Journal of Applied Polymer Science

The Performance of 7-Hydroxycoumarin-3-carbonitrile and 7-Hydroxycoumarin-3-carboxylic Acid as Fluorescent Probes for Monitoring of Cationic Photopolymerization Processes by FPT

Joanna Ortyl, Roman Popielarz
Department of Biotechnology and Renewable Materials, Faculty of Chemical Engineering and Technology, Cracow University of Technology, Warszawska 24, 31-155 Cracow, Poland
Correspondence to: R. Popielarz (E-mail: rpopiel@pk.edu.pl)

ABSTRACT: The applicability of 7-hydroxycoumarin-3-carbonitrile (1) and 7-hydroxycoumarin-3-carboxylic acid (2) as fluorescent probes for monitoring of cationic photopolymerization processes by fluorescence probe technique (FPT) was evaluated in comparison to the response of 7-diethylamino-4-methylcoumarin (C1). Triethylene glycol divinyl ether and diphenyliodonium hexafluorophosphate were used as an example monomer and a cationic photoinitiator, respectively. It has been found that the probe 1 withstands the cationic polymerization conditions and provides correct probe response. The probes 2 and C1 undergo side reactions under the cationic polymerization conditions that make them unusable for monitoring of the polymerization progress at high monomer conversions. The application of 1 as an amine-free probe for monitoring of curing progress of photocurable coatings cured by cationic photopolymerization is proposed. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: photopolymerization; sensors and actuators; coatings

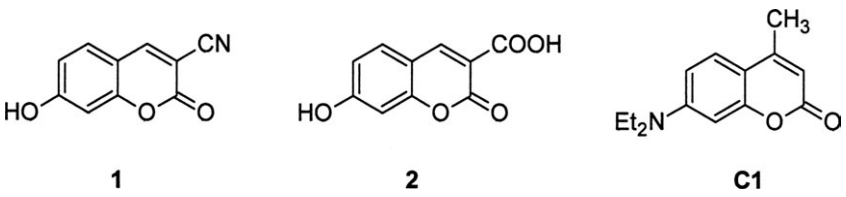
Received 30 May 2012; accepted 22 July 2012; published online
DOI: 10.1002/app.38378

INTRODUCTION

Fluorescence probe technique (FPT) is a modern spectroscopic method used mainly for monitoring of free radical photopolymerization processes.[1–6] It is well adaptable also for slow processes, such as crosslinking of epoxy resins.[7] However, an application of FPT for study of cationic photopolymerization processes encounters difficulties, because of the lack of easily available probes that would be stable under the cationic polymerization conditions. The fluorescent probes used for free radical polymerization usually do not perform well in cationic photopolymerization systems, because of the probe interaction with the strong protic acid generated in the system as the cationic polymerization initiator. Therefore, the development of sensitive and stable fluorescent probes suitable for the cationic systems is still in high demand.

The FPT method relies on the use of appropriate fluorescent molecular sensors, called probes, whose photophysical and photochemical properties depend on the properties of their environment.[8] These probes change their fluorescence characteristics upon changes occurring in their vicinity. In particular, the changes occurring during polymerization of monomers can be easily monitored by FPT. If a polymerizing system containing a fluorescent probe is illuminated with the light the probe absorbs, the probe molecules are excited to a higher electronic energy level. The excited molecules emit light in the form of fluorescence upon return to their ground state. The emitted wavelength depends on the state of the excited molecule at the moment of emission. During lifetime of the excited state, the excited molecules undergo relaxation to their more stable conformations and they interact with other molecules in their surroundings, which causes stabilization of the excited state by solvation. Hence, the state of the probe at the moment of emission depends on polarity and microviscosity of its surroundings. Consequently, photons emitted from the probe excited states carry information about the changes occurring in the system. During polymerization of monomers, the system polarity usually decreases, while overall system viscosity increases when a liquid monomer is converted into a solid polymer. The microviscosity, which is a measure of the system rigidity in vicinity of the probe molecules at a molecular scale, increases too. These changes cause shift of fluorescence spectrum of the probe to shorter wavelengths and increase of the fluorescence intensity.[9,10] Thus, by measurement of the changes of fluorescence characteristics of a probe, it is possible to monitor progress of polymerization processes at a molecular level, in contrast to conventional techniques, where macroscopic properties are usually monitored.

