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Quinoxaline derivatives as photoinitiators in UV-cured coatings

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Abstract

Photopolymerization of multifunctional acrylates with a series of quinoxaline derivatives as photoinitiator with *N*-methyldiethanol amine (MDEA) has been investigated by real-time Fourier transform infrared spectroscopy (RT-FTIR). The formulations were also coated onto tracing paper and cured by using Mini-UV-Cure unit. Curing was assessed until no visible deformation was observed. MEK resistance of films was also determined.

Keywords: Quinoxalines; Photoinitiators; RT-FTIR; UV-curing

1. Introduction

Photoinitiated free radical polymerization is of enormous commercial importance [1–5]. Techniques such as curing of coatings on various materials, adhesives, printing inks, and photoresists are based on photoinitiated radical vinyl polymerization. Photoinitiated radical polymerization may be initiated by both cleavage (type I) and H-abstraction type (type II) initiators [1].

Type II photoinitiators are based on compounds whose triplet excited states are reacting with hydrogen donors thereby producing an initiating radical [6,7] (Scheme 1). Because the initiation is based on bimolecular reaction, they are generally slower than type I photoinitiators which are based on unimolecular formation of radicals.

Typical type II photoinitiators include benzophenone and derivatives, thioxanthones, benzil and quinones while alcohols, ethers, amines and thiols are used as hydrogen donors [4,8,9].

The combination of various dyes with a tertiary amine provides an excellent type II photoinitiator system for the polymerization of acrylates and methacrylates. Quinoxalines are similar to dyes and they can be classified as type II photoinitiators [10–13]. Some earlier work by Davidson et al. established that quinoxalines are photoreduced by tertiary amines and their reduction products are reoxidised by oxygen to give the starting material [12].

RT-FTIR method has proved to be extremely valuable for measuring the polymerization rates and quantum yields of reactions that develop in the millisecond time scale [14–16]. The basic principle of this method of kinetic analysis consists in exposing the sample to the UV beam and to monitor simultaneously by IR the resulting decrease in the absorbance of the reactive double bonds.

In this study we have performed UV-cured coating of multifunctional acrylates with quinoxalines in the presence of a tertiary amine. Polymerization reactions were followed by RT-FTIR method and solvent resistance of cured films was tested by MEK rubs.

2. Experimental

2.1. Materials

2,3-Diphenylquinoxaline (DPQ), quinoxaline (Q), 2,3-dimethyl-quinoxaline (DMQ) were obtained from Aldrich. Acenaphthoquinoxaline (ACQ) was prepared as indicated in the literature [17,18]. The structures of initiator are given in Chart 1. Dichloromethane, methanol and methyl methacrylate (MMA) were obtained from Merck. MMA was washed twice with 5% NaOH and distilled over CaH_2 under vacuum before use. *N*-Methyl-diethanol amine (MDEA) and trimethylolpropanetriacrylate (TMPTA) were received from Aldrich and used as received. P-3038 (75% epoxyacrylate (EA) and 25% tripropyleneglycoldiacrylate (TPGDA)) was obtained from Cognis France.

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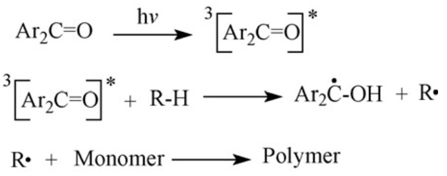

Scheme 1.

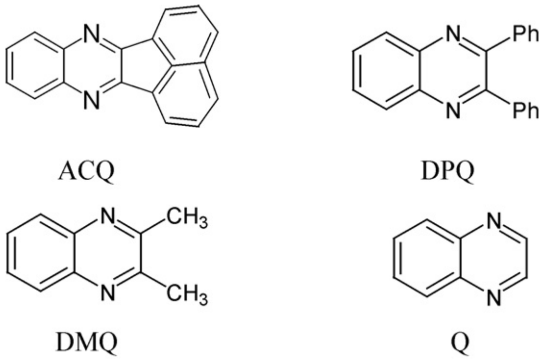

Chart 1.

