



Percolation of glassy regions during photopolymerization of epoxy acrylate in DMF



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ABSTRACT

The gelation of epoxy acrylate (EA) 80% and tripropyleneglycol diacrylate (TPGDA) 20% was studied through the use of photo-differential scanning calorimetric (photo-DSC) technique in the presence of a thioxanthone based initiator. Photo-induced polymerization reactions were performed under identical conditions of temperature, initiator concentration and UV light intensity in various N,N-dimethylformamide (DMF) contents. 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 DMF content. During gelation, it was observed that all conversion curves presented useful sigmoidal behavior which was predicted by employing a percolation model. Observations around the glass transition point, t_g , revealed that gel fraction exponent β obeyed the percolation picture. A significant solvent effect on the photopolymerization kinetics of EA/TPGDA was observed with changes in DMF content. DMF is used as solvent, which acts as a diluent and proton donor during photogelation.

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1. Introduction

It is well known that solvents have some effect on free radical homo- and copolymerization [1–3], particularly on propagation reaction [4]. The properties of the solvent strongly influence the rate of free radical polymerization of vinyl monomers [5]. Beuermann et al. studied the solvent effect on the propagation kinetics in radical polymerization, in terms of chain transfer reactions with solvents, polarity and polarizability of the medium [6,7]. They also studied the change of monomer reactivity as regards the solvent, in addition to reversible complex formations between radical and solvent molecules. Several studies have been conducted to examine water-based polymerizations [6,8,9], and it was generally found that they enhance the polymerization rate in water media [8,10]. Valdebenito and Encinas studied the solvent effect on the free radical polymerization of N,N-dimethylacrylamide [10], through studies of polymerization reactions in several solvents ranging from water to low polarity solvents such as THF.

In photopolymerization experiments, mainly type I (by bond cleavage) and type II (by H-abstraction) initiators are employed

[11]. Although type I photoinitiators are more effective than type II initiators, type II initiators operating in the visible range are advantageous in terms of energy policies. Recently, mercapto derivative [12], carboxylic acid derivatives [13,14], and morpholine-attached [15] TX initiators were used for the polymerization of acrylates and methacrylates as type II one component photoinitiators, and another approach was undertaken and thioxanthone–benzotriazole was synthesized, which presented stabilizer and initiator properties in one component [16].

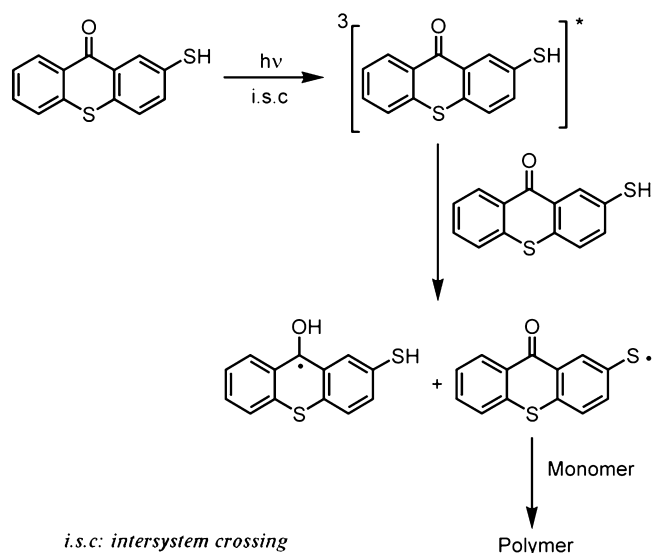
In previous studies we conducted, the efficiency of 2-mercaptothioxanthone (TX-SH) was investigated [12]. A thiol derivative of thioxanthone TX-SH photoinitiator serves as both a triplet photo-sensitizer [17] and a hydrogen donor for free radical polymerization. The mechanism of photoinitiation is based on the intermolecular reaction of the triplet, $^3\text{TX-SH}^*$, with the thiol moiety of ground state TX-SH. The resulting thyl radical initiates polymerization (Scheme 1) [12].

Since the solubility of TX-SH at high initiator concentrations creates some problems, the addition of a solvent was beneficial for the enhancement of the initiator's solubility. It is well known that the most commercial photoinitiators are not soluble in some of the monomers and oligomers. Moreover, as many reactions in industry are carried out in organic solvents rather than in bulk and many commercial photoinitiators are not dissolved in a presented bulk, it is useful to determine the effect of the solvent content on

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Scheme 1. Photoinitiated free radical polymerization by using 2-mercaptothioxanthone (TX-SH).

photogelation kinetics. There are significantly few studies in the literature which address solvent content, and this study intends to fill that gap.

