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Critical phenomenon during photoinitiated gelation at different temperatures: A Photo-DSC study

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ABSTRACT

The behaviour of photoinitiated radical polymerization of an 80 wt% epoxy diacrylate (EA) and 20 wt% tripropyleneglycoldiacrylate (TPGDA) mixture with 2-mercaptothioxanthone (TX-SH) photoinitiator was studied at different temperatures by using photo-differential scanning calorimetric (Photo-DSC) technique. All photopolymerization reactions were carried out under the same conditions. It was observed that all conversion curves during gelation at different temperatures present nice sigmoidal behaviour which suggests the application of the percolation model. Observations around the critical time, called the glass transition point (t_g), taken to reach the maximum rate of polymerization (Rp_{max}) show that the gel fraction exponent (β) obeyed the percolation model. The produced β values were found to be around 0.50, predicting that the system under consideration belongs to the same universality class. However, Rp_{max} and the final conversion (C_s) values were found to increase when the temperature was increased up to a certain value. On the other hand, t_g values decreased and became saturated as the temperature was increased.

1. Introduction

Photoinitiated polymerization of multifunctional acrylates provides an easy and instant method for producing highly crosslinked networks. The excellent physical properties and low curing time of these crosslinked materials have led to a growing demand and widespread applications for these materials. Applications, such as curing of coatings on various materials, adhesives, printing inks and photoresists are well known in the field of interest. 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 [1–5].

Photoinitiated radical polymerization may be initiated by bond cleavage (Type I) and H-abstraction (Type II) initiators [1]. Type II photoinitiators are based on compounds whose triplet-excited states readily react with hydrogen donors, thereby producing initiating radicals (Scheme 1) [2–4]. Because of the bimolecular radical generation process, they are generally slower than Type I photoinitiators, which form radicals unimolecularly.

Thiol and carboxylic acid derivatives of thioxanthone have recently been reported to initiate photopolymerization without co-initiators as they contain functional groups with a H-donating nature [6–8]. In addition, involvement of oxygen inhibition of photopolymerization suggests that thioxanthone–anthracene (TX–A) may find use in a variety of practical applications of photocuring in air [9]. A major advantage of thioxanthone-based initiators is related to their one component nature. They can serve as both a triplet photosensitizer [10,11] and a hydrogen donor. Thus, this photoinitiator does not require an additional co-initiator, i.e., a separate molecular hydrogen donor. We recently reported [7] the use of a thiol derivative of thioxanthone (TX-SH) as a photoinitiator for free radical polymerization. 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 thyl radical initiates the polymerization (Scheme 2).

Photoinitiated polymerization of multifunctional monomers results in crosslinked polymers that induce particular behaviours as regards kinetic reactions. Various parameters such as photoinitiator concentration, type of photoinitiator, light intensity and temperature affect the kinetic reaction processes during gelation [12]. Therefore, it is important to study the effect of temperature on the photopolymerization kinetics. Several researchers have been

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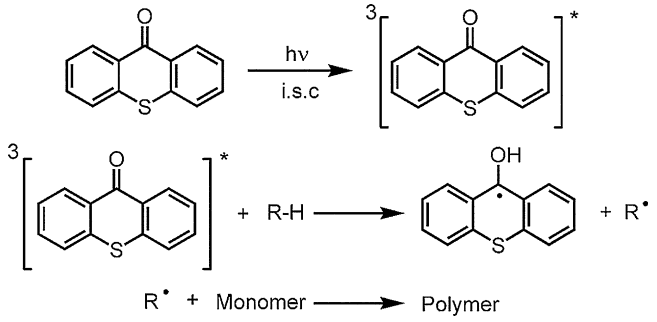
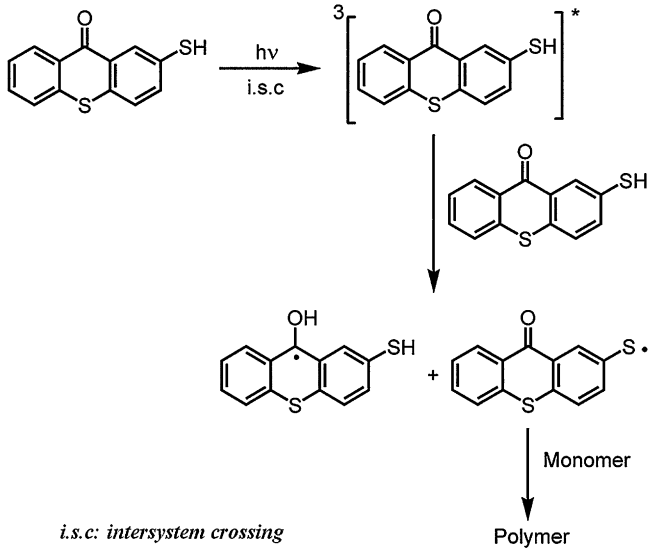


