

New fluorescent hyperbranched polymeric sensors as probes for monitoring photopolymerization reactions



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ABSTRACT

Two polychromophoric dansyl hyperbranched fluorescent probes (HBPs) have been used as fluorescent sensors to follow photopolymerization reactions of acrylic monomers through fluorescence monitoring. Simultaneously, photo-DSC measurements were conducted. The combined data obtained by both techniques allowed to measure precise and adequately the kinetics of the systems. Differences are found depending on the composition of the formulation, but no depending on the probe inserted in the systems. The behavior and sensitivity of the functional HBP's have been compared with their low molecular weight monochromophoric reference compounds. Hyperbranched polychromophoric probes showed the same sensitivity towards the process than the monochromophoric probes, confirming the high sensitivity of the hyperbranched probes. Also, the data obtained by fluorescence allow distinguishing the different steps involved in the mechanism of a radical crosslinking polymerization, which could not be observed only with calorimetric measurements. The advantages of the functional HBP fluorescent probes towards their low molecular weight homologues are discussed.

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1. Introduction

Fluorescent probes are perhaps the most popular and powerful tools that can be used to understand the physical and chemical processes that occur at the molecular level. It is possible because their fluorescence is sensitive to the polarity, mobility and/or (micro)viscosity of the molecular environment in which the probe molecules are located. This sensitivity can be achieved via a number of physical interactions: intramolecular reorientation (such as molecular rotors [1] and intramolecular excimer formation [2]), diffusion-controlled interactions [3], and solvent-dipole stabilization of the excited state of the probes (charge-transfer probes [4,5]). The physical origin of the sensitivity to the molecular environment, for a given probe molecule, is not necessarily determined by only one of the aforementioned interactions [6].

Fluorescence probes are usually designed to examine specific properties of their immediate environment or microenvironment by means of a shift in the maximum of their emission or changes in their emission intensity. Because its simplicity, the measuring of the fluorescence of a probe appears an ideal method to monitor processes occurring during polymerization. Probe fluorescence changes accompanying polymerization are related to both changes in the microviscosity and in the local polarity of the medium surrounding the probe. These changes are induced by both the growth of polymer chains and the resulting structure of the polymeric materials.

Photopolymerization reaction is a very useful technique to obtain polymeric materials and it has been extensively used since more than 40 years. It is still highly interesting and attracts a large attention in materials science. Elucidation of its mechanism and kinetics is of crucial importance for the development of new monomers [7], photoinitiators [8] and materials, such as optoelectronic materials [9], biomaterials [10], nanocomposites [11], IPNs [12], holographic recording [13], multilayer hydrogels [14], and many more. With the emergence of LEDs as new irradiation sources new environmental and economic possibilities have put increasing interest in the field [15,16].

Different types of fluorescent probes have been developed for monitoring photoinitiated polymerization processes, but charge transfer (CT) probes are probably the most used, since their photochemical properties are very convenient in terms of emission quantum yield, absorption and emission wavelengths. Recent examples have been published [17]. Fluorescence monitoring offers some advantages compared to others, such as DSC and FTIR, due to its high sensitivity, selectivity and because it is a non-invasive technique. Moreover, monitoring of UV-curing processes may be committed on line which is relevant from an applied point of view. Additionally, as the probe remains inside the material after the polymerization, its presence will allow the detection of future changes in the polymer structure, properties or morphology, such as degradation [18], swelling [19], thermal transitions [20] or mechanical stress [21,22].

In this work we study the behavior of two newly synthesized fluorescent hyperbranched polymeric probes functionalized with dansyl groups as sensors of viscosity, when applied to the monitoring of acrylic photopolymerizations. Their synthesis and properties have been recently described by us [23] and their photophysical behavior resulted very

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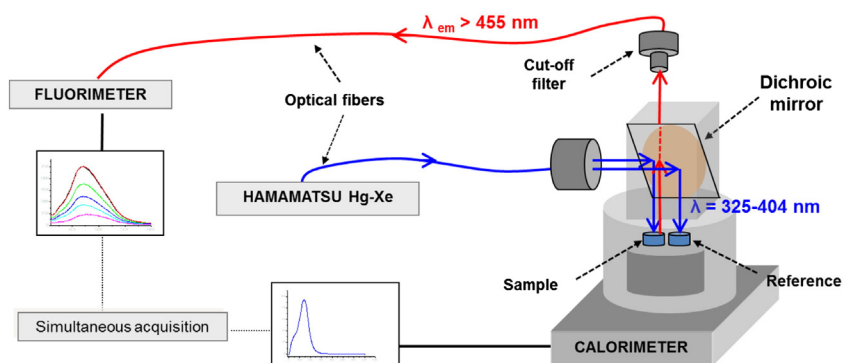


