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Photoinitiation ability of some pentaaza-1,4-dienes[*]

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1,5-bis(4-methoxyphenyl)-3-methyl-pentaaza-1,4-diene, 1,5-bisphenyl-3-(2`-oxyethyl)-pentaaza-1,4-diene and 1,5-bisphenyl-3-methyl-pentaaza-1,4-diene were studied by differential scanning photocalorimetry (DPC) and dilatometry methods as photoinitiators of radical polymerization of vinyl monomers. Photoinitiation abilities of the compounds investigated were compared with those of industrial photoinitiator IRGACURE 1 700. Pentaazadienes exibit a high initiation capacity, the activation energy of polymerization process in the presence of pentaazadiene compounds being lower than that for IRGACURE 1700. An increase of the initiator concentration results in a decrease of the rate of the process. The phenomenon can be explained by autoinhibition.

Key words: *pentaazadiene-1,4; photoinitiator; polymerization*

1. Introduction

Due to their photosensitive properties and relative thermal stability azo compounds may be applied in non-silver photographic processes [1]. The usage of azo compounds as photosensitive materials in photolithography and laser ablation is well known [2]. Their photosensitivity and superior structuring properties are mainly due to the liability of substituents binding to the N=N groups. During the ablation process, these bonds are cleaved, and nitrogen atoms as well as other small organic fragments of a molecule are released without leaving any residuals on the surface.

Pentaazadiene compounds under our investigation contain five nitrogen atoms in a row forming two conjugated azo groups. In view of the lability of this arrangement,

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they appear to be predestined for utilization in photochemical experiments [3, 4]. The first representative of these aromatic pentaaza-1,4-dienes was synthesized in 1866 by Griess [5] in the reaction of diazotized aniline with ammonia. Since then, a wide variety of aromatic pentaazadiene model compounds and polymers have been synthesized to investigate the influence of the substituents on the photolability [6]. A comprehensive discussion of the electronic structure of the pentaazadienes was made. With respect to the electronic structure and therefore to the photochemical properties, the class of pentaazadienes is similar to aromatic triazenes and aromatic diazonium salts [7].

The studies of a photochemical reaction under UV-Vis exposition and thermolysis behaviour have been carried out. It was found that electron-donating aromatic substituents increase photosensitivity and decrease their thermostability [6]. The quantum yield of photolysis is quite high compared with relative triazenes, which is attributed to the sterical hindrance of the competitive reaction channel, i.e. isomerization [8]. The thermolysis in the solution was followed with NMR spectroscopy [6]. Electronic paramagnetic resonance (EPR) experiments of pentaazadiene compounds were performed to establish whether an ionic or radical reaction take place during the UV -photolysis. Using a spin trap, aryl and alkyl radicals have been detected for all model compounds. For photolysis (mercury lamp), the photocleavage mechanisms were postulated. Depending on the solvent polarity, the compound is cleaved either into ionic or radical transient products after an initial isomerization. In acetonitrile and benzene as solvents, radical intermediates were verified by EPR spectroscopy [9].

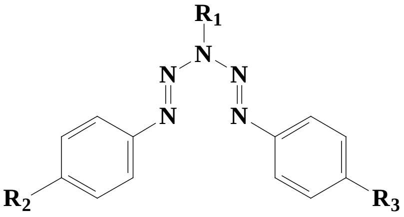
For the study of initiation ability of the titled compounds and thus their application possibility as photoinitiators of radical polymerization processes, a convenient method of differential scanning photocalorimetry (DPC) was chosen [10, 11]. The DPC method is based on differential scanning calorimetry DSC, making possible a delicate thermal analysis (measurement of heat flow as a function of time). The exothermal character of the polymerization of vinyl monomers allows one to study it by thermal analysis.

Differential scanning photocalorimeter Du Pont 930 with differential calorimeter 912 was used. The apparatus allows heating two samples simultaneously with Indium as a standard. Program selection, monitoring and calculations were fulfilled with computer IBM PC-2 connected with the calorimeter. The apparatus was supplied by UV light source (Hg high-pressure lamp, 200 W), fitted for irradiation the samples which were heated to assigned temperature.

