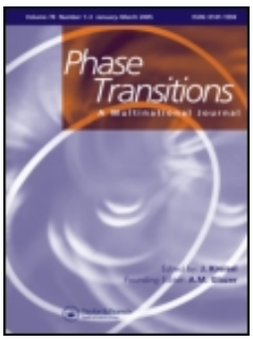

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Universality in gelation of epoxy acrylate with various photoinitiators: a photo differential scanning calorimetric study

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Photo-differential scanning calorimetric (Photo-DSC) technique was used to study the gelation of P-3038 (epoxy acrylate (EA) 75% and tripropyleneglycoldiacrylate (TPGDA) 25%) in the presence of various thioxanthone-based initiators, namely, thioxanthone (TX), 5-thia-naphtacene-12-one (TX-NP), 2-(carboxymethoxy) thioxanthone (TX-OCH_2COOH), 2-thioxanthone-thioacetic acid (TX-SCH_2COOH), and 2-mercaptothioxanthone (TX-SH). Photopolymerization reactions were performed under identical conditions of temperature, initiator concentration, and UV light intensity. Photo-DSC technique allowed us to monitor the gelation, without disturbing the system mechanically, and to test the universality of the gelation as a function of some kinetic parameters like initiator concentration. During gelation, it was observed that all conversion curves present a good sigmoidal behavior by predicting to employ percolation model. Observations around the glass transition point, t_g shows that the gel fraction exponents β obeyed the percolation picture. On the other hand, t_g was found to be much higher for the crosslinked networks obtained with TX-OCH_2COOH and TX-SCH_2COOH initiators than those with the other initiators.

Keywords: critical exponent; photoinitiator; epoxy acrylate; photo-DSC; glass transition point

1. Introduction

In general, gels can be classified according to the type of cross-linkages. Some gels are cross-linked chemically by covalent bonds, whereas physical interaction achieved by hydrogen or ionic bonding is responsible for the formation of some other gels [1,2]. Gels formed by chemical bonding are irreversible gels since they cannot be dissolved by a given solvent. However, moderate heating can reversibly dissolve a physically cross-linked gel. A chemical gel forms during a random linking process of monomers to larger molecules called macromolecules. This process of the bulk free-radical polymerization can usually be divided into three different stages: low-conversion stage, gel effect stage, and glass effect stage [3]. Monomer conversion first increases very slightly but later it

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accelerates because of the gel effect referred as the point where the rate of reaction reaches a maximum [4,5], which is a well-known phenomenon for both some of the linear polymers and the cross-linked bulk polymers [6,7]. The glassy state occurs as the last stage of polymerization, if the reaction temperature is lower than the glass transition point of the polymeric system under consideration. The characteristic temperature varies from one polymeric system to another. For example, methyl methacrylate (MMA) polymerization in bulk shows a very pronounced gel effect caused by the diffusion control of the termination reaction [4,8]. This is the result of the increased viscosity of the medium, with a concomitant rise in the rate of reaction, with the trapping of free radical [9,10]. However, compared to MMA [11,12] the diffusion control of the termination reactions and the resulting gel effect is less obvious in styrene gelation [13,14].

On the other hand, it has been known that most free-radical polymerizations are exothermic [14] and the heat generated during autoacceleration causes a sharp temperature increase. Therefore, the isothermal studies performed on 'test-tube scale' free-radical polymerizations are, in fact, not isothermal in the region of autoacceleration or in the region of the 'gel' effect.

The onset of the autoacceleration, for MMA polymerization was defined as the point in a reaction at which a sharp temperature increase begins to appear during the differential scanning calorimetric DSC measurements [15].

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 [16–20].

Photoinitiated radical polymerization may be initiated by bond cleavage (Type I) and H-abstraction-type (Type II) initiators [21]. Type II photoinitiators are a second class of photoinitiators and are based on compounds whose triplet-excited states readily react with hydrogen donors, thereby producing initiating radicals [22–24] (reactions 1–3). Because of the bimolecular radical generation process, they are generally slower than Type I photoinitiators which are based on unimolecular formation of radicals.

