Direct Determination of Absolute Light Intensity in UV-Transmitting and UV-Dispersive Fluoro Polymer Tubes

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(Received November 25, 1986)

To determine the absolute light intensity (including the reflective, scattered, and incident light intensity) in a UV-transmitting and UV-dispersive fluoro polymer tube, a new chemical actinometer, DPOF system, was introduced which was composed of dilute potassium tris(oxalato)ferrate(III), 0.03 mol m^{-3}; 1,10-phenanthroline, 0.135 mol m^{-3}; and potassium oxalate, 1.5 mol m^{-3}. The overall light intensity was determined with a simple procedure based on a precise analysis of the photochemical kinetics of a DPOF system. The absolute intensities at 366 nm in the UV-transmitting and UV-dispersive Teflon FEP and Folaflon PVdF tubes were detected to be higher than that in a fused-silica tube of similar size while the incident light intensities in the former tubes were always lower than that in the latter. In addition, the dispersive effect of a Teflon FEP tube was rather independent of the wall thickness and the tube diameter under the experimental conditions studied, owing to its high dispersibility of light. The dispersive effect was much more remarkable for the Folaflon PVdF tube. The property of light transmission with dispersion, with the characteristic of antifouling, would make the fluoro polymer tubes useful for novel photoreactors in various areas.

Photoreactions offer promising new processes for synthesis, conservation, and energy conversion. Sterilization by means of irradiation with ultraviolet rays(UV-sterilization process), for example, has recently attracted the attention not only of the pharmaceutical, biological and medical fields, but also the hygienic and electronic engineering fields concerning the antibacterial pretreatment.[1] The UV-sterilization may well be expected to play an important role in the future. However, UV-sterilizers and conventional photochemical reactors have an intrinsic problem in that they generally need restricted reactor-wall materials which are light-transmitting and resistant to fouling. In addition, a precise estimatiom of the light intensity is required for a design and performance evaluation for high quality-control standards. Even though it is permissible to estimate the incident intensity with the use of a conventional potassium tris(oxalato)ferrate (III) chemical actinometer[2] for a photoreactor with negligible reflection and dispersion, it is generally inconvenient to apply the system to other types of photoreactors which have considerable light reflection and dispersion at the reactor wall.[3] The estimation of light intensity is the characteristic and principal parameter required for the design of photoreactors (as stated above); thus, information concerning both hardware and software has long been desired. These include information concerning of new materials, other than fused-silica glass for the reactor wall, which are light-transmitting and resistive to fouling, and of new chemical actinometer system which readily determines the number of reflective and dispersive as well as the incident photons.

In the 1970's it was discovered that some fluoro polymers transmitted ultraviolet light and were stable under long-term irradiation.[4] In 1984, Funayama and coworkers developed a new chemical actinometer[5] (DPOF sysyem, named after the initial letters of dilute, potassium, oxalato, and ferrate) which detects the reflective and dispersive light as well as the incident absolute intensity in any type of photoreactor. The DPOF system has also the characteristic that the analytical procedure is very simple: the extent of conversion can be spectrophotometrically determined without any additional treatment for the reaction product. In the present paper, we determined the absolute light intensity at 366 nm in two kinds of UV-transmitting and UV-dispersive fluoro polymer tubes, compared with that in a fused-silica tube, with the use of the newly developed DPOF chemical actinometer to get fundamental information of novel wall-materials for photoreactors.

Experimental

Materials. All chemicals used were of special reagent grade distributed by Nakarai Chem. Co. Solutions were prepared with distilled and deionized water. Fluoro polymer tubes and sheets made of copolymer of tetrafluoroethylene with hexafluoropentene (denoted as Teflon FEP afterwards) and poly(vinylidene fluoride) (denoted as Folaflon PVdF afterwards) were supplied by Chiyoda Kohan Co. and Showa Denko Co., respectively.

