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Effect of UV light source intensity and spectral distribution on the photopolymerisation reactions of a multifunctional acrylated monomer

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Abstract

The goal of this study was to examine the possibilities of preparing thin surface spatial crosslinked polymer films by UV curing using 1,6-hexandioldiacrylate as a multifunctional monomer and 1-hydroxycyclohexyl acetophenone as a radical photoinitiator. Different UV light sources were used with different light spectral distributions and light intensities. It is found that the light source characterised at least by a particular overlap of its emission spectrum with the photoinitator's absorption spectrum is the best system used for effective cure. Low polymerisation rate achieved in the case of smaller overlap of spectrums is easy to regulate by extending the energy of the emitted light.

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Keywords: Photopolymerisation; UV lamps; IR spectroscopy

1. Introduction

Light induced process running in a polymer system is nowadays the subject of intensive study. One of the most effective methods of fast creating spatial crosslinked polymers is based on a multifunctional monomer exposure by UV light in the presence of a photoinitiator. The liquid resin is then transformed in a very short time into a solid polymer that is absolutely insoluble in organic solvents and has a high level of thermal and mechanical resistance [1]. This progressive technology is widely used in the fields of IT, imaging and electronic industries. Monomer is the most important fraction of any photopolymeric system. Monomers determine the properties of input systems and final products by their chemical structures and physical parameters [2].

Apart from the monomers there are other factors that influence the photopolymeric reactions such as: photoinitiator type and its concentration, presence of oxygen, temperature, spectral distribution and intensity of used the light source [3–5].

Photoreactions use energy from natural resources (sun radiation) or energy produced by controlled electric energy conversion into emission of UV, VIS and IR wavelengths [6–8]. Suitable light sources for photopolymerisation and photocuring are light sources with emission in the wavelengths' range from 254 to 450 nm, e.g. mercury lamps.

2. Experimental

In our study were used: multifunctional monomer 1,6-hexandioldiacrylate (Sartomer 238, Sartomer, France) and radical photoinitiator 1-hydroxycyclohexyl acetophenone (Irgacure 184, CIBA, Switzerland, with the initial molar concentration 0.05 M) dissolved in the monomer. Samples were irradiated by UV light sources with different spectral distributions and intensities. As a monochromatic light source a low pressured mercury lamp was used with light emitted at 253.7 nm and the power 3 W (Applied Photophysics, UK). As polychromatic light sources were used medium pressured mercury lamps: 250 W (RVC, Czech Republic) and 400 W (Narva, Germany), metalhalogen lamp 120 W (Philips, UK), high pressure mercury lamp 500 W (Narva, Germany). The regulation of applied light intensity was realised by changing the sample-lamp distance. The vacuum photodiode was used to measure the light source intensity.

Photocuring reactions were realised on aluminium and sodium chloride plates. The constant sample volume (approximately 0.8 μl) was spread on the plate and the thickness of the layer was 40 μm. Consequently, the layer was covered with polyethylene foil. The polyethylene foil eliminated