Scheme 1. Photoinitiated free radical polymerization by using aromatic carbonyl compounds.

interested in this matter. Cook [13], Young and Bowman [14], and Andrzejewska [15] have thoroughly studied the temperature effect on the photopolymerization of multifunctional acrylates. Significantly, Cook [16] investigated the reactivity of a homologous series of bisphenol-A-based dimethacrylate resins from −40 °C to 160 °C and also, low-temperature photopolymerization of different acrylates was studied by Gao and Nie [17]. They found generally that the maximum rate of cure for photopolymerized acrylates increased with an increase of temperature due to an increase in propagation rate. Maffezzoli et al. reported that photopolymerization of an epoxy resin for stereolithography by Photo-DSC and increasing the irradiation intensity or the cure temperature led to an increase of both the rate of reaction and the degree of reaction [18].

When the glass transition temperature (T_g) of the polymer network is lower than the isothermal cure temperature, the polymerization reaction is kinetically controlled. When T_g of the network equals the isothermal cure temperature, vitrification occurs and diffusion of the reactive species becomes the limiting stage in the crosslinking reaction.

It is well known that free radical cross-linking polymerization (FCP) produces a network called a gel. The whole course of the bulk FCP is divided into three stages: low conversion stage, gel effect stage and glass effect stage [19–21]. It was observed that monomer conversion first increases very slowly, but then accelerates because of the gel effect [22]. When the reaction temperature is lower than the glass transition temperature of the polymer, the glass effect stage occurs as the last stage of polymerization. The glass transition



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

temperature of polymers is customarily defined as the temperature at which the relaxation time on the monomer scale reaches about 100 s [23]. Radical chain polymerizations are often characterized by the presence of autoacceleration in the polymerization rate as the reaction proceeds [24].

Since the monomer and initiator concentrations decrease with time, usually one would expect the reaction rate to drop with the extent of conversion. However, exactly the opposite behaviour has been observed in many polymerization processes (the reaction rate increases with the conversion during the first stage of polymerization). This behaviour during the polymerization is referred to as the gel effect, also named the Trommsdorf effect or Norrish–Smith effect [25]. The gel effect corresponds to a dramatic increase in the rate of free radical polymerization and of the viscosity of the reaction medium. It is caused by the diffusion limitations in the reaction medium, which slows down the termination but not the propagation reaction. Norrish and Smith [25] postulated that the increased viscosity caused by monomers being converted to polymers 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 [26]. Burnett and Melville [26], Schultz and Harbort [27] each independently performed polymerizations in the presence of solvent and both reached the conclusion that the gel effect was caused by increasing the bulk viscosity, as the solvent reduces the viscosity and delays the onset of the gel effect.

Quite 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 [28,29] and at different UV light intensities with TX-SH as the photoinitiator [29,30].

In this work, the behaviour of photopolymerization kinetics of 80 wt% EA and 20 wt% TPGDA acrylates mixture with TX-SH photoinitiator was investigated at increasing temperatures from −15 to 125 °C by using the Photo-DSC technique. It was observed that all conversion curves during gelation present sigmoidal behaviour as predicted by the percolation model from which the critical exponents, β were produced. The averaged value for the critical exponents β was found to obey the percolation model, predicting that the universal behaviour holds near the glass transition point. The produced glass transition point t_g, maximum rate of polymerization Rp_{max} and final conversion C_s values were found to be strongly correlated with the temperature in which the photoinitiated polymerization took place.

