Polymer Testing 32 (2013) 708–715

Contents lists available at SciVerse ScienceDirect

Polymer Testing

journal homepage: www.elsevier.com/locate/polytest

Material characterisation

Applicability of aminophthalimide probes for monitoring and acceleration of cationic photopolymerization of epoxides

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ARTICLE INFO

Article history:
Received 27 January 2013
Accepted 11 March 2013

Keywords:
Fluorescent molecular probes
Photopolymerization
Cure monitoring
Photosensitizers

ABSTRACT

Applicability of a series of 5-substituted 3-amino-4-cyano-phthalimides as novel fluorescent probes for monitoring and acceleration of cationic photopolymerization of epoxy monomers has been studied. The performance of the following probes/accelerators were evaluated in ring opening photopolymerization of 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (CADE) monomer: 3-amino-4-cyano-5-phenylphthalimide, 3-amino-5-(4-carboxyphenyl)-4-cyanophthalimide, 3-amino-5-(4-chlorophenyl)-4-cyano phthalimide, 3-amino-4-cyano-5-(4-methoxyphenyl)phthalimide, 3-amino-5-([1,1′]biphenyl-4-yl)-4-cyanophthalimide and 3-amino-4-cyano-5-(2-naphthyl)phthalimide. It has been found that these probes are stable under the cationic photopolymerization conditions of CADE and sensitive enough to enable monitoring the entire range of monomer conversions by Fluorescence Probe Technology, while 3-amino-4-cyano-5-(4-methoxyphenyl) phthalimide showed the best performance. At typical probe concentrations, all of the probes studied accelerated the cationic photopolymerization of CADE up to seven times compared to the compositions without any probe. Moreover, these probes shift their fluorescence spectra to longer wavelengths upon polymerization of CADE, that is in the opposite direction to most fluorescent probes. This unusual behavior of the aminophthalimide probes in CADE monomer has been explained on the basis of their solvatochromic data.

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1. Introduction

A lot of fluorescent organic compounds have found practical applications in science and technology as fluorescent molecular probes and labels [1–3]. Among them, the best known are xanthenes, coumarins, naphthalimides, cyanines, various arylazoles, acridines and phenazines [4]. Fluorescent probes are the most powerful tools that can be used for measurement of bulk solvent polarity or viscosity [5,6], as well as for monitoring changes of these properties in the probe surroundings, occurring at a molecular level. This is possible, because fluorescence characteristics of most of fluorescent probes is sensitive to changes in solvation of the excited and ground states of the probe molecules, which in turn depends on the polarity and mobility of the molecules present in the probe surroundings. One important application of fluorescence probes is for monitoring progress of polymerization processes, especially photopolymerization [7,8]. When a fluorescent probe is dissolved in a polymerizing medium, the probe responds to changes occurring in the system by changing its fluorescence characteristics. These changes are easy to measure quantitatively with an appropriate fluorimeter. Therefore, Fluorescence Probe Technology (FPT) is a quick and effective method for photopolymerization monitoring and quality control of photocurable coatings [9,10].

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0142-9418/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymertesting.2013.03.009

Since the first application of fluorescent probes for following progress of rapid photopolymerization processes, a lot of fluorescent probes suitable for monitoring free radical polymerization have been developed. In the case of cationic polymerization, however, only a few probes can resist harsh cationic polymerization conditions [11–13]. Most of the known fluorescent probes suitable for monitoring free radical photopolymerization, usually do not perform well in cationic photopolymerization systems, because of probe interaction with the strong protic acid generated during the photopolymerization process. Therefore, the synthesis of highly fluorescent compounds that would perform well in cationic polymerization systems has gained considerable interest.