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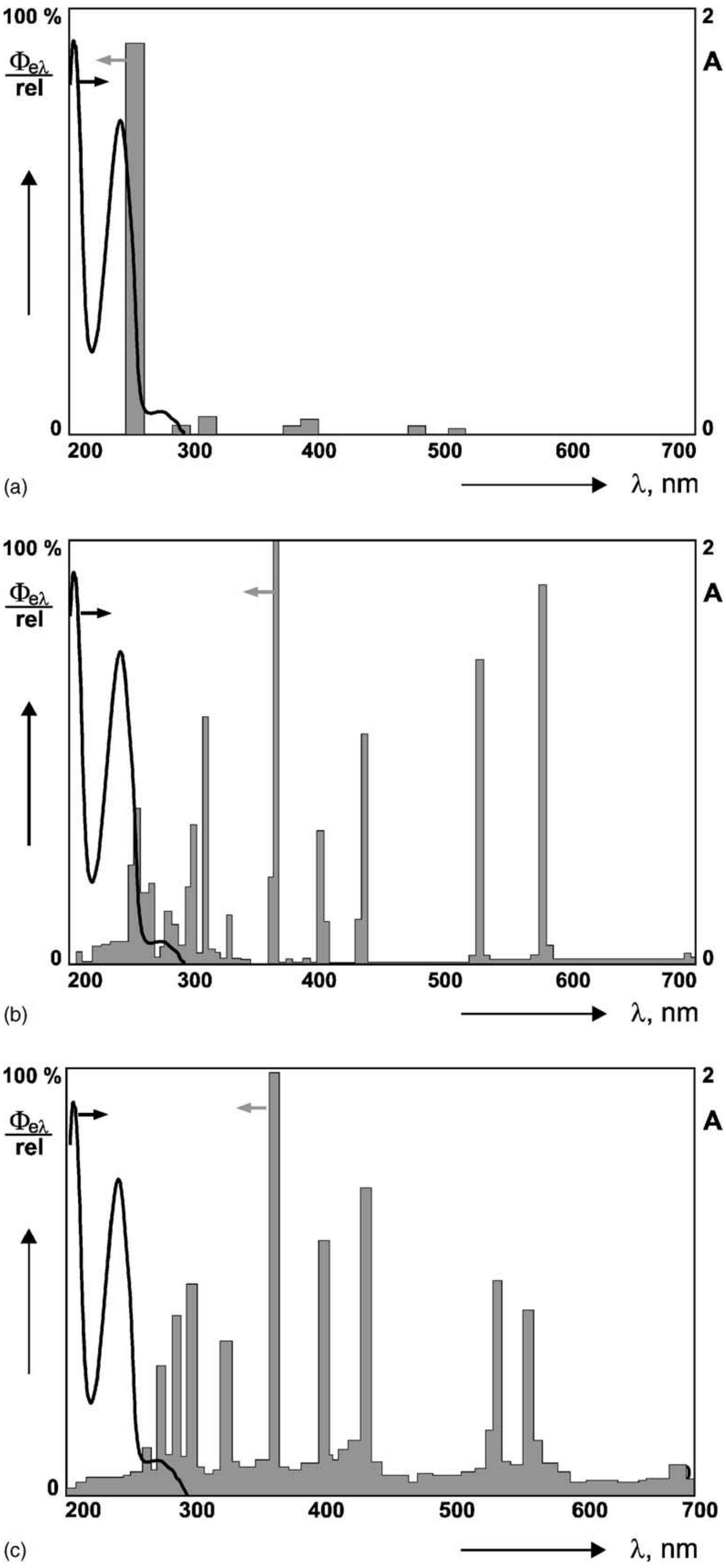


Fig. 1. Emission spectrums of low pressured (a), medium pressured (b), high pressured (c), and metalhalogen mercury lamp (d) vs. UV absorbance spectrum of initiator 1-hydroxycyclohexyl acetophenone.

