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New photoinitiators for cationic polymerization^{**)}

Summary — Four new diaryliodonium photoinitiators have been developed and their performance in initiation of cationic polymerization of example vinyl and epoxy monomers has been tested by Fluorescence Probe Technology (FPT). The photoinitiators exhibit absorption characteristics compatible with the emission characteristics of medium pressure mercury lamps, which are main sources of UV light in the industry. This solves the technological problem related to poor match between the absorption characteristics of commercial photoinitiators and the emission characteristics of industrial UV light sources.

Keywords: cationic photoinitiators, FPT, diaryliodonium salts.

NOWE FOTONICJATORY POLIMERYZACJI KATIONOWEJ

Streszczenie — Opracowano nowe fotoinicjatory diaryljodoniowe przeznaczone do stosowania w procesie fotopolimeryzacji kationowej monomerów winylowych oraz epoksydowych i oceniano ich skuteczność przy użyciu technologii sond fluorescencyjnych (FPT). Badane fotoinicjatory wykazują charakterystykę absorpcji kompatybilną z charakterystyką emisji średniociśnieniowych lamp rtęciowych, które są podstawowymi źródłami światła UV w przemyśle. Fakt ten rozwiązuje dotychczasowy problem technologiczny, polegający na niedopasowaniu charakterystyki absorpcji handlowo dostępnych fotoinicjatorów polimeryzacji kationowej do charakterystyki emisji przemysłowych źródeł światła UV.

Słowa kluczowe: fotoinicjatory polimeryzacji kationowej, FPT, sole diaryljodoniowe.

INTRODUCTION

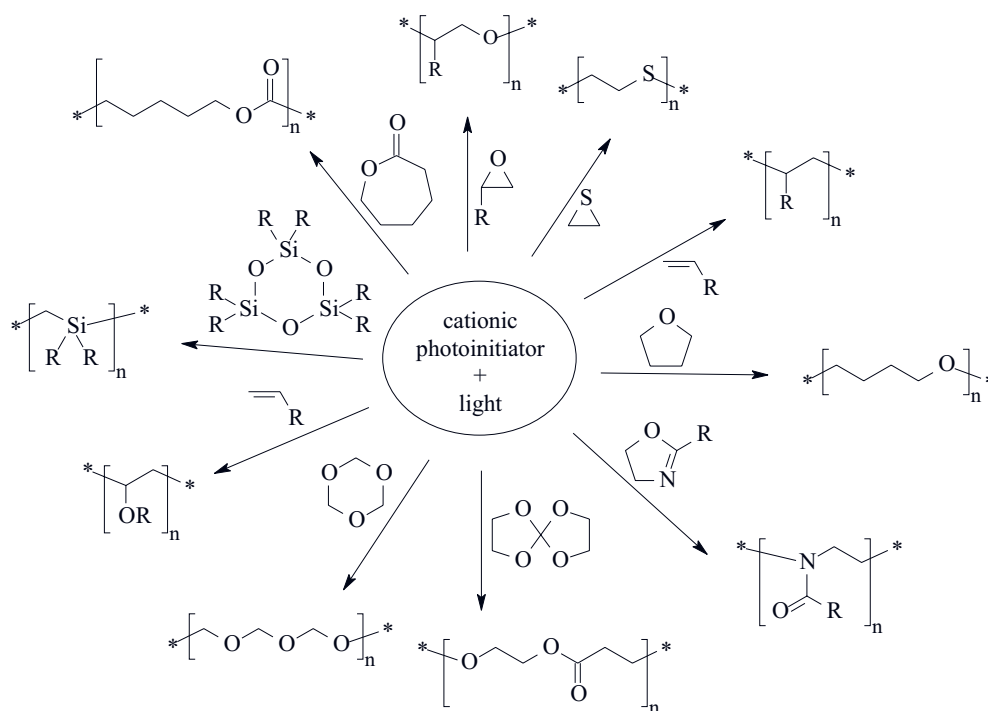
Photoinitiated polymerization is an important industrial process widely used in different applications. For instance, photocurable coatings, inks, and adhesives can be applied without the use of solvents, so a potential source of air and water pollution with volatile organic compounds is eliminated. Depending on the polymerization mechanism, photocurable compositions can be classified into two major categories, which require different types of photoinitiators: compositions cured by free radical photopolymerization and compositions cured by the cationic polymerization mechanism [1].

