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Applicability of decahydroacridine-1,8-dione derivatives as fluorescent probes for monitoring of polymerization processes

Roman Popielarz, Shengkui Hu, D.C. Neckers *

Center for Photochemical Sciences, [1] Bowling Green State University, Bowling Green, OH 43403, USA

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Abstract

The behavior in polymerizable media of 3,3,6,6-tetramethyldecahydroacridine-1,8-diones substituted with aromatic rings at the 9- or 10-position has been studied. It has been found that the fluorescence of acridinediones shifts to shorter wavelengths upon polymerization of the medium, and this qualifies them as fluorescent molecular probes for monitoring the progress of polymerization processes. The shift in fluorescence is accompanied by a slow decomposition of the acridinediones to a fluorescent product under photopolymerization conditions. Acridinedione decay was slower than the polymerization of a typical photocurable formulation, thus allowing one to follow the progress of polymerization by fluorescence. The influence of the photoproduct on the monitoring of polymerization has been avoided by optimization of the monitoring parameters. Application of the acridinediones as fluorescent molecular probes for large scale applications in the coating industry is proposed. © 1997 Elsevier Science S.A.

Keywords: Fluorescent molecular probes; Photocurable coatings; Polymerization monitoring

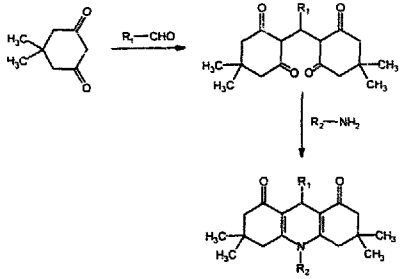
1. Introduction

Fluorescent molecular probes have been used to measure solvent polarity and viscosity [1,2], in biochemical applications [3,4], and in materials science [5]. Recently such probes have been used to monitor the progress of polymerization (including photopolymerization) [6,7]. This has been particularly suitable for the monitoring of polymerization in the thin layers used as photocurable coatings as well as for quality control of coating formulations [8,9]. The large scale application of fluorescent probes in monitoring processes with photocurable coatings now manufactured requires a non-expensive source. This prompted us to search for easily available fluorescent compounds that can be used as probes for free radical polymerization.

Decahydroacridine-1,8-dione derivatives have been reported to have high fluorescence efficiency and have been proposed as laser dyes. Several synthetic procedures have been developed [10]. A large abundance of aliphatic and aromatic amines and aldehydes available commercially and the easy synthesis make the acridinediones good candidates for large scale applications. Hence, in this paper we evaluate acridine-1,8-diones as fluorescent probes for monitoring free radical polymerization with an aim to their application in the coating industry.

2. Experimental details

Triethylene glycol diacrylate (TEGDA, from Sartomer) and Irgacure 907 (Ciba-Geigy) were used as received. The acridinediones studied were prepared as depicted in Scheme 1, following the procedure reported recently for other acridinediones of similar structure [11].



Scheme 1. Synthesis of the decahydroacridine-1,8-diones.

* Corresponding author.

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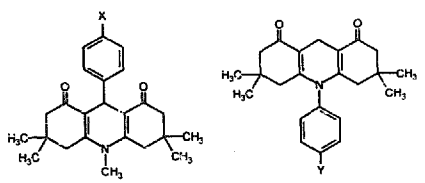
All of the fluorescence measurements were done with a fiber optic-based rapid scan fluorometer called CM-1000 Cure Monitor recently made commercially available from Spectra Group Ltd (1722 Indianwood Circle, Suite H, Maumee, OH 43537). The sample tested was positioned on the sensor head of the CM-1000 and measured in the absence of room light to avoid stray light interference. For recording the probe response of the acridinediones during the polymerization of TEGDA, fluorescence intensity ratios were taken automatically at 1 s intervals during the continuous irradiation of the sample with the excitation beam of the CM-1000 set at 360 nm. The samples for testing were prepared by squeezing a drop of the monomer containing the probe and the initiator between glass slides (25×75 mm^2) separated with 0.1 mm spacers on the sides. The area illuminated was about 5 mm in diameter (i.e. the size of the light beam coming out of the fiber optic cable of the CM-1000) and 0.1 mm thick (i.e. as set by the spacers). The incident light beam was at 45° angle relative to the sample surface, which prevented reflection of the excitation beam back to the spectrometer.