2. Experimental

Compounds of the following general structure were synthesized for investigations of initiation ability of pentaazadienes. They were obtained by the reaction of aromatic diazonium salts and primary amines [6].

For polymerization studies 1,6-hexandioldiacrylate (HDODA) $CH_2{=}CH{-}COO{-}(CH_2)_6{-}OOC{-}CH{=}CH_2$ was used as a monomer, which does not polymerize in such conditions without an initiator. Initiators were dissolved in monomer in the amount of 1 wt. %. Samples of (1.5±0.5) mg weight were set up in standard Du Pont aluminium pans. For equal distribution of the solution layer, the samples were covered with a thin polyethyleneterephthalate film. Pans were fitted in a thermostated head of the calorimeter and the samples were irradiated with integral UV light of 3 mW/cm^2 intensity.



I. $R_1 = –CH_3$, $R_2 = R_3 = –H$
II. $R_1 = –CH_3$, $R_2 = R_3 = –OCH_3$
III.$R_1 = –CH_3$, $R_2 = R_3 = –NO_2$
IV. $R_1 = –CH_3$, $R_2 = R_3 = –COOBu$
V. $R_1 = –CH_2–CH_2–OH$, $R_2 = R_3 = –H$

According to a selected program, samples were heated to pre-set temperatures, kept at the final temperatures for 1 min isothermally and then were subjected to 15 min irradiation in isothermal conditions. The reaction of polymerization can manifest itself as an exothermal dependence of the heat flow versus time [8].

Dilatometry investigations were carried out in a quartz dilatometer, thermostated at 30 °C. The measurements of volume contraction were conducted with a katetometer. Samples were irradiated with the integral light of a high pressure Hg lamp. The methyl methacrylate (MMA) was chosen as a monomer and its 15% DMF solution was examined. Kinetics curves of polymerization in the presence of 1% (of monomer weight) pentaazadienes of different structures were obtained.

3. Calculations

From the dependences heat flow versus time, the enthalpy of polymerisation (ΔH_{exp}, J/g); induction time (time of 1% monomer conversion); time of achievement of maximum on DPC curve (peak maximum, s) and monomer conversion in this maximum (reacted at THE peak) were obtained. The monomer conversions were calculated according to equations

$$C = \frac{\Delta H_{\mathrm{exp}}}{\Delta H_t}$$

where ΔH_{exp} – experimental enthalpy at the time t (J/g), ΔH_{theor} – theoretical enthalpy (J/g),

$$\Delta H_{\text{theor}} = \frac{f\left(\Delta H_f\right)}{M}$$

where f – the number of double bonds in the molecule (only for similar double bond), ΔH_f – enthalpy of double bond opening (J/mol), M – molecular weight of the monomer. For HDODA $f = 2$, $M = 226$ g/mol, $\Delta H_f = 80.3$ kJ/mol [10], $\Delta H_t = 710$ J/g.

For kinetic calculations we assumed that the reaction rate can be described by differential equation [11]:

$$\frac{d\alpha(t,T)}{dt} = k_{(T)} f(\alpha)$$

where α – fraction of the monomer converted, $k_{(T)}$ is given (according to Sestak and Berggren [11]) by the following differential equation:

$$R_{(T)} = \frac{dC_{(t,T)}}{dt} = k_{(T)} C^{m} (1-C)^{n} [-\ln(1-C)]^{p}$$

where C – conversion of monomer; m, n, p – partial reaction orders for the initiation, propagation and termination stages, respectively. As at the beginning of reaction $p = 0$, the above expression reduces to:

$$R_{(T)} = \frac{dC_{(t,T)}}{dt} = k_{(T)} C^{m} (1-C)^{n}$$

The values of $k_{(T)}$ were calculated at the primary step of reaction, in an interval between opening of diaphragm and achievement the maximum on DPC curve. The parameter n was fixed and equal 1.5, and the parameter m was calculated.

The measurements for each of the compounds studied were carried out at several temperatures and then the values of the activation energy of the polymerization process were calculated using the Arrhenius equation.

