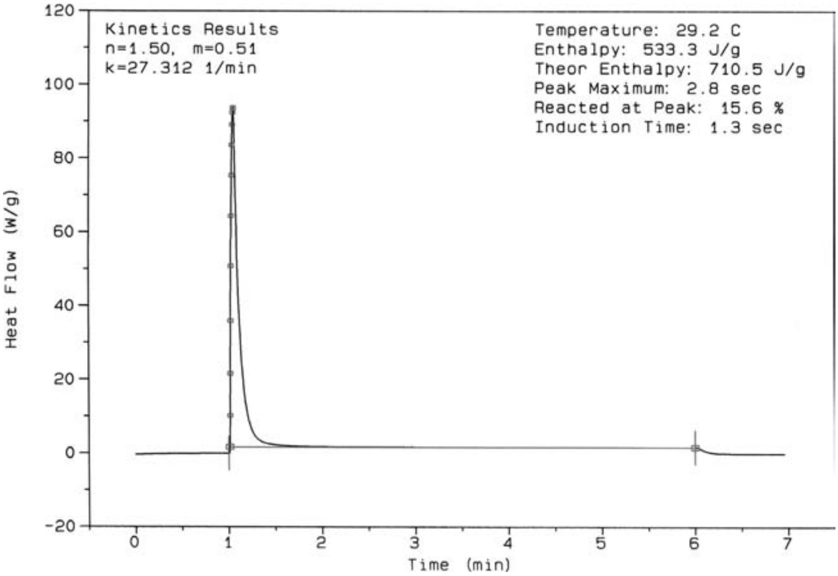
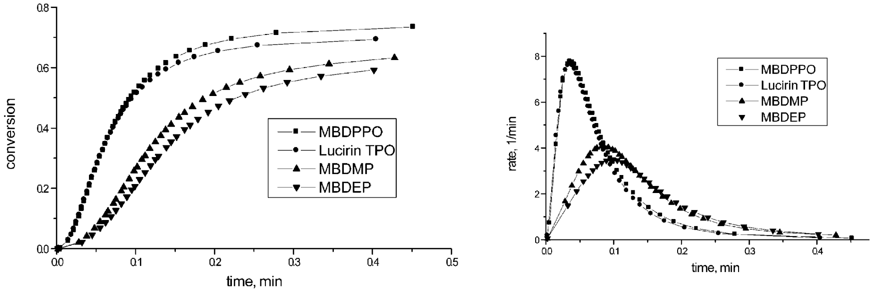


FIGURE 1 Typical thermogram of photoinitiated polymerization of HDDA with MBDPPO in the presence of TEA.

TABLE 3 Photoreactivity Parameters for the Polymerization of HDDA with Synthesized Photoinitiators, in Isothermal Conditions (t° = 30°C), in the Presence of Various Amines

Photoinitiator	Amine	Enthalpy, J/g	Peak maximum, sec	Reacted at peak, %	Induction time, sec	k, 1/min
MBDMP	TEA	536.9	6.0	20.4	2.1	13.721
	DEA	472.0	6.4	19.5	2.4	13.283
	BDMA	480.2	8.0	21.0	2.6	10.066
	without amine	527.2	21.2	24.0	6.9	3.572
MBDEP	TEA	504.5	6.4	20.7	2.4	12.175
	DEA	454.8	6.8	19.0	2.6	11.734
	BDMA	491.8	9.0	23.9	2.9	9.877
MBDPPO	TEA	533.3	2.8	15.6	1.3	27.312
	DEA	504.0	3.4	16.8	1.5	22.618
	BDMA	416.6	5.2	15.8	2.5	16.644
Lucirin TPO	–	517.37	2.8	16.3	1.3	26.281



a b

FIGURE 2 Conversion (a) and rate of polymerization (b) of HDDA with synthesized photoinitiators at a concentration of 3%, in the presence of 3% TEA.

and MBDEP have also short induction time and they perform good photoinitiating activity.

In Figures 2 and 3 are shown the variation of conversion and polymerization rate versus time of UV exposure in comparison with Lucirin TPO.

It can observe that the best values of conversion and rate were obtained using MBDPPO, better than Lucirin TPO.

The photoreactivity parameters depend on amine. In the case of photoinitiated polymerization of HDDA using MBDMP without amine, the induction time is greater that in case when amine is added. The role of amine is of an oxygen scavenger. It is well known that phosphorus radicals rapidly react with oxygen and thus probably partially consumed by this reaction [8]. The best results were obtained by adding TEA and DEA (Figure 3 a, b).