Fluorescent probes used for monitoring of free radical polymerization usually contain an amino group in their structure in



Scheme 1. Structure of the fluorescent probes studied.

combination with an electron withdrawing substituent, that generate a push–pull effect in the probe excited state, responsible for intramolecular charge transfer and high probe sensitivity to polarity changes. When such a probe is applied for a cationically polymerized system, the amino group usually neutralizes the strong acid generated as the cationic polymerization initiator that affects the polymerization kinetics. Moreover, the probe undergoes protonation, that changes the probe response.[11,12] The protonation of an electron-donating amino group converts it to an electron-withdrawing ammonium group, that in most cases disturbs the push–pull system in the probe structure and consequently leads to loss of the probe sensitivity. Therefore, amine-free fluorescent probes seem to be the best choice for the systems where acidic species are involved.

The first amine-free fluorescent probe proposed for monitoring of cationic polymerization processes was *N*-dodecyl-1-hydroxy-2-naphthalenecarboxamide (DDHNA probe).[13] Later on, a few other fluorescent probes suitable for monitoring both free radical and cationic polymerization processes were developed, but those were fluoro-organic compounds prepared by a multistep synthesis from relatively expensive fluorinated reagents, that limited their availability for large scale applications in industry.[14] From among amine-free fluorescent probes, recently we have evaluated applicability of N-substituted phthalimides,[15] amidocoumarins[9] and various stilbene derivatives[10] for monitoring of cationic photopolymerization processes.

In this article we report the performance of two new amine-free probes, one of which provides very good response under the cationic polymerization conditions. This makes it a good candidate for cure monitoring of photocurable coating formulations, cured by cationic polymerization mechanism, in large scale applications.

EXPERIMENTAL

Materials

Triethylene glycol divinyl ether (TEGDVE, Sigma Aldrich) and diphenyliodonium hexafluorophosphate (Alfa Aesar) were selected as a model monomer and a cationic polymerization photoinitiator, respectively. The 7-hydroxycoumarin-3-carbonitrile (**1**) and 7-hydroxycoumarin-3-carboxylic acid (**2**) were selected for the role of fluorescent probes in this study, while 7-diethylamino-4-methylcoumarin (Coumarin-1, Sigma–Aldrich), which is a typical probe used for free radical polymerization, was selected as a reference probe for comparison (Scheme 1).

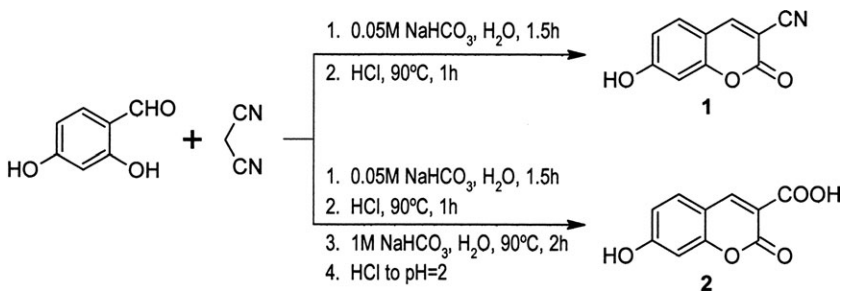
The probes **1** and **2** were obtained in a one-pot reaction, by condensation of 2,4-dihydroxybenzaldehyde with malonitrile (Scheme 2), using the procedure described by Fringuelli et al.[16]

Measurements

The photopolymerization monitoring system was composed of a narrow-bandwidth UV light source (which was a UV LED, type: T9B31C, emitting at the wavelength $\lambda_{max} = 320$ nm, from Seoul Optodevice, Korea), a miniature CCD spectrometer (EPP2000C, StellarNet, USA) interfaced to a microcomputer, and, an appropriate sensor head, where the sample was placed. For transmission of fluorescence light from the measurement site to the spectrometer a fiber optic cable was applied. The system worked by excitation of the probe dissolved in the composition with UV light, and, analysis of the fluorescence emitted from the probe, using the spectrometer. Simultaneously, the UV light caused decomposition of the photoinitiator to form hexafluorophosphoric acid, which initiated cationic polymerization of the sample.