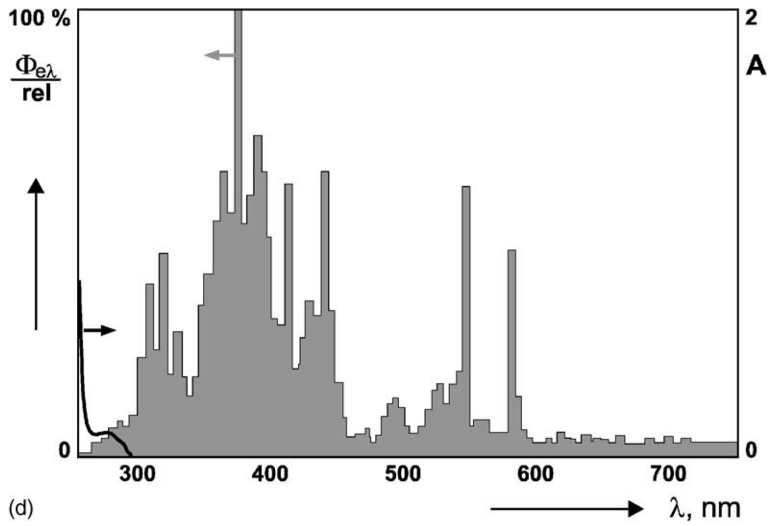
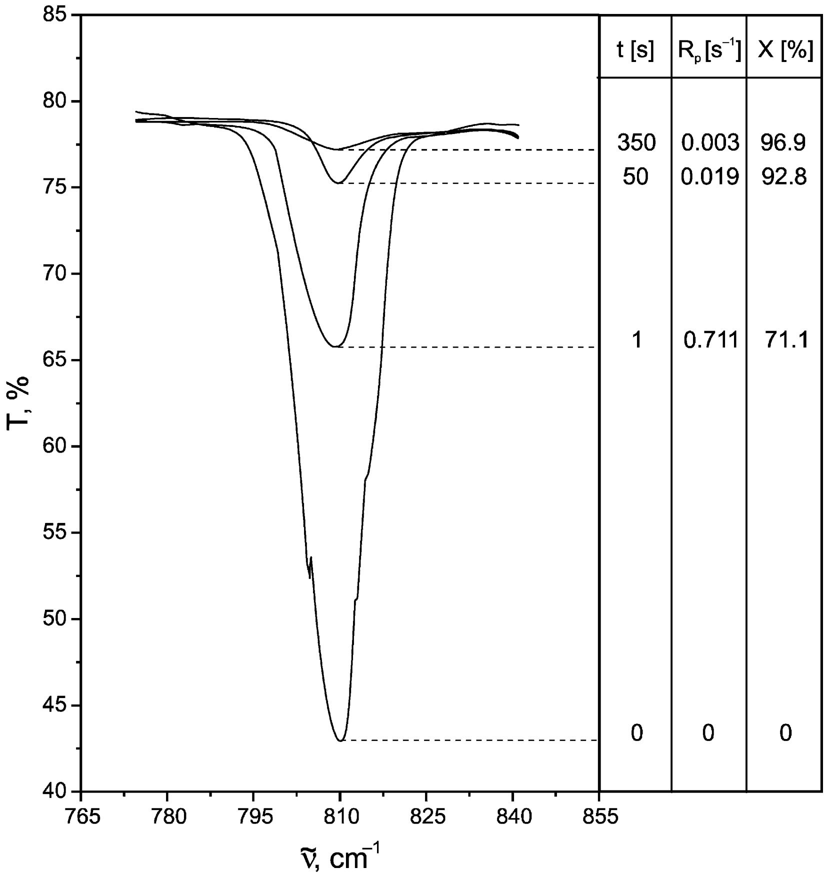


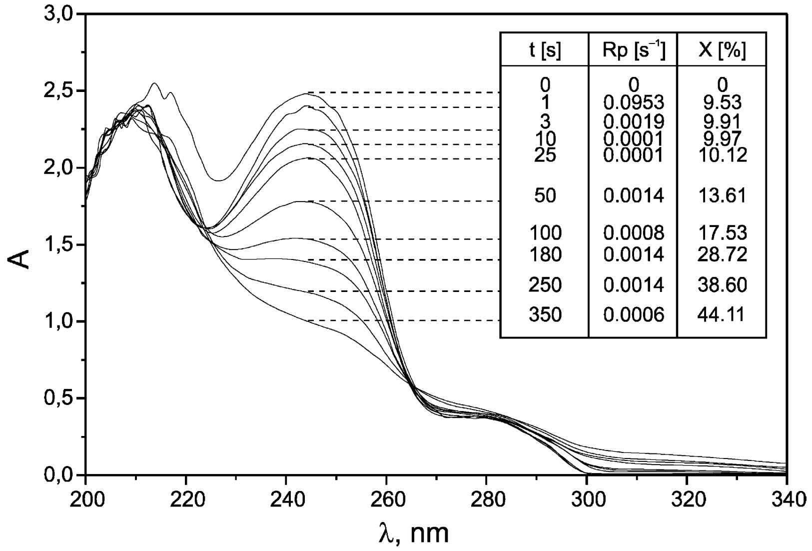
Fig. 1. (*Continued*).

