Central European Science Journals
www.cesj.com

Central European Journal of Chemistry
Central European Science Journals
CEJC 3(4) 2005 721–730

The influence of temperature and photoinitiator concentration on photoinitiated polymerization of diacrylate monomer

Lavinia Macarie*, Gheorghe Ilia†

Institute of Chemistry Timisoara,
Romanian Academy,
24 Mihai Viteazul Bvd., 300223 Timisoara, Romania

Received 14 March 2005; accepted 21 June 2005

Abstract: The behavior of *p*-methoxybenzoyldiphenylphosphine oxide, previously synthesized, as a photoinitiator for the polymerization of diacrylate monomer, in the presence of 3 % (w/w) tertiary amine (triethyl amine) as synergist additive, was studied. The influence of temperature in the range 30-90 °C at 3 % (w/w) photoinitiator concentration and the influence of the photoinitiator concentration in the range 0.5-3.5 % (w/w) at 30 °C was investigated by differential scanning photocalorimetry (photo-DSC). In all experiments the photopolymerization was performed at constant light intensity (3 mW cm^{-2}). The maximum conversion was obtained at temperature of 90 °C at 3 % (w/w) photoinitiator concentration and 3 % (w/w) triethyl amine. The optimal concentration of photoinitiator to obtain maximum conversion was 3 % (w/w), at 30 °C. No thermal polymerization occurred at higher temperature.

Keywords: Photoinitiated polymerization, dimethacrylate monomer, differential scanning photocalorimetry

---

1 Introduction

The UV-curing of photopolymerizable systems, containing monomer/oligomer, photoinitiator and additive, has found industrial application, mainly in the coating and printing domain, and 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

---

* E-mail: lavi_mac@yahoo.com
† E-mail: ilia@acad-icht.tm.edu.ro

systems by generating the reactive species, free radicals or ions, able to initiate the polymerization of the multifunctional monomers and oligomers. UV-curing coating systems have advantages such as: good cost/performance relationship, 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 meet these requirements. Phosphorus containing photoinitiators of the acylphosphine oxide and acylphosphonate classes have been found effective in photoinitiation of the polymerization of olefin monomers [2].

Epoxy acrylates are the mostly widely used group of UV-curable oligomers since they exhibit the highest reactivity. They are highly reactive and usually give hard, glossy and chemically resistant coatings.

This paper reports the influence of photoinitiator concentration and temperature on photoinitiated polymerization of diacrylate monomer. Differential scanning photocalorimetry (photo-DSC) was used to follow the reaction. The aroylphosphine oxide derivative: *p*-methoxybenzoyldiphenylphosphine oxide, previously obtained [3], was used as the photoinitiator, because it showed high photoinitiating efficiency compared with the commercial product Lucirin TPO (BASF) [4].

In photoinitiated polymerization by phosphorus compounds (i.e. acylphosphine oxides and acylphosphonates) the role of tertiary or secondary amine is either as synergist additive or to reduce the extent of oxygen inhibition [5]. The effectiveness of different amines, at a concentration of 3 % (w/w), in these systems was studied using photo-DSC [4]. Our experiments indicate that a concentration greater than 3 % could decrease the coating pendulum hardness.

2 Experimental section

2.1 Differential scanning photocalorimetry

2.2 Materials

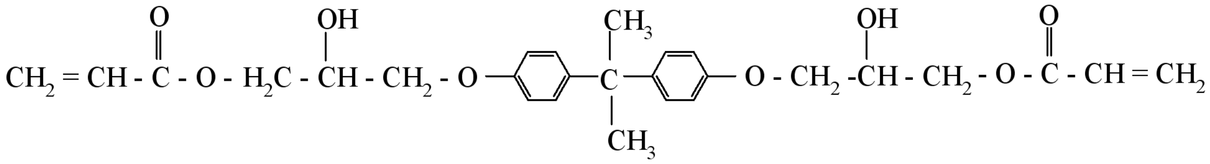
Photomer 3015 (from Henkel) - bisphenol A epoxy diacrylate (EDA), commercial product for coatings (Figure 1) was studied as the acrylate.

p–Methoxybenzoyldiphenylphosphine oxide (MBDPPO) (Figure 2 (a) and (b)) was used as the photoinitiator. Its photoinitiation efficiency had previously been evaluated. It showed a good solubility in monomer.