3. Results and discussion

The results of DPC investigations are shown in Figs. 1–6 and in Tables 1 and 2. From the kinetic curves (Fig. 1) and calculated parameters (Table 1) one can see that in the presence of pentaazadiene compounds (I, II, V) the maxima on DPC curves can be achieved a little later than in the presence of IRG, but the maxima of conversion are higher in the presence of compounds I, II, V. Moreover, as is clear from Fig. 1, the polymerization proceeds further attaining a higher conversion. The initiation ability is higher for the compound II with electron donating OCH_3 substituent in the phenyl ring.

These results are in a good accordance with the degree of photosensitivity and values of the photolysis quantum yields of the data compounds [8].

Table 1. DPC data of HDODA polymerization
in the presence of the compounds investigated at various temperatures

Compound	Temperature /°C	Enthalpy /(J/g)	Peak maximum/s	Induction time/s	Reacted at peak/%
I	24.8	560.6	9.6	5.1	16.0
	38.9	450.8	8.8	3.7	14.8
	49.0	634.1	6.8	2.6	21.1
	59.1	614.0	7.1	2.6	23.8
	69.3	479.9	5.0	2.2	13.9
	79.3	754.2	4.9	2.0	20.5
II	27.2	570.7	6.9	3.4	20.3
	33.8	660.7	5.5	2.2	23.0
	43.9	648.3	5.2	2.0	20.5
	54.0	591.7	4.8	1.9	17.6
	64.1	664.4	4.5	1.8	21.7
	74.2	593.6	4.4	1.7	20.4
V	25.4	470.0	9.6	4.9	16.1
	33.8	482.3	7.9	3.4	15.0
	43.9	616.6	7.5	3.0	18.1
	54.0	564.1	6.9	2.8	19.0
	64.1	529.4	4.9	2.3	10.9
	74.3	606.6	5.3	2.1	19.3
	84.5	660.8	4.9	2.1	15.5
IRGACURE 1700	23.9	420.0	4.6	2.8	15.7
	33.8	489.2	3.4	1.7	15.2
	43.8	522.4	3.4	1.7	17.0
	53.9	584.3	3.7	1.6	21.9
	64.1	570.0	3.6	1.7	15.7

Upon increasing the temperature in the range of 25–75 °C, the polymerization rates increase (Figs. 2, 3). The activation energies determined from these experiments are given in Table 2. As results from the measurements, the activation energies in the experiments with pentaazadienes are lower than those in the experiments with IRG. The dependences of $\ln k_{(T)}$ versus $10^3/RT$ for pentaazadienes (I, II, V) are shown in Figs. 4–6, respectively.

The kinetics of MMA polymerization (Fig. 7) shows that the polymerization rate in the presence of pentaazadienes is only weakly dependent on the electronic structure of substituents in the aromatic rings of the molecules. It was found that with the increasing of pentaazadiene concentration from 0.5% to 4%, the rate of MMA polymerization decreases to some extent (Fig. 8) and when the concentration of the initiator was 5%, the process did not occur at all.