DPOF Chemical Actinometer. The composition of DPOF chemical actinometer is listed in Table 1, as introduced in a previous paper.[5] The stoichiometry of this actinometer, Eq.1, holds in the photolysis of dilute potassium tris(oxalato)ferrate(III) (species A) aqueous solution with 1,10-phenanthroline (species B, denoted as phen afterwards), and potassium oxalate (species S), based on a preliminary

Table 1. Composition of DPOF Chemical Actinometer

Component	C_{j0} / mol m^{-3}
A : $K_3Fe(C_2O_4)_3$	0.03
B : 1,10-Phenanthroline(phen)	0.135
R : $Fe(phen)_3C_2O_4$	0.0
S : $K_2C_2O_4$	1.5

study[6] of the interaction of potassium tris(oxalato)ferrate(III) with phen and potassium oxalate:

$$A + 3B \longrightarrow R + (3/2)S + I_g. \qquad (1)$$

Here, species R and I_g represent iron(II)oxalate-phen complex and carbon dioxide, respectively. Kinetics were examined at the wavelength 366 nm with the use of the apparatus combined with the batch-photochemical reactor and the spectrophotometric system which was a part of the stopped flow unit (as discussed in a previous paper).[5] The observed overall rate for reactant species A is

$$(-r_A) = 2\phi_1 I_a C_A/(C_A + k), \qquad (2)$$

where ϕ_1, I_a, and k represent the primary quantum yield of DPOF chemical actinometer, the absorbed light, and the ratio of the rate constants of elementary two steps, respectively. Equation 2 holds for any light field irradiated from an arbitrary direction. When we use the DPOF system with a negligible optical thickness (within a few centimeters for the case of irradiation at 366 nm), we can obtain the overall light intensity I_1 in a general form,[5] as

$$I_1 = \{K(1/Z_A - 1) - \ln Z_A\}/(K_1'\theta), \qquad (3)$$

where Z_A and θ represent the unconverted fraction of species A and the irradiation time, respectively. Values of K_1' and K, or ϕ_1 $(=K_1'/(2\alpha_A))$ and $k(=KC_{A0})$, experimentaly determined by changing the temperature from 20 to 40 °C are summarized in Fig. 1, (α_A and C_{A0} mean molar absorption coefficient and initial concentration of species A, respectively).

Experimental Apparatus and Procedures. To determine the absolute light intensity in fluoro polymer tubes, the monochromatic and parallel light of a 100 mm circular beam at 366 nm was irradiated on a sample tube by means of a parallel light irradiation unit L_1 (Ushio Electric Co., UI-501C) and a monochromator M_0 (JASCO, CT-25N) as shown in Fig. 2. The light source used was a 500 W superhigh-pressure mercury lamp(Ushio, USH-500D). The absolute light intensity (including the reflective and dispersive as well as incident light) was determined with the use of the DPOF chemical actinometer. On the other hand, the incident light intensity was determined with the use of the Parker's chemical actinometer.[2] The concentration of reaction product, iron(II)oxalate-phen complex, for the both chemical actinometers was quantitatively determined at the wavelength of 510 nm with the use of spectrophotometer (JASCO, UVIDEC-510). A neutral filter was used to change the radiant intensity. All of the procedures were carried out in a dark and constant-temperature room at 25 °C.

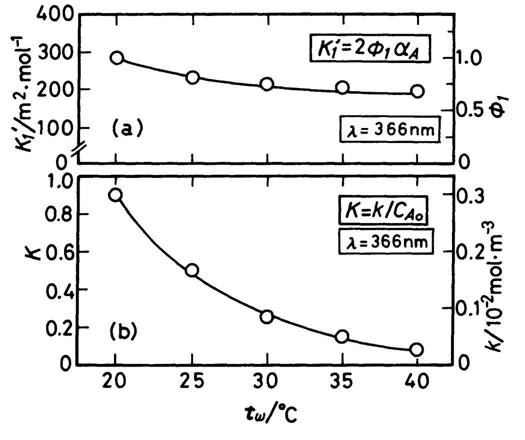

Fig. 1. Effect of temperature on (a) K_1' or ϕ_1, and (b) K or k for the irradiation at 366 nm.