1.1. Percolation

It is known that the gelation phase is not a transition one in the thermodynamic sense, being a geometrical one. As the subject of the critical phenomenon, it behaves like a second order phase transition constituting a universal class by itself. The exact solution of the gelation was given first by Flory and Stockmayer [31,32] 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 [33] where monomers are thought to occupy the sites of a periodic lattice and the chemical bonds corresponding to the edges randomly joining 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 viscoelastically rigid [34,35].

The predictions of these two theories about the critical exponents for the gelation are different from the point of universality.

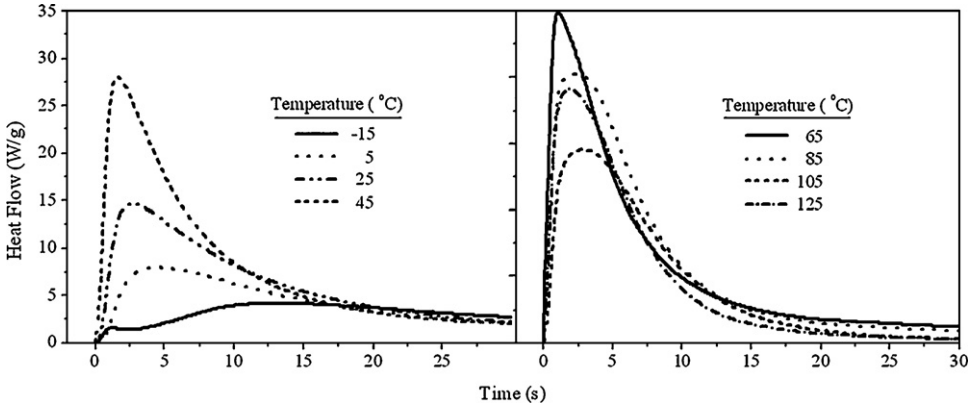


Fig. 1. Heat flow during photopolymerization of EA/TPGDA with TX-SH versus time.

Consider, for example, the exponents 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):

$$G \propto (p - p_c)^{\beta}, \quad p \to p_c^{+} \tag{1}$$

where the Flory–Stockmayer theory (the so-called classical or mean-field theory) gives $\beta = 1$ which is independent of the dimensionality, while the percolation studies based on computer simulations give β around 0.43 in three-dimensions [32,36]. These two universality classes for the gelation problem are separated by a Ginzburg criterion [37] 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 [33–35].

2. Experimental

2.1. Materials

2-Mercaptothioxanthone (TX-SH) was synthesized according to the previously described procedure [7]. Dimethylformamide (DMF, 99+%, Aldrich) was distilled over CaH_2 under reduced pressure. Epoxy diacrylate (EA) and tripropyleneglycoldiacrylate (TPGDA) were obtained from Cognis France.

2.2. Photo differential scanning calorimeter (Photo-DSC)

The heat of the photoinitiated polymerization reaction was measured by means of a photo differential scanning calorimeter, as a good control of the reaction temperature [38]. The photoinitiated polymerization of EA/TPGDA in the presence of TX-SH (0.5 wt%) was performed in a Photo-DSC setup (TA-DSCQ100) separately at elevated temperatures from −15 to 125 °C. UV light was applied from a medium pressure mercury lamp at a constant intensity of 40 mW/cm^2 for 3 min under a nitrogen flow of 50 mL/min at a prescribed temperature (isothermal mode). 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. The sample was maintained at a prescribed temperature for 4 min before each measurement run began. Measurements were recorded at a sampling interval of 0.05 s/point. The thickness of cured thin films was about 0.25 mm.