sample contact with atmospheric oxygen and simultaneously avoided the sample to flow from the vertical oriented plate after it was placed into a measuring gap of the spectrophotometer. The curing process was measured in two different ways. The measuring method was IR spectrophotometry (IR spectrophotometer PERKIN-ELMER type 599, USA; IR spectrophotometer HITACHI EPI-G3, Japan) based on the transmittance measured at a frequency of 810 cm^{-1}. IR



t [s]	R_p [s^{-1}]	X [%]
350	0.003	96.9
50	0.019	92.8
1	0.711	71.1
0	0	0

Fig. 2. Decline of carbon–carbon monomers' bounds of 1,6-hexandioldiacrylate evaluated from IR absorbance band ($\tilde{\nu} = 810\,\mathrm{cm}^{-1}$) (initiator IRGACURE 184, $c_0 = 0.08\,\mathrm{M}$) during irradiation using low pressured mercury lamp ($E = 95\,\mathrm{W\,m}^{-2}$, exposure time: 0–350 s).



t [s]	Rp [s^{-1}]	X [%]
0	0	0
1	0.0953	9.53
3	0.0019	9.91
10	0.0001	9.97
25	0.0001	10.12
50	0.0014	13.61
100	0.0008	17.53
180	0.0014	28.72
250	0.0014	38.60
350	0.0006	44.11

Fig. 3. Change of UV absorbance band of 1,6-hexandioldiacrylate (initiator IRGACURE 184, $c_0 = 0.08\,\mathrm{M}$) during irradiation using low pressured mercury lamp ($E = 95\,\mathrm{W\,m^{-2}}$).

absorbance bands were interpreted by the base line method. The degree of conversion X and polymerisation rate R_p were calculated from the following equations [9,10]:

$$X = 1 - \frac{[A_\lambda]_t}{[A_\lambda]_0}, \qquad (1)$$

where $[A_\lambda]_0$ is an absorbance of monomers' C=C bounds at $t = 0\,\mathrm{s}$ and $[A_\lambda]_t$ an absorbance at given exposure time t.

$$R_\mathrm{p} = -\frac{\Delta X}{\Delta t}[M_0] = k(x)[M_0]^\alpha E_0^\beta \qquad (2)$$

where X is a conversion degree of monomers' C=C bounds, t the exposure time, M_0 a monomers' initial molar equilibrium concentration (at $t = 0\,\mathrm{s}$), $k(x)$ a parameter dependent on the C=C bounds concentration, E_0 the applied light intensity, α and β are the exponents considering the real conditions and the polymerising system state. The values of maximum conversion degree X_max and maximum polymerisation rate $R_\mathrm{p\,max}$ were obtained from plots of X and R_p versus time [11,12].

