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

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A B S T R A C T

Photoinitiated radical polymerization of an 80 wt% epoxy diacrylate (EA) and 20 wt% tripropyleneglycoldiacrylate (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 concentration present nice sigmoidal behavior which suggests application of the percolation model. The critical time, where polymerization reaches the maximum rate (Rp_{max}) is called the glass transition point (t_g). The gel fraction exponents, β 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. Rp_{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}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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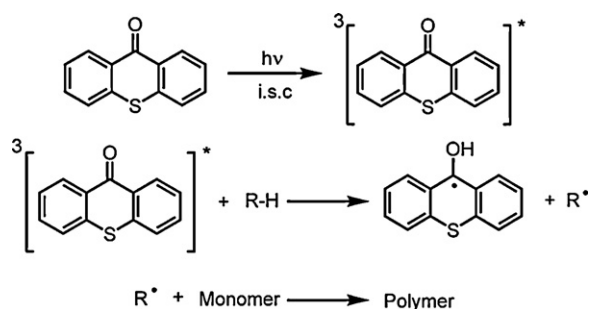
Scheme 1. Photoinitiated free radical polymerization by using aromatic carbonyl compounds.

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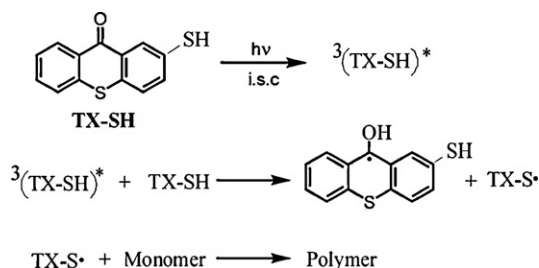
Scheme 2. Photoinitiated free radical polymerization by using 2-Mercaptothioxanthone (TX-SH).

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 (β) were produced. The averaged value for the critical exponent β 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 Rp_{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 β for the gel fraction G (the strength of the infinite network in percolation language) near the gel point, can be defined as Eq. (1),

$$G\alpha(p - p_c)^{\beta}, \qquad p \to p_c^+ (\text{above percolation}) \qquad (1)$$

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 β 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 CaH$_2$ under reduced pressure. Epoxy diacrylate (EA) and Tripropyleneglycoldiacrylate (TPGDA) were obtained from Cognis France.
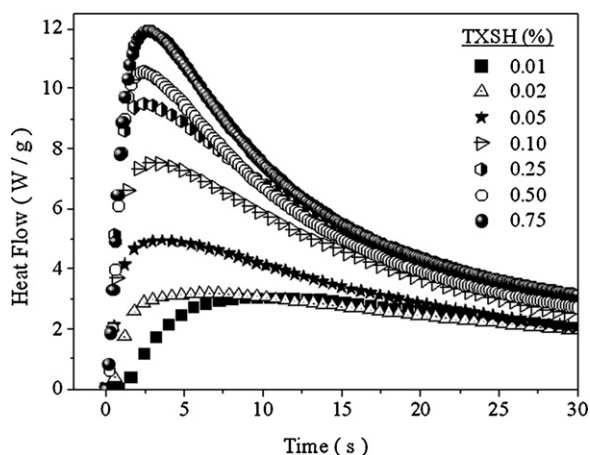
Fig. 1. Heat flow spectra of photopolymerization of EA/TPGDA with various photoinitiator (TX-SH) concentrations irradiated at 25 °C by UV light with an intensity of 40 mW/cm².

Fig. 2. 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/cm².

2.2. Photo differential scanning calorimetry (Photo-DSC)

The photoinitiated polymerization of EA/TPGDA in the presence of varying (0.01, 0.02, 0.05, 0.10, 0.25, 0.50 and 0.75 wt%) TX-SH concentration was performed in a Photo-DSC setup (TA-DSCQ100). UV light was applied from a medium pressure mercury lamp with 40 mW/cm² light intensity for 5 min. The weight of the samples 2 ± 0.1 mg was placed into an open aluminum liquid DSC pan. The measurements were carried out under identical conditions (i.e. an isothermal mode at room temperature (24.92 °C) and a nitrogen flow of 50 mL/min).