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 $\Delta H_0^{\text{theory}} = 86.25$ kJ/mol was used [39]. The rate of polymerization (R_p) is directly related to the heat flow (dH/dt) as in Eq. (3):

$$R_p = \frac{dC}{dt} = \frac{dH/dt}{\Delta H_0^{\text{theory}}} \tag{3}$$

3. Results and discussion

Photo-DSC experiments are capable of providing reaction 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 as in Eq. (3). It is important to study the effect of the temperature on the photopolymerization kinetics although photopolymerization reactions proceed at room temperature. However, the temperature at which the cure proceeds can affect the kinetics and the final cure values. Therefore, experiments were performed starting from −15 °C to 125 °C. Light intensity was held constant at 40 mW/cm^2 during the changes of temperature.

A typical heat flow curve versus reaction time of EA + TPGDA formulations is presented in two parts (Fig. 1) to clearly demonstrate the effect of temperature on the photopolymerization reaction.

The efficiency of the photoinitiator is not dependent on the temperature, but it might be dependent on the viscosity of the medium; decreasing the segmental mobility mainly decreases the efficiency of the photoinitiator due to prevention of the initiator radical from escaping the surrounding solvent cage as reported by Cook et al. [40]. Besides this, changing of the temperature – either lower or higher – will affect the molecular mobility. As the temperature and molecular mobility drops, the rate of reaction becomes markedly slower (Fig. 2). Figs. 1 and 2 show there is nearly no polymerization at −15 °C, but even when the temperature increased to 5 °C, this is still quite a low temperature for the viscosity of the medium. Heat flow reaches the maximum value for this experiment at 65 °C and then starts to decline above 65 °C (85, 105 and 125 °C) possibly due to depolymerization.

The rate of photopolymerization spectra of EDA/TPGDA versus reaction time for various curing temperatures at 40 mW/cm^2 light intensity is shown in Fig. 2. A similar trend was observed for the rate of polymerization as was expected. Increasing the temperature

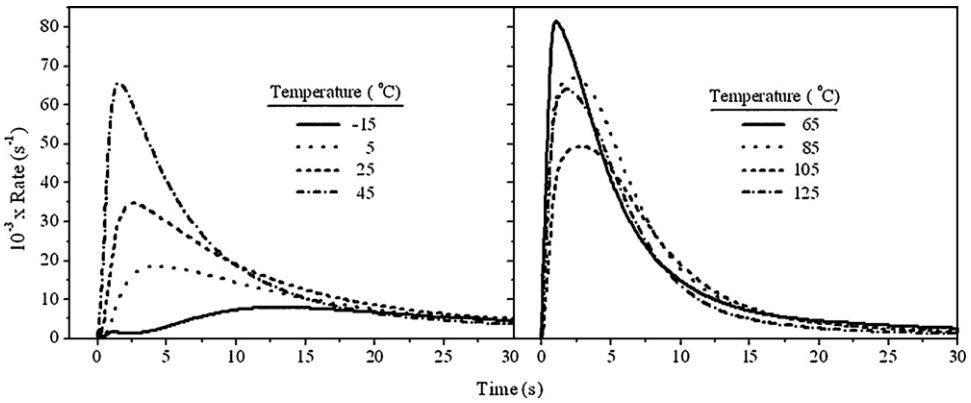


Fig. 2. Rate of polymerization spectra of photopolymerization of EA/TPGDA with TX-SH against time.

affects the polymerization medium and results in an increase of mobility of the reactive species.

From the results presented in Fig. 3 related to the conversion percentage values, the final conversion values of 32% and 43% were quite low at −15 °C and 5 °C, respectively. This is mainly due to the hindrance of molecular mobility in the medium. The highest conversion percentage of EA/TPGDA was obtained when the cure temperature increased to 45 °C. A further increase of cure temperature to 65 °C led to a slight decrease in the conversion percentage value and when the temperature was increased to 125 °C, conversion percentage values dropped to 52 and at that point depolymerization or decomposition had already started. It is obvious that increasing the temperature provides higher efficiency for initiation of the reaction by leading to the formation of primary radicals and small glass formers to evaluate the percolation cluster in the formulation.