The concentration of the photoinitiator in the compositions studied was 1.0% by weight, while the probe concentration was 5.0×10^{-3} mol dm^{-3}. The compositions were prepared in dimmed light in vials made of brown glass, and, they were used shortly after dissolution of the solid components in the monomer, because when the composition was exposed to daylight, spontaneous polymerization started.

Thin-layer samples with the thickness comparable to the thickness of photocurable coatings used in industry were applied in this study. Two drops of each composition were placed between



Scheme 2. Synthesis of the probes **1** and **2**.

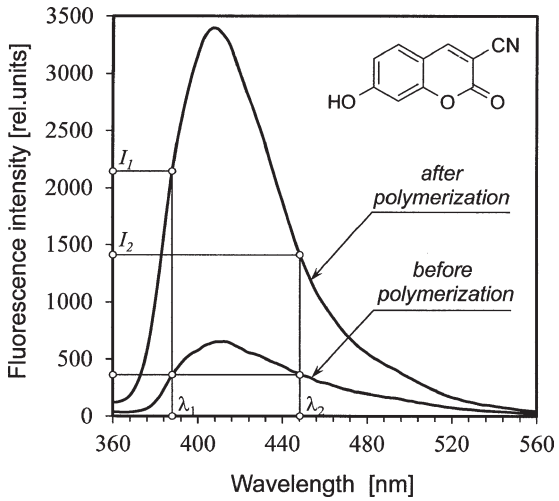


Figure 1. Fluorescence spectra of probe **1** before and after cationic photopolymerization of TEGDVE monomer.

microscope slides (25 × 75 × 1 mm^3), separated on their sides with appropriate spacers to form 0.1-mm-thick spot about 2 cm in diameter. So prepared sandwich-type samples were placed on the sensor head, located 4.5 cm below the UV LED. Drawings of the sensor head and the thin-layer sample were published previously.[17] For the purpose of this study, the sample was illuminated only with the light from the UV LED located above the sample, while the core fiber of the sensor head was used for transmission of fluorescence to the spectrometer. During the cure monitoring, the UV LED was supplied with 20 mA current from a stabilized DC power supply, while the fluorescence data were acquired to a microcomputer at the rate of 1 spectrum s^{-1}.

RESULTS AND DISCUSSION

Coumarin fluorophores have raised our interest, because of relatively high fluorescence efficiency of many coumarins substituted with electron donating and/or electron withdrawing substituents, and, good probe response of their representative: Coumarin 1 in many polymerizing systems. Unfortunately, Coumarin 1 contains an amino group in its structure, which limits its application to noncationic polymerization processes. As the presence of both an electron-donating group and an electron-withdrawing group on a conjugated system is usually necessary to achieve good probe response, hydroxyl group was applied as the electron donor, while cyano and carboxyl groups were applied as the electron acceptors in **1** and **2**, respectively (Scheme 1). The groups were localized on opposite sides of the coumarin moiety. Such arrangement of the substituents with opposite donor–acceptor abilities is characteristic for ICT probes. The ICT probes exhibit intramolecular charge transfer in their excited state that makes the excited state much more polar than the corresponding ground state. Therefore, the ICT probes are sensitive mostly to changes of polarity of their environment.

First, to check whether the compounds **1** and **2** would be applicable for monitoring of cationic polymerization processes, their fluorescence spectra were recorded in TEGDVE monomer before and after cationic photopolymerization of the monomer. These spectra are shown in Figures 1 and 2, while the corresponding spectra of Coumarin 1 probe in the same system have been reported previously.[18]

Figures 1 and 2 indicate that the fluorescence spectra of **1** and **2** shifted to shorter wavelengths upon polymerization of the monomer (as indicated by larger increase of the fluorescence intensity at λ_1 relative to that at λ_2), while the overall fluorescence intensity increased significantly. The magnitude of the spectrum shift was not large; it was only about 5 nm in the case of probe 1, while in the case of probe 2 it was hard to determine precisely due to the spectra distortion by inherent instrumental noise overlapped with the spectra. Nevertheless, the changes of the fluorescence characteristics upon polymerization of the medium were large enough for the application of **1** and **2** as fluorescent probes.