The reaction heat liberated in the polymerization is directly proportional to the number of acrylates reacted in the system. By integrating the area under the exothermic peak, the conversion of the acrylate groups (C) or the extent of the reaction was determined according to Eq. (2):

$$C = \frac{\Delta H_t}{\Delta H_0^{\text{theory}}} \tag{2}$$

where ΔH_t is the reaction heat evolved at time t and $\Delta H_0^{\text{theory}}$ is the theoretical heat for complete conversion. A reaction heat for an acrylate double bond polymerization of $\Delta H_0^{\text{theory}} = 86$ kJ/mol was used [30]. The rate of polymerization (Rp) is directly related to the heat flow (dH/dt) by Eq. (3):

$$Rp = \left(\frac{dC}{dt}\right) = \frac{(dH/dt)}{\Delta H_0^{\text{theory}}} \tag{3}$$

3. Results and discussion

3.1. Photo-DSC results

Photo-DSC measurements supply the reaction data in which the measured heat flow can be converted directly to the ultimate percentage conversion and polymerization rate for a given formulation. A typical heat flow and rate of polymerization curves versus reaction time for different initiator concentrations are presented in Figs. 1 and 2, respectively.

Conversion curves produced from Fig. 2 are shown in Fig. 3 against reaction time. It is seen in Figs. 1–3, that, with increasing initiator concentration, the extent of heat flow, the rate of polymerization and conversion increased.

Increased initiator concentrations provide higher efficiency for initiation, leading to more formed primary radicals in the solution. This enhances both the polymerization rate and final conversion
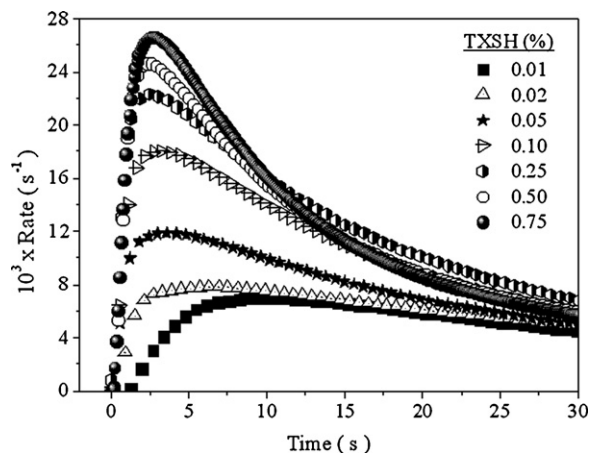
ratio. The reduction of the induction period is also favored by a high concentration of photoinitiator.

3.2. Kinetic assessment of photopolymerization

The effects of photoinitiator concentration on the photopolymerization kinetics were presented as shown in Figs. 4–6. It is interesting to note that t_g values decrease as the photoinitiator concentration increase, following the opposite behavior of Rp_{max} and final conversion, C_s.

One naturally may expect that the higher photoinitiator concentration should reduce the time required to achieve glass formation and their percolation during gelation process. On the other hand, as expected, both Rp_{max} and C_s increase as the photoinitiator concentration is increased.

3.3. Critical exponents during gelation

The above experimental findings can be quantified in terms of gelation theories 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 temperature, light intensity and concentration are kept constant, then p will be directly proportional to the reaction time,
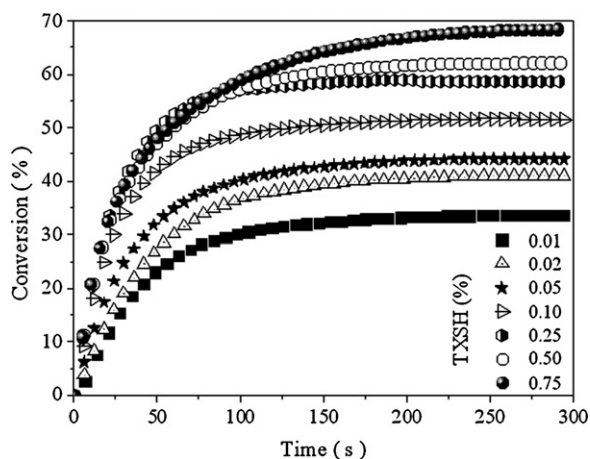