It has to be noted that the conversion curves in Fig. 3 are typical for the phase transition and can be used to determine the critical exponents of the percolation picture in which the conversion factor, p, alone determines the behaviour of the gelation process, though p may depend on temperature, concentration of monomers, and time. If the temperature, light intensity and the concentration of all components are kept constant, 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 around the critical point that $|p - p_c|$ is linearly proportional to the $|t - t_c|$. The position of the glass transition on the time axis, t_c, can be determined with great precision, assuming:

$$|p - p_c| \propto |t - t_c|, \tag{4}$$

at least in the narrow region about the glass transition point, 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, conversion measures solely the gel fraction G, the fraction of the monomers that belongs to the macroscopic network.

Here, our goal is to measure the values of the critical exponents, β with sufficient accuracy to determine its universality class to verify that it indeed has the non-classical values for percolation computed from series expansion and Monte Carlo studies as well as renormalization theory. In this work, our results were interpreted by considering the quasi-static properties of the gel near the glass transition point in the language of percolation [36].

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 while fitting the data in Fig. 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 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 behaviour over the greatest range in $|t - t_c|$, if the experiments are performed against time. The time, t_m corresponding to the maximum of the 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. In fact finite size scaling predicts [33] that the difference $(t_m - t_c)$ vanishes as $L^{-1/\nu}$, where L is the size of the system as measured in units of the lattice spacing, and ν is the correlation length exponent [41]. Therefore, it is believe in that our system under consideration satisfies above condition. The plot of log (conversion) versus log $|t - t_g|$ above t_g for the gelation of EA/TPGDA with different temperatures is presented in Fig. 4.

The gel fraction exponents β produced by the slopes of the straight lines for the temperatures 5, 45, 85 and 125 °C are

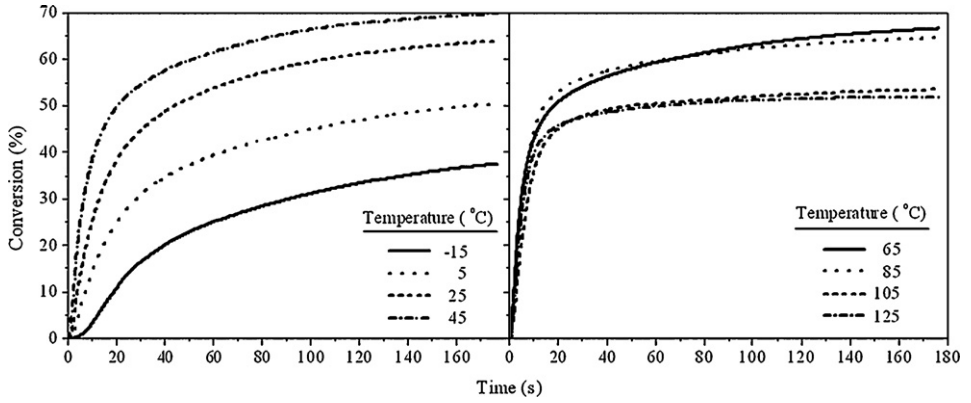


Fig. 3. Conversion spectra of photopolymerization of EA/TPGDA with TX-SH against time.

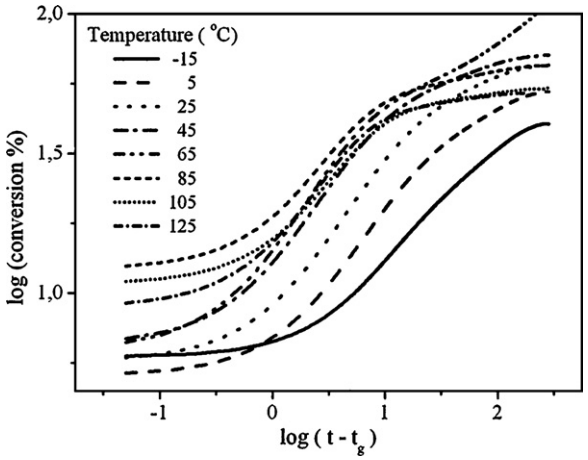


Fig. 4. Double logarithmic plot of the conversion versus time curves above t_g for various temperatures.

presented in Fig. 5a, b, c and d, respectively. The β values calculated for the gelation of EA/TPGDA mixture for all temperatures are given in Table 1 together with t_g, Rp_{max} and C_s. Here it has to be noted that the average value (=0.50) of the calculated β values above t_g strongly suggest that the glassy regions percolate during photoinitiated gel formation for all the samples under consideration, which predicts that they belong to the same universality class, i.e., they obey the percolation theory.