UV-initiated cationic photopolymerization exhibits several advantages compared to the free-radical photopolymerization. First of all, the cationic photopolymerization is not inhibited by oxygen. This feature provides a significant practical advantage for industrial processes since it is not necessary to blanket the system with nitro-

gen to achieve rapid cure rates as in the case of free radical polymerization [2]. Secondly, in contrast to the free-radical photopolymerization, which experiences rapid termination of the polymerization process when the light source is removed (due to radical-radical termination reactions), the cationic polymerization processes proceed long after the irradiation has ceased, until nearly all of the monomer has been consumed [3]. Furthermore, the cationic photopolymerization is a technique that may be used to polymerize important classes of monomers, which cannot be polymerized by free radical means, such as epoxides, vinyl ethers, propenyl ethers, siloxanes, oxetanes, cyclic acetals and formals, cyclic sulfides, lactones and lactams (Scheme A). These cationically polymerizable monomers include both unsaturated monomers that undergo chain polymerization through the carbon-carbon double bonds and cyclic monomers that undergo ring-opening polymerization [4, 5]. In particular, the cationic ring-opening polymerization of epoxides found a number of applications due to unique advantages inherent to the epoxy systems, such as low shrinkage of 1–2 % compared to 5–20 % in the case of acrylates, resulting in better adhesion of the epoxy coatings than that of acrylic ones [6, 7]. Furthermore, the

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Scheme A. Monomers used in photoinitiated cationic polymerization

epoxy coatings usually exhibit excellent clarity, strong adhesion to various surfaces, high chemical resistance, high gloss, high mechanical strength and abrasion resistance [8].

Growing interest in cationic photopolymerization of monomers as a facile, economic and environmentally friendly method to prepare crosslinked polymer coatings generates the need to develop new efficient photoinitiators. Usually, diaryliodonium and triarylsulfonium salts have been used in the industry as the cationic polymerization photoinitiators [9–11]. Diaryliodonium photoinitiators are most popular, because of their better solubility in non-polar monomers than the solubility of the corresponding triarylsulfonium salts [12]. Critical functions of the iodonium salts in the role of cationic polymerization photoinitiators depend on the nature of anionic and cationic portions of these compounds. The nature of the anion determines the strength of the protic acid formed during photolysis, which affects the initiation rate. Moreover, the anion type determines the nature of the ion pair involved in the chain propagation step. The rate of the propagation is influenced by the strength of interaction between the anion and the growing macrocation. Consequently, for the four most commonly used anions, the cationic polymerization rate follows the following order: $\text{BF}_4^- < \text{PF}_6^- < \text{AsF}_6^- < \text{SbF}_6^-$ [9]. However, from practical point of view, the most important feature of the photoinitiators is their optical characteristics, in particular the range and extent of light absorption. The cationic part of the iodonium photoinitiators plays the role of the light absorber. Hence, the structure of the iodonium cations is critical to the photoinitiator performance. Only the iodonium salts, that contain at least one light absorbing

aromatic chromophore, are suitable for the use as cationic polymerization photoinitiators. To-date, various substituted diphenyliodonium salts have been used in the photocurable coatings industry. Unsubstituted diphenyliodonium salts exhibit absorbance maximum in the deep UV region at around 220 nm. This absorption can be red-shifted by addition of substituents such as alkoxy groups or additional aromatic rings. Nevertheless nowadays, all of the iodonium photoinitiators used in the industry exhibit similar absorption characteristics with the absorption maximum (λ_{max}) in the range 220–280 nm

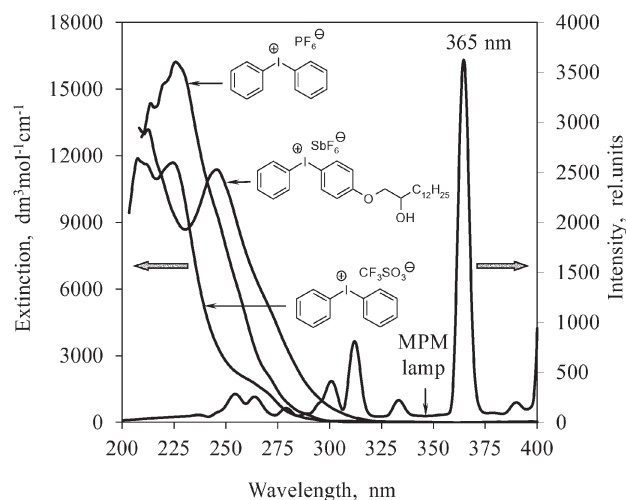


Fig. 1. Comparison of the absorption characteristics of commercial iodonium photoinitiators with the emission characteristics of industrial light sources (MPM lamp — emission spectrum of medium pressure mercury lamp)

[9, 13, 14]. This creates a technological problem, because there are no economical and simultaneously enough powerful light sources that would emit UV light in that range. Low pressure mercury lamps, deuterium bulbs and UV LEDs emitting deep UV light are low-power light sources, while xenon lamps are broadband UV-Vis-NIR light sources, which emit only a fraction of the supplied energy in the range below 300 nm [15]. In the photocurable coatings industry medium pressure mercury lamps are used, which emit most of energy at about 365 nm and only a fraction in the absorption range of commercial iodonium photoinitiators (Fig. 1). Hence, there is a mismatch between the absorption characteristics of the commercial photoinitiators and the emission characteristics of the light sources, which lowers the photopolymerization rate.