Bulk free-radical polymerization can usually be divided into three different stages: a low-conversion stage, a gel effect stage and a glass effect stage which occurs in the last stage of polymerization [18]. Monomer conversion first increases very slightly, but then accelerates because of the gel effect and the rate of reaction reaches a maximum [19,20], which is a well-known phenomenon for some of the linear polymers and the cross-linked bulk polymers [21].

Historically, in the lattice percolation model, monomers are thought to occupy the sites of a periodic lattice. A bond between these lattice sites is formed randomly with probability p . For a certain bond concentration p_c , defined as the percolation threshold, the infinite cluster is started to form. The critical exponents for the sol-gel transition are different from the point of the universality. Consider, for example the exponents γ and β for the weight average degree of polymerization, DP_w , and the gel fraction G (average cluster size) near the gel point, where the Flory–Stockmayer theory (so-called the classical or mean-field theory) gives $\beta = \gamma = 1$, independent of the dimensionality, while the percolation studies based on computer simulations give γ and β around 1.7 and 0.43 in three-dimension. These two universality classes for gelation problem are separated depending on the chain length N between the branch points as well as the concentration of the nonreacting solvent. For example, the vulcanization of long linear polymer chains (large N) belongs to the mean-field class; however the critical percolation (small N) describes the polymerization of small multifunctional monomers.

It is known that the gelation phase is not a transition in the thermodynamic sense, but is rather geometrical. As the subject of critical phenomenon, it behaves like a second order phase transition constituting a universal class by itself. The exact solution of gelation was given first by Flory and Stockmayer [22,23] on a special lattice called the Bethe lattice, on which the closed loops were ignored. An alternative to the chemical-kinetic theory is the lattice percolation model [24] in which monomers are thought to occupy the sites of a periodic lattice and the chemical bonds corresponding to the edges randomly join these sites with some probability p , where p is the ratio of the 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 in a manner that is viscoelastically rigid [25].

The predictions of these two theories about the critical exponents for gelation are different from the point of universality. Consider, for example, the exponent β for the gel fraction G (the strength of the infinite network in percolation language) near the gel point, which is defined in Eq. (1)

$$G \propto (p - p_c)^\beta, \quad p \rightarrow p_c^+ \quad (1)$$

where the Flory–Stockmayer theory (the so-called classical or mean-field theory) gives $\beta = 1$ which is independent of dimensionality, while the percolation studies based on computer simulations give β around 0.43 in three-dimensions [22,23,26]. These two universality classes for the gelation problem are separated by a Ginzburg criterion [27] that depends upon the chain length between the branch points as well as the concentration of the non-reacting solvent. Critical percolation describes the polymerization of small multifunctional monomers [24,25,28].

Critical exponents at the glass transition in free-radical crosslinking copolymerization have been studied for different monomeric systems. The fluorescence lifetimes of Py were used to monitor the gelation process, where the changes in the viscosity of the pregel solutions due to glass formation dramatically enhance the fluorescent yield of aromatic molecules. This effect is used to study the glass transition upon gelation of these systems as a function of time, at various temperatures and cross linker concentrations, where the results were interpreted in the view of percolation theory. The gel fraction and weight average degree of polymerization exponents are found to be in agreement with percolation results.

Findings in this work are similar to the findings in our previous works [29,30] where methyl methacrylate (MMA) and ethyl methacrylate (EMA) and their mixtures (MMA–EMA) produced the results accordance with the percolation model. Bulk linear poly methyl methacrylate (PMMA) also gave the similar findings [31] as was observed here with EA and TPGDA. From here we predict and conclude that acrylate resins most probably obey the percolation picture where glassy regions percolate during gelation as given in the cases of EA and TPGDA.

Recently, it has been shown that photo-DSC can be successfully applied to measure the critical exponents during photopolymerization reactions of epoxy acrylate and tripropyleneglycol diacrylate mixtures near the glass transition point [32,33].