The behaviours of t_g, Rp_{max} and C_s against temperature are summarized in Figs. 6, 7 and 8, respectively. It is interesting to note that t_g values decrease as the temperature is increased which predicts that the formation of glassy regions shows some delay at lower

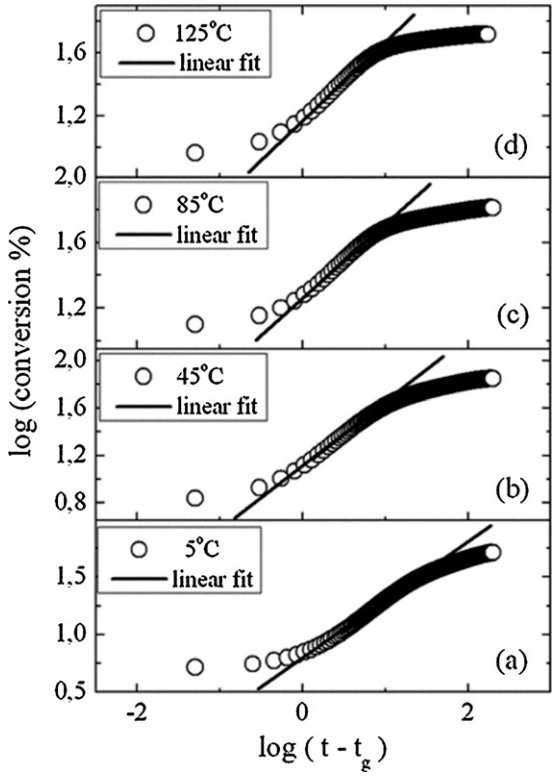


Fig. 5. Double logarithmic plot of the conversion versus time curves above t_g for the onset temperatures of (a) 5 °C, (b) 45 °C, (c) 85 °C and (d) 125 °C respectively. The values of β exponent were determined from the slope of the straight lines.

Table 1
Experimentally observed parameters measured by "Photo-DSC" and calculated via "percolation theory" at various temperatures during diacrylate, EA/TPGDA, photopolymerization.

Temperature (°C)	t_g (s)	Rp_{max} ($\times 10^{-3}$ s^{-1})	Final conversion (%)	β value
−15	13	8	32	0.46
5	4	18	43	0.55
25	3	34	59	0.55
45	2	65	66	0.55
65	1	81	61	0.56
85	2	66	62	0.47
105	3	49	52	0.47
125	2	64	52	0.52

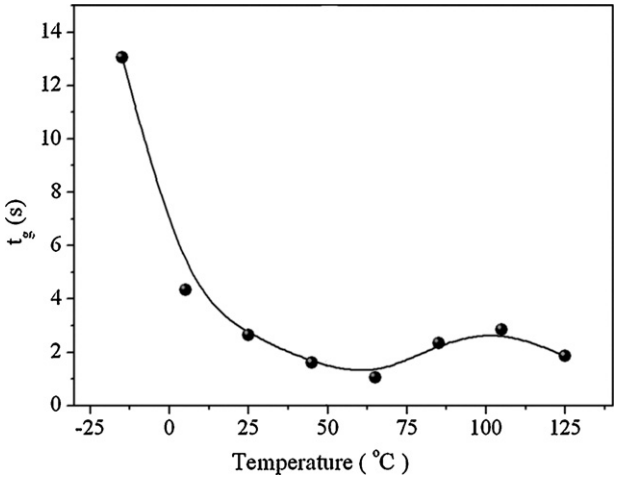


Fig. 6. t_g versus temperature for EA/TPGDA photopolymerization.

temperatures, however at higher temperatures glassy regions form particularly fast especially above t_g (Fig. 6).