The acridinedione concentration in TEGDA was 0.10 wt.% which corresponded to a $(3.3–3.8) \times 10^{-3}$ M solution depending on the acridinedione. The concentration of the photoinitiator, Irgacure 907, was 1.0 wt.% and was identical in all of the samples tested.

The stability of the acridinediones under photopolymerization conditions was tested by exposure of a 0.1 mm layer of each solution between glass slides to non-filtered UV light from 2×400 W medium pressure mercury lamps at the distance of 20 cm. The fluorescence intensity was measured with the CM-1000 before and after exposure.

3. Results and discussion

In order to evaluate the factors that can influence the acridinedione characteristics and to study their applicability as fluorescent probes, two families of acridinediones were studied (Scheme 2). Triethylene glycol diacrylate (TEGDA) containing Irgacure 907 as the photoinitiator was chosen as the medium for testing. Diacrylates are typical components of commercial photocurable coating formulations, which makes TEGDA a good representative for evaluation of the probes response in the formulations used in practice.



1a: X = CN
1b: X = H
1c: X = OMe

2a: Y = CN
2b: Y = H
2c: Y = OMe

Scheme 2. The decahydroacridine-1,8-diones studied.

The acridinones **1a–1c** have the phenyl ring in non-conjugated position relative to the photoactive chromophore, while the other series **2a–2c** have the ring in conjugation with the fluorescing chromophore (Scheme 2). Thus, one can expect some difference in characteristics of the acridinediones **1a–1c** compared to **2a–2c**. What we were looking for was the influence of substitution on the fluorescence characteristics and the stability of the acridinediones, when used as probes in polymerizing media.

Only fluorophores that shift their fluorescence spectrum, or change their fluorescence characteristics in other ways upon change of micropolarity and microviscosity of the medium, can be used as probes for monitoring polymerization processes [12]. A variety of probes sensing their microenvironment have been developed [13], and the most sensitive probes usually have electron donating and electron withdrawing substituents appropriately positioned on a rigid aromatic ring system. Such probes have been shown to exhibit intramolecular charge transfer in the excited state, which changes the excited state geometry. So called twisted intramolecular charge transfer probes (TICT) are typical examples [6,13].

The fluorescing chromophore in the target acridinediones has no aromatic ring structure because there is an sp3 carbon at the 9-position. There are essentially two electron withdrawing groups (i.e. the carbonyl groups) in conjugation with the intramolecular amine functionality that serves as the electron donor. Hence, one can expect some sensitivity of the acridinediones to the molecular environment.

Fig. 1 shows the fluorescence spectrum of the acridinedione **1b** in TEGDA before and after polymerization. The observed spectral shift indicated that the acridinediones can be used as fluorescent probes if they meet the other criteria expected from the probes. However, in non-polar media, the acridinediones bleached slowly when exposed to UV radiation [14]. A decrease in fluorescence intensity after polymerization (Fig. 1) confirms this observation; the acridinediones studied are also partly bleached under the photopolymerization conditions. Therefore, we first studied

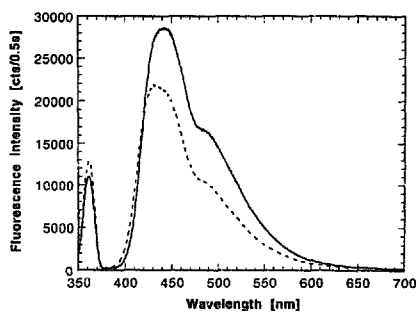


Fig. 1. Fluorescence spectra of acridinedione **1b** in TEGDA: (———) before polymerization, and (- - -) after polymerization.

Table 1
Characteristics of the acridinedione probes studied

Acridinedione	Center of emission (nm)	Relative stability	Relative sensitivity (%)
1a X ≡ CN	461	0.29	94
1b X ≡ H	459	0.29	66
1c X ≡ OMe	457	0.38	60
2a Y ≡ CN	467	0.13	105
2b Y ≡ H	473	0.19	207
2c Y ≡ OMe	474	0.25	270

acridinedione stability under the photopolymerization conditions.

