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# TEMPERATURE MODULATED DSC STUDY OF THE KINETICS OF FREE RADICAL ISOTHERMAL NETWORK POLYMERIZATION

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Temperature modulated differential scanning calorimetry (TMDSC) is used to study the kinetics of the free radical isothermal polymerization of triethyleneglycol dimethacrylate (TEGDMA). Azo-*bis*-isobutironitrile was used as initiator. The polymerization's temperature is lower than the final glass transition temperature of the polymer network. The measurement of the average heat flow released and the heat capacity during the reaction allows identifying the different stages of the reaction. The presence of double peaks in the heat flow is ascribed to the autoacceleration. The influence of temperature, measuring conditions and oxygen are described. Vitrification is detected by the drop in heat capacity. It occurs at increasing conversion rates for increasing temperatures. After vitrification, the diffusion-controlled reaction continues.

***Keywords:*** *free radical isothermal polymerization, TEGDMA, TMDSC, triethyleneglycol dimethacrylate*

## Introduction

Triethyleneglycol dimethacrylate (TEGDMA) monomer easily forms a glass upon cooling with a glass transition around –86°C [1, 2]. The free radical polymerization of TEGDMA produces a high glass transition temperature polymer network. This polymer has been used sometimes as a model material for the study of the highly cross-linked networks used as coatings, information storage systems, spherical lenses and dental cements [3–7].

Temperature modulated differential scanning calorimetry (TMDSC), has been used in particular to monitor time dependent properties as is the case of crystallization [8–10] and polymerization, where the heat flow released by the exothermal reaction is measured simultaneously to the heat capacity of the reacting mixture of monomer and growing polymer chains or polymer networks [11–21]. In TMDSC the conventional DSC temperature program is superimposed with a dynamic temperature change. Due to the phase lag, $\varphi$, between the calorimeter response function (i.e. the heat flow) and the time derivative of the temperature modulated program, a complex apparent heat capacity is defined, $C^*$, whose modulus is

$$\left|C^*\right| = \frac{\dot{Q}_\mathrm{a}}{\omega T_\mathrm{a}} \tag{1}$$

where $\dot{Q}_\mathrm{a}$ is the amplitude of the oscillating heat flow (or the first harmonic of the periodic component of the heat flow in the usual case the profile is not sinusoidal); $T_\mathrm{a}$ is the amplitude of the temperature wave; and $\omega$ is the modulation frequency. Data treatment is done through a Fourier analysis and the first harmonic is considered in the calculations. In this way, selecting the adequate combinations of the underlying heating rate, frequency and temperature amplitude values, three temperature dependent magnitudes are obtained as representative of a TMDSC experiment [22–24]:

$$C_\beta = \frac{\dot{Q}_\mathrm{u}}{\beta} \tag{2a}$$

$$C' = \left|C^*\right| \cos\varphi \tag{2b}$$

$$C'' = \left|C^*\right| \sin\varphi \tag{2c}$$

Equation (2a) describes the heating rate dependent heat capacity obtained from the underlying component of the heat flow, $\dot{Q}_\mathrm{u}$, i.e. the frequency independent component in the Fourier analysis. $C_\beta$ is equivalent to the trace of a conventional DSC analysis at the average heating rate, $\beta$. Equation (2b) gives the real part of the complex heat capacity, i.e., the component in phase with the heat flow; and Eq. (2c) gives the imaginary part, i.e., the out-of-phase component that appears when time dependent processes take place in the sample.

The main feature of isothermal polymerization at temperatures below the glass transition temperature of the final network is the heat capacity drop due to the vitrification of the reacting mixture. During polymerization, the glass transition temperature of the mixture continuously increases as a result of the changes in the composition of the monomer/polymer

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mixture. When the glass transition temperature of the mixture approaches the value of the polymerization temperature the reacting system becomes a glass, the mobility of the reacting species becomes much more restricted, and the reaction is controlled by diffusion. In many systems the reaction practically stops so that the full conversion is not attained. The change in heat capacity that accompanies this process can be directly measured by TMDSC.

