

NEAR-IR TWO-PHOTON INDUCED POLYMERIZATIONS USING EITHER BENZOPHENONE OR THIOXANTHONE-BASED PHOTOINITIATORS

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Introduction

Two photon induced photopolymerization of acrylates using a light source in the near infrared range of the spectrum has become an attractive alternative to the traditional ultraviolet cure since greater cure depths as well as higher resolutions are now possible. Initiator systems for these types of polymerizations usually require highly fluorescent chromophores which are needed to excite the initiator.¹⁻⁴ Disadvantages of these dyes are that they usually have to be custom made and that they leave a highly colored product. Additionally, in order to incorporate them into the monomer formulation, they sometimes need to be dissolved in organic solvents, which may be undesirable.

We present our research on traditional UV initiators for use in near-IR polymerizations. These systems do not rely on additional chromophores and consequently the final products are clear and most are colorless. Our study examined type I initiators (1-hydroxycyclohexyl phenyl ketone **1** and 2,2-diethoxyacetophenone **2**) and type II initiators (benzophenone **3**, Esacure TZT **4** (a blend of 4-methylbenzophenone and 2,4,6-trimethylbenzophenone), 4,4'-bis(diethylamino)benzophenone **5**, 2-amino-5-nitrobenzophenone **6** and isopropylthioxanthone **7** (a mixture of the 2- and 4-isomers)) with triethanolamine as co-initiator (see **Figure 1**).⁵

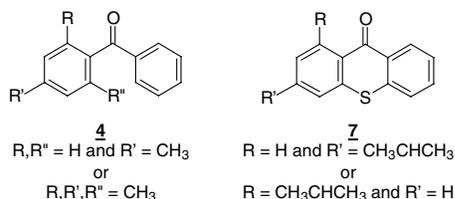


Figure 1. Chemical structures of two of the studied initiators.

Experimental

Materials. 2-Amino-5-nitrobenzophenone, benzophenone, 4,4'-bis(diethylamino)benzophenone, 2,2-diethoxyacetophenone and isopropylthioxanthone were purchased from Aldrich Chemical Company. Esacure TZT (a blend of 4-methylbenzophenone and 2,4,6-trimethylbenzophenone), ethoxylated (15) trimethylolpropane triacrylate (SR-9035) and dipentaerythritol pentaacrylate (SR-399) were obtained from Sartomer and were used without the removal of inhibitor (see **Figure 2**). 1-Hydroxycyclohexyl phenyl ketone (Irgacure 184) was purchased from Ciba Specialty Chemicals and triethanolamine was obtained from Eastman Kodak Chemicals and used without further purification.

Formulation. SR-9035 [2.00 mL, 2.226 g, 2.326 mmol] and SR-399 [0.280 g, 0.534 mmol] were measured into a vial and stirred until homogeneous. The initiator (approximately 2%, see **Table 1** for the amounts) was added and the mixture was heated to 50 °C for 15 minutes to aid in dissolution. Finally, triethanolamine [0.073 g, 0.482 mmol] was added and stirred to complete the formulation.

Curing. The monomer sample was poured into a 1 cm path-length poly(styrene) cuvette which was mounted in a confocal geometry with the focal point beyond the sample. The sample was cured using a titanium sapphire laser operating at 800 nm with a repetition rate of 500 Hz at 90 fs pulse duration with an average power at the sample of approximately 400 mW. Curing time was a maximum of 4 minutes.

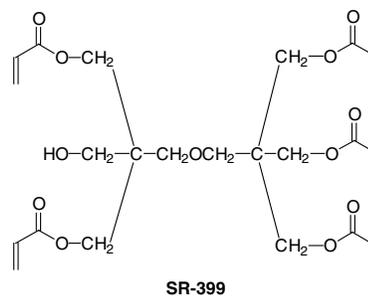
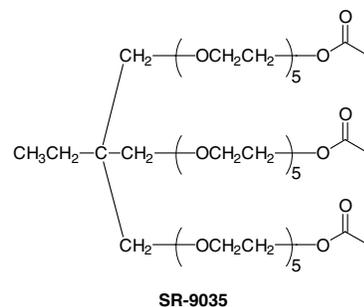


Figure 2. Chemical structures of the two monomers.

Results and Discussion

Two sets of seven formulations were made by combining the monomers with an initiator and either including (for the first set) or omitting (for the second set) the addition of triethanolamine. These samples, along with two control samples (the monomers with and without triethanolamine), were poured into 1 cm path-length poly(styrene) cuvettes and cured for four minutes. The resulting cured polymer weights and average diameters are shown in **Table 1**.

It is apparent that for this monomer system, an amine co-initiator may not be necessary, even with type II initiators. These results can be explained by the fact that the initiator is able to extract an α -hydrogen found in the ethylene glycol units in SR-9035 and therefore no longer requires an amine.⁶ Since amines tend to cloud and color polymer products over time, the advantage of eliminating this compound is obvious.

Table 1. Amount of Initiator Added as well as the Diameter and Weight of Rods Written in the Cuvette (All Rods Were 10 mm in Length Except Where Noted, -- Indicates the Monomer Did Not Cure)

	Initiator	Amount of Initiator	Average Cured Rod Diameter (mm) and Weight (g)	
			With Amine	Without Amine
1	1-Hydroxy cyclohexyl phenyl ketone	0.046 g (0.223 mmol)	1.08 mm (3.85 mm long) 0.003 g	--
2	2,2-Diethoxy acetophenone	45 μL (0.223 mmol)	--	--
3	Benzophenone	0.041 g (0.222 mmol)	2.59 mm 0.048 g	--
4	Esacure TZT	40 μL	3.00 mm 0.096 g	--
5	4,4'-Bis(diethyl amino) benzo phenone	0.073 g (0.223 mmol)	6.36 mm 0.336 g	4.54 mm 0.214 g
6	2-Amino-5-nitro benzophenone	0.054 g (0.223 mmol)	4.98 mm 0.266 g	--
7	Isopropyl thioxanthone	0.057 g (0.224 mmol)	6.28 mm 0.337 g	4.06 mm 0.161 g
	Control	None	--	--

While two of the initiators are liquids (Esacure TZT and 2,2-diethoxyacetophenone), the other initiators were chosen for their low melting points and were easily dissolved into the monomers by warming the samples at 50 °C for 15 minutes. Consequently, the need for organic solvents was avoided. Additionally, all the initiators produced clear and colorless samples except for 4,4'-bis(diethylamino)benzophenone and 2-amino-5-nitrobenzophenone which produced clear and pale yellow products. Finally, most initiators did not fluoresce during the curing process except for 4,4'-bis(diethylamino)benzophenone which produced a blue-green light and isopropylthioxanthone which fluoresced purple.

Conclusions

A new photoinitiator system for two-photon induced polymerizations has been presented with several advantages over currently used initiator systems. Perhaps the most unique feature is that these systems do not rely on dyes and therefore do not fluoresce during polymerization. Consequently, a deeper cure is now possible and the final polymer is not brightly colored. Additionally, the initiators are either liquids or solids with low melting points which allows easy incorporation into monomers without the use of solvents. Another advantage is that these initiators are commercially available and no complex or costly synthesis is needed.

Most notable of the initiators tested were Esacure TZT for its ease of incorporation into monomer formulations and isopropylthioxanthone for its enhanced curing properties. Both initiators also resulted in colorless products.

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