Application of aminocoumarins for the role of fluorescent molecular probe of cationic photopolymerization process

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Summary - In this research an attempt has been made to demonstrate the use of the technique of molecular fluorescence probe FPT (*Fluorescence Probe Technology*) to monitor the cationic photopolymerization process of the triethylene glycol divinyl ether (TEGDVE), using for that purpose five commercially available coumarin derivatives: *Coumarin 1*, *Coumarin 120*, *Coumarin 102, Coumarin 153* and *Coumarin 6H*. In the spectroscopy studies, the changes of the probe fluorescence were collected, monitoring the physicochemical changes occuring in the composition, ie. changes of both microviscosity and polarity of enviroment in which the coumarin probe was located. The utility of the aminocoumarins for the monitoring of progress of photopolymerization reactions were tested using fluorescence intensity ratio R, the probe sensitivity S and the number of progress of the reaction β.
Obtained results revealed that the majority of the compounds tested can be successfully qualified for the role of molecular fluorescent probes capable of monitoring the cationic photopolymerization. It has been found that the presence of amino groups in the basic structure of the coumarin derivative is not a factor limiting the usefulness of these compounds as molecular probes of FPT method.

Keywords: Fluorescent probes; cationic photopolymerization; aminocoumarins

INTRODUCTION

Today, coating polymers are very important group of materials and there is a necessity to obtain possibly the best properties of these products. Polymer coatings are applied for photocurable solvent-free paints, photocurable lacquers, photocurable inks and other coating materials, microelectronics, printing plates, etc., wherever fast drying or setting is important. Therefore, there is a need to monitor the photopolymerization process during the production (*on-line*) and also in the laboratory (*off-line*) **[1]**. Knowledge of the nature of this process allows to obtain a high quality product by keeping the reaction parameters constant or by manipulating them during the reaction process **[2]**.

The modern method of monitoring photopolymerization process is Fluorescent Probe Technology (FPT), which can be used when there is no possibility to use traditional methods such as photo-differential calorimetry (PDSC), nuclear magnetic resonance (NMR) or real infrared spectroscopy (RFT-IR) **[3,4]**. FPT technology involves the use of chemicals compounds called fluorescent molecular sensor or fluorescent molecular probe, which exhibit fluorescence changes during the process of polymerization or photopolymerization, when the physico-chemical changes occurring i.e. the changes of microviscosity and/or polarity of the environment **[5]**.

Fluorescence Probe Technology (FPT) offers the possibility of monitoring the photopolymerization processes on-line during the process of production of polymer coating in industry. FPT method does not cause the destruction of the material **[5]**. Also using the FPT method there is no need to sampling. This technique is characterized by high sensitivity and selectivity, because we use fluorescence as signal and the response time is very short ($<10^{-9}$s). Fluorescent probe method gives many information about microscopic (not only macroscopic) characteristic of the reaction environment **[3]**.

Into monomer composition, molecular probe absorbs light of a particular wavelength. After radiation exposure, the excitation of the molecules to higher electronic excited state takes place. Excited molecules undergo stabilization as a result of interaction with the environment. When the properties of the environment change, stabilization of the excited states and their degree of relaxation also change as can be seen by the differences in energy states in the quantum yield of radiation **[1]**.

In this paper, applicability of various substituted aminocoumarin derivatives as fluorescent probes for monitoring progress of cationic polymerization processes of vinyl monomer by FPT, and, the

effect of substituent on performance of the probes are evaluated. Coumarin derivatives are huge and very important group of chemical compounds. They are characterized by low toxicity, therefore can be used in biology, medicine, perfumery and cosmetic industry **[6]**. Coumarins have interesting ability to emit fluorescence in the visible range upon excitation of the molecule to a higher energy level after exposure to UV radiation **[7]**. For this reason, many research are carried out to check the utility of coumarins as a molecular fluorescent probe. In example 7-benzamido-4-methylcoumarin, 7-acetamido-4-methylcoumarin was used as a fluorescent sensors in cationic photopolymerization of triethylene glycol divinyl ether **[8]**.

EXPERIMENTAL

Materials

Triethylene glycol divinyl ether (TEGDVE) from Sigma Aldrich (**Figure 1**) and diphenyliodonium hexafluorophosphate from Alfa Aesar (**Figure 2**) were applied as a model monomer and the photoinitiator, respectively.