Either the spectrum shift toward shorter wavelengths or the change of fluorescence intensity has been used in literature for following the polymerization progress. Direct measurement of the spectrum shift in terms of the position of fluorescence spectrum maximum would not be accurate, because the fluorescence spectra of organic molecules are broad. Hence, the fluorescence intensity ratio method, developed by Neckers et al.,[19] was applied first as the polymerization progress indicator resulting from the spectrum shift. Figure 3 shows the kinetic profile obtained using the ratio R defined as the ratio of fluorescence intensity at a shorter wavelength (λ_1), located on the short-wavelength side of the peak maximum, to that at a longer wavelength (λ_2), located on the opposite side of the maximum. For comparison of the response of different probes, the pairs of wavelengths ($\lambda_1$and λ_2) were selected individually for each probe so as to correspond to half of the fluorescence intensity at the peak maximum before monomer polymerization, as marked in Figure 1. So defined R started from 1 and increased with progress of the photopolymerization.

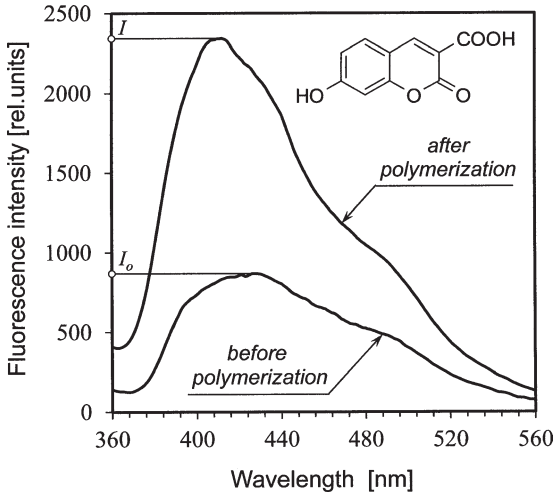


Figure 2. Fluorescence spectra of probe **2** before and after cationic photopolymerization of TEGDVE monomer.

Applied Polymer SCIENCE

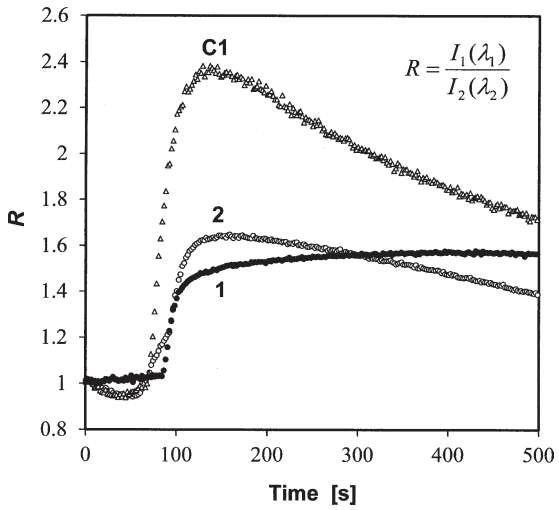


Figure 3. Monitoring of the progress of cationic photopolymerization of TEGDVE by FPT, using the probes studied and the fluorescence intensity ratio (R) as the progress indicator.

It is evident from Figure 3, that only the probe 1 shows correct polymerization profile. After a short induction period, where the carbocations generated during the initiation process were neutralized by traces of moisture and stabilizers present in the monomer, the photopolymerization started, as indicated by sharp increase of R. As the monomer was used up, the polymerization rate decreased, as indicated by decreasing slope of the kinetic profile, and finally a plateau was reached after the polymerization had ended. However, no correct polymerization profiles were obtained in the case of the probes **2** and **C1** (Figure 3). In both cases R increased during the monomer photopolymerization and then started decreasing in time (Figure 3).