In order to solve that problem, we developed several new iodonium photoinitiators with the absorption characteristics better matching the medium pressure mercury light sources than that of commercial photoinitiators. In this paper, spectral characteristics of the new cationic polymerization photoinitiators and their performance in photopolymerization of example monomers are reported.

EXPERIMENTAL

Materials

Triethylene glycol divinyl ether (TEGDVE, from Sigma Aldrich) and 3,4-epoxy cyclohexylmethyl 3,4-epo-

xycyclohexanecarboxylate (CADE, Sigma Aldrich) were applied as model monomers.

The stilbene derivative *trans*-1-[2-(2',5'-dimethoxyphenyl)ethenyl]-2,3,4,5,6-pentafluorobenzene was applied as a fluorescent probe to monitor progress of the cationic photopolymerization by FPT (*i.e.*, Fluorescence Probe Technology). This probe was synthesized according to the procedure described in article [16].

The following photoinitiators were studied: four new photoinitiators: (7-ethoxy-4-methylcoumarin-3-yl)phenyliodonium hexafluoroantimonate [**P3C-Sb**, formula (I)], (7-ethoxy-4-methylcoumarin-6-yl)phenyliodonium hexafluoroantimonate [**P6C-Sb**, formula (II)], (7-ethoxy-4-methylcoumarin-3-yl)phenyliodonium hexafluorophosphate [**P3C-P**, formula (III)], (7-ethoxy-4-methylcoumarin-6-yl)phenyliodonium hexafluorophosphate [**P6C-P**, formula (IV)] and a commercial photoinitiator: [4-(2-hydroxytetradecyloxy)phenyl] phenyliodonium hexafluoroantimonate [**CD1012**, formula (V), Sigma-Aldrich), used as a reference. The new photoinitiators were synthesized according to the procedures described in the patent applications [17, 18].

Preparation of photocurable compositions

The compositions were prepared by dissolution of the probe and each photoinitiator in TEGDVE or CADE monomer in such proportions as to obtain the concentrations $5 \cdot 10^{-3}$ mol/dm³ of the probe and $1.5 \cdot 10^{-2}$ mol/dm³ (about 1 wt. %) of the photoinitiator. The solutions were prepared in glass vials made of dark glass, and were stored in dark until needed. Just before the measurement, two drops of the composition were placed in the middle of a microscope slide (75 mm × 25 mm × 1 mm), equipped with two 0.08 mm thick spacers located on the slide sides and the slide was covered with another microscope slide to form a sandwich structure. The composition spread between the slides into a broad spot of about 0.08 mm thick and about 20 mm in diameter. The sandwich structure was kept together using paper clips placed on the sides.

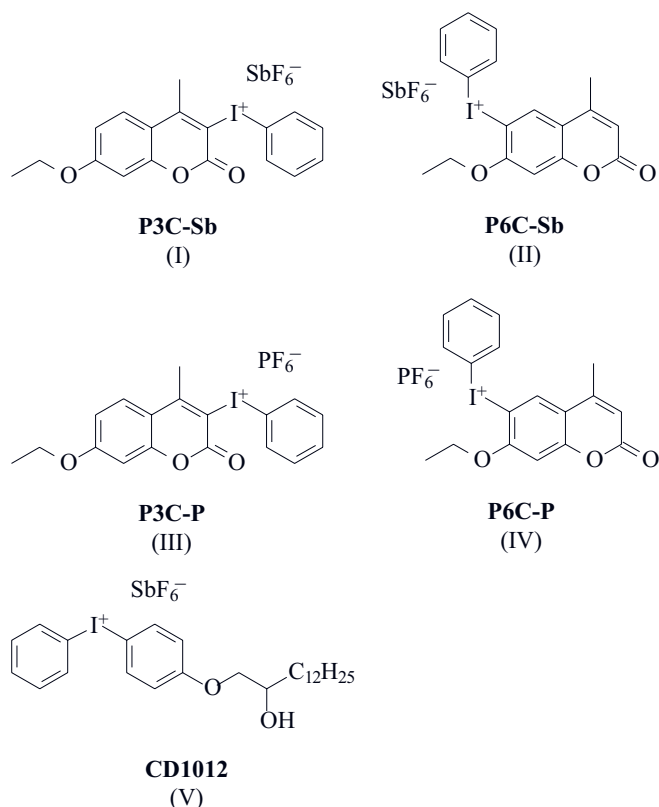
Methods of testing

UV-Vis spectroscopy

Absorption spectra of the photoinitiators were recorded in methanol, using EPP2000C spectrometer (StellarNet, Inc., USA) in combination with a broadband tungsten-deuterium UV-Vis light source and a quartz cuvette with 1.0 cm optical path. For relative comparisons, the absorbance data were converted into extinction coefficient data, expressed in classical units [dm³·mol⁻¹·cm⁻¹].

