MAREK PIETRZAK, AGNIESZKA GŁUSZAK, ANDRZEJ WRZYSZCZYŃSKI*)

University of Technology and Life Sciences
Faculty of Chemical Technology and Engineering
ul. Seminaryjna 3, 85-326 Bydgoszcz, Poland

Photopolymerization of multifunctional monomer initiated with redox system dye-sulfur compounds

RAPID COMMUNICATION

Summary — Radical photopolymerization of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA), photoinduced with redox system: electron donor-acceptor has been presented. Xanthene dye *i.e.* 5,7-diiodo-3-pentoxy-6-fluorenone (DIPF) was used as acceptor. Electron donor in the system investigated was benzenesulfinic or (phenylthio)acetic acid tetrabutylammonium salt (BSAAS or PTAAAS). Calculated from Rehm-Weller negative value of the free energy of activation of the photoinduced electron transfer (ΔG_{el}) suggests that transfer of the electron from BSAAS to DIPF is possible and that obtained in this proces sulfonyl radicals or products of disproportionation reactions of the ones are the photoinitiating radicals. There is no correlation between the rate of the photopolymerization (R_p) of TMPTA and square root of BSAAS as on electron donor concentration. R_p is approximatelly proportional to the square root of absorbed light intensity (I_a), however some deviation from the fit at low intensity is observed.

Key words: photopolymerization, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate, redox photoinitiators, xanthene dyes.

FOTOPOLIMERYZACJA MONOMERU WIELOFUNKCYJNEGO INICJOWANA ZA POMOCĄ UKŁADU REDOKS BARWNIK-ZWIĄZKI SIARKI

Streszczenie — Przedstawiono polimeryzację triakrylanu 2-etylo-2-(hydroksymetylo-1,3-propanodiolu) fotoinicjowaną za pomocą układu redoks: donor-akceptor elektronów. Jako akceptor zastosowano barwnik ksantenowy: 5,7-dijodo-3-pentoksy-6-fluorenon (DIPF). Donorem elektronów była sól tetrabutyloamoniowa kwasu benzenosulfinowego lub fenylotiooctowego (BSAAS lub PTAAAS). Obliczona na podstawie równania Rehma-Wellera wartość potencjału termodynamicznego (ΔG_{el}) w przypadku BSAAS była liczbą ujemną, co wskazuje, że możliwe jest przeniesienie elektronu z cząsteczki donora (BSAAS) na cząsteczkę akceptora (DIPF). Otrzymane w tym procesie rodniki sulfonylowe (bądź produkty reakcji tych rodników) mogą inicjować fotopolimeryzację monomeru. Stwierdzono, że nie ma zależności pomiędzy szybkością polimeryzacji (R_p) a pierwiastkiem kwadratowym ze stężenia BSAAS użytego jako donor elektronów (rys. 4). Szybkość polimeryzacji jest natomiast proporcjonalna do pierwiastka kwadratowego z zaabsorbowanego promieniowania, chociaż przy małym jego natężeniu zaobserwowano odchylenia od tej zależności (rys. 5).

Słowa kluczowe: fotopolimeryzacja, triakrylan 2-etylo-2-(hydroksymetylo-1,3-propanodiol, fotoinicjatory, redox, barwniki ksantenowe.

Redox polymerization, initiated with free radicals formed by oxidation-reduction reactions, is characterized by very short induction periods, hight polymer yield in a short time, and the possibility of polymerization running at room temperature or below [1, 2]. Several authors reported a redox system in polymerization of monomers [3—6]. These include benzophenone, thioxanthone, and dye structures as the acceptor species and amines, sulfinates, sulphur-containing amino or carboxylic acids as electron donors.

In this work we present a new redox system, xanthene dye: 5,7-diiodo-3-pentoxy-6-fluorenone (DIPF) as electron acceptor and benzenesulfinic acid tetrabutylammonium salt (BSAAS) as electron donor in the photopolymerization of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA).

---

*) To whom all correspondence should be addresed; e-mail: wrzyszcz@utp.edu.pl

As in the case of (phenylthio)acetic acid tetrabutylammonium salt (PTAAAS), benzenesulfinic acid tetrabutylammonium salt also exist in the ionic form [5].