Such behavior suggests that the probes **2** and **C1** undergo slow photolysis or another side reaction not necessarily involving light, under the cationic polymerization conditions. For example, it is possible that these probes react with the carbocations generated during the cationic polymerization, because both the carboxyl group in **2** and the diethylamino group in **C1** are nucleophilic. If some of the side reactions lead to formation of another fluorescent species emitting at longer wavelengths than the original probe molecules, then the fluorescence from the side product overlaps with the fluorescence spectra of the probe at the wavelength λ_2, which makes the total intensity at λ_2 decreasing slower than that at λ_1. Consequently, the intensity ratio (R) decreases at prolonged irradiation times (Figure 3).

To verify whether the fluorescence intensity change at a single wavelength can be used as an alternative polymerization progress indicator, where the ratio method fails, the intensity measured at the peak maximum at every given polymerization time (I) was normalized to the initial intensity before start of the photopolymerization (I_o) and so obtained normalized intensity (I/I_o) was plotted as a function of time (Figure 4).

Figure 4 indicates that in the case of the probes **1** and **2**, the normalized fluorescence intensity (I/I_o) can be used as the polymerization progress indicator within a broad range of monomer conversions. However, the I/I_o parameter is not a good choice for following the polymerization progress at high monomer conversions, because the I/I_o started decreasing upon further irradiation, when the polymerization was over, and, the probe response became ambiguous (Figure 4). Such intensity decrease proves that both probes (**1** and **2**) undergo side reactions under the cationic polymerization conditions that cause gradual decrease of the probe concentration. However, the probes decay is much slower than the rate of cationic polymerization of the vinyl ether, which in the case of probe **1** allowed monitoring entire range of monomer conversions using the ratio (R) as the conversion indicator (Figure 3). The I/I_o parameter cannot be used at all in the case of probe C1 (Figure 4).

In summary, when the performance of 7-hydroxycoumarin-3-carbonitrile (**1**) in the role of a fluorescent probe for monitoring of cationic photopolymerization processes is compared with the corresponding performance of previously reported amine-free probes, it turns out that the probe **1** is better than the N-substituted phthalimides,[15] because at the same low concentration the probe **1** provides less noisy kinetic profiles of the cationic photopolymerization than the phthalimides, due to higher fluorescence quantum yield of **1** compared to that of the phthalimides. Amidocoumarin probes showed significant decrease of the fluorescence intensity ratio (R) at high monomer conversions (Figure 4 in Ref. [9]), which is not observed in the case of the probe **1** (Figure 3). Finally, the response of the probe **1** is as good as that of the best stilbene probes (e.g., the probe **2** in Ref. [10]), while 7-hydroxycoumarin-3-carbonitrile (**1**) is easier to synthesize than any of the stilbene probes reported previously.

CONCLUSIONS

The 7-hydroxycoumarin-3-carbonitrile (**1**) is a new amine-free fluorescent probe suitable for monitoring of the progress of cationic photopolymerization reactions by the fluorescence probe technique, using fluorescence intensity ratio (R) as the progress indicator. This probe is stable enough under cationic

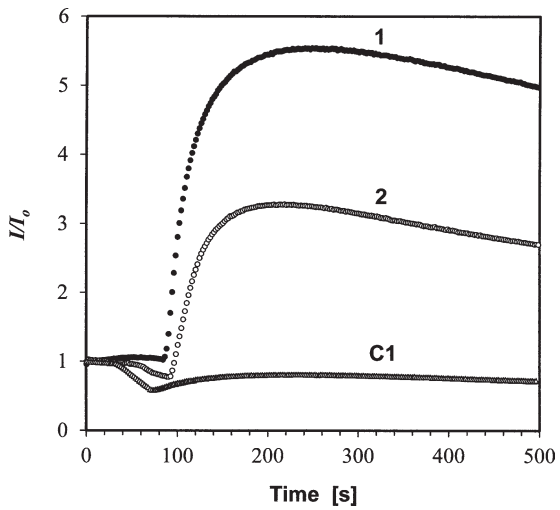


Figure 4. Monitoring of the progress of cationic photopolymerization of TEGDVE, using the normalized fluorescence intensity at peak maximum (I/I_o) as the progress indicator.

polymerization conditions of vinyl ethers, and, it affords correct response even at high monomer conversions. Easy one-pot synthesis of **1** from readily available reagents makes it a good candidate for practical applications in photocurable coatings industry.