Monitoring of photopolymerization by FPT

A stationary cure monitoring system was applied for comparison of the initiators effectiveness. The system



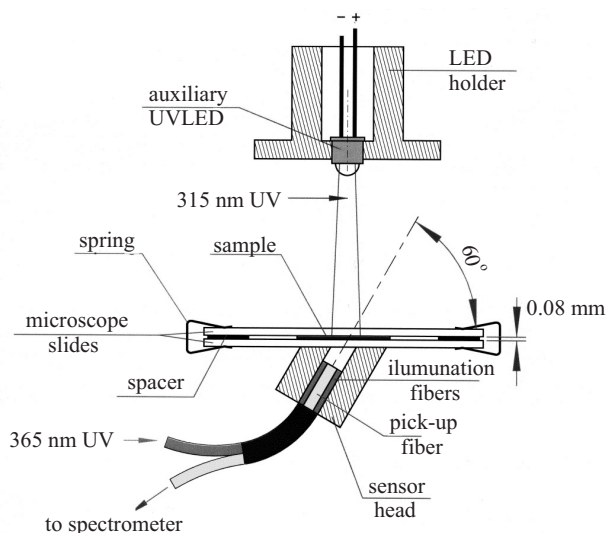


Fig. 2. The measurement setup

was composed of a microcomputer-controlled miniature spectrometer (EPP2000C from StellarNet, Inc.), a specially designed sensor head and two UV light sources based on UV LEDs. This was a two-beam version of the one-beam cure monitoring system described in [19]. The system enabled irradiation of the sample with UV light of two different wavelengths and monitoring the photopolymerization progress by FPT simultaneously, whenever necessary. Schematic drawing of the measurement setup is shown in Fig. 2.

Two UV LEDs were applied. The UV light from the first UV-LED (Roithner LaserTechnik, GmbH; $\lambda_{\text{max}} = 365 \text{ nm}$) was injected into a fiber optic cable and was transmitted into the measurement site, where the light illuminated about 5 mm spot on the thin-layer sample at the angle 60° relative to the sample surface. The second UV-LED (T9B31C, from Seoul Optodevice Co. Ltd.; $\lambda_{\text{max}} = 315 \text{ nm}$), equipped with a ball lens, focused the UV light on the same spot within the sample from above (see Fig. 2). The illumination area of the top UV-LED was adjusted by changing the distance of the UV-LED from the sample so as to match exactly the diameter of the spot illuminated by the light from the other UV-LED. Both UV-LEDs were supplied with constant current of 20 mA from appropriate stabilized power supplies. The fluorescent light from the probe was picked up by the central optical fiber and was transmitted into the spectrometer.

The UV light from the LEDs caused decomposition of the photoinitiator present in the sample and excitation of the probe molecules to induce their fluorescence. The fluorescent light was analyzed with the spectrometer at constant time intervals. All measurements were done at the ambient temperature (25°C).

RESULTS AND DISCUSSION

Effectiveness of any photoinitiator in initiation of monomers polymerization depends on two primary

factors: (1) ability of the initiator to absorb light within the wavelength range emitted by the light source used to induce the photopolymerization process, and (2) initiation efficiency of the photoinitiator itself, which is a measure of how many active species are generated per one photon absorbed. In the case of cationic photopolymerization there is a third factor that affects the photopolymerization rate. It is the type of the protic acid generated as the actual cationic polymerization initiator. In particular, strength of the acid affects the rate of initiation, while the strength of interaction of the counterion derived from the acid with the cationic sites involved in the propagation step of cationic polymerization has influence on the propagation rate. Therefore, both hexafluoroantimonates and the corresponding hexafluorophosphates of the coumarin-based iodonium photoinitiators were synthesized and studied.