Triethylamine (TEA) (Merck) was used as received as the synergist additive [6].

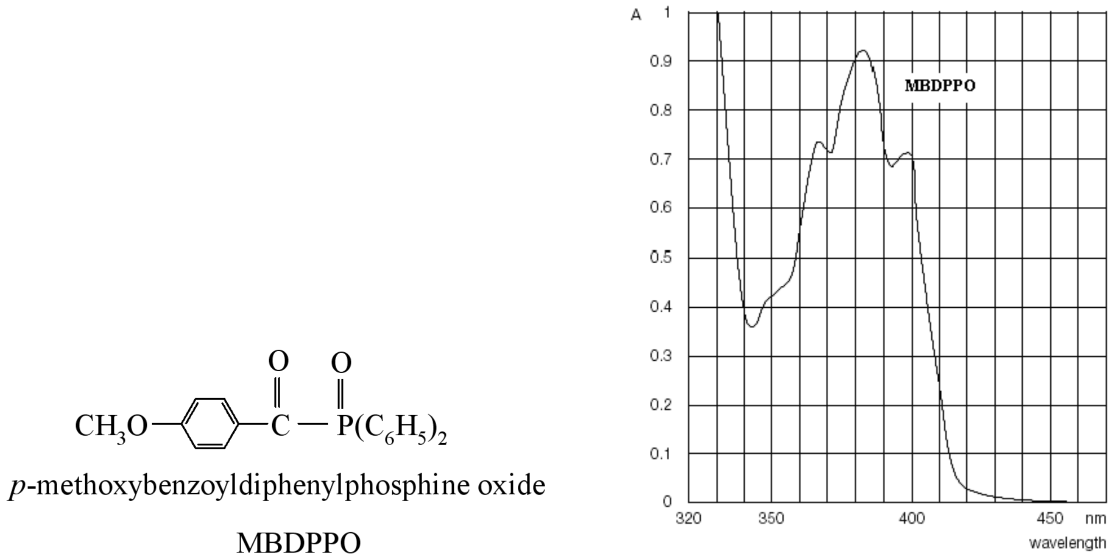
2.3 Sample preparation

About 1.5±0.5 mg sample containing monomer EDA, photoinitiator MBDPPO in various concentrations % (w/w), and amine 3 % (w/w), were added in an aluminum DSC pan,



EDA

Fig. 1 Chemical formula of monomer.



p-methoxybenzoyldiphenylphosphine oxide

MBDPPO

(a)

(b)

Fig. 2 Chemical formula of photoinitiator (a) and UV absorption spectrum for MBDPPO in toluene (c=0.0015 mol l^{-1}).

and then covered with 2.5 μm PET film in order to minimize the oxygen inhibition effect. A reference sample containing only EDA was also prepared. This reference sample was pre-exposed to UV light, to achieve a complete reticulation.

2.4 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. The experiments were carried out under an inert N_2 atmosphere.

2.5 Measurement

Photo-DSC experiments were carried out using computer controlled isothermal methods. First, the samples were equilibrated at a preselected temperature followed by isothermal treatment without exposure for 5 min. The heat flow (W/g) versus exposure time (min) was recorded for each sample to obtain photoreactivity parameters: polymerization enthalpy, time to reach maximum, conversion at peak maximum, induction time (time to reach 1 % conversion) and rate constant.

The viscosity of the monomer was determined using a Brookfield RV viscometer, at a rate of 5 rot min^{-1} and the DSC thermogram was recorded in a N_2 atmosphere using a TG 209 Netzsch instrument.

3 Results and discussion

The photoinitiator *p*-methoxybenzoyldiphenylphosphine oxide, MBDPPO, synthesized in our laboratory, has not previously been studied and reported as a photoinitiator for radical polymerization of acrylate monomers. A photo-DSC study on the polymerization of 1,6-hexandioldiacrylate, HDDA, in the presence of MBDPPO and triethylamine reveals that this compound is an effective photoinitiator, giving very good values of conversion. It is as reactive as the commercial product Lucirin TPO (from BASF), which has a similar structure, in the same conditions (Figure 3). For this reason the efficiency of this compound was further studied in the polymerization of the commercial product Photomer 3015 – bisphenol A epoxy diacrylate.