The 7-hydroxycoumarin-3-carboxylic acid (**2**) undergoes a side reaction under the cationic polymerization conditions, that disturbs the probe response. Even though **2** shifts its fluorescence spectrum upon cationic polymerization of a monomer, its use as a fluorescent probe is rather limited only to a narrow range of monomer conversions, where the effect of the side reactions is small compared to the changes caused by monomer polymerization. Hence, **2** cannot be recommended for use as a probe, because **1** works better, while both these probes are obtained from the same reagents just by changing the reaction conditions.

Both **1** and **2** undergo side reactions under cationic polymerization conditions, which cause decrease of their fluorescence intensity with irradiation time. However, the intensity loss of the probe **1** caused by the side reactions is compensated in excess by over fivefold intensity increase caused by polymerization of the monomer. Hence, there is no risk the probe **1** will be bleached within the irradiation time required to cure the compositions based on vinyl ethers. In the case of slower curing coating formulations, such as the ones based on aliphatic epoxy monomers, the probe stability will need to be tested separately.

ACKNOWLEDGMENT

This research was supported by the Ministry of Science and Higher Education (Poland) within the research project: Iuventus Plus—0394/IP3/2011/71.

REFERENCES

1. Kabatc, J.; Jędrzejewska, B.; Pączkowski, J. *J. Appl. Polym. Sci.* **2006,** *99*, 207.
2. Bosch, P.; Peinado, C.; Martín, V.; Catalina, F.; Corrales, T. *J. Photochem. Photobiol. A Chem.* **2006,** *180*, 118.
3. Hu, S.; Popielarz, R.; Neckers, D. *C. Macromolecules* **1998,** *31*, 4107.
4. Jager, W. F.; Norder, B. *Macromolecules* **2000,** *33*, 8576.
5. Popielarz, R.; Sarker, A. M.; Neckers, D. C. *Macromolecules* **1998,** *31*, 951.
6. Jager, W. F.; Sarker, A. M.; Neckers, D. C. *Macromolecules* **1999,** *32*, 8791.
7. Sawicz, K.; Ortyl, J.; Popielarz, R. *Polimery* **2010,** *55*, 539.
8. Pączkowski, J. *Polimery* **2005,** *50*, 520.
9. Ortyl, J.; Sawicz, K.; Popielarz, R. *J. Polym. Sci. A Polym. Chem.* **2010,** *48*, 4522.
10. Ortyl, J.; Sawicz-Kryniger, K.; Galek, M.; Popielarz, R. *Przem. Chem.* **2010,** *89*, 1642.
11. Eckberg, R. P.; Marino, T. L.; Popielarz, R.; Neckers, D. C. *Proc. Rad. Tech* **1996,** *1*, 399.
12. Ren, K.; Serguievski, P.; Gu, H.; Grinevich, O.; Malpert, J. H.; Neckers, D. C. *Macromolecules* **2002,** *35*, 898.
13. Neckers, D. C.; Specht, K. G.; Feng, K.; Popielarz, R. (Spectra Group Ltd) US Patent 5,955,002, **1999.**
14. Strehmel, B.; Malpert, J. H.; Sarker, A. M.; Neckers, D. C. *Macromolecules* **1999,** *32*, 7476.
15. Ortyl, J.; Sawicz, K.; Popielarz, R. *Czasopismo Tech. Ser. Chem.* **2009,** *1-Ch*, 67.
16. Fringuelli, F.; Piermatti, O.; Pizzo, F. *J. Chem. Educ.* **2004,** *81*, 874.
17. Ortyl, J.; Galek, M.; Milart, P.; Popielarz, R. *Polym. Test.*, **2012,** *31*, 466.
18. Ortyl, J.; Popielarz, R. Modyfikacja Polimerów, Stan i Perspektywy w roku 2011, Ryszard Steller ed. (ISBN: 978-83-86520-09-1); Tempo s.c.: Wrocław, **2011;** p 423 (Eng).
19. Pączkowski, J.; Neckers, D. C. *Macromolecules* **1991,** *24*, 3013.