Absorption characteristics of the photoinitiators studied

First, absorption characteristics of the new photoinitiators was determined and compared to that of the commercial photoinitiator (Fig. 3). The commercial cationic polymerization photoinitiator (**CD1012**), which is a diphenyliodonium derivative does not absorb light significantly above 300 nm. It shows only an absorption shoulder reaching up to 320 nm. This is because the phenyl chromophores usually show absorption maximum at around 250 nm. No wonder, our first attempts to initiate cationic photopolymerization with the commercial photoinitiator using only the irradiation at 365 nm failed, because of no absorption at that wavelength. When one of the phenyl substituents was replaced with the coumarin chromophore, the absorption spectrum of the diaryliodo-

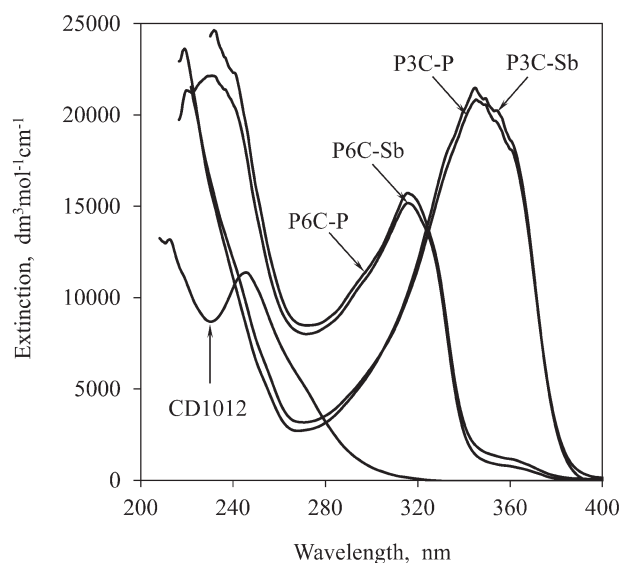


Fig. 3. Comparison of absorption characteristics of the newly developed iodonium photoinitiators with that of a typical commercial one

nium salts shifted to longer wavelengths, which coincided with 365 nm (Fig. 3). The photoinitiators with phenyliodonium substituent located at the position 3 of the coumarin moiety (*i.e.*, **P3C-Sb** and **P3C-P**) turned out to be better absorbers at 365 nm, than the corresponding 6-substituted isomers (**P6C-Sb** and **P6C-P**), due to higher bathochromic shift of the absorption of 7-ethoxy-4-methylcoumarin chromophore upon the substitution in the position 3 compared to that of 6-substituted isomer. This effect can be attributed to more extended π -d- π electron delocalization when the electron-donating ethoxyl group and the electron-withdrawing phenyliodonium group are located on the opposite sides of the coumarin moiety, compared to cross-coupling only, when the phenyliodonium substituent is in the position 6. In fact, the extinction coefficient of **P3C-Sb** and **P3C-P** at 365 nm is at the level of 75 % of that at the peak maximum located at $\lambda_{\max} = 345$ nm, while that of the isomers **P6C-Sb** and **P6C-P** is at the level of about 10 % of that at $\lambda_{\max} = 315$ nm, compared to zero absorption in the case of **CD1012**.

On the other hand, when the second of most intense emission bands of medium pressure mercury lamps is taken into account, which is composed of a series of closely-spaced spectral lines of mercury in the range 302–320 nm, the iodonium salts **P6C-Sb** and **P6C-P** show maximal absorption, while the absorption of **P3C-Sb** and **P3C-P** reaches half of its maximal value, compared to less than 10 % absorption of the maximal value in the case of **CD1012**. This makes the coumarin-based iodonium salts good candidates for the role of photoinitiators in cationic polymerization with medium pressure mercury light sources. Moreover, the magnitude of the extinction coefficient of **P3C-Sb** and **P3C-P** at the peak maximum indicates that the longest-wavelength absorption band of these compounds corresponds to π - π^* type of electronic transition, while the weak longest-wavelength absorption band of **P6C-Sb** and **P6C-P**, located at around 360 nm, corresponds to a symmetry-forbidden n - π^* transition.

Table 1. Spectral characteristics of the photoinitiators studied

Compound	λ_{\max} nm	Extinction coefficient, ϵ , $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$			
		λ_{\max}	365 nm	320 nm	302 nm
P3C-Sb	345	21 500	16 300	12 200	6 470
P3C-P	345	20 800	15 800	11 700	6 640
P6C-Sb	316	15 200	629	14 600	12 000
P6C-P	316	15 700	964	15 200	12 400
CD1012	245	11 400	0	65	581

The extinction coefficients of the photoinitiators at critical wavelengths, determined from the UV spectra, are summarized in Table 1. These data indicate that the type of anion in the iodonium salts with same cation has no effect on position of the absorption maximum, while

its influence on the magnitude of extinction coefficients is negligible.

Comparison of the photoinitiator performance by FPT

In order to evaluate the performance of new cationic polymerization photoinitiators in comparison to the commercial one, tests of photopolymerization of two example monomers under identical reaction conditions were carried out, using the photoinitiators studied. Triethylene glycol divinyl ether (TEGDVE) and 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (CADE) were selected as the model monomers, because they are representatives of vinyl ethers and epoxy monomers, which are most often used for coating formulations cured by the cationic polymerization mechanism.

