



## Producing critical exponents from gelation for various photoinitiator concentrations; a photo differential scanning calorimetric study

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### ABSTRACT

Photoinitiated radical polymerization of an 80 wt% epoxy diacrylate (EA) and 20 wt% tripropylene glycol diacrylate (TPGDA) mixture with various 2-Mercaptothioxanthone (TX-SH) photoinitiator concentrations was studied by using photo-differential scanning calorimetric (Photo-DSC) technique. Photopolymerization reactions were carried out under the same conditions of temperature and light intensity. It was observed that all conversion curves during gelation at various photoinitiator concentrations present nice sigmoidal behavior which suggests application of the percolation model. The critical time, where polymerization reaches the maximum rate ( $R_{p,max}$ ) is called the glass transition point ( $t_g$ ). The gel fraction exponents,  $\beta$  were produced from the conversion curves around  $t_g$ . The observed critical exponents were found to be around 0.55, predicting that the gel system obeys the percolation model.  $R_{p,max}$  and final conversion ( $C_s$ ) values were found to be increased as the photoinitiator concentration was increased. On the other hand  $t_g$  values decreased as photoinitiator concentration was increased, indicating higher TX-SH concentration causes early glass transition during radical polymerization.

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### 1. Introduction

Photopolymerizable formulations consist of three major components: a pre-polymer, monomer as a diluent and a photoinitiator. In addition to these components, additives (pigments, co-initiators, etc.) are also often a part of these systems. The most expensive part of the formulations and playing a key role in UV-curable systems is a photoinitiator capable of absorbing light of the appropriate wavelength and producing reactive species, ions, or radical species, which are able to initiate polymerization of the multifunctional monomers or oligomers [1,2]. Photoinitiated radical polymerization may be initiated by bond cleavage (Type I) and H-abstraction type (Type II) initiators [3]. Type II photoinitiators are based on compounds whose triplet excited states readily react with hydrogen donors, thereby producing initiating radicals (Scheme 1) [4–6]. Because of the bimolecular radical generation process, they are generally slower than Type I photoinitiators, which form radicals unimolecularly.

Typical Type II photoinitiators include benzophenone and derivatives, thioxanthones, benzyl, and quinones, while alcohols,

ethers, amines and thiols are used as hydrogen donors. Among Type II photoinitiators, thioxanthone (TX) derivatives in conjunction with tertiary amines are efficient photoinitiators with absorption characteristics that compare favorably with benzophenones [7]. We have reported [8] the use of a thiol derivative of thioxanthone (TX-SH) as a photoinitiator for free radical polymerization. A major advantage of this initiator is related to its one component nature. It can serve as both triplet photosensitizer [9] and a hydrogen donor [10]. Thus, this photoinitiator does not require an additional co-initiator, i.e., a separate molecular hydrogen donor. The mechanism of the photoinitiation is based on the intermolecular reaction of the triplet  $^3\text{TX-SH}^*$  with the thiol moiety of ground state TX-SH. The resulting thiyl radical initiates the polymerization (Scheme 2).

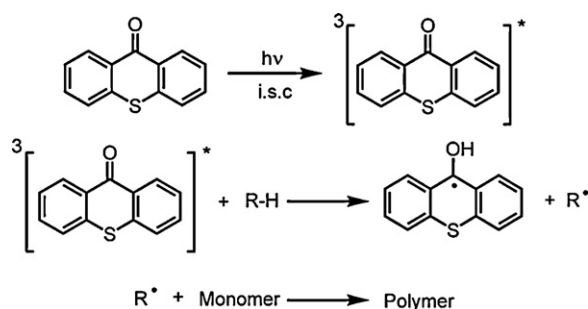
The rate of photoinitiation is directly proportional to the square root of the photoinitiator concentration, an increase in the level of photoinitiator would be expected to enhance the cure speed of formulation. Several reports claim that the cure rate and the degree of polymerization of a formulation will at first increase with increasing photoinitiator concentration, and after passing through a maximum or optimum concentration, the effect will rapidly fall off. This effect will largely depend upon the absorbance characteristics of the photoinitiator and that of the curable formulation [11].

At higher photoinitiator concentrations the absorbance of UV light appears to generate a higher concentration of free radicals

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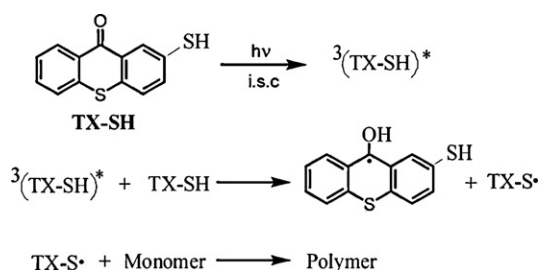
**Scheme 1.** Photoinitiated free radical polymerization by using aromatic carbonyl compounds.

near the surface of the film. This higher concentration of photoinitiator and therefore free radicals at the surface is thought to block sufficient energy from penetrating film, preventing photoactivation below a given thickness. Below this level an insufficient number of free radicals are generated in order to initiate and sustain the polymerization process, and therefore the rate of polymerization decreases.