EXPERIMENTAL

Materials

2-Ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA) used as monomer and benzenesulfinic acid sodium salt were purchased from Aldrich. 5,7-Diiodo-3-pentoxy-6-fluorenone (DIPF) used as a dye was synthesized according to the method described in [7, 8]. Benzenesulfinic and (phenylthio)acetic acid tetrabutylammonium salts (BSAAS and PSAAAS, respectively) were prepared using standard organic chemistry method [9].

Photopolymerization

The polimerization was carried out in a mixture consisted of monomer (TMPTA), the dye (DIPF) in concentration of 0.001 M and one of the electron donors (BSAAS or PTAAAS) in concentration up to 0.005 M under the influence of irradiation. The light was emitted by Omnichrome model 543-500 MA argon ion laser. The light intensity was 25 mW/cm^2 in the position of the sample and was measured by a Coherent model Fieldmaster power meter. The system was arranged this way in order to make possible that all incident light is absorbed by the dye.

Methods of investigations

The kinetics of the photopolymerization was studied by measuring the polymerization heat release from a sample, irradiated with a laser beam throught an optical system, in a home made microcalorimeter [10, 11]. The rate of reaction was determined from kinetic curvers on the assumption that it is directly proportional to the amount of heat released.

The reduction potential of the electron donor was measured by cyclic voltammetry. An Electroanalitycal MTM (Krakow) Model EA 9C-4z was used for the measurements, and an Ag-AgCl electrode (SCE) served as a reference electrode. The supporting electrolyte was 0.5 M tetrabutylammonium perchlorate.

RESULTS AND DISCUSSION

As it was shown prieviously [5, 9] the photoreduction of the dye (DIPF) by PTAAAS yielded a stable DIPF radicals (DIPF$^\bullet$) or radical anions (DIPF$^{\bullet-}$) and also radicals of the electron donors. The latter are responsible for the polymerization of TMPTA. We believe that the photopolymerization of the monomer in the presence of redox system dye-tetrabutylammonium salt of benzenesulfinic acid proceeds by similiar mechanism. The radicals able to initiate the polymerization are formed in bimolecular electron transfer process between the dye (DIPF) triplet state and electron donor (BSAAS). The basic Rehm-Weller requirement for such reaction is that free energy of activation of photoinduced electron transfer (ΔG_{el}) process should have negative value. The free energy change can be calculated using the Rehm-Weller equation (1).

$$\Delta G_{el} = E_{\text{ox}}(D/D^{\bullet+}) - E_{\text{red}}(A^{\bullet-}/A) - Ze^2/\varepsilon a - E_{oo} \qquad (1)$$

where: *E_{ox} $(D/D^{\bullet+})$ — oxidation potential of the electron donor, E_{red} $(A^{\bullet-}/A)$ — reduction potential of the electron acceptor, E_{oo} — triplet excitation energy, $Ze^2/\varepsilon a$ — Coulombic energy gained by bringing the formed radical ions to an encounter distance in a solvent with dielectric constant ε.*

Generally, for the electron transfer reaction in solution, where the reaction occurs within a collision distance, Coulombic energy is neglected, in contrast to the electron transfer reaction in rigid matrix or in donor-acceptor system where donor and acceptor are separated by a rigid spacer. The reduction potential of DIPF measured by square-wave voltammetry in acetonitryle is -0.9 V (vs. SCE) and the triplet excitation energy determined from the phosphorescence spectrum is 2.3 eV [12]. The oxidation potential of BSAAS can be deducted from the voltammetric curve of BSAAS in acetonitrile presented in Fig. 1. Determined value of E_{ox} $(D/D^{\bullet+})$ is equal 258 eV. Assuming that the Coulombic energy is small, the calculated ΔG_{el} value is -0.142 eV. Negative value of ΔG_{el} indicates that the electron transfer from benzenesulfinic ion (RSO_2^-) to the dye triplet state (^{3}DIPF*) is thermodynamically allowed. As a result sulfonyl radicals and the dye anion radicals are formed according to the equation:

$$^3\text{DIPF*} + RSO_2^- \rightarrow \text{DIPF}^{\bullet-} + RSO_2^\bullet \qquad (2)$$