For quantitative comparison of the photoinitiators performance, fluorescence probe technology (FPT) has been applied [20, 21]. The FPT method is based on specially designed fluorescent compounds, called probes, which change their fluorescence characteristics upon changes occurring in the environment they are dissolved. When a fluorescent probe is dissolved in a monomer and the system is polymerized, usually the change of the medium polarity and/or microviscosity causes shift of the fluorescence spectrum of the probe to shorter wavelengths. The shift can be monitored with a rapid-scan spectrofluorometer, like the one applied in this study. While many fluorescent compounds can be used as probes for monitoring progress of free radical polymerization, few probes have been reported for the cationic systems, because during the cationic polymerization a strong acid is usually generated from a photoinitiator as the actual cationic polymerization initiator. When a probe structure contains a basic or an acid-sensitive functional group, usually the acid affects the probe response. Therefore, in order to minimize the interaction between the probe and the photo generated acid, an amine-free fluorescent probe reported by Neckers *et al.* [16] has been selected for this study. Figure 4 shows the structure of the probe and its fluorescence spectra obtained before and after cationic photopolymerization of an example monomer, initiated with **P6C-Sb** photoinitiator.

Figure 4 indicates that the fluorescence spectrum of the probe shifted to shorter wavelengths upon polymerization of the monomer, while its intensity doubled. This enabled monitoring of the photopolymerization progress in real time. The increase in the fluorescence intensity upon crosslinking of the probe environment is a typical behavior of most fluorophores, which results from decrease of the efficiency of non-radiative decay of the probe excited states in rigid media due to restricted motion of the probe molecules responsible for the non-radiative dissipation of the excited state energy. Both, the change of the fluorescence intensity or the spectrum shift have been used in literature as the indicators of the poly-

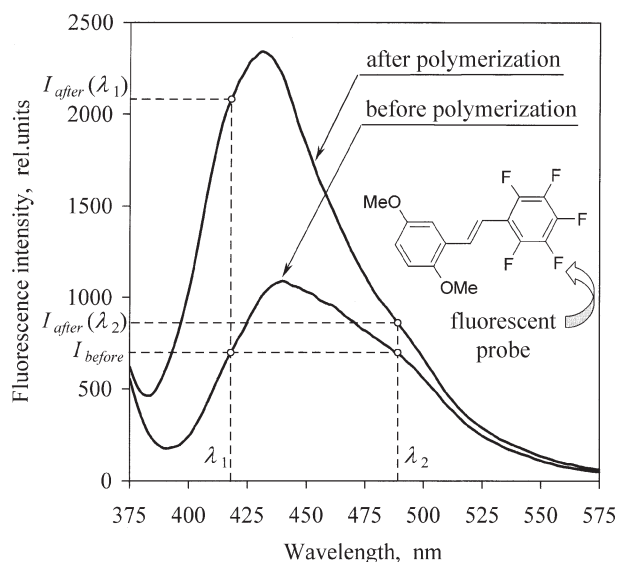


Fig. 4. Fluorescence spectra of the probe *trans*-2-(2',5'-dimethoxyphenyl)ethenyl-2,3,4,5,6-pentafluorobenzene before and after polymerization of CADE monomer

merization progress [22, 23]. However, for practical reasons the spectrum shift, measured in terms of fluorescence intensity ratio at two wavelengths, was applied in this study. The ratio was calculated by division of the fluorescence intensity at the shorter wavelength (λ_1 in Fig. 4) by the intensity at the longer wavelength (λ_2 in Fig. 4), while the monitoring wavelengths were selected so as to correspond to the same fluorescence intensity on both sides of the peak maximum within the highest slopes of the fluorescence spectrum before polymerization of the monomer [equation (1)].

$$R = \frac{I(\lambda_1)}{I(\lambda_2)} \quad (1)$$

So defined ratio (R) started from (1) and increased with progress of the polymerization as the spectrum shifted to shorter wavelengths.

First photopolymerization tests of the compositions containing identical molar concentrations of the photoinitiators and the probe in TEGDVE monomer were carried out using irradiation with one beam only. Figure 5 shows the kinetic curves of the photopolymerization initiated with particular photoinitiators, obtained by FPT, using only the UV LED emitting at 365 nm. These data confirm that at the wavelength corresponding to the strongest emission line of medium pressure mercury lamps used in the industry, the new photoinitiators are much more effective than the **CD1012** photoinitiator. In fact, the composition containing **CD1012** did not polymerize at all within the irradiation time applied, because of the lack of significant light absorption by **CD1012** above 325 nm (Figs. 3 and 5). At 365 nm, the hexafluoroantimonates (**P6C-Sb** and **P3C-Sb**) are more effective than the corresponding hexafluorophosphates (**P6C-P** and **P3C-P**), as indicated by shorter induction time and higher polymerization rate in the case of the former