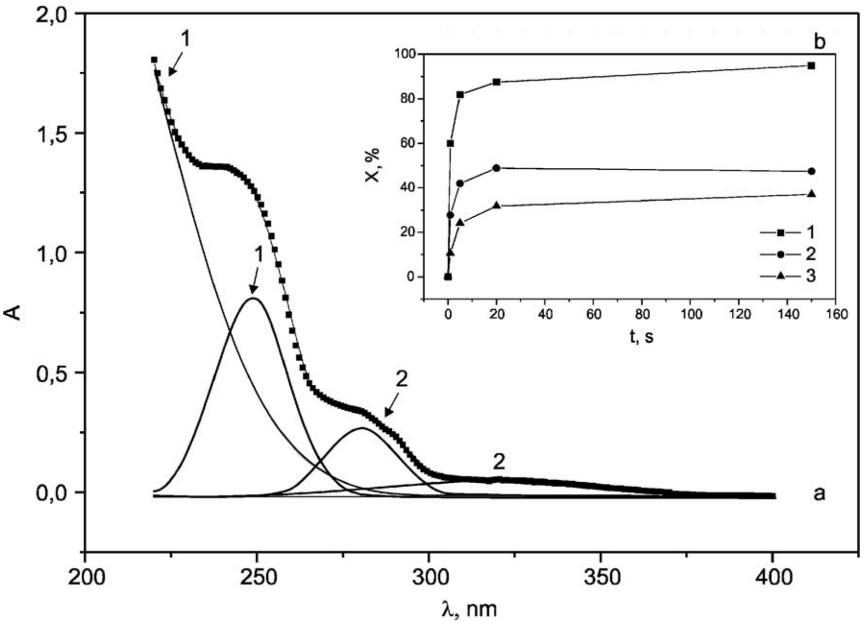


Fig. 4. (a) UV spectrum decomposition of the mixture composed of the monomer 1,6-hexandioldiacrylate (1) and the initiator (2) IRGACURE 184, ($c_0 = 0.08\,\mathrm{M}$, irradiation time $t = 150\,\mathrm{s}$, used medium pressured mercury lamp with $E = 150\,\mathrm{W\,m^{-2}}$) into basic bands; (b) conversion increase of 1,6-hexandioldiacrylate during irradiation calculated from: (1) decrease of IR absorbance band at $\tilde{\nu} = 810\,\mathrm{cm^{-1}}$; (2) monomers' peak area after UV spectrum decomposition ($\lambda_\mathrm{max} = 246\,\mathrm{nm}$); (3) decrease of maximum absorbance values of UV/VIS spectral band at $\lambda_\mathrm{max} = 246\,\mathrm{nm}$.

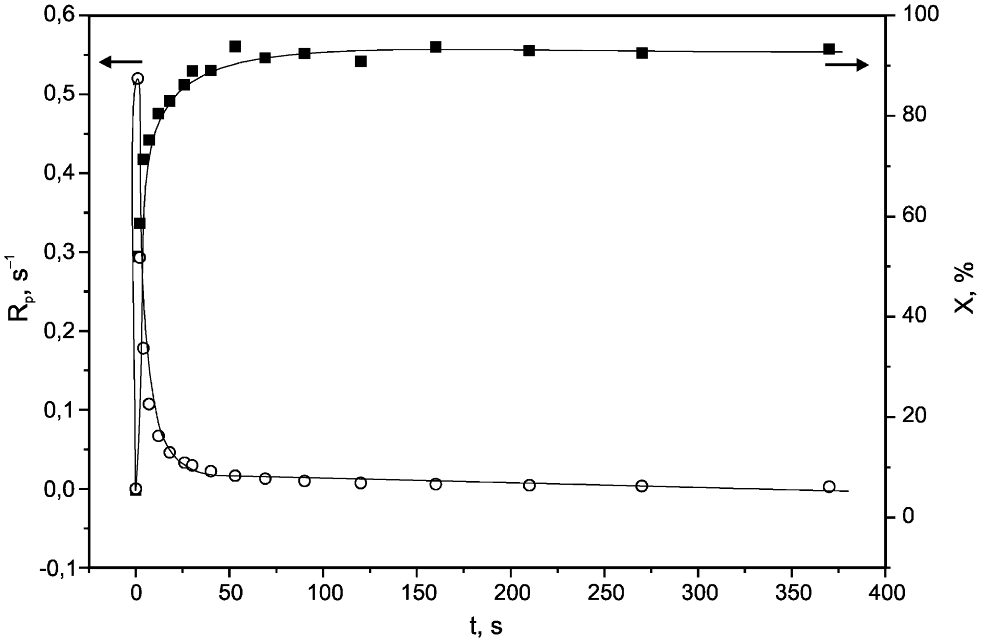


Fig. 5. Conversion's X increase and relative polymerisation rate's R_p course of 1,6-hexandioldiacrylate in the relation to exposure time using low pressured mercury lamp ($E = 95\,W\,m^{-2}$, $c_0 = 0.08\,M$).