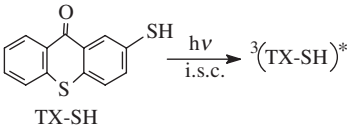
$$Ar_2C{=}O \xrightarrow{h\nu} {}^3[Ar_2C{=}O]^* \tag{1}$$

$${}^3[Ar_2C{=}O]^* + R{-}H \longrightarrow Ar_2\dot{C}{-}OH + R\bullet \tag{2}$$

$$R^\bullet + \text{Monomer} \longrightarrow \text{Polymer} \tag{3}$$

Typical Type II photoinitiators include benzophenone and derivatives, thioxanthones, benzil, and quionones while alcohols, ethers, amines, and thiols are used as hydrogen donors. Among Type II photoinitiators, thioxanthone derivatives in conjunction with tertiary amines are efficient photoinitiators with absorption characteristics that compare favorably with benzophenones [25]. We have recently reported [26] the use of a thiol derivative of thioxanthone (TX-SH) as photoinitiator for free radical polymerization. A great advantage of this initiator is related to its one-component nature. It can serve both as triplet photosensitizer and a hydrogen donor. 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 triplet, ^{3}TX-SH*, with the thiol moiety of ground state TX-SH. The resulting thiyl radical initiates the polymerization (reactions 4–6).



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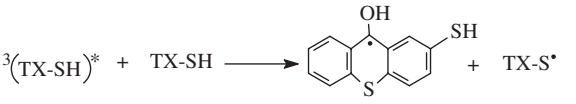


(5)

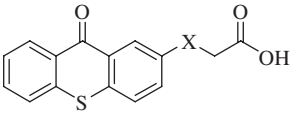
$$TX-S^{\bullet} + \text{Monomer} \longrightarrow \text{Polymer} \tag{6}$$

We have also reported [27,28] another photoinitiator belonging to the same class of photoinitiator family, i.e., exhibiting a one-component nature, namely, acetic acid derivatives of thioxanthone with the following structure (Figure 1). In both cases, the light absorbing and hydrogen donating sites are composed in the photoinitiator molecules.

Notably, these one-component photoinitiators initiate the polymerization much more efficiently than two-component systems in which the related functions are composed in independent molecules.

Photo-DSC has been widely used to elucidate key cure-process parameters such as the extent of crosslinking and conversion, the rate of polymerization, and the order of reactions. This technique is based on the interpretation of the change in heat flow from the particular system under consideration.

Several theories have been developed in the past half century to describe gelation during free radical crosslinking copolymerization (FCC), among which Flory–Stockmayer theory and percolation theory provide bases for modeling the gelation [29–32]. Statistical theories based on the Cayley tree approximation are called classical theories, originated from Flory [29] and Stockmayer [30], and assume equal reactivities of functional groups and absence of cyclization reactions. However, percolation suggests a more simple, yet detailed picture in terms of which one may seek to understand gelation [31,32]. In percolation model, monomers are considered to occupy the vertices of a periodic lattice, and the chemical bonds as corresponding to the edges joining these vertices at any given moment with some probability p. Then, the gel point can be identified with the percolation threshold p_c, where, in the thermodynamic limit, the incipient infinite cluster starts to form. Identifying the weight average degree of polymerization with the average



X= O, S

Figure 1. Structure of thioxanthone acetic acid derivatives.

cluster size and the gel fraction, G, with the probability of an occupied site that belongs to the incipient infinite cluster, one can predict the scaling behavior of these and related quantities near the gel point as a function of p. The critical exponents in percolation theory differ from those found in Flory–Stockmayer.

Fluorescence technique has been successfully used to perform the experiments on chemical gel formation [33]. Studies, using the extrinsic fluoroprobe, have shown that percolation exponents could describe the glass transition for the gels. In these studies, the fluoroprobe monitors the change occurring in the rigidity of the medium near the glass transition. Therefore, this method seems particularly suitable for studying the sudden changes occurring during the glass transition of poly(methyl methacrylate) gelation. More recently, the critical exponents for bulk copolymerizations [34,35] and hydrogels [36] near the gel points were determined by using fluorescence technique.

In this work, Photo-DSC technique, which elaborates photoinitiation during the gelation of multifunctional acrylates was used to study glass transition in bulk free radical crosslinking copolymerization. Photopolymerization of P-3038 (epoxy acrylate (EA) 75% and tripropyleneglycoldiacrylate (TPGDA) 25%) were monitored by Photo-DSC technique in the presence of various thioxanthone-based initiators. Heat flows against gelation time were measured using the Photo-DSC technique to determine the critical exponents for the bulk polymerization of P-3038. It was observed that the universal behavior near the glass transition point was satisfied for the systems investigated. The averaged value for the critical exponent β was produced and found to obey the percolation model. The observed glass transition point, t_g, was found to be strongly correlated with the choosen photoinitiator.