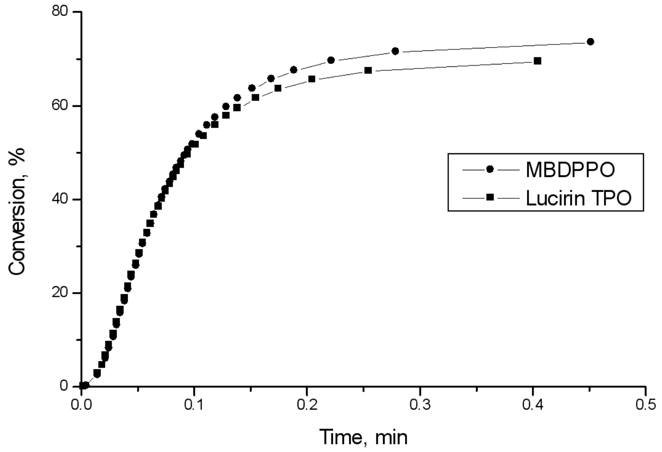


Fig. 3 Conversion of **HDDA** using **MBDPPO** and **Lucirin TPO** as photoinitiator (conc. 3 % w/w), in the presence of 3 % w/w triethylamine at 30 °C.

Figure 4 shows a typical exotherm plot for EDA photopolymerization initiated by MBDPPO at concentration of 3 % w/w, in the presence of 3 % w/w triethylamine as additive. The total area under the exotherm curve corresponds to the polymerization enthalpy ΔH of the sample. The very sharp peak represents the high reactivity of EDA in the presence of MBDPPO. From this exotherm plot, one can obtain the induction time, polymerization enthalpy, percent conversion (right side), and rate constant (left side).

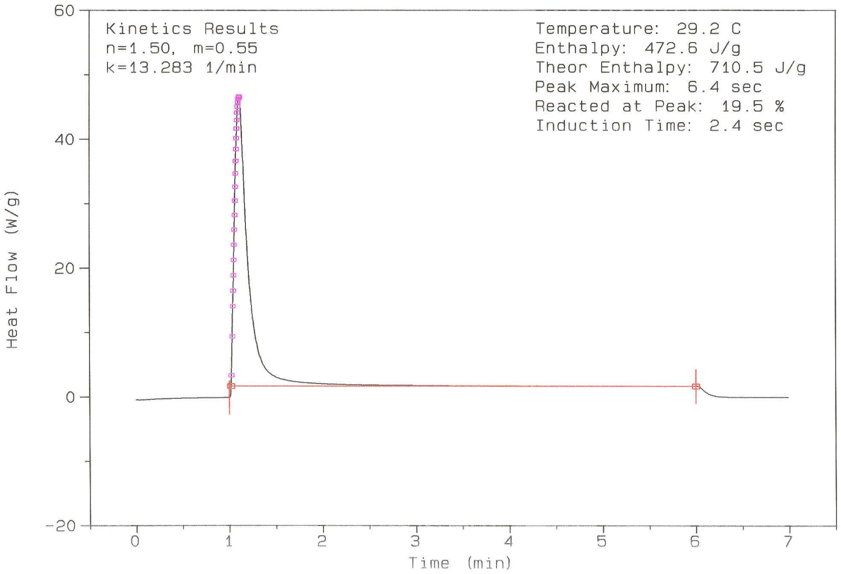


Fig. 4 Typical exotherm plot of the polymerization of EDA photoinitiated by MBDPPO (conc. 3 % w/w), additive triethylamine 3 % w/w at 30 °C.

3.1 Influence of the temperature

Influence of the temperature on reaction was studied in the range 30-90 °C, for a photoinitiator concentration of 3 % (w/w) and triethylamine additive 3 % w/w. In this range it is possible that the monomer might undergo a thermal polymerization. The DSC thermogram (Figure 5) was recorded maintaining the monomer at 95 °C for 12 hours, in an inert atmosphere. No thermal polymerization was observed even at this higher temperature (95 °C). In the investigated temperature range only photoinitiated polymerization was occurring.

The 30-90 °C temperature range studied is comparable with the temperatures that arise in practical applications for coatings. The possibility of thermal polymerization in this range therefore needs to be considered. The DSC thermogram (Figure 5) reveals that thermal polymerization did not occur even after 12 hours at 95 °C. We considered that the study of the monomer behavior at higher temperature is not necessary because the temperature in photopolymerization did not exceed 90 °C. We therefore conclude that in our studies there was no thermal polymerization taking place as a side reaction.