Photoinitiators which have a high molar extinction coefficient would be expected to give rise to this uneven distribution more readily than photoinitiators which have a low extinction coefficient and do not absorb UV light intensity. The photoinitiated polymerization of acrylates and methacrylates is one of the most efficient processes for the rapid production of polymeric materials with well defined properties. These materials have found widespread use as coatings, imaging materials, photoresists and polymeric materials for many other applications. The photoinitiator plays a key role in UV-curable systems by generating the reactive species, free radicals or ions, which will initiate the polymerization of the multifunctional monomers and oligomers [3–6,21].

The bulk free radical cross-linking copolymerization (FCC) is divided into three stages: low conversion stage, gel effect stage and glass effect stage [12–14]. It was observed that monomer conversion first increases very slowly but then it accelerates because of the gel effect [15]. When the reaction temperature is lower than the glass transition point of the polymer the glass effect stage occurs as the last stage of polymerization. The glass transition temperature of polymers is customarily defined as the temperature at which the relaxation time on the monomer scale reaches 100 s [16]. Radical chain polymerizations are often characterized by the presence of an auto-acceleration in the polymerization rate as the reaction proceeds [17].

Norrish and Smith [18] postulated that the increased viscosity caused by monomers being converted to polymer resulted in a decrease in the mobility of the growing chains, making it more difficult for them to diffuse together and terminate. The term gel effect was used due to the characteristic rise in viscosity accompanying the dramatic increase in polymer conversion [19]. Burnett and Melville [19], Schulz and Harbort [20] each independently



**Scheme 2.** Photoinitiated free radical polymerization by using 2-Mercaptothioxanthone (TX-SH).

performed polymerizations in the presence of solvent and both reached the conclusion that the gel effect was caused by increasing bulk viscosity, as solvent reduces the viscosity and delays the onset of the gel effect.

Recently photopolymerization of 75 wt% EA and 25 wt% TPGDA mixture was monitored by employing the Photo-DSC technique in the presence of various thioxanthone based initiators [21] and with TX-SH as an initiator at different UV light intensities [22] respectively.

In this current study, the photopolymerization kinetics of 80 wt% EA and 20 wt% TPGDA mixture acrylates with various TX-SH photoinitiators concentration was investigated by using Photo-DSC technique. It was observed that all conversion curves during gelation present sigmoidal behavior as predicted by the percolation model from which the critical exponents ( $\beta$ ) were produced. The averaged value for the critical exponent  $\beta$  was found to obey the percolation model, predicting the universal behavior holds near the glass transition point. The produced glass transition point  $t_g$ , maximum conversion rate  $R_{p_{max}}$  and final conversion values  $C_s$  were found to be strongly correlated with the introduced photoinitiator concentration.

In general gelation process has been known as a geometrical phase transition rather than a thermal phase transition and owns a universal class by itself. However, as far as the critical phenomenon is concerned behavior of gelation may be made analogous to second order phase transition.

Understanding the gelation phenomenon was first introduced by Flory and Stockmayer [23,24] on a special lattice called Bethe lattice on which the closed loops were ignored. An alternative to the classical theory is the lattice percolation model [25] where monomers are thought to occupy the sites of a periodic lattice and the chemical bonds as corresponding to the edges joining these sites randomly with some probability  $p$ , which is the ratio of actual number of bonds that have been formed between the monomers, to the total possible number of such bonds. The gel point can be identified with the percolation threshold  $p_c$ , where, in the thermodynamic limit, the incipient infinite cluster starts to form and the system exhibits viscoelastic rigidity [26,27].

From the point of the universality, the predictions of these two theories about the critical exponents for the gelation are quite different. The critical exponent  $\beta$  for the gel fraction  $G$  (the strength of the infinite network in percolation language) near the gel point, can be defined as Eq. (1),

$$G \propto (p - p_c)^\beta, \quad p \rightarrow p_c^+ (\text{above percolation}) \quad (1)$$

where the Flory–Stockmayer theory (so-called the classical or mean-field theory) gives,  $\beta = 1$  independent of the dimensionality, while the percolation studies based on computer simulations give  $\beta$  around 0.43 in three-dimension [25,28]. These two universality classes for gelation problem are separated by a Ginzburg criterion [29] that depends upon the chain length between the branch points as well as the concentration of the non-reacting solvent. The vulcanization of long linear polymer chains belongs to the mean-field class. Critical percolation describes the polymerization of small multifunctional monomers [25,27].

## 2. Materials and methods

### 2.1. Materials

2-Mercaptothioxanthone [8] (TX-SH) was synthesized according to the previously described procedure. Dimethylformamide (DMF, 99+%, Aldrich) was distilled over  $\text{CaH}_2$  under reduced pressure. Epoxy diacrylate (EA) and Tripropyleneglycol diacrylate (TPGDA) were obtained from Cognis France.

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