1.1. *Theoretical considerations*

It has been known that the gelation is not a phase transition in a thermodynamic sense, being a geometrical one, as a subject of critical phenomenon, it behaves like a second-order phase transition and constitutes a universal class by itself. The exact solution of the gelation was first given by Flory and Stockmayer [29,30] on a special lattice called Bethe lattice on which the closed loops were ignored. An alternative to the chemical-kinetic theory is the lattice percolation model [32] 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 behaves viscoelastically rigid [37,38].

The predictions of these two theories about the critical exponents for the gelation are different from the point of the universality. Consider, for example, the exponents β for the gel fraction G (the strength of the infinite network in percolation language) near the gel point is defined as

$$G \propto (p - p_c)^{\beta}, \quad p \to p_c^{+}, \tag{7}$$

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 β around 0.43 in three-dimension [32,39]. These two universality classes

for gelation problem are separated by a Ginzburg criterion [40] that depends upon the chain length between the branch points as well as the concentration of the nonreacting solvent. The vulcanization of long linear polymer chains belongs to the mean-field class. Critical percolation describes the polymerization of small multifunctional monomers [32,38].

In order to understand the physical nature of polymerization processes underlying the gelation, one must follow the reaction kinetics and compare results with experiments directly measuring some physical properties in the course of the polymerization reaction. Experimental techniques must be used for just monitoring and should not disturb the system mechanically.

2. Experimental

2.1. *Material*

2-Mercaptothioxanthone [26], thioxanthone thioacetic acid and thioxanthone phenoxyacetic acid [22] were synthesized according to the previously described procedure. Dimethylformamide (DMF, 99+%, Aldrich) was distilled over CaH_2 under reduced pressure. *N*-methyldiethanolamine (MDEA) were also obtained from Aldrich. Epoxy acrylate (EA) and Tripropyleneglycoldiacrylate (TPGDA) were obtained from Cognis, France.

2.2. *Synthesis of TX-NP*

Thiosalycylic acid (1.6 g, 0.010 mol) was slowly added to 15 mL of concentrated sulfuric acid, and the mixture was stirred for 5 min to ensure thorough mixing. Naphtalene (5.6 g, 0.044 mol) was added slowly to the stirred mixture over a period of 30 min. After the addition, the reaction mixture was stirred at room temperature for 1 h and then at 60°C for 4 h, after which it was left to stand at room temperature overnight. The resulting mixture was poured carefully with stirring into a 10-fold excess of boiling water, and it was boiled further for 5 min. The solution was cooled and filtered. The residue was recrystallized from dioxane–water (50 : 50), m.p.: 180°C.

Anal. Calcd. for $C_{17}H_{10}OS$ ($262\,g\,mol^{-1}$): C, 77.83%; H, 3.84%; S, 12.22%. Found: C, 76.71%; H, 3.11%; S, 12.56%. ^1H NMR (250 MHz) in DMSO: δ 8.52–7.65 (m, 9H, aromatic).

IR (KBr) : $\nu\,(cm^{-1})$ 3457, 3056, 2921, 2852, 1631, 1617, 1438, 1387, 1211, 1161, 1033.

2.3. *Photo differential scanning calorimetri*

The photoinitiated polymerization P-3038 were carried out by TA-DSCQ100 equipped with a medium pressure mercury arc lamp. This unit emits radiation predominantly in the 220–400 nm range, and provides light intensity of $40\,mW\,cm^{-2}$ as measured by a UV radiometer capable of broad UV range coverage. The mass of the samples was $\sim 2 \pm 0.1$ mg and the measurements were carried out in an isothermal mode at room temperature under a nitrogen atmosphere (nitrogen flow: $50\,mL\,min^{-1}$).