Fig. 3. Conversion spectra of photopolymerization of EA/TPGDA with various photoinitiator (TX-SH) concentrations irradiated at 25 °C by UV light with an intensity of 40 mW/cm².
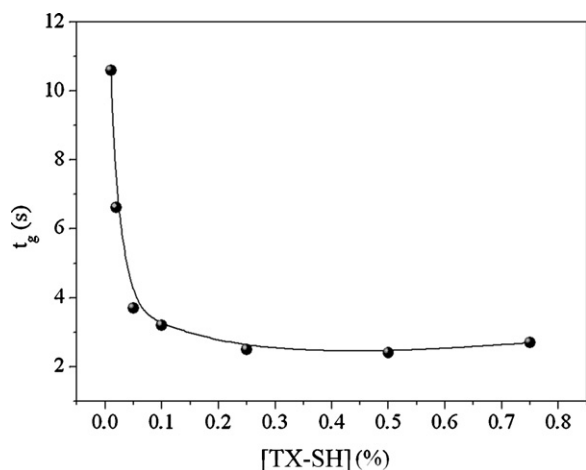
Fig. 4. The effect of photoinitiator (TX-SH) concentration on t_g value for EA/TPGDA.
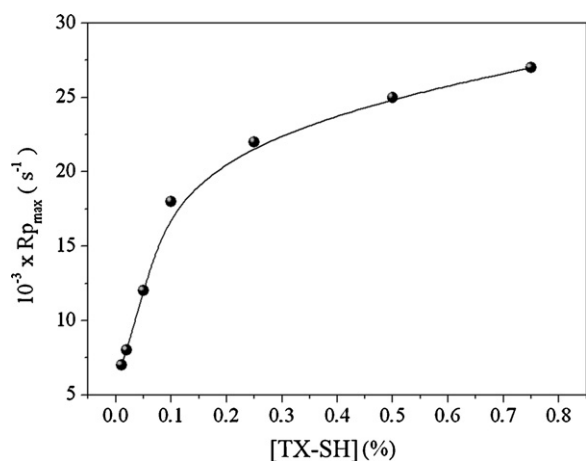

Fig. 5. The effect of photoinitiator (TX-SH) concentration on the rate of photopolymerization for EA/TPGDA.

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 critical point (i.e., for $t < t_c$) conversion measures the weight average degree of polymerization. Above t_c, however
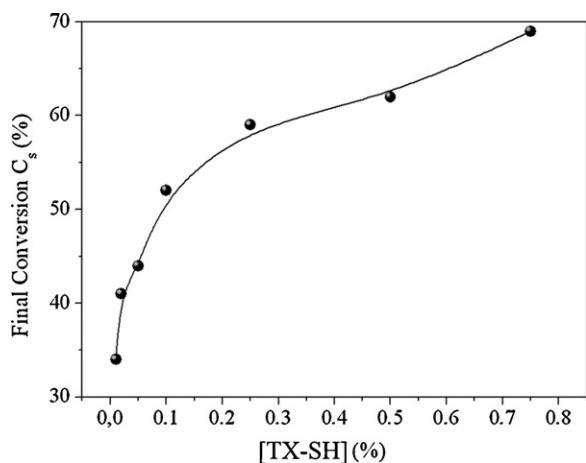

Fig. 6. The effect of photoinitiator (TX-SH) concentration on the final conversion of photopolymerization for EA/TPGDA.
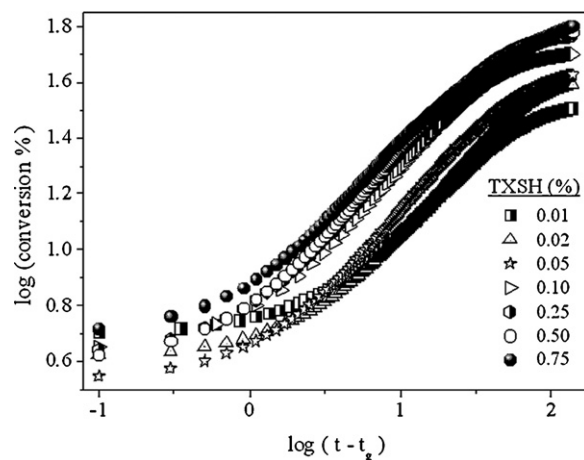

Fig. 7. Double logarithmic plot of the conversion versus time curves above t_g for various photoinitiator (TX-SH) concentrations.

conversion measures solely the gel fraction G, the fraction of the monomers that belong to the macroscopic network.

Now our experimental findings were interpreted by considering the quasi-static properties of the gel near the glass transition point in the language of percolation [31]. The double logarithmic plot of the conversion versus $|t - t_c|$ was analyzed, which produced the critical exponent, β from the slope of the straight line during fitting the data in Fig. 7.