The conversion increases with temperature (Figure 6). High temperatures speed up the radical reactions and the temperature effects are manifested in the acceleration and increase of conversion. Film formation, which involves transtion from a liquid state to solid state, is dependent on the ability of photoinitiator to diffuse through monomer to active sites. The most important property required for coatings is a mechanical property:

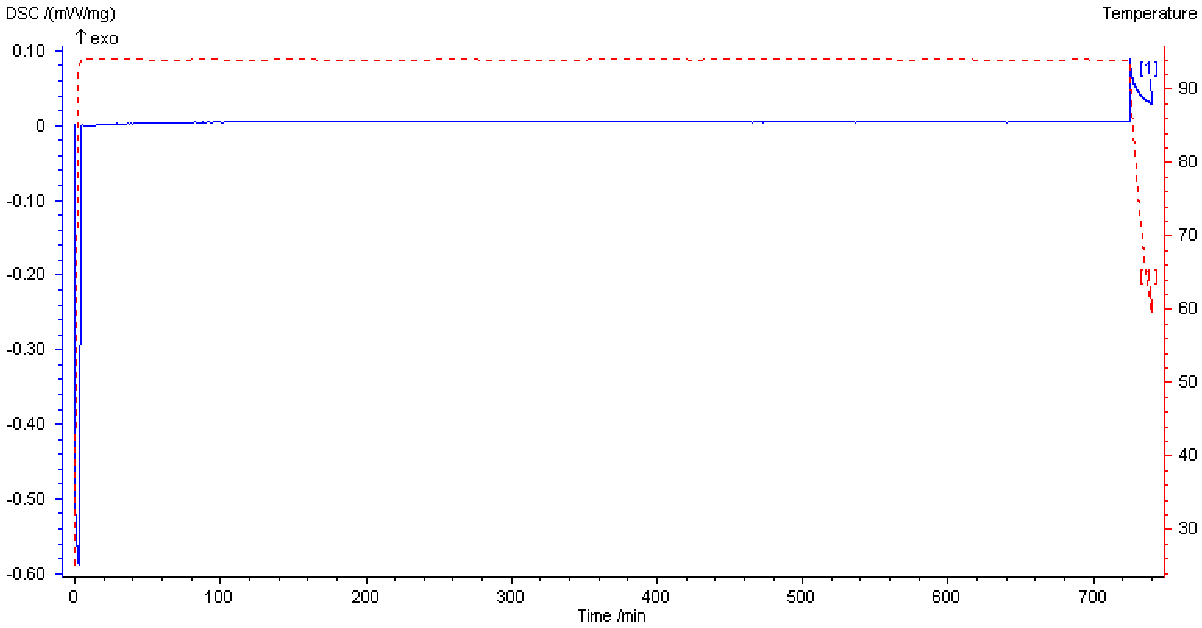


Fig. 5 DSC thermogram of monomer.

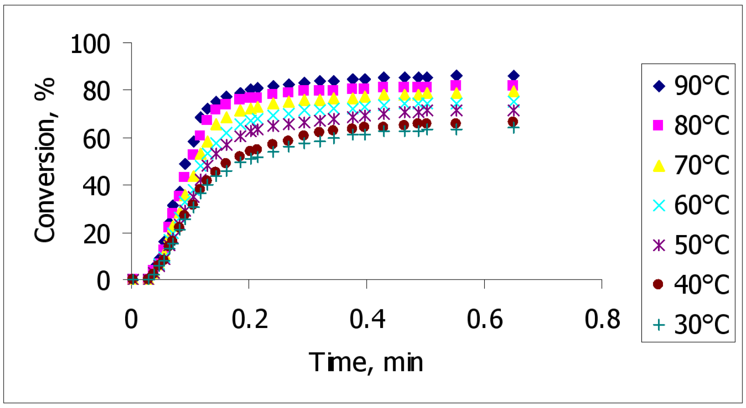


Fig. 6 Conversion versus time of exposure for temperature range 30-90 °C (photopolymerizable system: monomer EDA, photoinitiator MBDPPO 3 % (w/w) and triehtylamine as additive 3 % (w/w)).

pendulum hardness. An elevated temperature reduces the viscosity of the formulation (Figure 7), leading to increased conversion. High conversion in photopolymerization means a good mechanical property. The results of this study show that MBDPPO could successfully be used as an efficient photoinitiator to obtain a high cure degree.