The most sensitive fluorescent probes usually contain an amino group in their structure in combination with an appropriate electron-withdrawing substituent that generate an intramolecular electron transfer in the excited state, necessary for high probe sensitivity [14,15]. Moreover, the presence of an amino group in the structure of a fluorophore usually boosts its fluorescence quantum yield. Hence, replacement of the amino group with another electron-donating substituent usually worsens the probe performance. On the other hand, if a fluorescent probe containing an amino substituent is applied for monitoring of progress of cationic photopolymerization, the basic amino groups neutralize strong protic acid generated as the cationic polymerization initiator until all of the groups have been protonated, which usually results in a significant delay of the polymerization start, considered not acceptable for some technological applications [16]. Recently, we have discovered that some amino derivatives of phthalimide, containing an electron withdrawing cyano group in the vicinity of the amino group, show very good probe response in monitoring of cationic photopolymerization of vinyl ethers [17]. An important feature of these probes is that the delay in the cationic polymerization start, caused by the probe, is insignificant (i.e., less than 5% of the induction time increase at the typical probe concentration of 0.1% by weight), while the aminophthalimides accelerate the rate of cationic photopolymerization of vinyl ethers. Simple synthesis, good probe response under cationic polymerization conditions and the accelerating effect of the aminophthalimides makes them good candidates for mass applications in the coatings industry for simultaneous monitoring and acceleration of the production of coatings cured by cationic photopolymerization. However, the question arises whether these probes will perform equally well in other cationically-cured systems, in particular in cationic ring-opening polymerization of epoxides, which are the other type of monomers used for coatings cured by the cationic polymerization mechanism. Vinyl ethers are very rapidly polymerizing monomers, while the epoxides polymerize much more slowly, so the epoxide-based photocurable formulations are usually exposed to much higher doses of UV light than that required for vinyl ethers to complete the photopolymerization process. Many organic fluorophores are decomposed on prolonged exposure to UV light. Hence, another question that needs to be answered is whether the aminophthalimide probes will be stable enough in the epoxy-systems to enable monitoring entire conversion range of the monomers before the probe has been photolyzed. In this paper, the posed questions are answered. Moreover, an unusual behavior of these probes during cationic photopolymerization of 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate (CADE) monomer is explained on the basis of their solvatochromic characteristics.

2. Experimental section

2.1. Materials

3,4-Epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (CADE from Sigma Aldrich) and diphenyliodonium hexafluorophosphate ($Ph_2I^+PF_6^-$, Alfa Aesar) were applied as a model epoxy monomer and a cationic photoinitiator, respectively. Triethylene glycol divinyl ether (TEGDVE from Sigma Aldrich) was applied as a reference monomer for comparison with CADE. The aminophthalimide derivatives shown in Fig. 1 were synthesized and studied. All of these probes were prepared by the two-step procedure outlined previously [17].

2.2. Monitoring of the cationic photopolymerization by FPT

The compositions were prepared by dissolution of the photoinitiator and each probe in CADE monomer in such proportions as to obtain the concentrations $2.3 \cdot 10^{-2}$ mol/dm^3 (about 1% by weight) of the photoinitiator and $5 \cdot 10^{-3}$ mol/dm^3 of the probe, unless specified otherwise. The same probe and photoinitiator concentrations were applied for the reference composition based on TEGDVE. Before measurement, two drops of the composition were placed in the middle of a microscope slide (75 mm × 25 mm × 1 mm), equipped with two 0.09 mm thick spacers located on the slide sides, and the slide was covered with another slide to form a sandwich structure. The sandwich structure was kept together using paper clips placed on the sides.

The cure monitoring system and measurement parameters were analogous to those described in detail previously [17], except that longer irradiation times were applied. All measurements were done at ambient temperature (25 °C).

2.3. Monitoring of cationic photopolymerization by Photo-DSC

The compositions used for PDSC studies were the same as those used for FPT. The PDSC measurements were performed under isothermal conditions at room temperature (25 °C), using a TA 100Q Differential Scanning Calorimeter (TA Instruments, USA), equipped with a 200 W OmniCure S2000 medium-pressure mercury lamp (Exfo-Omnicure, Canada). The average irradiation power was 50 mW/cm^2. The composition samples (about 6 mg ± 2 mg) were polymerized in open aluminium pans (about 5 mm in diameter). The calorimeter was equipped with a quartz window that let UV light pass through, and appropriate lenses which focused the UV light onto the sample and a reference pan. Although the cationic photopolymerization is not sensitive to oxygen, the sample space was kept under nitrogen to avoid any potential side reactions that could

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