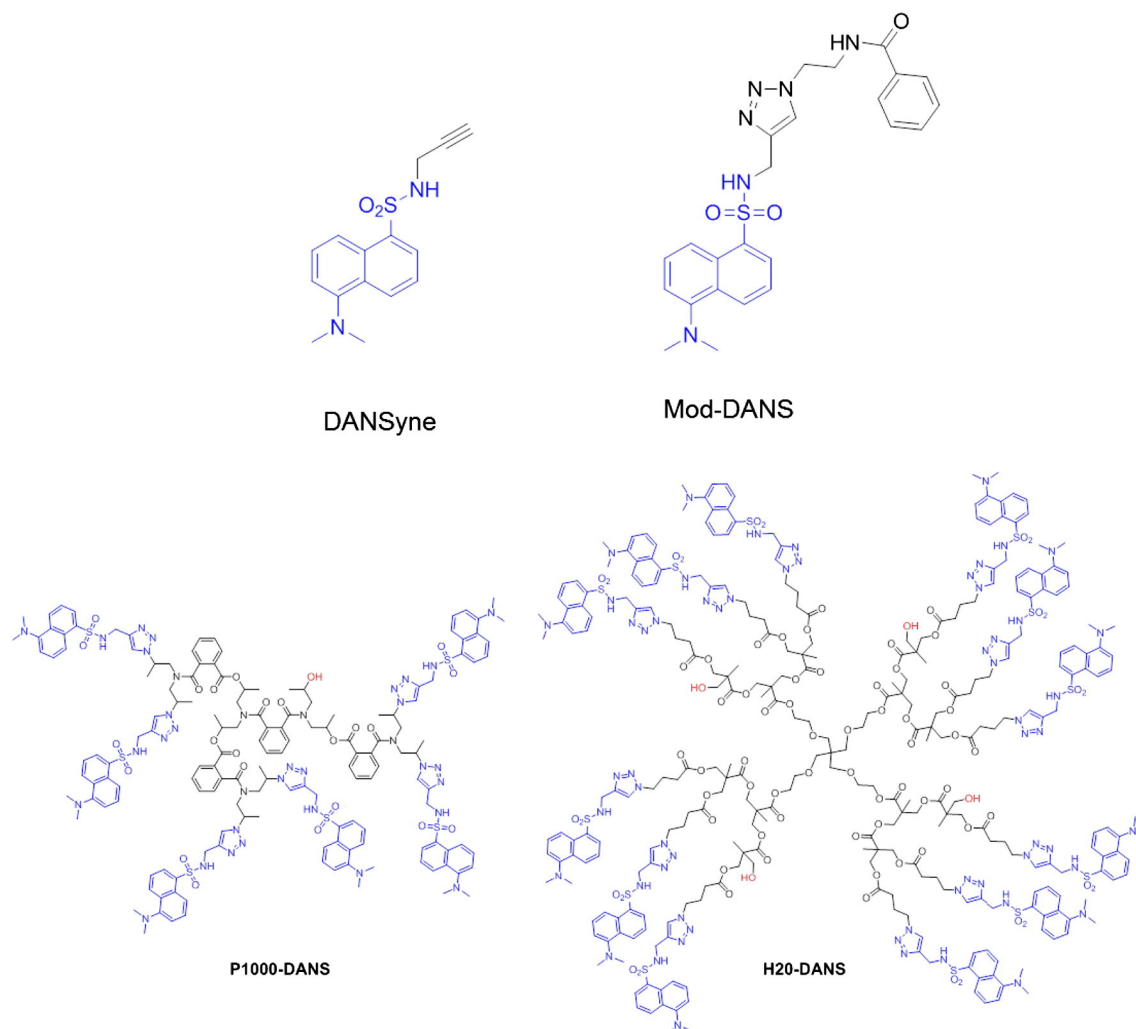
Fig. 1. Set-up for measurements. DSC-fluorimeter coupling.

convenient to use them as sensors, because no quenching effects were observed when the fluorescent group was attached to the hyperbranched macromolecular skeleton. To the best of our knowledge, this is the first time that polychromophoric probes are used for accurately follow polymerization reactions. We report herein the studies on the copolymerization reaction between mono- and difunctional methacrylates, and on the homopolymerization of dimethacrylates of variable chain length, and conclusions are obtained combining the data from fluorescence and DSC measurements.

2. Experimental

2.1. Materials

Monomers: 1,6-hexanediol dimethacrylate (HDDMA), 2-hydroxyethylmethacrylate (HEMA), ethylenglycol dimethacrylate (EGDMA), diethylenglycol dimethacrylate (DEGDMA), triethylenglycol dimethacrylate (TEGDMA) and polyethylenglycol dimethacrylate (PEGDMA₅₅₀) were from Aldrich and used as received. Photoinitiator



Scheme 1. Structures of the probes.

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