In this study, our aim is to understand the universal behavior of gelation and the influence of photopolymerization kinetics in the presence of various amounts of DMF. The cure characteristics of EA/TPGDA were analyzed in terms of solvent content. DMF was chosen for two reasons: firstly, our component type II initiator is easily solubilized even at high concentrations in DMF, and secondly, this approach makes it possible to see the solvent effect on the rate of polymerization by means of controlling sudden increases in the viscosity of the medium. In particular, controlling auto-acceleration may help explain the percolation of glassy regions.

In order to understand the physical behavior of the polymerization processes underlying gelation, one may follow reaction kinetics through experiments utilizing fluorescence [20] and photo-DSC [32–35] techniques, which do not mechanically disturb the system.

2. Experimental

2.1. Materials and method

2-Mercaptothioxanthone [12] was synthesized according to the previously described procedure. Dimethylformamide DMF

(99%, Aldrich) was distilled over CaH_2 under reduced pressure. Epoxy acrylate (EA) and tripropyleneglycoldiacrylate (TPGDA) were obtained from Cognis France.

The photoinitiated polymerization of EA 80 wt% and TPGDA 20 wt% was carried out in various amounts of DMF 15, 20, 25, 30, 35 and 50 wt% by TA-DSCQ100 equipped with a medium pressure mercury arc lamp. This unit emits radiation predominantly in the 220–400 nm range, and provides a 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 approximately $2 \pm 0.1 \text{ mg}$ and the measurements were carried out in isothermal mode at room temperature under a nitrogen atmosphere with nitrogen flow of 50 mL/min . The samples were irradiated for 100 s at room temperature. Measurements were recorded at a sampling interval of 0.05 s/point . The thickness of the cured thin films was approximately $0.20 \pm 5 \text{ mm}$.

Heat flow (W/g) as a function of reaction time was monitored using photo-DSC under isothermal conditions, and both the rate of polymerization (s^{-1}) and conversion (%) were then calculated from the heat flow values as a function of time. The heat of the reaction value $\Delta H_p^{\text{theory}} = 86 \text{ kJ/mol}$ was used as the theoretical heat evolved for acrylate double bonds [36]. Rates of polymerization were calculated according to Eq. (2)

$$R_p = \left(\frac{dC}{dt} \right) = \frac{dH/dt}{\Delta H_0^{\text{theory}}} \quad (2)$$

where H is the reaction heat evolved at time t , $\Delta H_0^{\text{theory}}$ is the theoretical heat for complete conversion and C is the percentage of conversion.

3. Results and discussion

Photo-DSC is a unique method for obtaining more information about the photopolymerization system, and 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 the polymerization rate for a given amount of formulation [32].

In order to reveal the effect of solvent (DMF) content on photopolymerization, a mixture of EA + TPGDA formulation was chosen to be initiated by TX-SH. It is well known that epoxy resins provide an excellent combination of properties, such as high abrasion resistance, very low shrinkage during and after cure, excellent adhesion to most constructing materials, high mechanical strength and a wide range of cure schedules [37].

Photopolymerization reactions were performed under identical conditions of temperature, initiator concentration, mass of samples, nitrogen flow rate and UV light intensity. In Fig. 1 the rate of polymerization curves versus reaction time for various DMF contents are presented.

DMF content in the formulations changed from 15 to 50% (w/w). As can be seen from Fig. 1, the lowest concentration of DMF formulation led to the highest rate of polymerization. The initial viscosity of a photocurable system has a strong impact on polymerization, and the initial viscosity of the reaction system determines the initial polymerization rate; the greater the viscosity, the higher the rate of polymerization. Our results confirmed this, and an increase in solvent concentration inversely affected the rate of polymerization (Figs. 1 and 7).

However, the highest final conversion value, C_s , was obtained when the solvent content was increased to 25–30%, and nearly 50% conversion was achieved. The gap between the highest rate of polymerization ($33 \times 10^{-3} \text{ s}^{-1}$) and the lowest rate of polymerization ($16 \times 10^{-3} \text{ s}^{-1}$) was reduced, while the C_s values did not change to the same extent. C_s value was calculated as 45% where formulation