The second measuring method was UV/VIS spectrophotometry (UV/VIS spectrophotometer PU 8800 Philips, UK) where the results were interpreted via the absorbance band decrease for the monomers' C=C bounds at 246 nm.

3. Results and discussion

Free radicals, ions and ion radicals can initiate the polymerisation of unsaturated monomers. The simplest case to start a radical chain reaction is direct photoinitiation by UV light induced splitting of a photoinitiator system during irradiation [13,14]. The main request to choose a suitable light source is mostly via its convenient emission spectral maximum that must at least partially overlap the area of initiator absorbance [6,7,15] and high intensity of emitted irradiation. The proper combination of these two factors is required to gain a sufficient polymerisation rate.

The comparison of emission spectrums (of used light sources) to that of the UV absorbance spectrum of

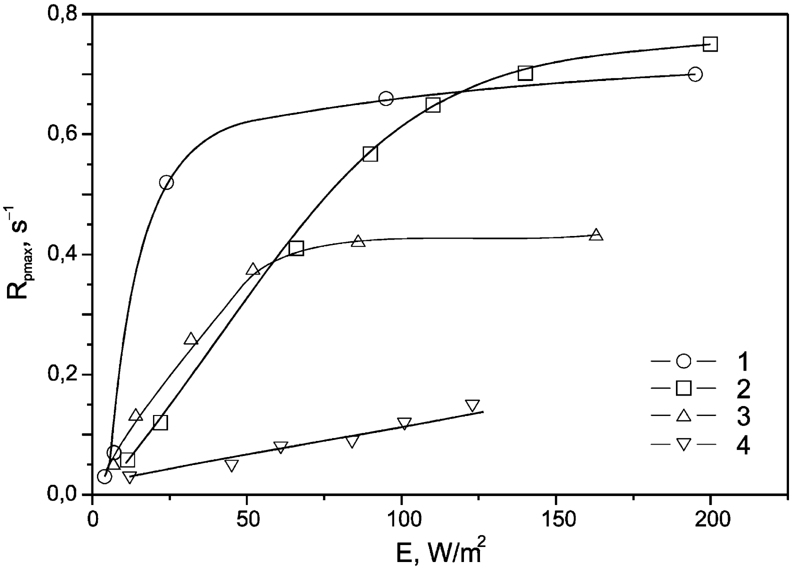


Fig. 6. Change of maximum polymerisation rate of 1,6-hexandioldiacrylate (initiator IRGACURE 184, $c_0 = 0.08\,M$) in relation to energy of used lamps: (1) low pressured mercury lamp; (2) metalhalogen lamp; (3) medium pressured mercury lamp (400 W) and (4) medium pressured mercury lamp (250 W).

initiator 1-hydroxycyclohexyl acetophenone is mentioned in Fig. 1a–d.

Radical polymerisation kinetics of 1,6-hexandioldiacrylate were studied according to the characterised monomer band changes in their IR and UV spectrums (Figs. 2 and 3). After examination of the results there was determined, that the calculation of maximum conversion $X_{\max}$ and maximum reaction rate $R_{\mathrm{p\,max}}$ are suitable only for the decreasing transmittance band values of C=C bounds measured at $\tilde{\nu} = 810\,\mathrm{cm}^{-1}$. X values gained from the UV spectra analysis were lower by 50%. UV spectral evaluation and interpretation were difficult because of their additive character. Absorbance band positions caused by chromophores can considerably vary and are dependent on the molecule's product residue that changes during irradiation. Besides measuring the UV/VIS absorbance spectrum it is also substantially responsive in relation to experimental conditions and spectral environmental purity.