The samples were irradiated for 4 min at room temperature. The heat flow as a function of reaction time was monitored using Photo-DSC under isothermal conditions, and both the rate of polymerization and conversion were then calculated as a function of time. The heat of reaction value $\Delta H_p^{\,theor} = 86\,kJ\,mol^{-1}$ was used as the theoretical heat

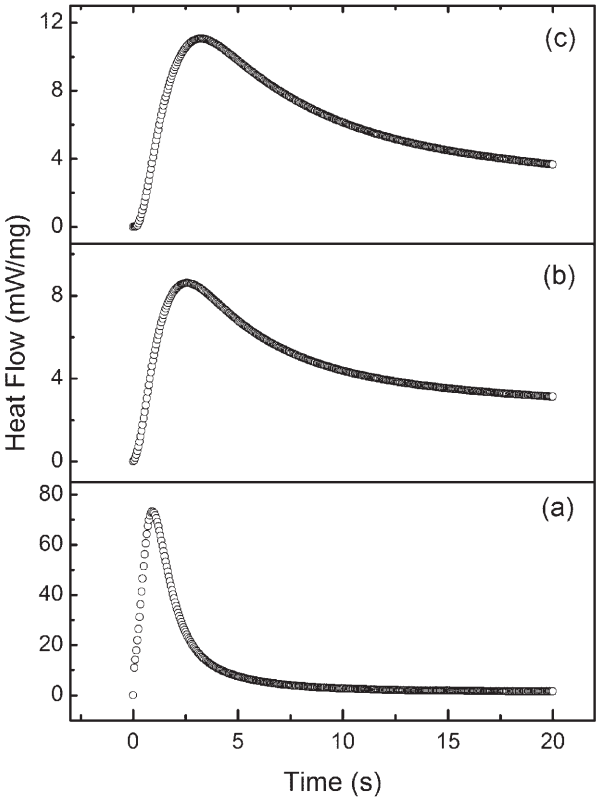


Figure 2. Heat flow spectra of polymerization of P-3038 with (a) TX + NMDEA, (b) TX-OCH_2COOH, and (c) TX-SCH_2COOH photoinitiators.

evolved for acrylate double bonds [41]. Rates of polymerization were calculated according to the following equation; $R_p = (Q\ s^{-1})M/n\ \Delta H_p m$ where $Q\ s^{-1}$ is heat flow per second, M the molar mass of the monomer, n the number of double bonds per monomer molecule and m the mass of monomer in the sample.

3. Results and discussion

Photoinitiation can occur from the interaction of an excited initiator with the monomer and/or the co-initiator [42]. Photo-DSC experiments are capable of providing kinetics data in which the measured heat flow can be converted directly to the ultimate percentage conversion and polymerization rate for a given amount of formulation, with the data obtained reflecting the overall curing reaction of the sample. Photo-DSC is a unique method to obtain a fast and accurate indication of the photoinitiator performance. Gelations of P-3038 were monitor by Photo-DSC in the presence of various thioxanthone-based initiators. Photopolymerization reactions were performed under identical conditions of temperature, initiator concentration, and UV light intensity. A typical heat flow and rate of polymerization curves *versus*

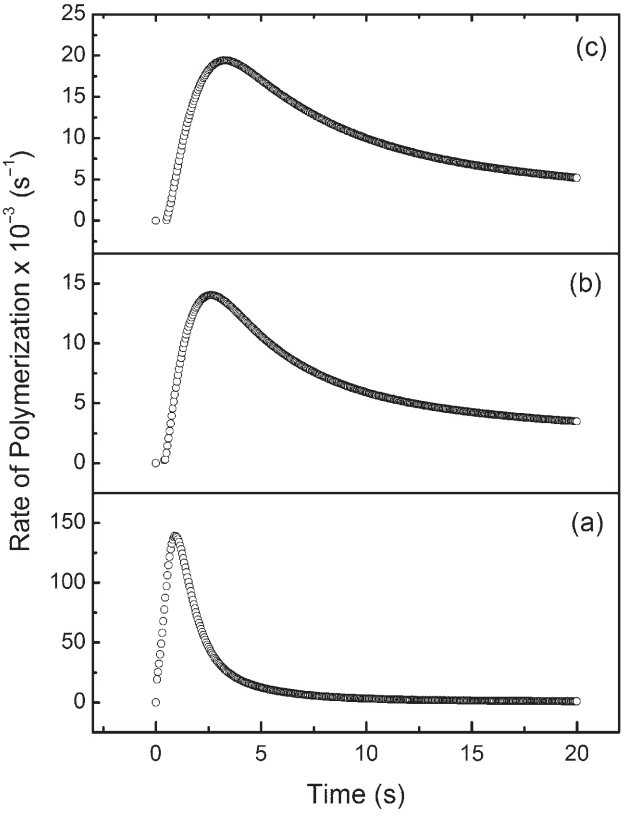


Figure 3. Rate of polymerization spectra of polymerization of P-3038 with (a) TX + NMDEA, (b) TX-OCH_2COOH, and (c) TX-SCH_2COOH photoinitiators.

reaction time for various thioxanthone-based initiators are presented in Figures 2 and 3, respectively. Conversion curves produced from Figure 3 are shown in Figure 4 against reaction time. These sigmoidal curves are typical for a gelation predicted by the percolation model.