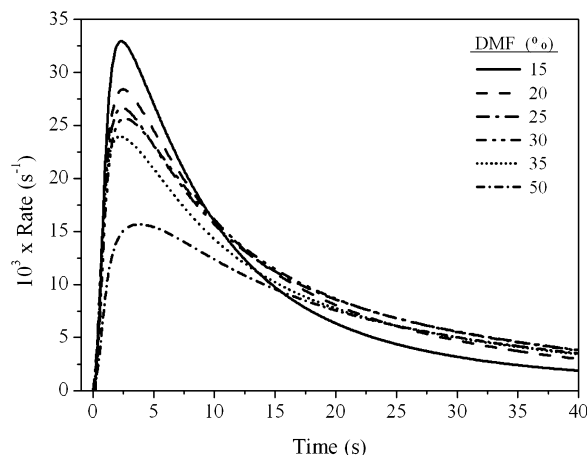


Fig. 1. Rate of polymerization spectra of photopolymerization of EA/TPGDA with various photoinitiator (TX-SH) concentrations irradiated at 25°C by UV light with an intensity of 40 mW/cm^2 .

Table 1

Experimentally observed parameters measured by “photo-DSC” and calculated via the “percolation theory” during diacrylate, EA/TPGDA, and photopolymerization with various DMF content.

[DMF](%)	t_g (s)	$10^{-3} \times R_{p_{\text{max}}}$ (s^{-1})	Conv. at t_g (%)	C_s (%)	β
15	2.4	33.0	5	45	0.551
20	2.5	28.4	5	49	0.554
25	2.5	26.7	4	52	0.554
30	2.6	25.7	4	52	0.564
35	2.3	23.9	4	47	0.568
50	3.8	15.7	4	41	0.558

consists of 15% DMF when DMF content was increased to 50% for the formulation C_s value gradually decreased to 41% (Table 1).

As seen from Fig. 2, when the reaction continues, the increased cross-linking level may eventually limit monomer mobility and the propagation and termination reaction may become diffusion controlled. Moreover, the final conversion decreases with increasing initial viscosity. This is because the resin system with a higher solvent content leads to a more buried monomer and consequently a lower conversion value.

As part of our continuing interest in the percolation model of gelation (photopolymerization), we studied the changing of the parameters of the photopolymerization. Interestingly, these sigmoidal curves (conversion %) are typical for the gelation process

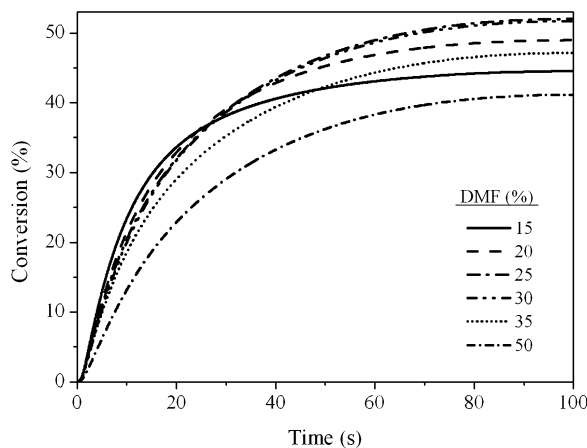


Fig. 2. Conversion spectra of photopolymerization of EA/TPGDA with various photoinitiator (TX-SH) concentrations irradiated at 25°C by UV light with an intensity of 40 mW/cm^2 .

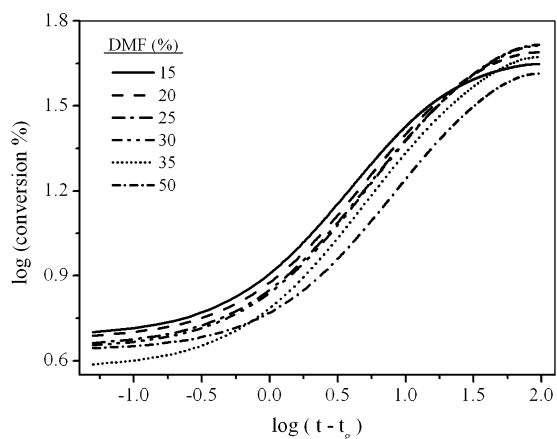


Fig. 3. Double logarithmic plot of the conversion versus time curves above t_g for various photoinitiator (TX-SH) concentrations.

predicted by the percolation model, which can be elaborated as follows: in gelation theory the conversion factor, p , alone determines the behavior of the gelation process, though p may depend on temperature, concentration of monomers, viscosity of medium and time.