In fact, most organic compounds undergo various photoreactions upon prolonged exposure to UV light, though on various time scales. For monitoring the progress of photopolymerization, bleaching of the probe is not a real problem provided that the probe is not bleached totally before completion of the polymerization. We assumed that if the fluorescence intensity of a probe does not decay more than five times within the exposure required to complete the polymerization, the probe is suitable for practical applications. In order to evaluate the photostability of the acridinediones studied, solutions of the acridinediones in TEGDA containing the photoinitiator were exposed to strong doses of UV light, and the relative stability was determined as the ratio of fluorescence intensity at the peak maximum after exposure to the intensity before exposure.

Table 1 lists the relative stability of the target acridinediones in TEGDA under overexposure conditions. We found that under the conditions used, the monomer was practically 3polymerized within the first 20 s of exposure, while the samples tested were exposed for 5 min. Even under such obvious overexposure conditions the fluorescence from the acridinediones **1a–1c** decayed less than five times, while in the case of **2a–2c** the stability was slightly lower (Table 1). Hence, when it is taken into account that the light dose used in this experiment was at least 15 times greater than the dose required to polymerize the monomer, it becomes evident that these acridinediones meet the stability requirement. In both families of the acridinediones tested, the methoxy substituted derivatives are the most stable, though the effect of substituents in the phenyl rings on stability is rather small. Moreover, the acridinediones substituted with phenyl at the 9-position (i.e. **1a–1c**) are slightly more stable than the acridinediones substituted with phenyl at the 10-position (i.e. **2a–2c**, Table 1). The minor influence of substituents on the stability of acridinedione creates some flexibility in the selection of amines and aldehydes for acridinedione synthesis. Thus, commercial factors like the availability of starting materials, or other factors, like the probe sensitivity, may be taken into account in the design of acridinedione probes for large scale applications, without concern for the probe stability.

Next, the probe response of the acridinediones during polymerization of TEGDA was studied. For monitoring changes occurring during polymerization processes with a probe, the fluorescence intensity ratio at two wavelengths is used [8]. Since the fluorescence spectrum shifts to shorter wavelength as the polymerization progresses, the intensity at the wavelength on the short wavelength side of the peak maximum increases, while the intensity on the long wavelength side decreases. Thus, the ratio of the former intensity to the latter intensity increases with the progress of polymerization and becomes an indicator of reaction progress. The ratio can be calibrated to measure the degree of monomer conversion or can be used without calibration as a quantitative measure for quality control of photocurable coatings as reported previously for the DASD-probe [8]. If the fluorescence from a probe decays owing to photodecomposition of the probe itself (or other photostimulated reactions of the probe with the components of the medium), without generating other fluorescing species, then the intensity at each wavelength becomes proportional to the immediate probe concentration, while the ratio of the intensities at two wavelengths is concentration independent. By rationing fluorescence intensities, the influence of the probe decay is cancelled. Thus, the fluorescence intensity ratio method was also applied in these experiments.

Preliminary tests of TEGDA photopolymerization using the acridinediones **2a–2c** as the probes gave unusual results (Fig. 2). When the monitoring wavelengths were selected so as to correspond to the peak half height on both sides of the fluorescence peak maximum, instead of a regular increase in the fluorescence intensity ratio with a plateau when the polymerization reached completion, as in the case of the DASD-probe [8], the ratio started decreasing immediately after reaching the maximum (Fig. 2). Such behavior indicates that the photodecomposition of the probe was accom-

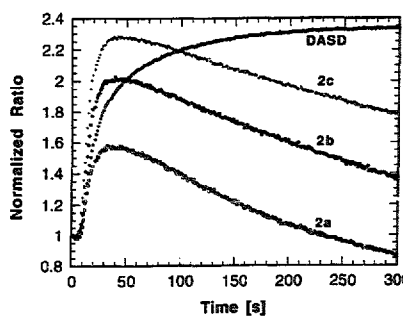


Fig. 2. Fluorescence intensity ratio change as a function of time for acridinediones **2a–2c** during photopolymerization of TEGDA, when the monitoring wavelengths are selected at the fluorescence peak half-height. (DASD = 5-dimethyamino-1-naphthalenesulfonyl-*N,N*-di(*n*-butyl)amide; the ratios were normalized to the same scale by dividing them by the starting ratio value before polymerization.)