Another interesting feature that was observed and characterized by TMDSC was the appearance of a peak in the real component of the complex heat capacity during isothermal polymerization. At the beginning of the polymerization process the measured value of $C'$ is that of the monomer. An increase in $C'$ with time during the first stages of polymerization has been reported both in network [11, 12] and chain [13] polymerizations. $C'$ then goes through a maximum and subsequently it decreases. If the reaction temperature is above the final $T_g$ of the polymer, the system is in the liquid or rubbery state during the whole process and a maximum is clearly observed [14]. If the polymerization temperature is below the final $T_g$ the vitrification of the material produces the fall of $C'$ [15, 16, 20] and sometimes it is uncertain whether the maximum observed in $C'$ takes place before vitrification [17] or whether it is produced by it [17, 18]. Wang and Johari [19] using polymer chain statistical have recently explained the appearance of this peak in $C'$ as a consequence of the balance between two contributions to the configurational component of $C_p$, one of them coming from the fraction of vacancies in the lattice and the other one from the chain flexibility.

The kinetics of free radical addition polymerization is the result of the kinetics of different simultaneous reactions: the decomposition of the initiator which continuously produces free radicals, propagation which consumes the monomer available in the reaction mixture, chain transfer and the termination reactions. Probably the most important termination mechanism is the interaction of two active chain ends [25, 26]; termination rates strongly depend on the viscosity of the medium. An increase in the viscosity of the medium may cause a decrease in the rate of the termination reaction. This produces a rapid increase in the polymerization rate called the Trommsdorff–Norrish or gel effect [25–28].

In this work the kinetics of TEGDMA isothermal polymerization using azo-*bis*-isobutyronitrile, AIBN, as initiator, will be studied by TMDSC.

## Experimental

Commercial TEGDMA, from Sigma-Aldrich (cat. Nr. 26,154-8) containing hydroquinone as inhibitor was used in the experiments. Hydroquinone was eliminated using a column also from Aldrich (cat. Nr. 306312-1).

DSC and TMDSC experiments were performed in a Perkin Elmer Pyris1 calorimeter; aluminium pans were used. Quasi-isothermal experiments were performed. The programmed modulation was a teeth saw with varying peak-to-peak amplitude between 0.2 and 1°C (the actual amplitude of the temperature oscillation is lower than the peak to peak temperature increment programmed), and a modulation period between 12 and 48 s. The DSC was calibrated using indium and zinc standards at a heating rate of 10°C $\text{min}^{-1}$. In TMDSC storage heat capacity was calibrated following a method similar to that proposed in [29] (second order calibration). Heat capacity values of TEGDMA monomer were measured in conventional DSC in the temperature interval of the isothermal TMDSC measurements, using an aluminium oxide standard for heat capacity calibration. The same procedure was used to determine the heat capacity of the polymer networks. The samples used in these measurements were those polymerized in the isothermal TMDSC experiments. A multiplicative calibration factor was obtained by comparing the modulus of the complex heat capacity measured by TMDSC in the monomer and in the polymer with that determined by DSC, $\psi_m$ and $\psi_p$, respectively. The calibration factor for intermediate polymerization times was considered proportional to the polymer fraction according to the conversion $x$ (Eq. (3)).

$$\psi(t)=\psi_m+\frac{x(t)}{x(t_{\max})}(\psi_p-\psi_m) \tag{3}$$

One of the main difficulties in the study of the kinetics of free radical polymerization is the reproducibility of the results. It was determined that the accuracy in the reproducibility of the initiator content in the samples was crucial in this sense. When a series of samples are taken from the same monomer/initiator mixture (with a 0.1 mass% of AIBN in TEGDMA) and sealed in nitrogen atmosphere in aluminium pan the reproducibility of the results can be considered acceptable to support the conclusions reached in this work. Figure 1 shows the result of two TMDSC experiments conducted on two different samples prepared in this way. Small differences between the different polymerization thermograms can come from differences in the small amount of oxygen dissolved in the monomer even when it was sealed in nitrogen atmosphere.