The coumarin derivatives containing amino groups from Sigma Aldrich, shown in Table 1, were selected as fluorescent probes for monitoring progress of cationic photopolymerization of monomer.

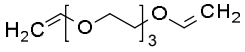


Figure 1 TEGDVE

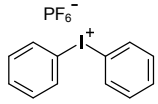
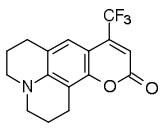
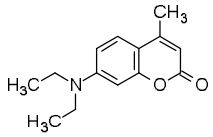
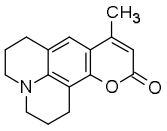
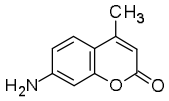
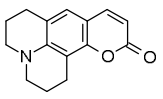


Figure 2 Diphenyliodonium hexafluorophosphate

Table 1 Coumarin derivatives.

				
COUMARIN 153 $C_{16}H_{14}F_3NO_2$	**COUMARIN 1** $C_{14}H_{17}NO_2$	**COUMARIN 102** $C_{16}H_{17}NO_2$	**COUMARIN 120** $C_{10}H_9NO_2$	**COUMARIN 6H** $C_{15}H_{15}NO_2$

Preparation of photocurable formulations

Samples preparation consisted of making a solution of coumarin derivative and photoinitiator (1 wt %) into the TEGDVE monomer, so as to obtain concentration of the probe $5.0 \cdot 10^{-3}$ mol/dm^3. The vials with the mixture were immediately wrapped tightly in aluminum foil to prevent uncontrolled photopolymerization. Samples with limited solubility were placed into ultrasonic bath for a two minutes.

Thin-layer samples of the thickness comparable to the thickness of photocurable coatings used in industry were applied in this study. Just before measurement, two drops of the composition were placed in the middle of a microscope slide (75 mm x 25 mm x 1 mm) (Thermo Scientific), equipped with two 0.1 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 0.1 mm thickness. The sandwich structure was kept together using paper clips placed on the sides. So prepared samples were maintained in horizontal position to avoid shift of the composition between slides during the measurements.

FPT measurements

The photopolymerization monitoring system was composed of a narrow-bandwidth UV light source, which was a UV LED emitting at the wavelength λ_{max} = 320 nm (UVTOP315-BL-TO39, Roithner Laser Technik, Austria), a miniature CCD spectrometer (EPP2000C, StellarNet Inc., USA) interfaced to a microcomputer. Sample was placed into a dark chamber of the spectrometer horizontally directly above the UV-LED light. Immediately after insertion of the sample, recording of emitted fluorescence spectra started. Measurements occurred automatically, and data were obtained and saved on a computer configured with a spectrometer in a specially created program. For transmission of fluorescence light from the measurement site to the spectrometer a fiber optic cable was applied. All measurements were done at ambient temperature (25 ^{o}C).

RESULTS AND DISCUSSION

During the monitoring of the cationic photopolymerization of vinyl monomer (TEGDVE), changes in aminocoumarins fluorescence intensity appeared, which indicates the sensitivity of these systems to changes in the environment surrounding the probe molecules **(Figure 3-7)**.

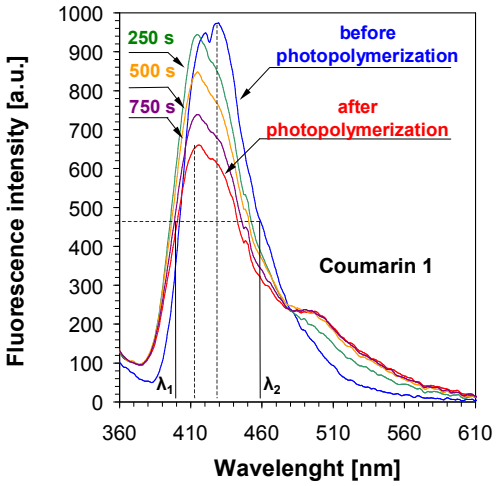


Figure 3 Fluorescence spectra of the Coumarin 1 before and after polymerization of TEGDVE.