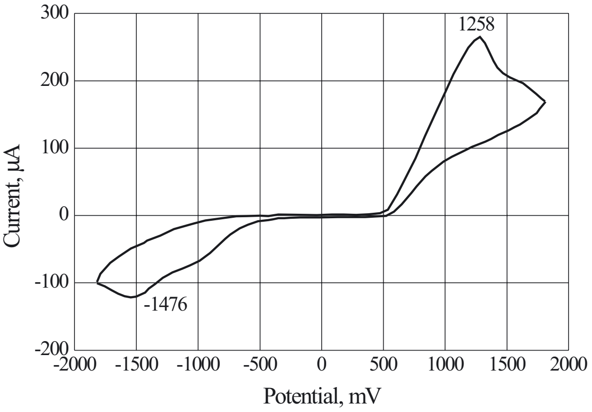

Fig. 1. Voltammetry curve of BSAAS in acetonitryle in the presence of tetrabutylammonium perchloride (0.1 M) as a supporting electrolyte

The sulfonyl radicals are very electrophilic ones and can undergo a series of oxidation and disproportiona-

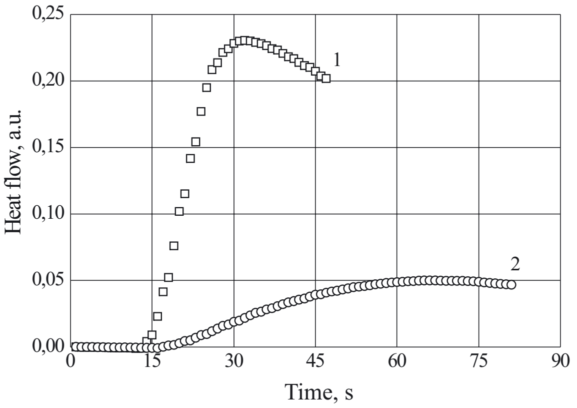

Fig. 2. Kinetic curves of TMPTA polymerization by DIPF (0.001 M) in the presence of electron donors (0.005 M): 1 — BSAAS, 2 — PTAAAS

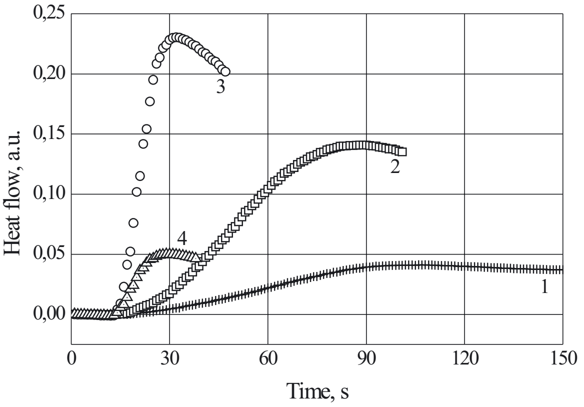

Fig. 3. Kinetic curves of TMPTA polymerization initiated by DIPF (0.001 M) and various BSAAS concentration: 1 — 0.002 M, 2 — 0.003 M, 3 — 0.005 M, 4 — 0.01 M

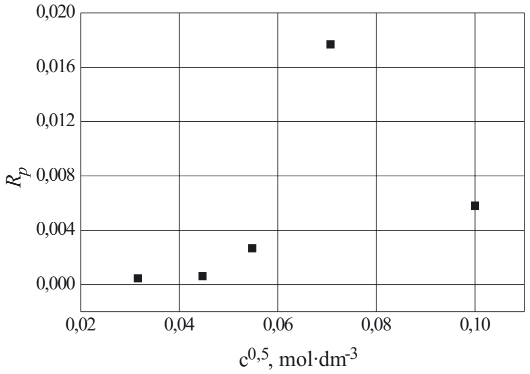

Fig. 4. Rate of photoinitiated polymerization (R_p) of TMPTA vs. square root of BSAAS concentration for initiating system DIPF (0.001 M)-BSAAS