After this preliminary studies two solutions were prepared by dissolving 0.1 mass% of AIBN in TEGDMA; the fresh mixtures were stored at –18°C and used in all the experiments to ensure no variability in the initiator content of the samples. One of the solutions was prepared in nitrogen atmosphere

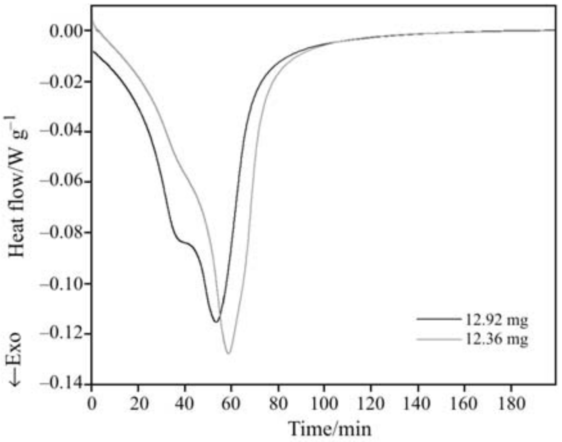

**Fig. 1** Normalized average heat flow measured by TMDSC during isothermal polymerization at 66°C of two samples prepared in nitrogen atmosphere to show the reproducibility of the experimental results

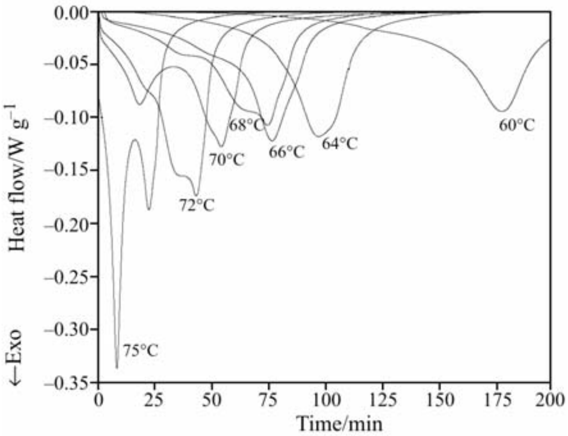

**Fig. 2** Normalized average heat flow measured by TMDSC during isothermal polymerization at different temperatures. Samples prepared in nitrogen atmosphere

and nitrogen flushing was continued during sealing. The other solution was prepared and sealed in air to study the influence of oxygen on the reaction kinetics. To check that no polymerization took place in the monomer/initiator mixture during storage at –18°C, several samples were encapsulated after several months of storage and some experiments reproduced. No significant deviation of the results from those obtained with the original samples was found.

## Results and discussion

### *Samples sealed in nitrogen atmosphere*

The average specific heat flow released by the sample during the quasi-isothermal polymerization, $\dot{Q}_u / m$, at different temperatures is shown in Fig. 2. The peak-to-peak amplitude of the temperature modulation was 0.2°C and the period 24 s. The sample mass, $m$, was around 11 mg in all the samples. Experiments were conducted for 200 min in the temperature interval ranging from 60 to 75°C. In this temperature range one or two exothermal peaks are clearly observed in the underlying heat flow within the experimental time interval. The AIBN decomposition kinetics determines that at lower temperatures the rate of the reaction is too slow for the experimental time, and at temperatures above 75°C a significant part of the reaction takes place before the stabilization of the calorimeter required to start temperature modulation. At the lowest temperatures a broad single peak is shown, but as temperature increases, the shape of the heat flow curve becomes more complex, and at the highest temperatures clearly a double peak appears.

After each isothermal experiment the sample was cooled from room temperature to –40°C and a conventional DSC scan followed until 220°C at 10°C min$^{-1}$. These scans showed an exothermal peak in the temperature range between the polymerization temperature and 200°C, corresponding to the polymerization of the unreacted methacrylate C=C bonds (Fig. 3). In several polymer networks it was reported that the system can vitrify during this kind of post-curing treatment and more than one heating scan is needed to reach full polymerization [17]. This seems not to be the case of our system at the heating rate of 10°C min$^{-1}$. The shape of the exotherm indicates that the system does not vitrify during heating, and that the reaction continues up to temperatures in the range of the final glass transition temperature of the network.