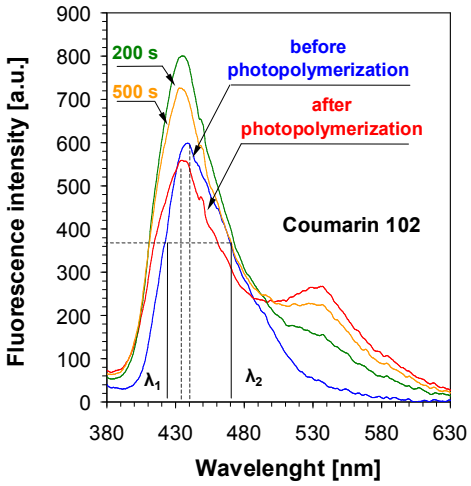


Figure 4 Fluorescence spectra of the Coumarin 102 before and after polymerization of TEGDVE.

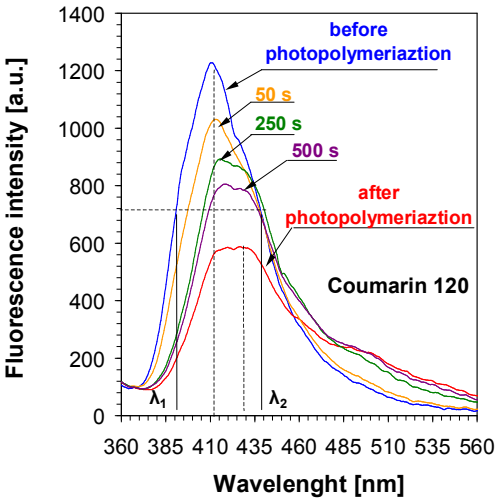


Figure 5 Fluorescence spectra of the Coumarin 120 before and after polymerization of TEGDVE.

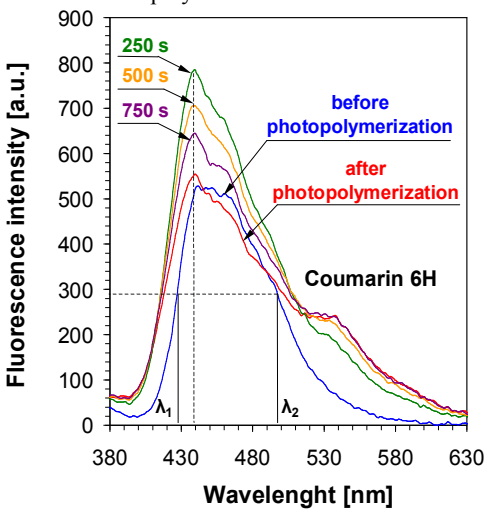


Figure 6 Fluorescence spectra of the Coumarin 6H before and after polymerization of TEGDVE.

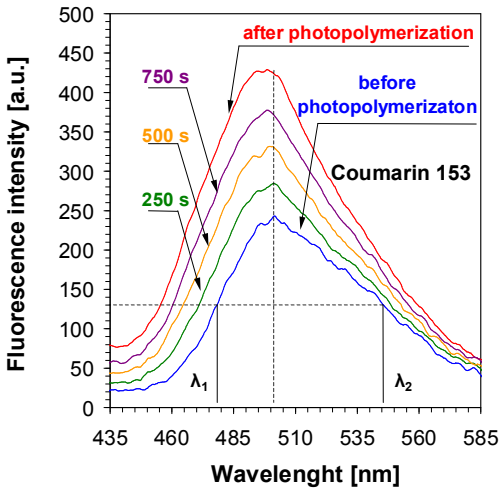


Figure 7 Fluorescence spectra of the Coumarin 153 before and after polymerization of TEGDVE.

The decrease of the compositions polarity is related to the transformation of the more polar double bonds of monomer into the less polar single bonds of polymer. Accordingly, with decreasing of the environment polarity, stabilization of the excited states of the fluorescent probes also decrease and there is formed a larger energy gap between the ground state and excited state energy. The increase of environment microviscosity causes the less number of probe molecules in the excited state achieved the most favorable conformation energy before emitting the quantum of radiation. The emission of photon from conformation of the excited states with more energy takes place and then the spectrum of fluorescence probe shift toward shorter wavelengths.