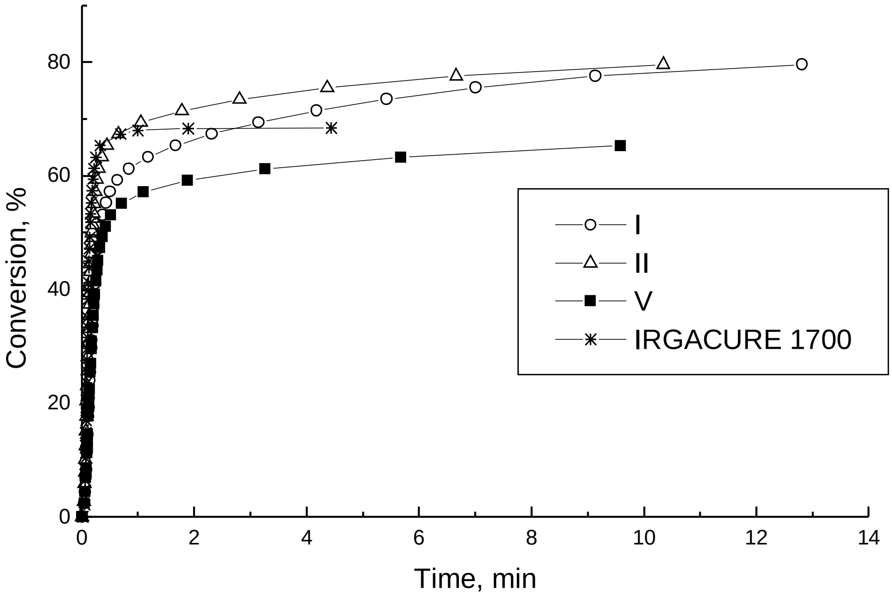


Fig. 1. Kinetic curves of HDODA polymerization in the presence of 1% (of monomer weight) of pentaazadienes and IRGACURE 1700 at room temperature

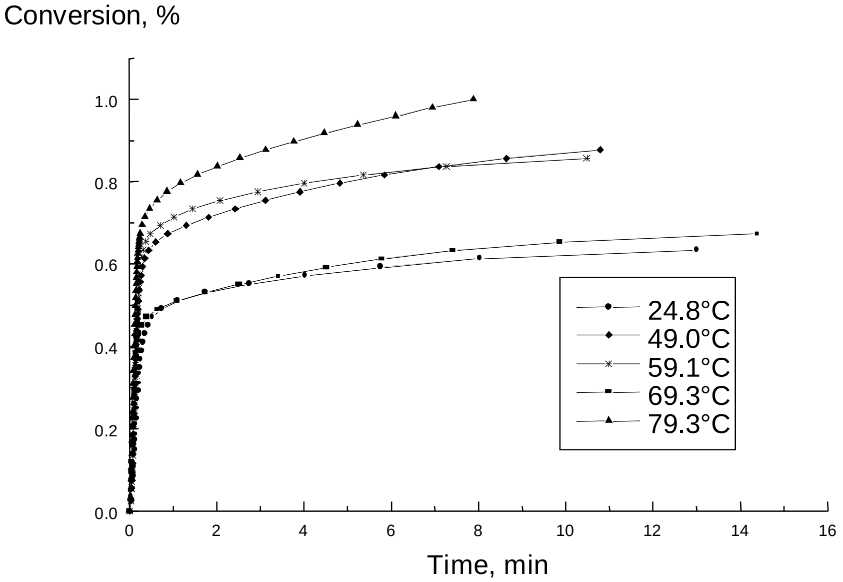


Fig. 2. Kinetic curves of HDODA polymerization in the presence of 1% (of monomer weight) of 1,5-bisphenyl-3-methyl-pentaaza-1,4-diene (I) at several temperatures

Table 2. Activation energy E_a of HDODA polymerization in the presence of pentaaza-1,4-dienes and Irgacure 1700, obtained graphically from dependence of ln$k_{(T)}$ versus 1/T and calculated from the Arrhenius equation

Compound	E_a, /(kJ/mol)	Coefficient of correlation
I	9.6	0.952
II	5.6	0.999
V	8.5	0.978
IRGACURE 1700	10.1	0.982

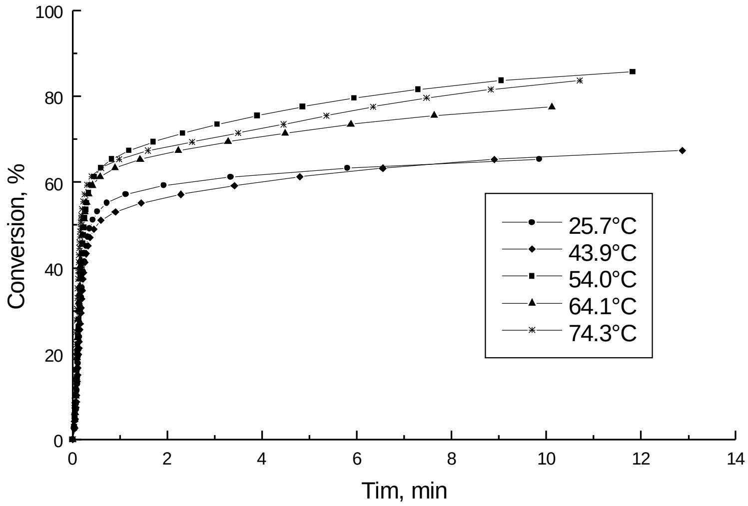


Fig. 3. Kinetic curves of HDODA polymerization in the presence of 1% (of monomer weight) of 1,5-bis(4-methoxyphenyl)-3-methyl-pentaaza-1,4-diene (II) at several temperatures