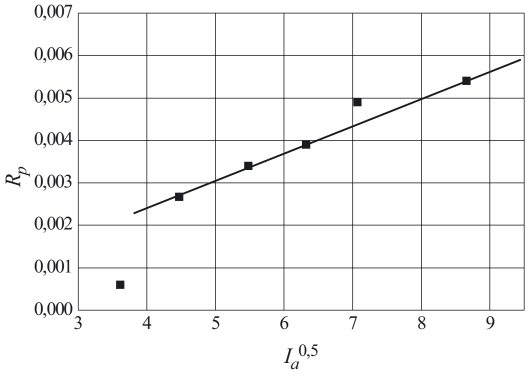

Fig. 5. Effect of absorbed light intensity (I_a) on the rate of photoinitiated polymerization (R_p) of TMPTA in the presence of BSAAS (0.003 M) and DIPF (0.001 M)

tion reactions [13] and also addition to vinyl monomers [14]. Therefore we suggest that sulfonyl radicals formed upon irradiation or product of the disproportionation reactions of the ones are the initiators of TMPTA polymerization. The dark bleaching of the dye was observed when tetrabutylammonium salt of benzenesulfinic acid was added to the polymerizing mixture. This is not due to electron transfer reactions, because these processes do not occur in the absence of light. The interaction of BSAAS and DIPF in the ground state is probably responsible for the bleaching process. Figure 2 shows the curves of heat flow during TMPTA polimerization initiated by DIPF (0.001M) in the presence of 0.005 M of BSAAS or PTAAAS as electron donors under the influence of irradiation with a laser beam of energy 25 mW/cm^2. Because the amount of heat released is directly proportional to the rate of polymerization it is evident from Fig. 2 that BSAAS is a coinitiator of the polymerization of TMPTA.

Similar kinetic curves, presented in Fig. 3, are determined for TMPTA polymerization in the presence of various amounts of BSAAS. The rate of the photopolymerization increases with increasing donor concentration (BSAAS) up to 0.005 M. At higher concentration of BSAAS the rate of the photopolymerization decreases.

Figure 4 shows the dependence of rate of photoinitiated polymerization (R_p) of TMPTA on square root of BSAAS concentration. It is evident from this figure that there is no correlation between presented quantites. This is probably due to the dye depletion in the bleaching process.

The effect of absorbed light intensity (I_a) on R_p was also studied. Fig. 5 indicates that R_p is approximatelly proportional to the square root of (I_a), however some deviation from the fit at low intensity is observed.

Finally we compared DIPF-BSAAS as initiating system with redox system DIPF — PSAAAS, which was investigated by us also prieviously [5, 9]. It is apparent from the inspection of the data shown in Fig. 2 that DIPF — BSAAS redox system is more efficient in the photopolymerization of TMPTA than the system DIPF-PSAAAS.

REFERENCES

1. Liu Z., Brooks W.: *J. Polym. Sci. Polym. Chem.* 1998, 37(A), 313.
2. Konar R. S., Palit S. R.: *J. Indian Chem. Soc.* 1961, 38, 481.

3. Linden L. A., Pączkowski J., Rabek J., Wrzyszczyński A.: *Polimery* 1999, 44, 161.
4. Pączkowski J., Neckers D. C.: „Electron transfer in Chemistry", Vol. 5, Wiley-VCH, Weinhem, New York, Chichester, Brisboane, Singapore, Toronto, 2001, pp. 516—580.
5. Wrzyszczyński A., Pietrzak M., Pączkowski J.: *Macromolecules* 2004, 37, 41.
6. Rust J. B., Miller J., Margerum J. D.: *Polym. Eng. Sci.* 1969, 9, 40.
7. Shi J., Zhang X., Neckers D. C.: *J. Org. Chem.* 1992, 57, 4418.
8. Shi J., Zhang X., Neckers D. C.: *J. Org. Chem.* 1993, 58, 2614.
9. Wrzyszczyński A., Pączkowski J.: *Polimery* 2004, 49, 606.
10. Pączkowski J., Pietrzak M., Kucybała Z.: *Macromolecules* 1996, 29, 5057.
11. Kabatc J., Kucybała Z., Pietrzak M., Ścigalski F., Pączkowski J.: *Polymer* 1999, 40, 735.
12. Hassoon S., Neckers D. C.: *J. Phys. Chem.* 1995, 99, 9416.
13. Chatagilialoglu Ch., Gilbert B. C., Gill B.: *J. Chem. Soc. Perkin II* 1980, 1141.
14. Takahara Y., Ino M., Matsuda M.: *Bull. Chem. Soc. Jap.* 1976, 49, 2268.

Received 16 III 2007.