On the other hand, Rp_{max} and C_s present the opposite behaviour, i.e., both values increase as the temperature is increased as is expected (Figs. 7 and 8). Here, it has to be noticed that t_g, Rp_{max} and C_s values all fluctuate against temperatures above 45 °C. Most probably, the formation of glassy regions above 45 °C poses some difficulties which result from instability during the formation of percolation clusters from the glassy regions under consideration.

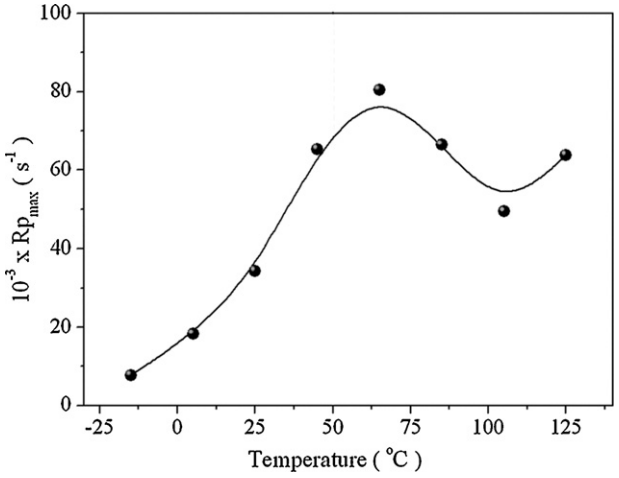


Fig. 7. Effect of temperature on the rate of photopolymerization of EA/TPGDA mixture.

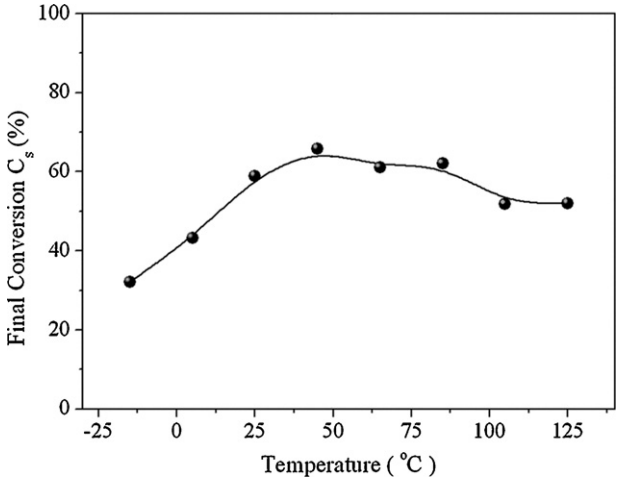


Fig. 8. Effect of temperature on the final conversion of photopolymerization of EA/TPGDA.

4. Conclusions

This work has presented a study in which the Photo-DSC technique was used to measure the critical exponents, β during the gel formation of EA and TPGDA mixtures with TX-SH photoinitiator for various curing temperatures at a constant light intensity (40 mW/cm^2). It has to be emphasized that (values do not vary at all during gelation for all samples conducted at various temperatures. However, it was observed that the other gelation parameters such as t_g, Rp_{max} and final conversion (C_s) presented considerable variations depending on the temperatures. The optimum curing temperature for a given formulation was found to be 45 °C according to the C_s values. Increasing the temperature to about 20 °C possibly helped to increase the propagation rate and resulted in higher conversion values. In fact, an increase of temperature to 65 °C led to an increase in the rate of polymerization at the beginning and then a slightly lower rate for the final conversion value. Above 65 °C, possibly depolymerization or decomposition occurred and the produced conversion values dropped.

The averaged value for the critical exponent β was found to obey the percolation model, predicting that the universal behaviour holds near the glass transition point for all the gels prepared at different temperatures. Here we have to note that producing exponent γ for $t < t_g$ conversion is not reliable with DSC measurements, which is the shortcoming of this method below t_g.

On the other hand, this present work and the others [28,29,42] strongly support the universality of glass transition during free radical polymerization processes by given the similar critical exponent β in various polymeric systems with different measurement techniques.

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