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Material Performance

Mechanism of interaction of coumarin-based fluorescent molecular probes with polymerizing medium during free radical polymerization of a monomer

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ABSTRACT

The effect of an electron-donating and an electron-withdrawing substituent at 4-position and selected electron-donating substituents at the 7-position of coumarin structure on its ability to monitor free radical photopolymerization of diethylene glycol dimethacrylate by the Fluorescence Probe Technique (FPT) has been evaluated. It was found that the fluorescence spectra position of the probes studied depends only on changes of the medium polarity and is not sensitive to changes of microviscosity. The changes of microviscosity of the medium upon monomer polymerization can be monitored only with probes that have fluorescence in liquid monomer partially quenched by the substituents, using relative fluorescence intensity measured at peak maximum. Mechanism of how the probes work has been discussed. Moreover, photostability of the probes studied under free radical photopolymerization conditions has been evaluated and the factors affecting the photostability have been suggested. 7-Amino-4-trifluoromethylcoumarin was found to be the most sensitive and photostable probe under the conditions studied.

1. Introduction

Recently, fluorescence spectroscopy has found wide use in polymer chemistry. The high degree of advancement and continuing development of fluorescence spectroscopic techniques allows reaching into internal structure of polymers and explaining sophisticated details of their formation. One of the methods useful in the study of polymerization processes is the Fluorescent Probe Technique (FPT) [1,2]. It is a novel method used for monitoring changes occurring in polymerizing media by means of appropriate fluorophores, called fluorescent molecular probes, which change their fluorescence characteristics with changes occurring in the reaction medium. The phenomenon of the FPT method relies on the dependence of emission spectrum of fluorescent probes on physical properties of their surroundings [3–5]. The mechanism of interaction of the environment with the probe is usually quite complex, and many factors have impact on changes of the fluorescence spectrum, such as: polarity of the medium, relaxation rate of solvent around the probe molecules, conformational changes of the probe, the environment microviscosity, etc. [6]. The FPT method plays a crucial role in monitoring fast photopolymerization processes, where other less rapid methods fail. In the case of photopolymerization processes, photons emitted from a light source cause decomposition of the photoinitiator and fluorescence of the probe, both dissolved in the same composition. Upon absorption of photons, the probe molecules are excited to a higher electronic energy level to form appropriate excited states, which relax to the most favorable excited state conformation at a rate dependent on the instant value of microviscosity and polarity of the polymerizing medium. Hence, the changes in rheology of the medium caused by monomer polymerization, and in physicochemical properties of the system, such as the medium polarity, caused by conversion of more polar double bonds in the monomer into less polar single bonds in the polymer formed, translate into appropriate changes of fluorescence spectrum of the probe [7,8]. Understanding the mechanism of how the fluorescent molecular probes work is crucial for careful design of the probe structure to optimize their performance by selection of appropriate functional groups, attached to an aromatic ring at an appropriate distance and orientation relative to each other, and with appropriate electron-donating and/or

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electron-withdrawing characteristics [9,10].

To elucidate in detail what factors influence the probes' response and in what way (i.e., the mechanism of how the probes work), in this article, we have evaluated the effect of different substituents in the position 7 and 4 of coumarin ring on the probes' performance in monitoring progress of free radical polymerization of a model monomer - diethylene glycol dimethacrylate (DEGDMA).

2. Experimental section

2.1. Materials

Diethylene glycol dimethacrylate (DEGDMA) was purchased from Aldrich. The purity of this monomer was 95% and it was stabilized with 300 ppm of hydroquinone monomethyl ether. 2,2-Dimethoxy-2-phenylacetophenone from Sigma-Aldrich was applied as the photoinitiator. The structures of the probes studied are shown in Fig. 1. 7-Amino-4-trifluoromethylcoumarin and 7-amino-4-methylcoumarin were purchased from Sigma-Aldrich. The other derivatives of 4-(trifluoromethyl)coumarin and 4-methylcoumarin were synthesized according to Fig. 2 and Table 1 using the procedures described previously [11–14]. Moreover, commercial fluorescent probe: 7-diethylamino-4-methylcoumarin (Coumarin 1 from Sigma-Aldrich) was applied for comparison.