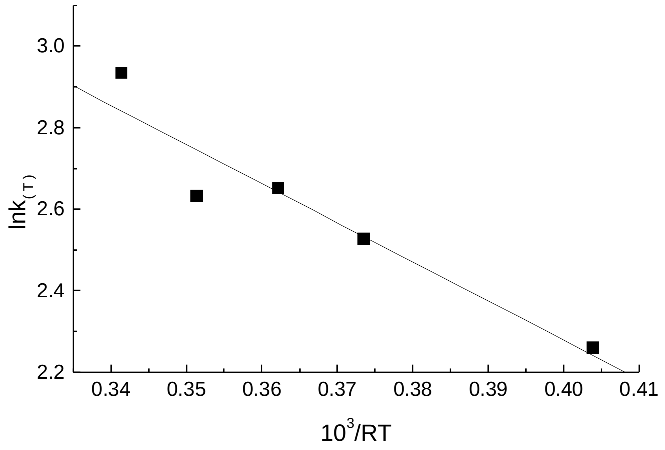


Fig. 4. Dependence of ln$k_{(T)}$ versus 1/T for HDODA polymerization in the presence of 1% (of monomer weight) of 1,5-bisphenyl-3-methyl-pentaaza-1,4-diene (I)

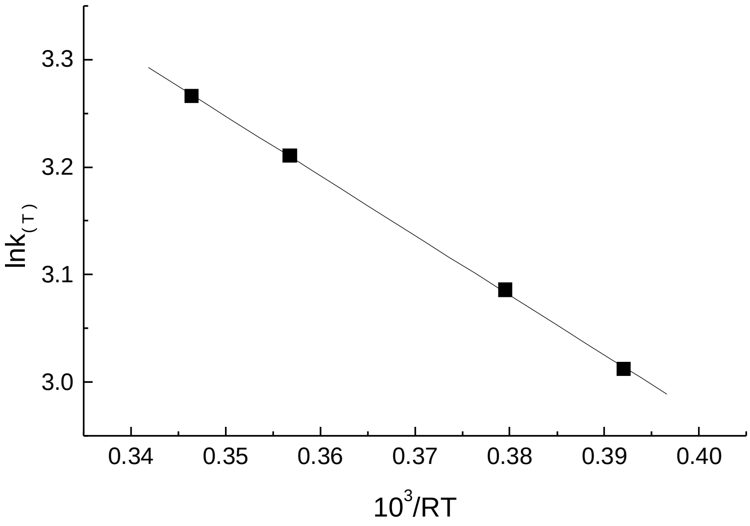


Fig. 5. Dependence of ln$k_{(T)}$ versus 1/T for HDODA polymerization in the presence of 1% (of monomer weight) of 1,5-bis(4-methoxyphenyl) -3-methyl-pentaaza-1,4-diene (II)