For the **C153** probe it was observed that shift of fluorescence spectra is very faint. During the photopolymerization the fluorescence intensity increases of approx. 55.5%. The very low intensity values are probably the result of presence of fluorine atom in the CF_3 group attached at position 4 of a coumarin ring. During the photopolymerization process, the fluorescence spectrum for the **C120** probe moves towards longer wavelengths. The observed phenomenon can be explained by the presence of a primary amine group located at 7 position of the coumarin ring. Analysis of **C102**, **C153** and **C6H** structures allowed to classify this chemical compounds to the ICT fluorescent molecular probes - compounds with intramolecular electron transfer in the excited state without functional group rotation. Absence of rotation is the result of presence of the 'rigid' group in 7 position of the coumarin ring. ICT probes are very sensitive to changes in the polarity of the environment (solvatochromic effect).

Monitoring of cationic photopolymerization of TEGDVE monomer

For the measurements, fluorescence intensity ratio (R) was used (**Figure 8**) which is expressed as the ratio of the fluorescence probe intensity measured on both sides of the spectrum peak in the middle of its height (1). This method is the most precise and allows to accurate monitor monomer conversion. Wavelength values (λ_1, λ_2) are selected individually for every single fluorescent probe. Using this parameter allows measurement to be independent from probe concentration and thickness of sample layer.

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

Values of R parameter started from unity and increased if the fluorescence spectrum shifted to shorter wavelengths, or decreased if the spectrum shifted to longer wavelengths. Shape of the kinetic profiles indicate that **C153** is not suitable for monitoring photopolymerization process of TEGDVE monomer. For the other coumarin derivatives it was possible to correctly determine the ratio of the fluorescence intensity (R). Studies confirmed that the **C120**, **C1**, **C6H** and **C102** have a sufficiently large fluorescence spectrum shift and can be successfully applied to the role of the fluorescent probes.

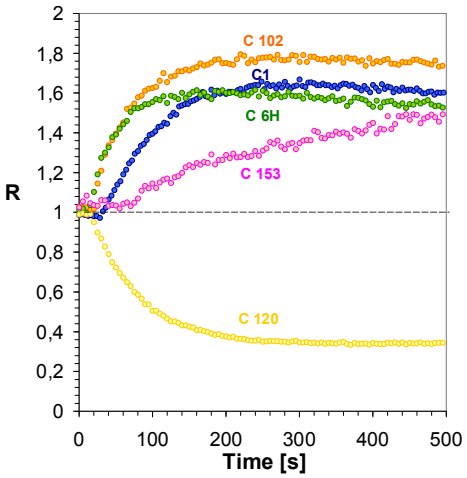


Figure 8 Progress of cationic photopolymerization of TEGDVE monomer monitored using Coumarin fluorescent probes, expressed as the fluorescent intensity ratio *R*.

The influence of the probes structure to their sensitivity '*S*' to changes occurring during the photopolymerization process.

Coumarin probes exhibit diverse sensitivity to changes appearing during the photopolymerization, depending on the nature of the functional groups attached to the defined position of aromatic ring. This dependency is correlated with the different ranges of *R* parameter (*1/R* for compounds shifted the fluorescence spectra to longer wavelengths). To compare sensitivity of different aminocoumarines, *S* parameter was introduced (2).

$$S = \frac{\left|R_k - R_0\right|}{R_0} \cdot 100\% \qquad (2)$$

R_0 – *R* value for the fresh composition
R_k – *R* value for the composition after photopolymerization

Influence of the type of the substituent at position 7 of the coumarin chromophore can be compared between derivatives of 4-methylcoumarin (**Figure 9**). A methyl group located at the 4 position is a relatively weak donor. In turn, the amino groups attached at the 7 position of the coumarin ring have the electron acceptor character, but significantly stronger than the -CH_3 substituent. The presence of strongly electron donating amino groups and the electron acceptor lactone ring conjugate to the aromatic system, resulting in an increased sensitivity to changes in probe microviscosity and polarity of the composition.

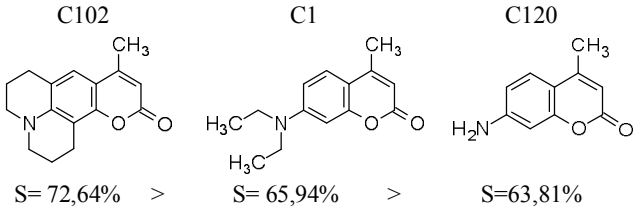


Figure 9 Influence of the type of functional group at '7' position to sensitivity of coumarin probe.