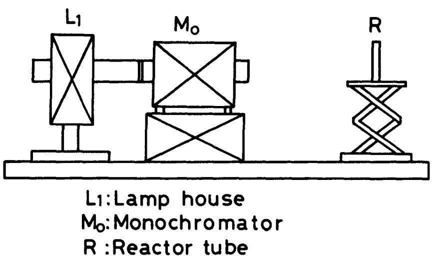

Fig. 2. Experimental apparatus for the measurement of overall and incident intensities in fluoro polymer tubes at 366 nm.

Results and Discussion

Light-Dispersibility of Fluoro Polymer Tubes. Figure 3 shows a spectral distribution of light transmitted through fluoro polymer films, where the transmitted intensity measured with a spectrophotometer (JASCO, UVIDEC-510) was restricted to a narrow beam in order to exclude most of the scattered light. We may well conclude from the figure that fluoro polymer is not as good a material as quartz for transmitting ultraviolet light, especially at shorter wavelengths. However, these fluoro polymer tubes are highly light-dispersive compared with a fused-silica tube as shown for the sample of a Teflon FEP tube in Fig. 4. The light-scattering patterns in a fused-silica tube and a fluoro polymer tube are schematically illustrated in Fig. 5. Figure 5(b) shows a more remarkable dispersion of light inside a fluoro polymer tube than a fused-silica tube in Fig. 5(a). We could not determine

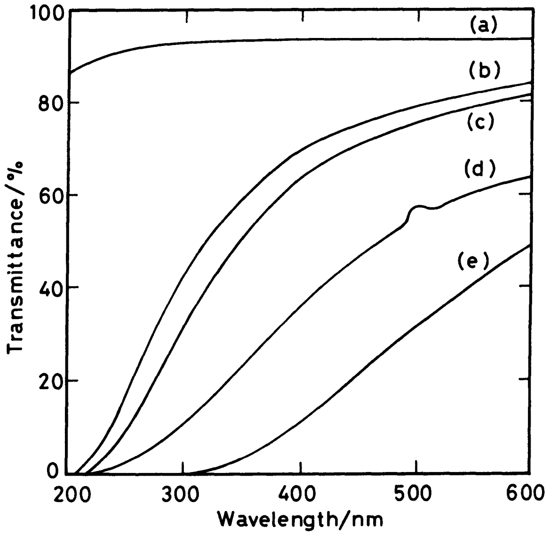

Fig. 3. Spectral distribution of light transmitted through a fluoro polymer film. (a) Fused-silica(thickness 1.0 mm), (b) Teflon FEP 1000 A(0.25), (c) Teflon FEP 1400 A(0.35), (d) Folaflon PVdF(1.0), (e) Teflon FEP 6000 L(1.75).