The volume fraction occupied by the total number of monomers incorporated into the glassy regions as the 'occupation probability', p , of the sites has a three dimensional lattice. In a glassy region the motion of the monomer is completely restricted due to vitrification. These glassy regions, which may be considered the initiation centers of vitrification on a microscopic scale, will grow in time as the polymerization proceeds. Furthermore, as percolate p_c reaches the critical exponent, β can be measured by using the double logarithmic plots of the conversion versus $(t - t_c)$. The critical exponents were produced from the slope of the straight lines during the fitting of data in Fig. 3.

The conversion curves produced from Fig. 1 by Eq. (2) are shown in Fig. 2 against the reaction time. The sigmoidal conversion curves in Fig. 2 are typical for a gelation process predicted by the percolation model, which can be elaborated as follows: 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 parameters that can change the reaction kinetics like temperature, concentration and light intensity etc. 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 $|t - t_c|$. 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 section, 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 [30]. 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 studies in the literature propose that the 3D glass transition is controlled by the percolation of small domains of slow dynamics, which allows us to explain the heterogeneous dynamics close to the glass transition [38,39]. 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 calculated the corresponding reduction in the glass transition temperature in quantitative agreement with the experimental results. Here it is assumed that

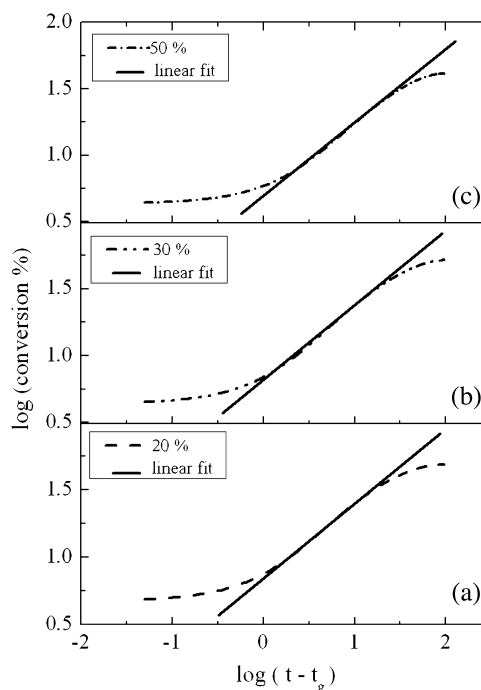


Fig. 4. Double logarithmic plot of the conversion versus time curves above t_g for (a) 0.02%, (b) 0.10% and (c) 0.50% TX-SH concentration, respectively. The values of β exponent were determined from the slope of the straight lines.

the volume fraction occupied by the total number of monomers incorporated into the glassy regions are the 'occupation probability', p , of the sites of a three dimensional lattice. In a glassy region, the motion of a monomer is completely restricted due to vitrification. These glassy regions, which may be considered the initiation centers of vitrification on the microscopic scale, will grow in time as polymerization proceeds, and percolate as p_c is reached.

The critical exponent, β , can be measured by using the double logarithmic plots of the conversion versus $|t - t_c|$. The critical exponents were produced from the slope of the straight lines during fitting of the data in Fig. 3.

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 large shifts in the critical exponent. Such a log-log plot reveals that the 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 behaviour over the greatest range in $|t - t_c|$, if the experiments are performed against time. Here, the time corresponds to the maximum of the rate of polymerization chosen as the critical time, t_c , which may be considered as the glass transition point, t_g , for the gelation under consideration. The plots of log conversion versus log $|t - t_g|$ above t_g for three different DMF content gels are shown in Fig. 4a, b and c, respectively, where the slopes of the straight lines produced the gel fraction exponent, β .

The β values produced for gelation are presented in Table 1 together with t_g and Rp_{max} values. Here it should be noted that the average value (≈ 0.55 of produced β values above t_g) strongly suggests that the glassy regions percolate during gel formation for all the samples under consideration, by predicting that they belong to the same universality class.