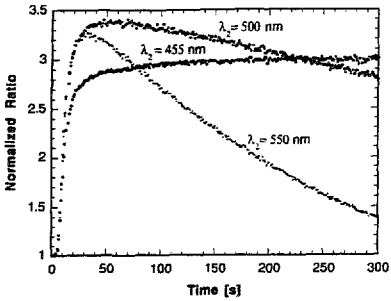


Fig. 3. Monitoring of TEGDA polymerization with probe **2b** at $\lambda_1 = 414$ nm and various second monitoring wavelengths.

panied by the generation of another fluorescing species whose fluorescence spectrum overlapped with the acridinedione emission at longer wavelengths. As a result, the intensity at the longer monitoring wavelength decayed more slowly than the intensity at the other wavelength, and the ratio decreased continuously after the polymerization had been completed. Such an artifact is not acceptable since one would be unable to tell whether the ratio corresponded to an undercure or an overcure condition just by measurement of a single ratio for a coating doped with the probe. However, it turned out that only the intensity at longer wavelength was affected by the fluorescent photoproduct while the short wavelength fluorescence intensity stayed intact. This suggested that if the second monitoring wavelength was selected sufficiently short, it might be possible to avoid the influence of the photoproduct on the intensity ratio. Fig. 3 shows polymerization profiles recorded with acridinedione **2b** under steady state irradiation conditions, monitored at different wavelengths. For relative comparisons absolute ratios were normalized to the same scale by dividing each ratio by the initial ratio before polymerization. In particular, the longer monitoring wavelength was varied, while the first wavelength was held constant at 414 nm. If the second monitoring wavelength is selected close to the fluorescence peak maximum, while still being on the longer wavelength side of the maximum (i.e. that corresponding to 455 nm in Fig. 3), a regular kinetic profile of the polymerization process is obtained.

Fig. 4 shows the progress of photopolymerization of TEGDA monitored by means of the fluorescence intensity ratios caused by steady-state irradiation with the excitation beam of CM-1000 at 360 nm. The first monitoring wavelength was optimized by subtraction of the normalized fluorescence spectra before polymerization from the spectra after polymerization, following the method described previously [8], while the second wavelength was selected to be as close as possible to the fluorescence peak maximum before polymerization. When the excitation beam of the CM-1000 was used as the curing source, the photopolymerization was practically complete within the first 50 s of irradiation, while the ratio remained stable up to 5 min (Fig. 4). In each of the cases regular polymerization kinetic profiles were obtained. This clearly indicates that by the appropriate selection of the monitoring wavelengths, artifacts resulting from the formation of a fluorescent photoproduct on the response of acridinedione probes can be avoided, thus making the acridinediones applicable for monitoring free radical photopolymerization. In the case of TEGDA, the optimized monitoring wavelengths for the ratio correspond to 414/450 nm for the acridinediones **1a–1c** and 414/455 nm for **2a–2c**. A shift of the kinetic profiles on the absolute ratio scale (Fig. 4) resulted from small differences in the emission wavelength position between the various acridinediones studied. For the same reason the second monitoring wavelengths for the acridinediones **2a–2c** had to be selected 5 nm longer than that used for acridinediones **1a–1c**, because the fluorescence maximum of **2a–2c** was shifted to a longer wavelength than that of **1a–1c**.