Usually in gelation theory the conversion factor, p, alone determines the behavior of the gelation process, though p may depend on temperature, concentration of monomers, and time. If the temperature and concentration are kept fixed, then p will be directly proportional to the reaction time, t. This proportionality is not linear over the whole range of reaction time but it can be assumed that in the critical region, i.e., around the critical point $|p - p_c|$ is linearly proportional to the $|t - t_c|$. Therefore, below the gel point, i.e., for $t < t_c$ conversion measures the weight average degree of polymerization (or average cluster size). Above t_c, however conversion measures solely the gel fraction G, the fraction of the monomers that belong to the macroscopic network.

In this work, we tried to interpret our results by considering the quasi-static properties of the gel near the glass transition point in the language of percolation [34]. Here the glassy region is defined as a region of sufficiently high viscosity, such that it inhibits the motion of molecules on a short time scale. The same works in the literature propose that the 3D glass transition is controlled by the percolation of

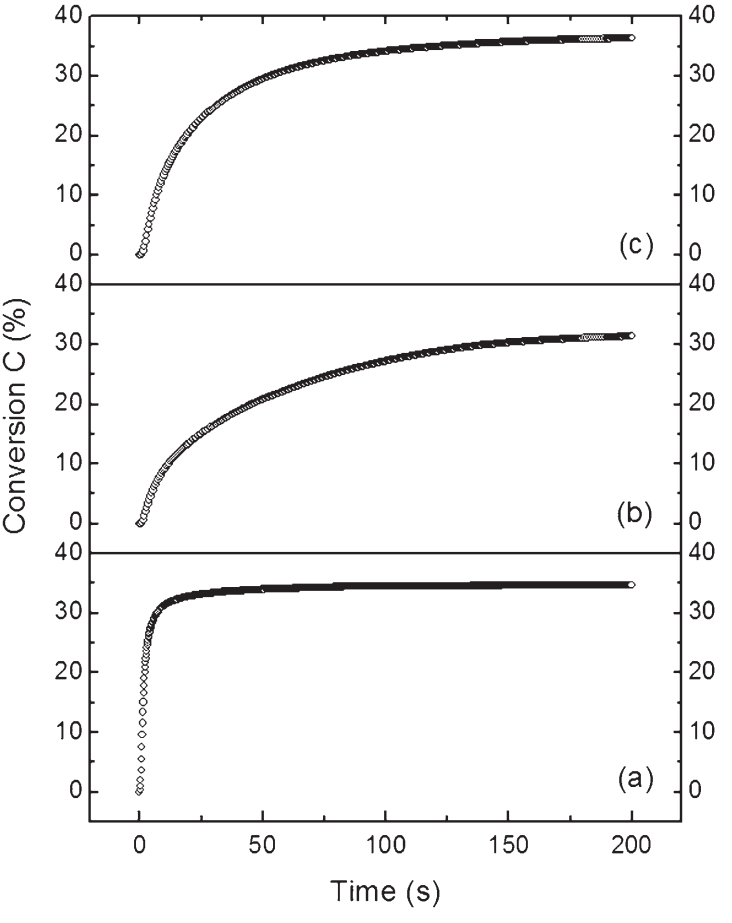


Figure 4. Conversion spectra of polymerization of P-3038 with (a) TX + NMDEA, (b) TX-OCH_2COOH, and (c) TX-SCH_2COOH photoinitiators.

small domains of slow dynamics, which allows us to explain the heterogeneous dynamics close to the glass transition [43,44]. These authors have suggested that domains of slow dynamics percolate at a lower temperature in the quasi-2D case of thin suspended polymer films and they calculate the corresponding reduction in glass transition temperature, in quantitative agreement with the experimental results. Here it is assumed that the volume fraction occupied by the total number of monomers incorporated into the glassy regions as the 'occupation probability', p, of the sites of a three-dimensional lattice. In a glassy region, the motion of monomer is completely restricted due to vitrification. These glassy regions, which may be considered as the initiation centers of the vitrification in microscopic scale, will grow in time as the polymerization proceeds, and percolate as p_c is reached.