Designation of sensitivity for **C153** probe was not possible due to the inability to determine the *plateau*. The highest sensitivity was exhibited by **C102** probe which has in a structure a relatively weak electron donating methyl group attached to the a strong electron accepting lactone ring. Presence

of the weak donor groups has the biggest influent to the *S* parameter than any group deficiency (**Figure 10**).

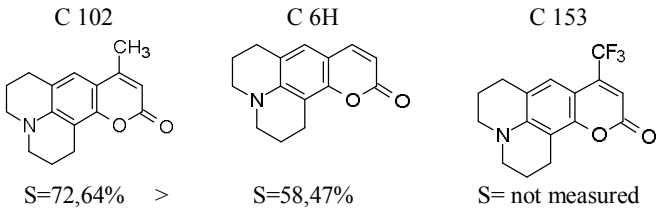


Figure 10 Influence of the type of functional group at '4' position to sensitivity of coumarin probe.

The influence of the coumarin derivatives structure to the accuracy of the measurements of process rate.

In order to make the response of the probe independent of sensitivity and to be able to use the slope of the kinetic profiles using different aminocoumarins - it is necessary to normalize the profiles expressed by using the values of *R* to the same range of variability (**Figure 11**). For this purpose number of the progress of the reaction (β) was defined (3).

$$\beta = \frac{R - R_{\min}}{R_{\max} - R_{\min}} \tag{3}$$

R_{min} – value of the initial ratio of the fluorescence intensity,
R_{max} -value of the fluorescence intensity after photopolymerization.

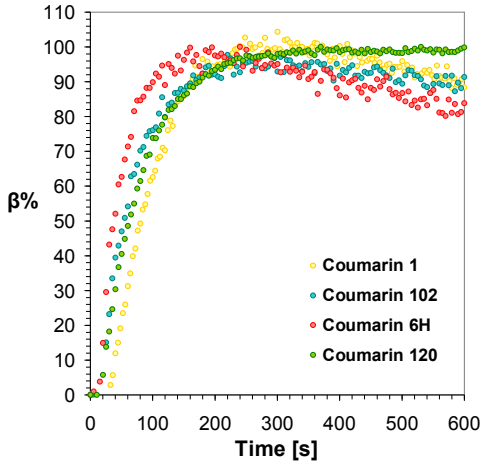


Figure 11 . Kinetic profiles of cationic photopolymerization of TEGDVE, using β parameter.

For **C153** probe it was impossible to define a *plateau* and calculate a β parameter. Δβ value for all compounds did not exceed 20%, which means that the profiles for the individual coumarins to a large extent overlap with each other in spite of varying chemical structure. However, overlap is not ideal - which can be seen at **Figure 11**. The sensitivity of the probes in the high conversion is slightly different depending on the structure of the probe. All probes tested show that photopolymerization reaction proceeded at the same speed, and after 250 s composition was polymerized.

CONCLUSION

Coumarin derivatives exhibited changes the shift of fluorescence spectrum and changes of its intensity during the cationic photopolymerization of TEGDVE. It has been found that the presence of a primary amino group in the 7 position of **C120** shits the fluorescence spectrum to longer wavelengths. From a group of five coumarin derivatives, four of them (**C1**, **C 6 H**, **C102**, **C120**) can be successfully used for the role of molecular fluorescent probes in the cationic photopolymerization process of TEGDVE monomer using for this purpose fluorescence intensity ratio *R* as indicator of progress of the reaction. One of them - **C153** were rejected due to the minimal range of variation of the *R* parameter. Coumarin probes which were tested, exhibited different sensitivity *S* to the environment changes depending on the type of the substituents attached to the coumarin ring. The highest sensitivity was demonstrated by **C102**. For four probes (with the exception of **C153**) it is possible to apply the number of progress of the reaction β as an indicator of the progress of the photopolymerization. Differences in the response of the individual probes we can see only in the high range of monomer conversion. Research described in this article may be the base for more advanced analysis, for example, examine the effect of concentration of the probe into monomer composition to the rate of photopolymerization process.

Acknowledgments

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