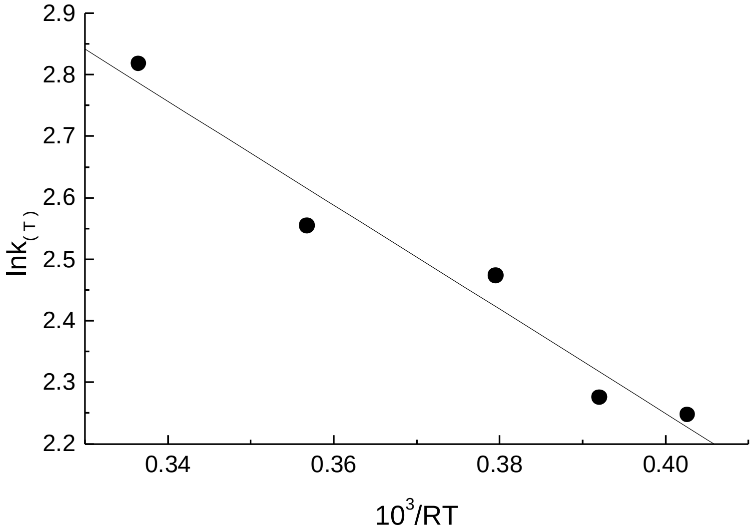


Fig. 6. Dependence of ln$k_{(T)}$ versus 1/T for HDODA polymerization in the presence of 1% (of monomer weight) of 1,5-bisphenyl -3-(2′-oxyethyl)-pentaaza-1,4-diene (V)

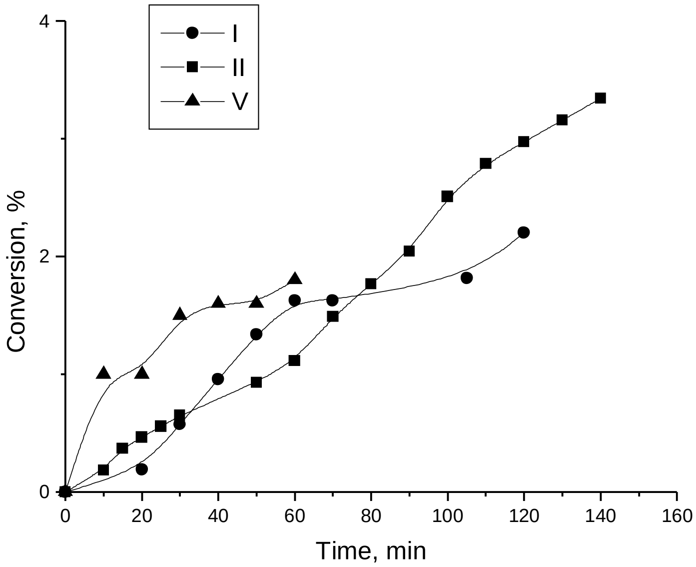


Fig. 7. Kinetic curves of polymerization of 15% MMA solution in DMF in the presence of pentaazadienes

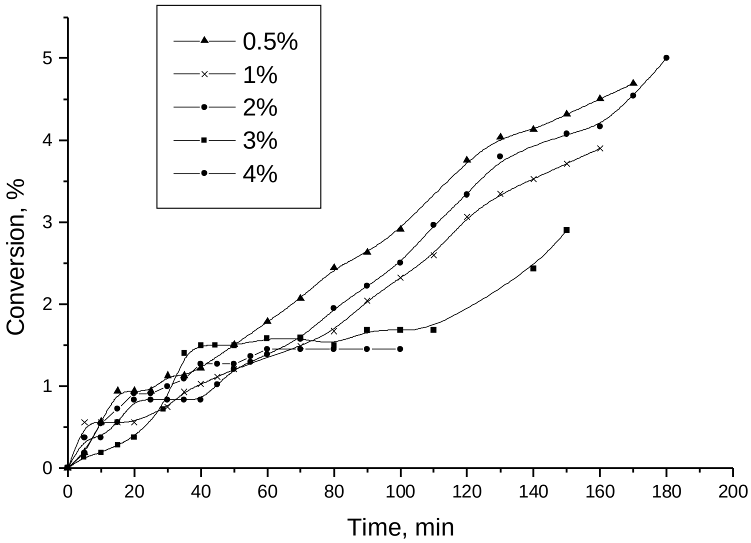


Fig. 8. Kinetic curves of polymerization of 15% MMA solution in DMF in the presence of 1,5-bis(4-methoxyphenyl)-3-methyl-pentaaza-1,4-diene (II). Concentrations of the initiator are given in % of the weight of monomer

As a result of this work, a conclusion can be made that the investigated pentaaza-1,4-diene compounds appear as effective photoinitiators of radical polymerization of vinyl monomers, which can be used in a suitable UV-Vis region (300–450 nm).

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