The autocatalytic model (equation 1) [7] has been used to calculate the kinetic parameters. The autocatalyzed reactions are characterized by a maximum heat evolution at about 40 % reaction in the isothermal DSC signal.

$$\frac{dC}{dt} = kC^m(1-C)^n \tag{1}$$

where: C = conversion; dC/dt = polymerization rate (sec^{-1}); $k(T)$ = specific rate con-

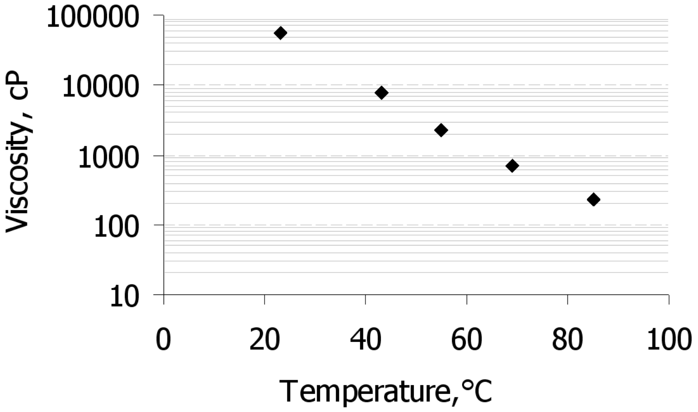


Fig. 7 Viscosity of Photomer 3015 vs. temperature.

stant at temperature T (min^{-1}); n, m = reaction orders.

The reaction constant $k(T)$ is assumed to follow the Arrhenius equation (2):

$$k(T) = A \cdot \mathrm{e}^{\frac{-E}{RT}} \tag{2}$$

The basic parameters C and dC/dt can be obtained from the (photo-DSC) exotherm. The polymerization rate can be calculated in connection with the heat flow, according to equation 3:

$$R_p = \frac{dC}{dt} = \frac{\left(\frac{dH}{dt}\right)}{\Delta H_0} \tag{3}$$

where: R_p = polymerization rate (sec^{-1}); ΔH_0 = theoretical enthalpy for EDA, 190 J g^{-1} [7].

The initiation and polymerization rates, R_i and R_p, respectively, are given by equations (4) and (5):

$$R_i = 2\phi\, I_a = 2\phi\, \varepsilon\, I_0\, [\text{PI}] \tag{4}$$

$$R_p = k_p\, [\text{M}^\cdot]\, [\text{M}] \tag{5}$$

where: ϕ = quantum yield of the photochemical reaction, ε = photoinitiator molar extinction coefficient; I_0 = light intensity of the u.v. radiation; [PI] = photoinitiator concentration; [M], [M$^\cdot$] = monomer and radical concentration.

Applying the steady-state assumption that [M$^\cdot$] is constant, meaning that the radicals are consumed at the same rate as they are generated, $R_i = R_t$. These rates are given by equations (6) and (7):

$$R_i = 2f\, k_i\, [\text{PI}] \tag{6}$$

$$R_t = 2\, k_t\, [\text{M}^\cdot]^2 \tag{7}$$

where: f = fraction of radicals that initiate chain growth.

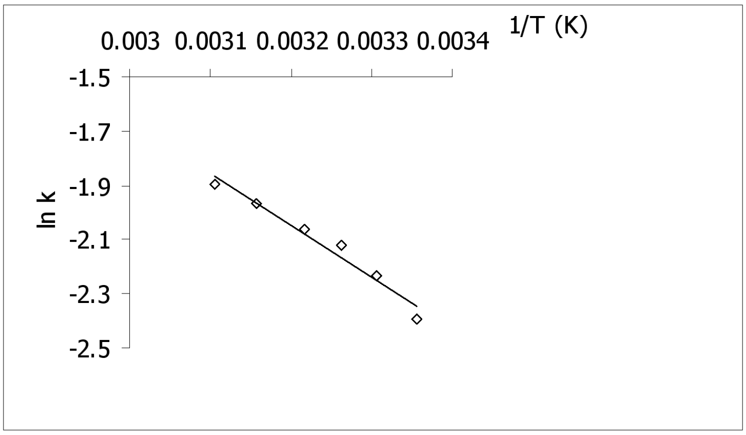
Using equation (5), the rate of polymerization can be expressed by equation (8):

$$R_p = k_p[\text{M}] \left(\frac{\phi\, \varepsilon\, I_0\, [\text{PI}]}{k_t}\right)^{\frac{1}{2}} \tag{8}$$