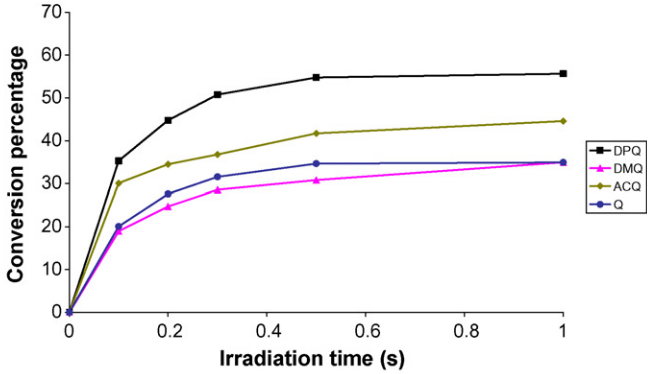

Fig. 1. Kinetic profiles demonstrating the photopolymerization of the TMPTA mixture (w/w) containing different quinoxaline photoinitiators in the presence MDEA with polychromatic light in an air atmosphere during 1 s of irradiation. Formulations: (1%) PI + (10%) MDEA + (94%) TMPTA.

2.2. Analysis

IR spectra were recorded on an ATI Unicam Mattson 1000 FT/IR-3 spectrophotometer on a KBr disc. Flexicure system was employed which consists of a medium pressure lamp and a light guide. Primarc Mini-UV-Cure system was employed for curing of films.

2.3. Real-time infrared spectroscopy photopolymerization studies

Uniform samples of photocurable formulations consisting of a photoinitiator, and trimethylolpropanetriacrylate (TMPTA) in the presence of various amines were prepared by casting on KBr pellets. The samples which were placed in the compartment of an infrared spectroscope were simultaneously exposed to a UV photolyzing light and an IR analyzing light beam. The photolyzing light was generated by a medium pressure mercury lamp (Flexicure UV system) and conducted through a flexible fiber optic to the IR compartment. The curves were obtained by monitoring the absorption decrease of the band at 810 cm^{-1} corresponding to the frequency of the twisting vibration of the double bonds. The degree of conversion expressed as a percentage can be expressed by the following equation: conv. %: $(A_0 - A_t)/A_0$.

3. Results and discussion

More recently [19], we have reported the use of benzaldehyde or *o*-phtaldialdehyde an alternative to the amine for free radical polymerization of MMA and TMPTMA in the presence of various quinoxalines.

Molecular oxygen is known to inhibit radical induced polymerization because of its high reactivity with radical species. If oxygen is present, an induction time is observed since the polymerization cannot proceed because the propagation reaction competes with the inhibition reaction. Therefore, polymerization experiments were carried out in the presence of a tertiary amine (MDEA). Several combinations of quinoxaline/amine were tested as photoinitiating systems for the polymerization of the acrylate monomers (Table 1). Four quinoxalines (DPQ, ACQ, DMQ and Q) (see Chart 1) were used as initiator.

The real-time infrared spectroscopy was used to follow up the cure of trimethylolpropanetriacrylate and EA + TPGDA in the presence of initiators and MDEA as co-initiator. By following the decrease in intensity of the absorption band at 810 cm^{-1} with the irradiation time, the progress of polymerization can be monitored. The results are shown in Figs. 1–6.

Table 1
List of formulation

Formulation	Photoinitiator (w/w)				Additive (w/w)	Acrylates (w/w)	
	Q (%)	ACQ (%)	DPQ (%)	DMQ (%)	NMDEA (%)	TMPTA (%)	P-3038 (%)
1	1	–	–	–	10	89	–
2	1	–	–	–	10	–	89
3	–	1	–	–	10	89	–
4	–	1	–	–	10	–	89
5	–	–	1	–	10	89	–
6	–	–	1	–	10	–	89
7	–	–	–	1	10	89	–
8	–	–	–	1	10	–	89