In order to compare the sensitivity of the individual acridinonediones, the relative sensitivity (Table 1) was defined by the following equation:

$$\text{Relative sensitivity} = \frac{r_m - r_0}{r_0} \times 100\%$$

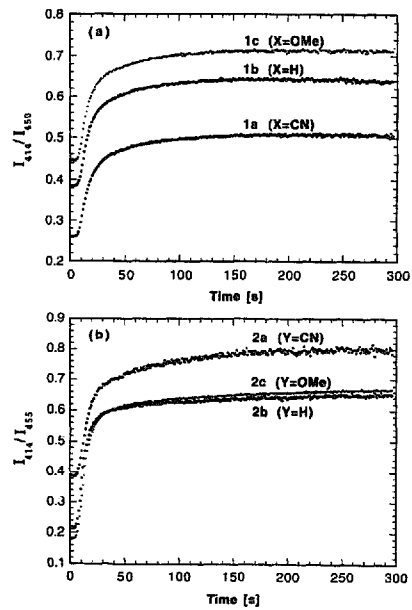


Fig. 4. Real-time monitoring of the progress of TEGDA photopolymerization with the acridinedione probes at optimized monitoring wavelengths (a) with the acridinediones **1a–1c**, and (b) with **2a–2c**.

where r_m is the fluorescence intensity ratio after polymerization, r_0 is the initial ratio before polymerization.

The effect of para substituents in the phenyl ring on probes 1a-1c is negligible. Sensitivity under the testing conditions increased from 60% to 94% in going from theelectron donating methoxy group to electron withdrawing cyano group, which is roughly 1.5 times (Table 1). This is not surprising since the phenyl ring at the 9-position is not conjugated with the fluorescing chromophore. In the case of 2a–2c the relative sensitivity of the methoxyphenyl derivative 2c is more than twice that of cyanophenyl acridinedione 2a at the wavelengths monitored. Moreover, the effect of the substituent on the sensitivity of the probes goes in the opposite direction in the series 1a-1c compared to 2a–2c. The electron donating methoxy group decreased the sensitivity in the former case, but increased it in the latter. The effect of the electron withdrawing cyano group is in the opposite direction (Table 1). This indicates that electron donors on nitrogen at the 10-position of the acridinedione chromophore enhance charge transfer from the nitrogen to the carbonyl group in theexcited statecausingan increase in sensitivity. The relative sensitivity of the probes depends on the monitoring wavelengths used and for the purpose of relative comparison. the same set of wavelengths was used within each family of the acridinediones tested. However, as the wavelengths used for the probes were optimized, the data can be compared to the sensitivity of other probes used for free radical polymerization at their optimized monitoring wavelengths. Thus. we determined that the relative sensitivity of the previously reported DASD [8] was 135% in the polymerization of TEGDA. which means that some of the acridinediones can be as sensitive as the DASD-probe or even more sensitive depending on substitution (Table 1), while their synthesis is easier than that of dansyl derivatives. Like DASD [8], the probes studied in this paper do not contribute color when added to a monomer. Therefore, they are suitable for large scale applications where colorless probes are needed, like for clear photocurable coatings.

4. Conclusions

Most of the acridinediones reported are sensitive enough to be applied as fluorescent probes for the monitoring of the free radical polymerization of acrylates. Even though the acridinediones are bleached upon prolonged exposure to UV iight, they are sufficiently stable under the conditions required to polymerize the monomer. Insensitivity to substitution on the phenyl ring in the 9-position creates flexibility in probe design. For example. by the appropriate selection of the aldehyde component. a vinylic functionality can be placed at that site such that the probe can be chemically bonded to the polymer without affecting significantly the probe response or stability, when compared to its non-functionalized anatog. Substitution at the nitrogen of the acridinedione chromophore effects probe response. Sensitivity can be maximized by substitution. with an electron donating group at that position.

The acridinediones represent a special case in that they generate a fluorescent photoproduct upon bleaching. Fortunately, the photoproduct has relatively weak fluorescence that overlaps with the fluorescence of the starting probe only at longer wavelengths. Thus, by the appropriate selection of the monitoring wavelengths. it becomes possible to avoid interference from the photoproduct with probe response.

Recently, decahydro-1,8-acridinediones were reported to be effective photoinitiators when combined with iodonium salts [15]. This suggests application of the acridinediones in performing two functions simultaneously, as initiator and as probe. When acridinediones are applied as co-initiators, the addition of other fluorescent probes to the formulation will be unnecessary for following polymerization progress, because most of the initiator remains in the polymer matrix when the polymerization is complete. If this is the remaining acridinedione. it can be used to determine the final monomer conversion by the fluorescent probe technology.

Acknowledgements

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