The plots of t_g and Rp_{max} versus the DMF content are presented in Figs. 5 and 6, respectively. It is seen in Fig. 5 that there is a long delay in glass transition during gelation of EA/TPGDA with the highest amount of DMF, which also results in a very low Rp_{max} value compared to the others. As expected, it can be clearly seen

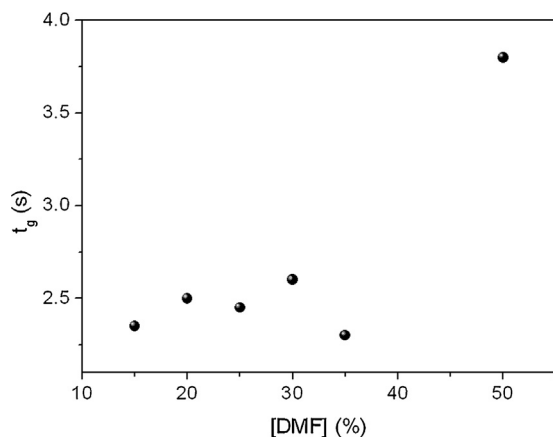


Fig. 5. The effect of photoinitiator (TX-SH) concentration on t_g value for EA/TPGDA.

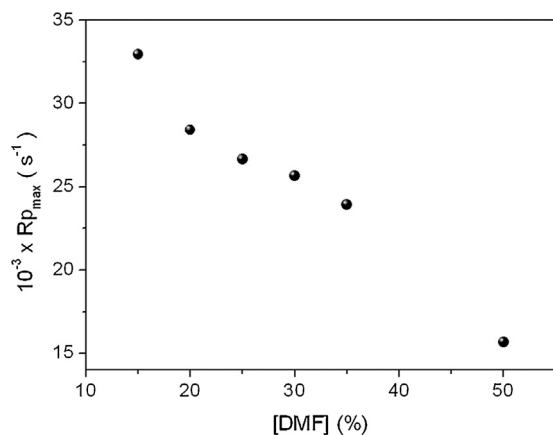


Fig. 6. The effect of photoinitiator (TX-SH) concentration on the rate of photopolymerization for EA/TPGDA.

in Fig. 6 that increasing the solvent content diluted the monomer concentration, hence slowing down the polymerization rate [40].

These results are expected because glassy regions have difficulty percolating in high amounts of solvent which results in a long t_g and a low rate of polymerization value. Here we should point out that all formulations produced approximately the same conversion values at t_g (see Table 1), indicating that high t_g and low $R_{p_{\max}}$ do not affect the production of the gelation at t_g . However, the highest final conversion, C_s , as seen in Fig. 7 with low and high DMF content

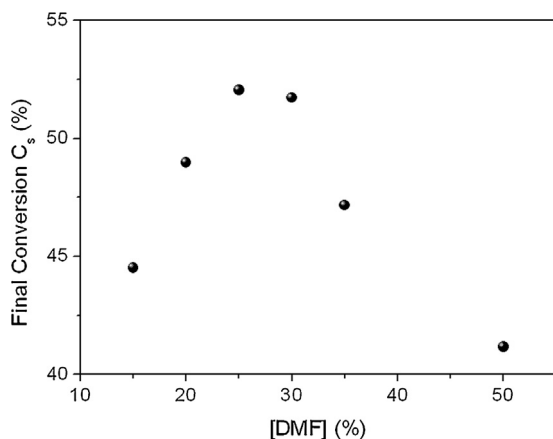


Fig. 7. The effect of photoinitiator (TX-SH) concentration on the final conversion of photopolymerization for EA/TPGDA.

gels, presents lower values than C_s in medium DMF content gel. In addition, the large amount of DMF can lead to a considerably low C_s value. It was also noted that changing the solvent content has little influence on the conversion values at t_g , which is defined in the early reaction (see Table 1).

This behavior can be explained with the assumption that polymerization in high and low viscous medium results in low conversion values compared to a medium viscous environment. Most probably in high and low viscous mediums, the polymerization reaction cannot be completed due to kinetic difficulties, which results in low conversion values. Moreover, while the solvent content demonstrates a dominant effect in terms of the rate of the early stage of polymerization (gelation region), in the last stage (glassy region) this effect becomes less pronounced.

4. Conclusions

In this study, a photo-DSC technique was used to measure the critical exponent, β , during gel formation for EA/TPGDA mixtures in various amounts of DMF. It should be emphasized that β values displayed no variation during gelation for all samples prepared with various DMF contents. However, it was observed that the other gelation parameters such as t_g , $R_{p_{\max}}$ and the final conversion C_s presented considerable variations, depending on the DMF content. The averaged value for the critical exponent β was found to obey the percolation model, predicting that universal behavior holds near the glass transition point for all gels prepared with differing DMF content.

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