Through the decomposition of UV absorbance bands it is evident as how single bands can affect and overlap with each other (Fig. 4a). Calculated conversion values (corresponding to the band at 246 nm) are different to those values calculated from the IR spectra (Fig. 4b) and this is in contradiction to results published by other authors [16].

Maximum conversion values were relatively high, e.g. 97% using medium pressured metalhalogen lamp and 90% using 250 W medium pressured mercury lamp.

The low pressured mercury lamp is the most efficient light source for our studied polymeric system. Fig. 5 shows typical increasing of conversion and reaction rate curves during irradiation using the low pressured mercury lamp at $95\,\mathrm{W\,m^{-2}}$ irradiation intensity. The mentioned light source emits the energy maximum (nearly 100%) at $\lambda = 254\,\mathrm{nm}$ that overlaps the absorbance range of the initiator ($\lambda = 243$–$300\,\mathrm{nm}$).

Actually it is impossible to use the low pressure lamp because of its environmental harmfulness (it emits almost 100% of "hard" UV irradiation).

Thus, not only does the spectral characterisation, but also the light source used considerably affect UV curing kinetics of multifunctional acrylates [7,8]. Fig. 6 shows maximum polymerisation rate values of 1,6-hexandioldiacrylate at the different energies of the lamps used.

It was determined that $R_{\mathrm{p\,max}}$ values sharply increase with increasing intensity of emitted UV irradiation. On the other hand, the photopolymeric reaction rate increases only to the point when there are no spare reactive radicals concerning in the reactive spaces monomers and recombination will not preferentially occur. Upon assessing results it was assumed that a less appropriate emitted irradiation from the spectral distribution of a metalhalogen lamp can be compensated by a sufficient irradiation intensity of this light source (see Fig. 7).

The energy, effectively usable for UV curing, decreases by a reduction of the emitted light in the UV part of the spectrum.

A plot curve of $R_{\mathrm{p\,max}}$ versus $E_0^{0.5}$ is usually linear and this is typical for a second order polymeric reaction (Fig. 8) [17].

Curves of $\log E_0$ dependent on $\log R_{\mathrm{p\,max}}$ are bent lines with slope curve values (identical to β values from the Eq. (2)) from 0.02 to 1.47. The courses of these curves are dependent on the light sources used (monochromatic or polychromatic irradiation) and provide information on the termination kinetic mechanisms [17]. UV curing in the initial stages of 1,6-hexandioldiacrylate run according to a first-order reaction ($\beta = 1$) and at the end according to a second-order reaction ($\beta < 0.1$ or 0.5).

With regard to these polymerisation kinetic results the parameters (at eliminated oxygen influence) are complex

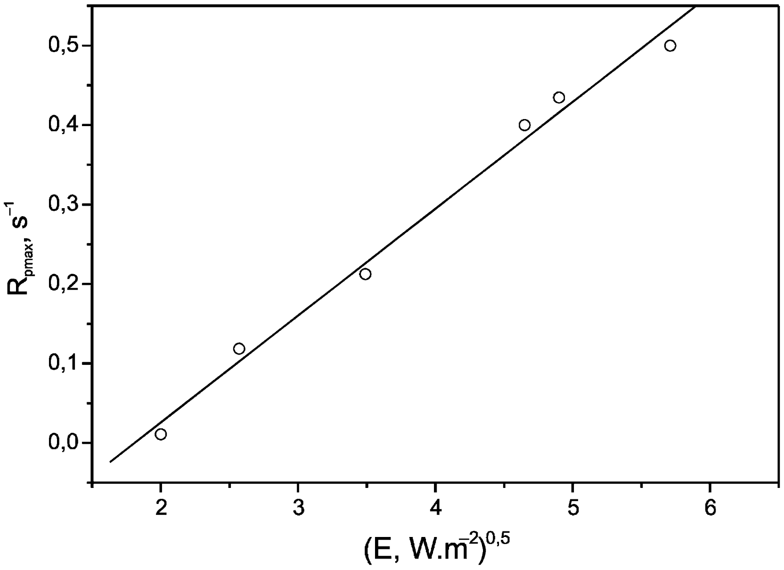


Fig. 7. Plot of reaction rate vs. ($E_0^{0.5}$) of 1,6-hexandioldiacrylate's ($c_{0\,\mathrm{int}} = 0.08\,\mathrm{M}$ IRGACURE 184) photocrosslinking using low pressured mercury lamp.