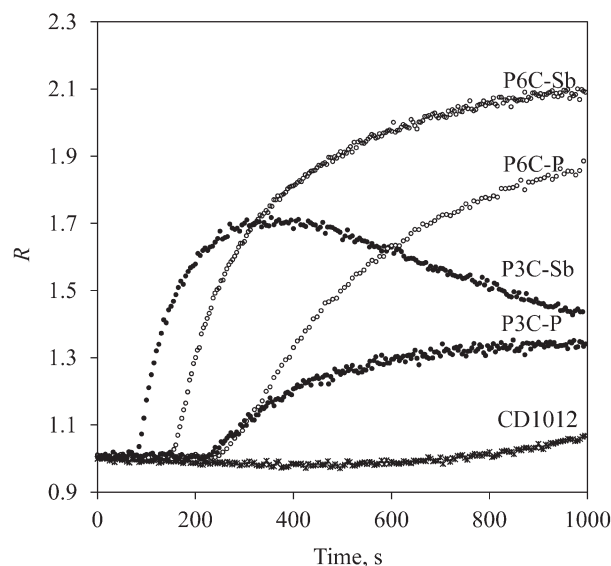


Fig. 5. Kinetic profiles of cationic photo-polymerization of TEGDVE monomer, obtained by FPT, using *trans*-2-(2',5'-dimethoxyphenyl)ethenyl-2,3,4,5,6-pentafluorobenzene as a fluorescent probe and different photoinitiators

photoinitiators compared to the latter ones (Fig. 5). This is consistent with the general trend observed with other photoinitiators [9] and it indicates that the hexafluoroantimonic acid released from the diaryliodonium hexafluoroantimonates protonates the PEGDVE monomer faster than the hexafluorophosphoric acid, which results in faster initiation rate, while the SbF_6^- anion binds more loosely with the cationic sites in the chain propagation step, which in turn results in faster overall polymerization rate. Moreover, in the case of hexafluoroantimonates, the 3-substituted isomer (**P3C-Sb**) is more effective than the corresponding 6-substituted isomer (**P6C-Sb**), because of higher extinction coefficient of the former photoinitiator around 365 nm (Figs. 3 and 5).

The fall of the polymerization progress indicator (R) at high monomer conversions in the case of **P3C-Sb** is an artifact, which probably results from protonation of the probe when hexafluoroantimonic acid is generated too fast, so that it is not consumed on protonation of the monomer molecules for kinetic reasons. The lack of the artifact in the case of **P6C-Sb** confirms that when hexafluoroantimonic acid was generated slower due to much lower absorption of **P6C-Sb** compared to that of **P3C-Sb**, no significant probe interaction with the acid occurred. Hence, the fluorescent probe applied in this study fails in monitoring the photopolymerization progress at high monomer conversions in the case of **P3C-Sb** photoinitiator; only the initial slopes right after the polymerization start can be compared. Moreover, similar initial slopes observed in the case of **P3C-Sb** and **P6C-Sb**, while much faster photogeneration of the acid from **P3C-Sb** suggest that in the case of hexafluoroantimonates, the overall polymerization rate of PEGDVE monomer was controlled by the rate of monomer protonation rather than by

the rate of generation of hexafluoroantimonic acid. Consequently, the excess of acid, not consumed fast enough on the protonation of monomer, altered the probe response in the case of **P3C-Sb**.

For quantitative comparison of the performance of new photoinitiators with that of the commercial one (**CD1012**), the photopolymerization tests of the epoxy monomer (CADE) were carried out using irradiation with both UV LEDs simultaneously, because when only 365 nm light was applied, the **CD1012** photoinitiator did not work at all. Such two-beam irradiation with 315 nm and 365 nm simultaneously mimicked the two most intense UV bands of medium pressure mercury light sources used in the industry, though not necessarily at exactly the same intensity. The kinetic profiles of the ring-opening cationic photopolymerization of CADE monomer, initiated with the particular photoinitiators under identical reaction conditions, are shown in Figure 6.

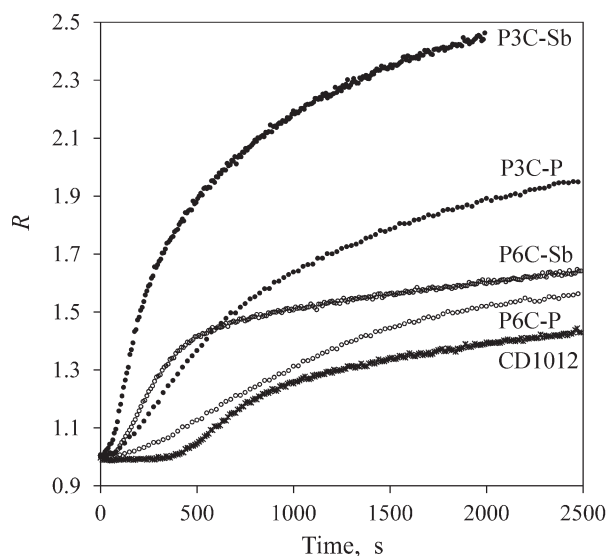


Fig. 6. The kinetic profiles of cationic photo-polymerization of CADE monomer, obtained for different photoinitiators, using irradiation with two beams (365 and 320 nm) simultaneously