In order to measure the values of the critical exponent, β, with sufficient accuracy to determine their universality class, the double logarithmic plot of the conversion *versus* $|t - t_c|$ was analyzed, which produced the critical exponent from the slope of the straight line during fitting the data in Figure 4. Here the important problem was the precise determination of the glass transition point and the critical region. In particular, a small shift in t_c results in a large shift in the critical exponent. Such a

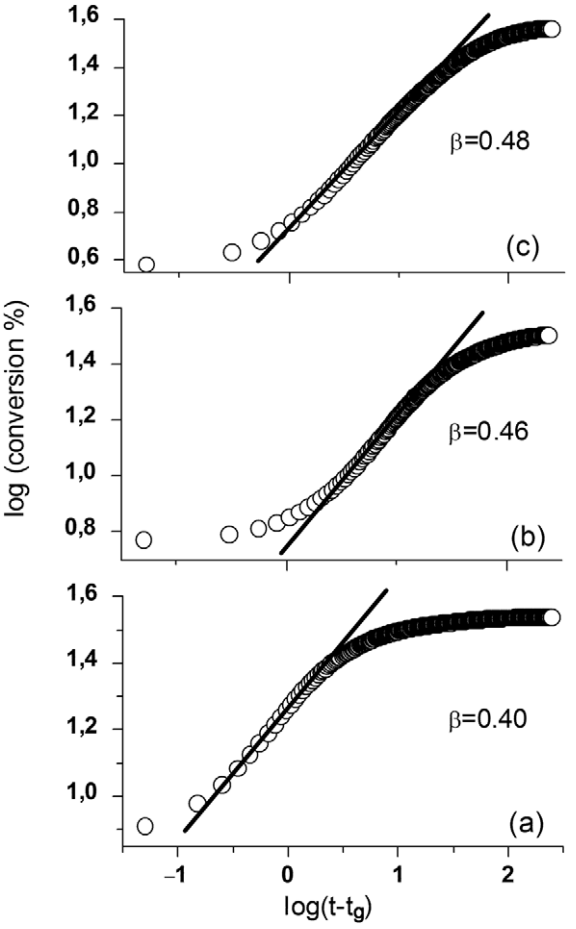


Figure 5. Double logarithmic plot of the conversion C *vs.* time curves above t_c for (a) TX + NMDEA, (b) TX-OCH_2COOH, and (c) TX-SCH_2COOH photoinitiators, respectively. The β exponents were determined from the slope of the straight lines.

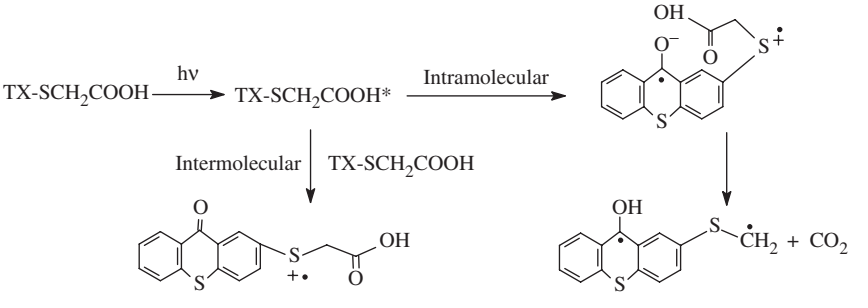
log–log plot reveals that data should be particularly accurate near the gel point. Usually the critical point can then be determined by varying t_c in such a way as to obtain good scaling behavior over the greatest range in $|t - t_c|$, if the experiments are performed against time. Here the time corresponding to the maximum of the rate of polymerization was chosen as the critical time, t_c, which may be considered as the glass transition point, t_g for the gelation under consideration. The plot of log (conversion) *versus* log $|t - t_g|$ above t_g for TX + NMDEA, TX-OCH_2COOH, and TX-SCH_2COOH initiators are shown in Figure 5(a)–(c), respectively, where the slopes of the straight lines produced gel fraction exponent, β. The produced β values for the gelation with the other initiators are presented in Table 1 together with t_g and R_{pmax} values. Here it has to be noted that the average value (=0.45) of produced β values above t_g strongly suggest that the glassy regions percolate during gel formation for all the samples under consideration, by predicting that they belong to the same universality class.