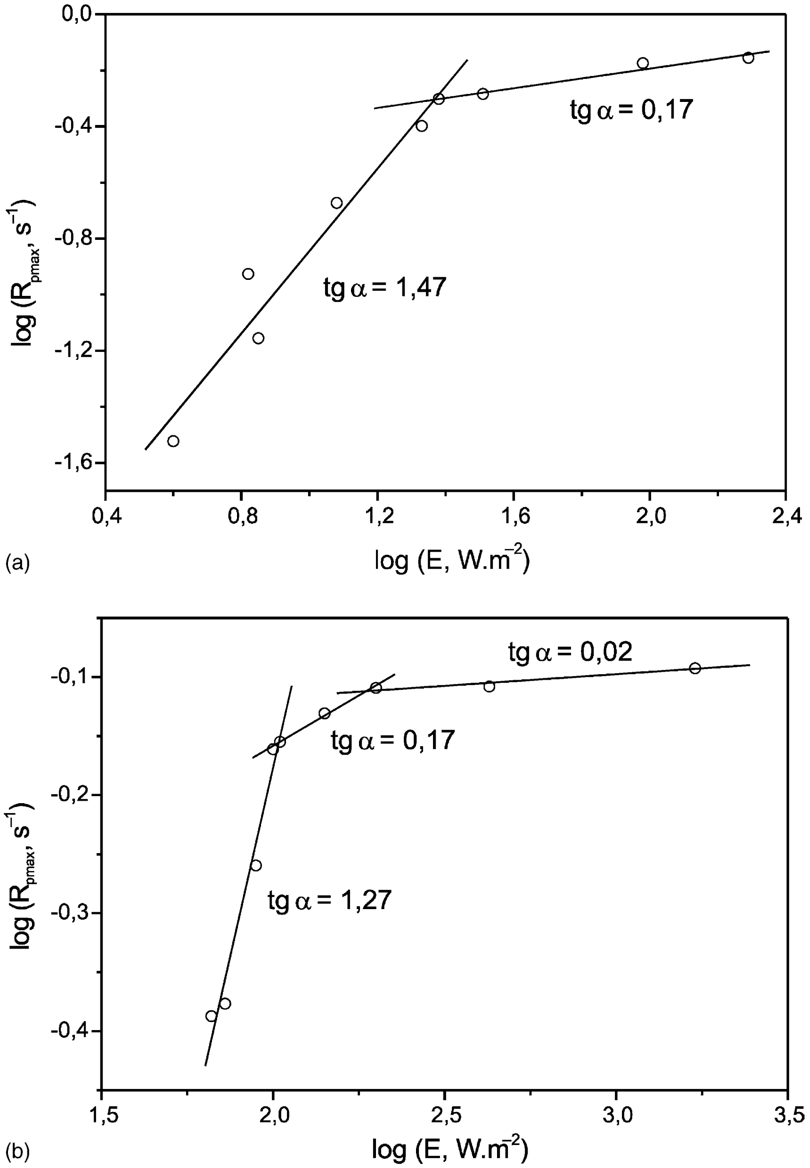


Fig. 8. Two logarithmic plots of reaction rates vs. incident light intensities *E* under monochromatic (8a) (lamp—Fig. 1a) and polychromatic irradiation (8b) (lamp—Fig. 1d).

functions of irradiation intensities and their spectral distributions.

Acknowledgements

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