Expressing the rate constants k_p and k_t by their Arrhenius law (equation 2), it follows equation (9):

$$\ln R_p = \ln \frac{A_p}{A_t^{1/2}} + \ln\Big((\phi\, \varepsilon\, I_0\, [\mathrm{PI}])^{\frac{1}{2}}\, [\mathrm{M}] \Big) - \frac{E}{RT} \tag{9}$$

The rate constant measured at various temperatures can be plotted in the form ln k vs $1/T$, as shown in Figure 8. Assuming that the system follows the Arrhenius equation, this plot can be used to determine the apparent activation energy.



$$y = -1910.4x + 4.0645; \quad R^2 = 0.9642.$$

Fig. 8 ln k versus $1/T$ for EDA.

The activation energy for EDA photopolymerization initiated by MBDPPO is 15.88 kJ mol^{-1} . This implies a high photopolymerizing reactivity of EDA using MBDPPO as radical photoinitiator.

Previous discussion in the literature [7] suggested that the kinetic parameters of the photoinitiated polymerization can be described by the autocatalytic model. The low value of the reaction order m=0.55 (Figure 4) indicates an autocatalytic model. In this photopolymerization the rapid consumption of the initiator, is followed by a first order decomposition reaction. The kinetics of the polymerization are satisfactorily described by first-order law. This model fits to our experimental data. The rate constants obtained at different temperatures are plotted in a log k vs $1/T$ plot in Figure 8. In the temperature range studied, this plot shows a linear dependence of ln k versus $1/T$, with a regression coefficient comparable with those obtained in literature data [7] for similar systems.

3.2 Influence of the concentration

The values of conversion change with the initiator concentration. Several photoinitiator concentrations varying in the range 0.5-3.5 % were studied at 30 °C, measuring conversion as a function of exposure time (Figure 9).

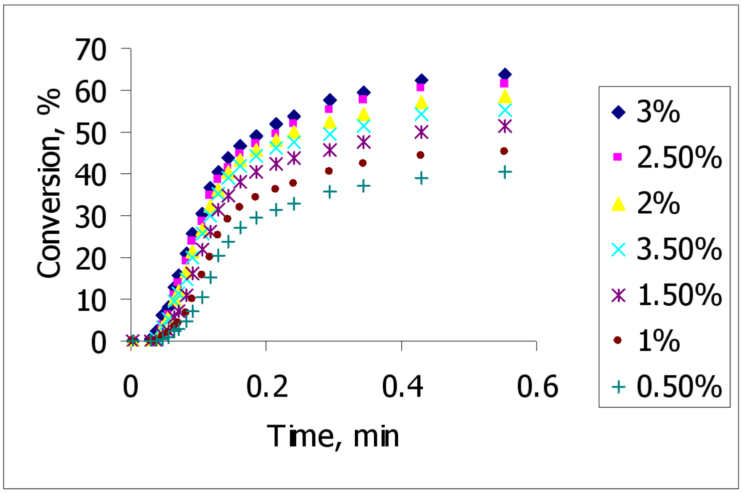


Fig. 9 Conversion versus exposure time for different photoinitiator concentration at 30 °C, in the presence of 3% (w/w) TEA.

Maximum conversion values as a function of exposure time are obtained for 3 % photoinitiator concentration. This is also seen in Figure 10, where values of ultimate conversion are shown. This result is directly connected to the optimum experimental conditions for final properties of the films, i.e. pendulum hardness, which gives maximum values for 3 % photoinitiator concentration [3]. Moreover, a photoinitiator concentration of 3 % is usual in practice for acylphosphine oxides [9].