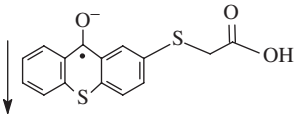
Table 1. Experimentally observed parameters measured by 'Photo-DSC' and calculated via 'percolation theory' for various types of photoinitiators during diacrylate gelation.

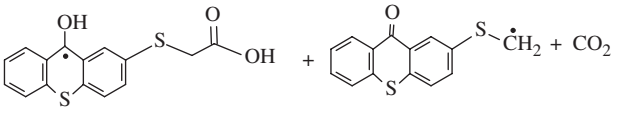
Polymer formulation							
Photoinitiator (PI)			Photo-DSC results				
PI formulation	%	Monomer Diacrylate	$R_{pmax} \times 10^{-3}$ [s^{-1}]	Conv. at t_g [%]	t_g [s]	Final conv. [%]	Gel fraction exponents β
TX + NMDEA[a]	0.5	P-3038	139	7.5	0.9	34.7	0.40
TX-NP + NMDEA[a]	0.5	P-3038	87	6.7	1.3	34.5	0.44
TX-OCH_2COOH	0.5	P-3038	14	2.2	2.6	31.6	0.46
TX-SCH_2COOH	0.5	P-3038	19	3.6	3.3	36.5	0.48
TX-SH	0.5	P-3038	41	4.9	1.9	41.8	0.49

Note: [a]NMDEA is a hydrogen donor with used type of second photoinitiators.

On the other hand, the diagram of R_{pmax} and t_g *versus* the initiator type, presented in Figure 6(a) and (b), show that TX-OCH_2COOH and TX-SCH_2COOH behave much different than the other initiators. In other words, there is a long delay in glass transition during gelation when TX-OCH_2COOH and TX-SCH_2COOH were used, which also results in very low R_{pmax} value compared to others. The special effects of TX-OCH_2COOH and TX-SCH_2COOH can be explained by generation of initiating radicals after several steps during gelation. In these cases, first excited states abstract hydrogen followed by decarboxylation leading to the formation of free radicals capable of initiating the polymerization process (reactions 8–10).







However with the other initiators, initiating radicals can only be produced after hydrogen abstraction. Obviously, the additional step in the cases of TX-OCH_2COOH and

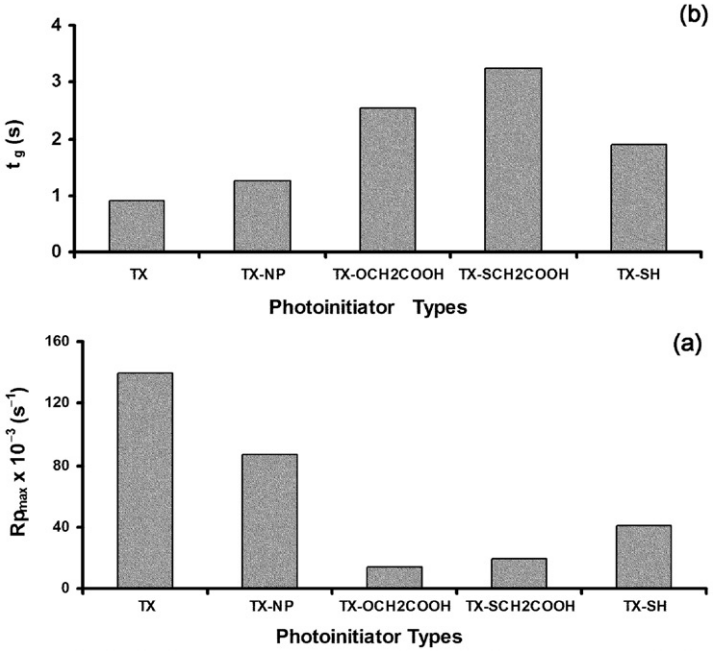


Figure 6. The diagrams of (a) R_{pmax} and (b) t_{g} *vs.* the initiator type.

TX-SCH_2COOH ground for the late glass transition, which then results low rate of polymerization at the glass transition point.

Here we have to point out that all formulations have approximately produced the same final conversion values (Table 1) by indicating that low t_{g} and high R_{pmax} do not effect the final production of the gelations under consideration.

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