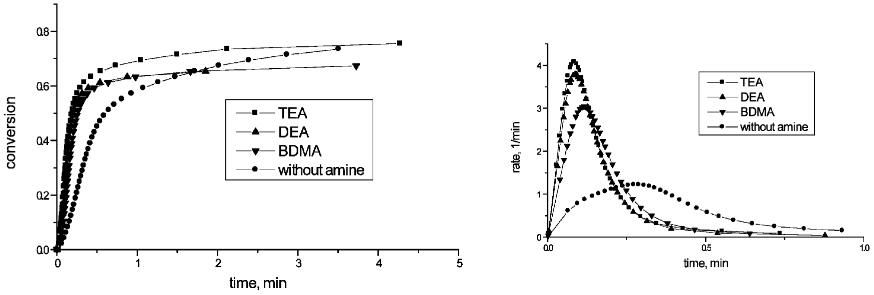


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FIGURE 3 Conversion (a) and rate of polymerization (b) of HDDA with MBDMP photoinitiator at a concentration of 3%, in the presence of various amines 3% and without amine.

By adding TEA and DEA it was obtained more efficient photoinitiating activity of MBDMP than by adding BDMA or without amine. BDMA is steric hindered and reacts slower with atmospheric oxygen.

Photoinitiator Applications

The synthesized compounds were used as UV curing photoinitiators of diacrylate Photomer 3015 (Henkel) films. Photopolymerizable formulation containing monomer, photoinitiator and additive (amine) was laid down on a glass panel with a film applicator. UV curing was carried out using Hg lamp, situated 15 cm above surface of formulation. The König pendulum hardness of cured film was determined using pendulum hardness test according with DIN 53157. The results are shown in Table 4.

It can observe from Table 4 that by adding amine the values of the pendulum hardness decrease, although in differential photocalorimetry experiments, by adding amines, were obtained better values for photoreactivity parameters. However, there are small differences between photoreactivity parameters obtained at photoinitiated polymerization with and without amine. In practical applications, great values of pendulum hardness means good resistance of the films to solvents and weathering.

The influence of photoinitiator concentration on pendulum hardness of acrylate films was studied.

In the Figure 4 are shown the variation of the pendulum hardness of Photomer 3015 films, using MBDMP as photoinitiator.

The pendulum hardness of the film pronounced increases from a concentration of 1% to 1.5% and slowly up to 1.5%. Good values for pendulum hardness were obtained from a concentration of 3%.

TABLE 4 Pendulum Hardness of UV Cured Films of Photomer 3015 in the Absence and in the Presence of TEA as Additive, After 1 min. Exposure Time

		Pendulum hardness, s	
Photoinitiator	Film thickness, μm	Without TEA	With TEA
MBDMP	120	254	149
	300	265	153
MBDEP	120	231	143
	300	239	148
MBDPPO	120	242	235
	300	264	259

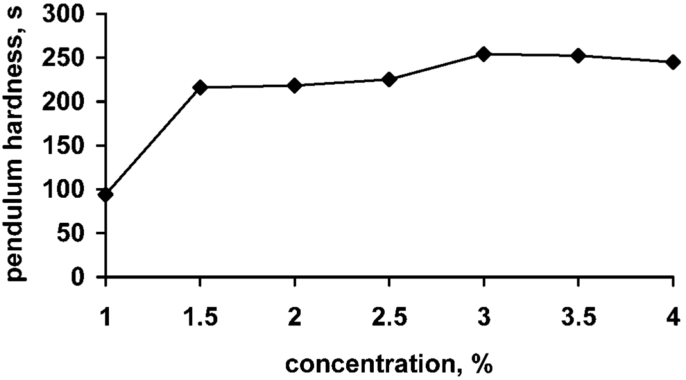

FIGURE 4 The influence of concentration on pendulum hardness.

CONCLUSION

p-Methoxybenzoyldialkylphosphonates, where alkyl = methyl, ethyl and *p*-methoxy-benzoyldiphenylphosphine oxide were synthesized by Michaelis-Arbuzov reaction. These compounds were tested as photoinitiator for radicalic polymerization of diacrylate monomer HDDA by differential photocalorimetry method. They showed a very good photoreactivity efficiency, comparable with commercial product Lucirin TPO. The influence of amine on photoreactivity parameters was studied. The best results were obtained in the presence of TEA. The influence of concentration on pendulum hardness was studied.

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