Figure 6 confirms that also in the case of the epoxy monomer (CADE) the new photoinitiators are more effective than **CD1012**. The slopes (dR/dt) of the kinetic profiles, obtained right after the polymerization start, can be used as quantitative indicators of the polymerization rates, which depend on the photoinitiator performance. The higher is the slope, the higher is the polymerization rate and the better is the photoinitiator, because the photoinitiators concentration and the testing conditions were maintained identical. Alternatively, the induction time, defined as the time between the start of irradiation and the start of polymerization, can be used for comparison of photoinitiators performance. In the case of the induction time, the relationship is opposite: longer induc-

tion time means poorer performance of the photoinitiator. However, it has to be pointed out that the magnitude of the induction time in cationic photopolymerization of monomers depends on the concentration of hydroxylic contaminants, such as moisture or stabilizers that are present in the monomer or may be introduced with the photoinitiator. If for example, a photoinitiator forms hydrates, it may induce increased induction time even if its intrinsic performance is not bad. In that sense, for qualitative comparison of the performance of different photoinitiators, the polymerization rate is better. Hence, the photoinitiator **P3C-Sb** showed the best performance, as indicated by the highest slope of the kinetic curve and the shortest induction period (Fig. 6 and Table 2).

Table 2. Comparison of the effectiveness of the photoinitiators studied in initiation of cationic photopolymerization of CADE monomer

Photo-initiator	Induction time, s	Polymerization rate (dR/dt), s^{-1}	Relative effectiveness ($(dR/dt)_i/(dR/dt)_{CD1012}$)
CD1012	403	0,000336	1
P3C-Sb	55	0,003310	9.8
P6C-Sb	81	0,001290	3.8
P3C-P	104	0,000913	2.7
P6C-P	202	0,000403	1.2

For quantitative comparisons of the performance of different photoinitiators under any particular reaction conditions, the relative effectiveness, defined as the ratio of the maximal photopolymerization rate (*i.e.*, that after the polymerization start), achieved with any particular photoinitiator, to the rate achieved using some reference photoinitiator (assumed as a standard), is the best parameter. Such comparison, where **CD1012** was applied as the standard, is illustrated in Table 2.

It turned out that under the irradiation conditions used in this study, the photoinitiator **P3C-Sb** is about 10 times more effective than **CD1012**, while the worst of the new photoinitiators (**P6C-P**) is still by about 20 % more effective than the reference. In industrial settings, under irradiation conditions with powerful medium pressure mercury lamps, the absolute values of the induction times and the polymerization rates will be different, but it can be expected that the general trend in the values of the relative effectiveness of particular photoinitiators will be similar. Hence, from among the photoinitiators tested, **P3C-Sb** can be considered as the best candidate for practical applications, where high speed of cationic cure is important. The performance of **P3C-Sb** is the best both in the photoinitiation of cationic polymerization of polyethylene glycol divinyl ether (PEGDVE) and the cationic ring-opening polymerization of the epoxy monomer (CADE). Thus, similar performance of that photoinitiator can be expected in other monomers used for photo-

curable formulations cured by cationic polymerization mechanism.

CONCLUSIONS

Replacement of one of the phenyl groups in commercial diphenyliodonium photoinitiators with a coumarin chromophore shifted the absorption spectrum to longer wavelengths, which made the new photoinitiators better matched to the emission characteristics of medium pressure mercury light sources used in the industry. All new coumarin-based photoinitiators described in this paper show better performance than the commercial photoinitiator **CD1012** in initiation of cationic polymerization of vinyl ethers and ring-opening cationic polymerization of cycloaliphatic epoxides. Under the irradiation conditions corresponding to strongest emission lines of medium pressure mercury lamps (7-ethoxy-4-methylcoumarin-3-yl)phenyliodonium hexafluoroantimonate (**P3C-Sb**) is about 10 times more effective photoinitiator than **CD1012**.

The coumarin-based photoinitiators substituted in the position 3 of the coumarin moiety (i.e., **P3C-Sb** and **P3C-P**) show better performance than the corresponding 6 substituted isomers. Moreover, also in the case of the coumarin-based photoinitiators, diaryliodonium hexafluoroantimonates form better cationic polymerization photoinitiators than the corresponding hexafluorophosphates.

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