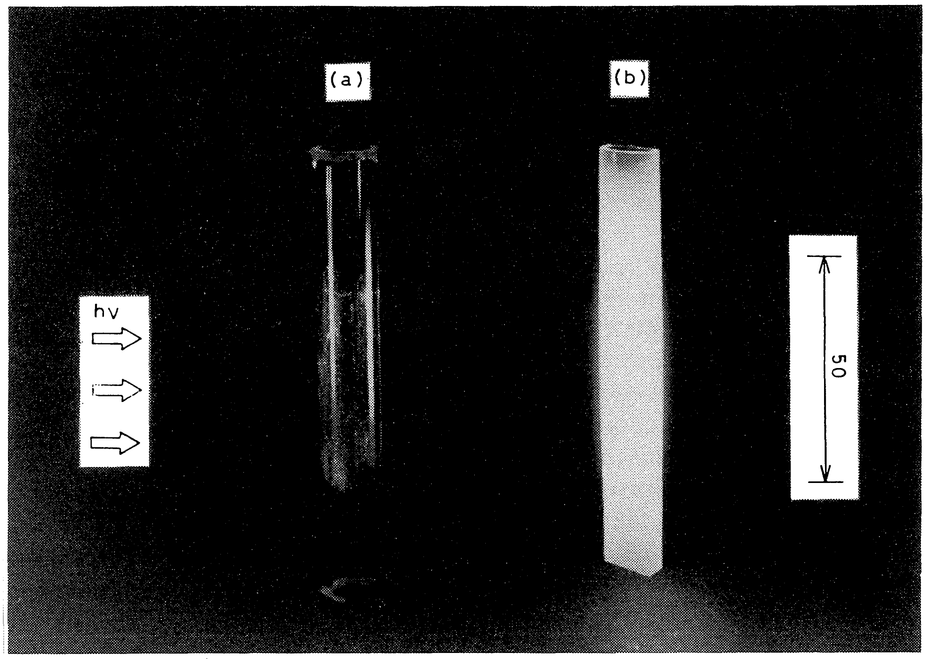

Fig. 4. Fused-silica tube (a) and Teflon FEP tube (b) irradiated with the parallel light from a superhigh-pressure mercury lamp.

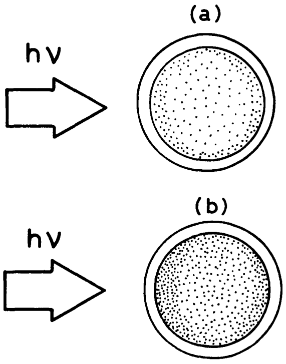

Fig. 5. Illustration of light-scattering pattern in a fused-silica (a) and a fluoro polymer tube (b).

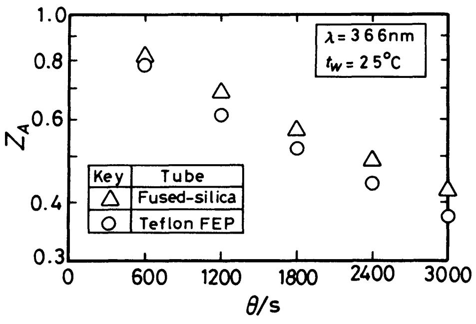

Fig. 6. Actinometry with the use of DPOF chemical actinometer in a fused-silica tube and a Teflon FEP tube having the same inside and outside diameters (10 mm×12 mm).

the absolute overall light intensity in this type of highly light-dispersive tube without the use of such a chemical actinometer as the DPOF system which detects reflective and dispersive as well as incident photons.

Determination of the Absolute UV-Intensity Involving the Effect of Dispersion. The overall light intensity, I_1, is obtained by substituting the relation of the fraction of A unconverted Z_A and irradiation time θ, and the values of K_1' and K into Eq. 3. An example of the experimental results of actinometry with the use of DPOF chemical actinometer is shown in Fig. 6. The figure indicates that the absolute light intensity I_1 is higher in a Teflon FEP tube than in a fused-silica tube having the same inside and outside diameters.

Determination of Incident UV-Intensity. The incident UV-intensity was determined with the use of conventional Parker's actinometer system. A batch analysis with the monochromatic irradiation (Fig. 7) gives

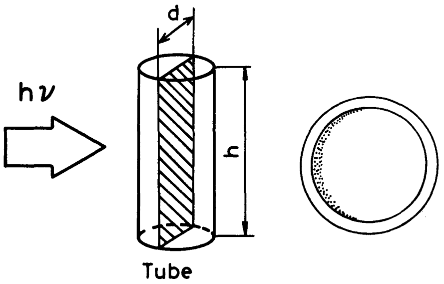

Fig. 7. Determination of incident intensity I_0 and illustration of light absorbed pattern.