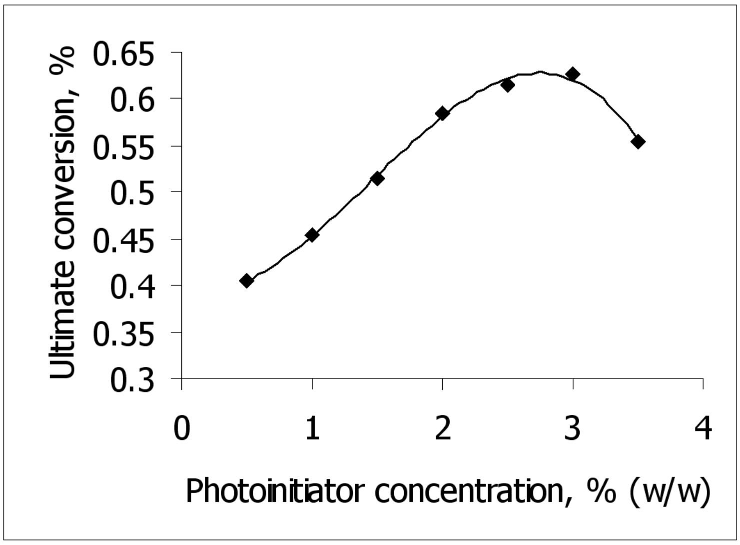


Fig. 10 Ultimate conversion vs. photoinitiator concentration at 30 °C.

According to equation (8), when [PI] increases, the polymerization rate must increase, assuming that other terms in this equation are constant.

With the increase of photoinitiator concentration to 3.5 %, conversion decreases. This can be explained by competition between the reactions of primary radical with a double bond during the initiation, due to higher concentration of active species, i.e. radicals.

4 Conclusions

In this study we have emphasized that differential scanning photocalorimetry is a good method for investigation of photoinitiated polymerization. In our experimental study of the photoinitiated polymerization of the dimethacrylate monomer in the presence of *p*-methoxybenzoyldiphenyl phosphine oxide as photoinitiator, the influence of the temperature and photoinitiator concentration were investigated. The conversion increases with temperature. High temperatures speed up the radical reactions due to decreased viscosity of the mixture. It was demonstrated that no thermal polymerization was occurring. The maximum conversion was obtained at a photoinitiator concentration of 3 % (w/w) when experiments were carried out at 30 °C.

References

[1] G.C. Roffey: *Photopolymerization of Surface Coatings*, Wiley Interscience Publications, London, 1982, p. 137.

[2] T. Majima and W Schnabel: „Photolytic α-scission in acyl phosphonic acid ester", *Bull. Soc. Chim. Belg.*, Vol. 99(11-12), (1990), pp. 911–917.

[3] L. Macarie, G. Ilia, S. Iliescu, A. Popa, G. Dehelean, I. Manoviciu, A. Petrean and M.J.M. Abadie: „Phosphorus Compounds as Photoinitiators for Radicalic Polymerization", *Mol. Cryst. Liq. Cryst.*, Vol. 416, (2004), pp. 165–174.

[4] L. Macarie, A. Petrean, G. Ilia, S. Iliescu, A. Popa and M.J.M. Abadie: „Photopolymerizable systems Containing Organophosphorus Compounds as Photoinitiators", *J. Polymer Research*, in press, accepted 07 dec 2004.

[5] K.K. Dietliker: *Photoinitiators for Free and Cationic Polimerisation*, Vol III of *Chemistry and Technology of UV & EB Formulation for Coatings, Inks and Paints*, P.K.T. Oldring, 1991, p. 177.

[6] J.E. Baxter, R.S. Davidson and H.J. Hageman: „Acylphosphine Oxides as Photoinitiators for Acrylate and Unsatured polyester resins", *Eur. Polym. J.*, Vol. 24(5), (1988), pp. 419–424.

[7] D. Wang, L. Carrera and M.J.M. Abadie: "Photopolymerization of Glycidyl Acrylate and Glycidyl Methacrylate Investigated by Differential Photocalorimetry and FT-I.R.", *Eur. Polym. J.*, Vol. 29(10), (1993), pp. 1379–1386.

[8] J.E. Moore: „Calorimetric Analysis of UV Curable Systems", In: *UV Curing: Science and Technology*, Technology Marketing Corp., Connecticut, USA, 1980.

[9] L.R. Gatechair and D. Wostratzky: „Photoinitiators: An Overview of Mechanism and Applications", *RadTechReport (RadTech Internat. North America)*, Vol. 13(4), (1999), pp. 34.