2.2. Sample preparation

The starting compositions were prepared by dissolution of the photoinitiator and a probe in DEGDMA monomer so as to obtain a concentration 5.0×10^{-3} mol/dm^3 of the probe and 1% by weight of the photoinitiator. Each sample contained the same probe and photoinitiator concentrations. The vials with freshly prepared mixtures were sonicated in an ultrasonic bath for two minutes to speed up dissolution of the ingredients, and then the compositions were stored in the dark until used. A 0.1 mm layer of each composition was prepared by squeezing two drops of the composition between glass slides separated by appropriate spacers [Fig. 3]. So-prepared samples were placed on the sensor head in horizontal position to avoid shift of the composition between slides during the measurement. All measurements were done at constant temperature (25 °C).

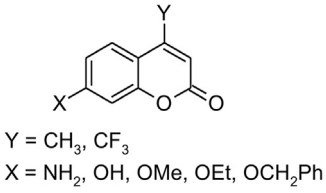

Fig. 1. The fluorescent probes studied.

2.3. Apparatus

For the measurements, a stationary cure monitoring system was applied. The system was composed of a miniature CCD spectrometer (EPP2000C from StellarNet); a specially designed sample compartment with a sensor head (similar to that depicted in Ref. [15]) equipped with an ultraviolet light emitting diode (UVTOP315-BL-TO39, Roithner LaserTechnik GmbH, Austria), which was supplied with constant current of 20 mA from a stabilized constant current source, and PMMA fiber optic cable with 2 mm core, which carried the light from the measurement site to the spectrometer. Additionally, the sample compartment was equipped with a specially designed thermostatic head (shown in Fig. 4) equipped with an electronically-controlled Peltier cell, which acted as a heat pump, pumping heat from inside out when the room temperature was higher than 25 °C or in the reverse direction when it was lower, so as to maintain the temperature inside the compartment constant. The spectral data were collected by a PC microcomputer in real time, directly into Excel spreadsheets using appropriate VBA macros to control the spectrometer.

3. Results and discussion

Unsubstituted coumarin shows no detectable fluorescence at room temperature in any solvent, so it cannot be used as a fluorescent probe. Substitution of coumarin with electron-donating and/or electron-withdrawing substituents that do not quench fluorescence usually induces coumarin fluorescence and increases its sensitivity to changes occurring in the probe environment. For example, the natural product umbelliferone, which is 7-hydroxycoumarin, or commercially available Coumarin 1, which is 7-dimethylamino-4-methyl-coumarin, are well known as highly fluorescent compounds. For application as fluorescent probes for monitoring progress of polymerization processes, the coumarin derivatives have to exhibit both high fluorescence efficiency and high sensitivity to changes occurring during the polymerization process. To elucidate how the type and position of substituents on the coumarin ring structure effect its performance, we studied two families of coumarins: derivatives of 4-methylcoumarin and 4-(trifluoromethyl)coumarin, substituted with a series of electron-donating substituents (X) at the position 7, (Fig. 1).

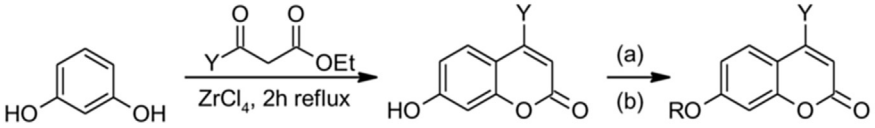

Fig. 2. Synthesis of 7-hydroxy- and 7-alkoxy-coumarins (Y = CH_3, CF_3).

Table 1
Experimental conditions used for the synthesis of 7-alkoxycoumarins.

R	Reagents (a)	Reaction conditions (b)
Me	Dimethyl sulfate, aq. NaOH	reflux 2 h
Et	Ethyl iodide, aq. NaOH, benzyltributylammonium chloride (catalyst)	reflux 4 h
$PhCH_2$	Benzyl chloride, K_2CO_3, EtOH	reflux 3 h