Eq. 4 for the performance of the reaction

$$\phi_0 I_a = (S/V)\phi_0 I_0\{1-\exp(-\mu_l l)\} = (S/V)\phi_0 I_0 \quad (\mu_l l \gg 1), \qquad (4)$$

where $S(=h\cdot d)$, $V(=h\cdot \pi d^2/4)$, and ϕ_0 denote the irradiation area, the reaction volume, and the quantum yield of Parker's actinometer, respectively. The term,

$\mu_l l$, represents the optical thickness. The incident photons are perfectly absorbed near the incident wall under the condition of the conventional actinometry: $\mu_l l \gg 1$ as illustrated in Fig. 7. The incident light intensity I_0 was evaluated using

$$I_0 = \frac{(h\cdot \pi d^2/4)}{(h\cdot d)}\cdot\frac{1}{\phi_0}\cdot\frac{dC_R}{d\theta} = \frac{\pi d}{4}\cdot\frac{1}{\phi_0}\cdot\frac{C_R}{\theta}. \qquad (5)$$

An example of the experimental results for the actinometry with the use of Parker's actinometer is shown in Fig. 8 for the same sample tubes as shown in Fig. 6. The figure indicates that the incident intensity I_0 is higher in a fused-silica tube than in a Teflon FEP tube having the same inside and outside diameters.

Absolute Light Intensity in Fluoro Polymer Tubes. A comparison of the overall intensity I_1 obtained from Fig. 6 through Eq. 3 and the incident intensity I_0 from Fig. 8 through Eq. 5 tells us that Teflon FEP is a UV-transmitting and highly UV-dispersive material: the characteristics of light scattering can be evaluated well by means of the DPOF actinometry by comparing it with the conventional Parker's actinometry (as discussed above). Table 2 shows an example of the data for the overall light intensity I_1 and the incident light intensity I_0 in both the Teflon FEP and the Folaflon PVdF tubes compared with those in a fused-silica tube as a reference. Three levels of incident intensity were achieved by means of the neutral filter (as mentioned in the experimental section).

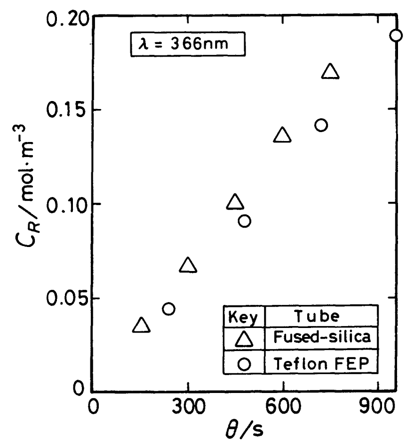

Fig. 8. Actinometry with the use of Parker's chemical actinometer in a fused-silica tube and a Teflon FEP tube having the same inside and outside diameters.

As for the case in the Teflon FEP tube, the overall light intensity I_1, is higher than in a fused-silica tube although Fig. 3 indicates the transmitted light apparently decreases to a considerable degree at 366 nm. In addition, it is noticeable that I_1 seems to be independent of the wall thickness and the tube diameter for the Teflon FEP tube. As for the Folaflon PVdF tube, the overall light intensity I_1 can also be inferred to be higher than that in a fused-silica tube of similar size, whereas it becomes lower as the wall gets thicker. The incident intensity I_0 in both the Teflon FEP and the Folaflon PVdF tubes is always lower than that in a fused-silica tube.

The characteristics of light transmission and dispersion of crystalline fluoro polymer are, in general, closely related to the crystallinity of polymer itself; the transmittance decreases with increasing crystallinity while dispersibility increases with it. First of all, from a comparison of the incident intensity I_0 in a Teflon FEP tube with that in a fused-silica tube having the same inside and outside diameters (Table 2), it is suggested that the crystallinity of fluoro polymer caused the decrease in transmittance in the former tube. Second, the fact that the overall intensity I_1 in a Teflon FEP tube is higher than that in a fused-silica tube whould indicate that the effect of dispersibility exceeds the effect of the decrease in the transmittance in the Teflon FEP tube. As for the Folaflon PVdF tubes, the effect of the decrease in transmittance owing to the crystallinity becomes more remarkable as the wall becomes thicker. Although the absolute values of data shown in Table 2 may slightly change with the sample tube selected, they would reflect the optical characteristics of fluoro polymer in general.