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 log–log plot reveals that data should be particularly accurate near the critical 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. The time corresponding to the maximum rate of polymerization was chosen as the critical time, t_c which may be named as the glass transition point, t_g for the photoinitiated gelation under consideration. The plot of log (conversion) versus log $|t - t_c|$ above t_g for the gelation of EA/TPGDA with three different photoinitiator concentrations are presented in Fig. 8.

The slopes of the straight lines produced gel fraction exponent β at the given initiator concentrations. The β values calculated for the gelation of EA/TPGDA in all initiator concentrations are listed in Table 1 together with t_g, Rp_{max} and final conversion, C_s. Here it has to be noted that the average value (=0.56) of the calculated β values above t_g strongly suggest that the glassy regions percolate during photoinitiated gel formation for all the samples under

Table 1
Experimentally observed parameters measured by "Photo-DSC" and calculated via "percolation theory" for various photoinitiator concentrations during diacrylate, EA/TPGDA, photopolymerization at 25 °C by UV light with an intensity of 40 mW/cm².

[TX-SH] (wt%)	t_g[a] (s)	$10^{-3} \times Rp_{max}$[b] (s^{-1})	C_s[c] (%)	β[d]
0.01	10.6	7	34	0.52
0.02	6.6	8	41	0.56
0.05	3.7	12	44	0.57
0.10	3.2	18	52	0.57
0.25	2.5	22	59	0.57
0.50	2.4	25	62	0.57
0.75	2.7	27	69	0.55

[a] Time to reach glass transition point.
[b] The maximum polymerization rate.
[c] The final conversion of double bond.
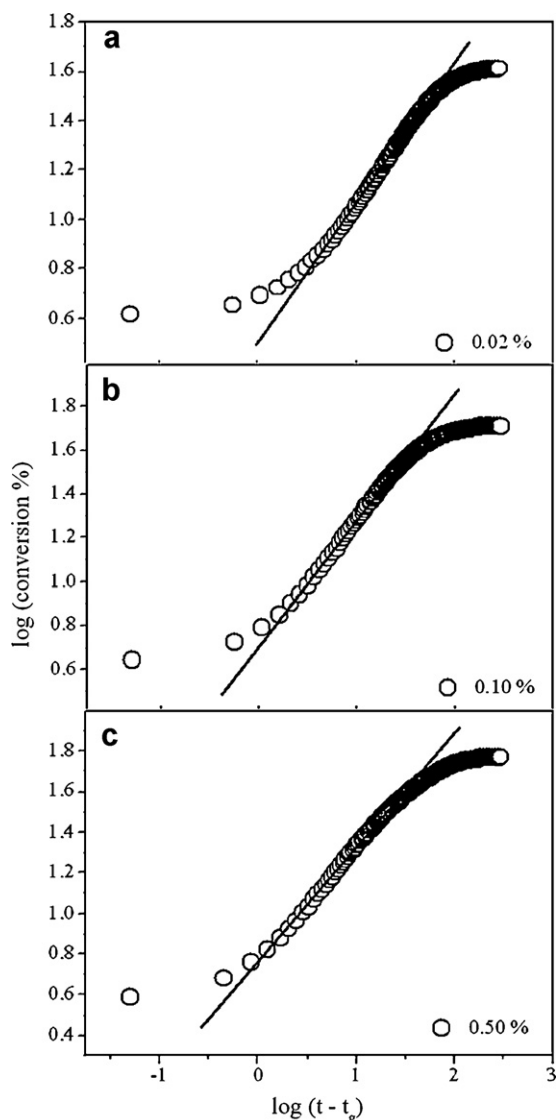[d] Beta value.

Fig. 8. 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.

consideration, by predicting that they belong to the same universality class, that is, they obey the percolation theory.

4. Conclusions

In this work it is seen that Photo-DSC technique can be used to measure the critical exponents, (during gel formation from EA to TPGDA mixtures for various photoinitiator concentrations. It has to be emphasized that (values do not vary during gelation for all samples prepared in various initiator concentrations indicating

that the gelation in this particular system obeys the universality of percolation model. However it was observed that the other gelation parameters such as t_g, Rp_{max} and C_s presented considerable variations depending on the photoinitiator concentration.

Acknowledgments

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