Figure 9 shows a comparison of the relative light intensities for the Teflon FEP and Folaflon PVdF tubes. The relative intensity in the fluoro polymer tubes studied is always higher than that in a fused-silica tube referred. It is remarkable that these effects seem to be practically independent of the wall thick-

Table 2. Overall Light Intensity I_1 and Incident Intensity I_0 in Fluoro Polymer Tubes at 366 nm Compared with Those in a Fused-Silica Tube

Tubes	Inside diameter	Wall thickness	I_1	I_0
	mm	mm	10^{-6} mol m^{-2} s^{-1}	
Teflon FEP	10	1.0	2.65	1.30
	10	0.5	2.51	1.35
	6	1.0	2.59	1.20
Fused silica	10	1.0	2.20	1.59
Folaflon PVdF	10	2.0	6.68	2.51
Fused silica	10	1.0	6.17	4.48
Folaflon PVdF	26	3.5	7.42	3.15
Fused silica	10	1.0	9.79	7.42

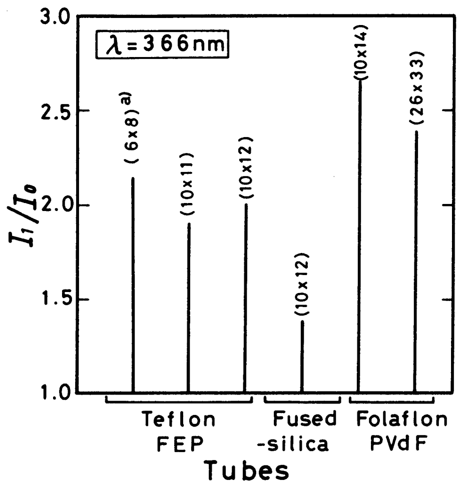

Fig. 9. Comparison of the relative light intensity in light dispersive fluoro polymer tubes.
(a) Inside diameter (mm)×outside diameter (mm).

ness and the tube diameter for a Teflon FEP tube under the experimental conditions studied. As for the Folaflon PVdF tube, the dispersive effect is much more considerable. Considering the observed results above, we conclude that UV-scattering effect is remarkable in these kinds of fluoro polymer tubes. The property of light transmission with dispersion, with the characteristic of antifouling, would make the fluoro polymer tubes useful for novel photoreactors in various areas.

Conclusion

To determine the reflective and scattered as well as the incident light intensity in UV-transmitting and UV-dispersive fluoro polymer tubes, a new chemical actinometer, the DPOF system, was introduced which was composed of dilute potassium tris(oxalato)ferrate, 0.03 mol m^{-3}; 1,10-phenanthroline, 0.135 mol m^{-3}; and potassium oxalate, 1.5 mol m^{-3}. The overall light intensity at 366 nm was determined with a simple procedure at 25 °C, based on the precise photochemical kinetics of the DPOF system.

The overall light intensities in UV-transmitting and UV-dispersive fluoro polymer tubes, Teflon FEP and Folaflon PVdF, were always higher than that in a fused-silica tube of similar size, although the transmitted light through the film apparently decreased to a considerable degree when observed with a restricted narrow beam. The incident intensity in the fluoro polymer tubes was always lower than that in a fused-silica tube. As for the Teflon FEP tube, the overall light intensity was practically independent of wall thickness and the tube diameter under the condition studied. The dispersive effect is much more remarkable for the Folaflon PVdF tube.

The authors wish to express their thanks to Associate Professor Nobumichi Ohno of Akita National College of Technology for his helpful discussion on the crystallinity of fluoro polymer. The present work was partially supported by a Grant-in-Aid for Scientific Research (59750752) from the Ministry of Education, Science and Culture. They would like to thank Chiyoda Cohan Co. for its financial assistance and offer of Teflon FEP tubes and sheets. Appreciation is also for Showa Denko Co. for the supply of Folaflon PVdF tubes and sheets. The assistance of student colleagues in Akita National College of Technology (Messrs. Hitoshi Kato, Yasumi Kaneya, Masayuki Watanabe, Shunji Tashiro, Katsuhiko Kikuchi, Akira Hashimoto, and Yoshikazu Yachi) is also appreciated.

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