The enthalpy increment in the isothermal experiment was determined by the area below the curves shown in Fig. 2. The sum of the heat released in the isothermal reaction and that measured in the DSC scan was $\Delta h_{\text{tot}}$=94±4 kJ mol$^{-1}$ of monomer. In spite of the high uncertainty, it can be said that this value is

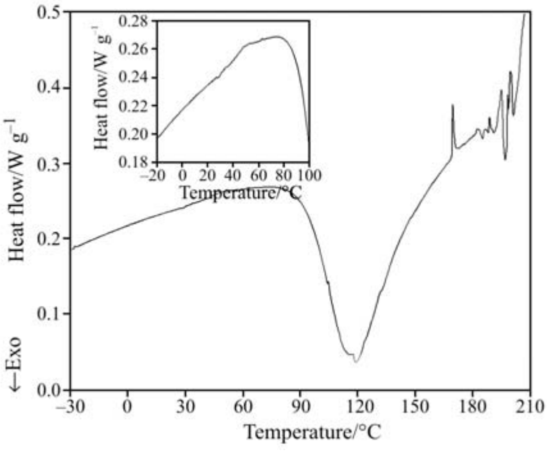

**Fig. 3** Conventional DSC scan obtained from –40 to 220°C at 10°C min$^{-1}$ for a representative sample sealed in nitrogen atmosphere and previously polymerized during 200 min at 66°C

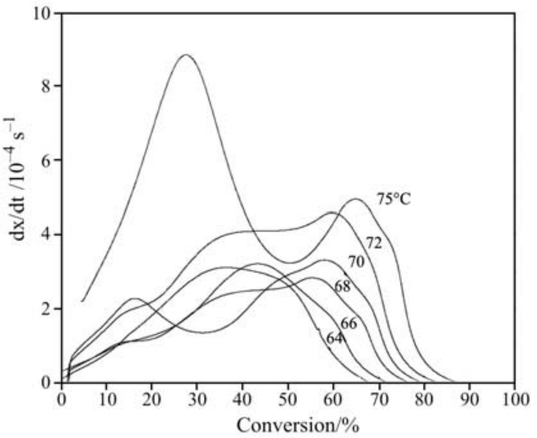

**Fig. 4** Conversion rate *vs*. conversion for the isothermal polymerization at different temperatures (indicated in the figure). Samples prepared in nitrogen atmosphere

similar to those found in the polymerization of other methacrylate polymers [30, 31].

Conversion was determined from the theoretical reaction heat per methacrylate double bond, $\Delta h_{\text{theor}}$=54.8 kJ mol$^{-1}$ [32]. The conversion $x$, and the conversion rate were calculated as:

$$x=\frac{M}{2\Delta h_{\text{theor}}}\int_0^t\frac{\dot{Q}}{m}\mathrm{d}t \qquad \frac{\mathrm{d}x}{\mathrm{d}t}=M\frac{\dot{Q}}{2m\Delta h_{\text{theor}}} \tag{4}$$

where $m$ is the mass of the sample and $M$ the molecular mass of the repeating unit. Plots of conversion rate *vs*. conversion are shown in Fig. 4, corresponding to some characteristic temperatures selected from those of Fig. 2. The maximum conversion attained depends on the polymerization temperature ranging from around 65% at 64°C to 80% at 75°C (abscissa in the plot of Fig. 4). Figure 5 presents the storage heat capacity at different polymerization temperatures.

The influence of some characteristic parameters on the experimental results was studied. Figure 6 shows the conversion rate *vs*. conversion curve measured at different modulation amplitudes for polymerization at 70°C. The strong dependence of the reaction kinetics on temperature results in a significant dependence of the heat flow on the modulation amplitude. However, the main features of this curve are preserved when increasing the peak-to-peak amplitude from 0.2 to 1°C. A conventional DSC heat flow curve is also shown for comparison. The influence of the modulation period in the range between 24 and 96 s was found irrelevant (results not shown).

*Samples sealed in air atmosphere*

The effect of oxygen inside the sample pan was studied by comparing the polymerization behaviour of samples

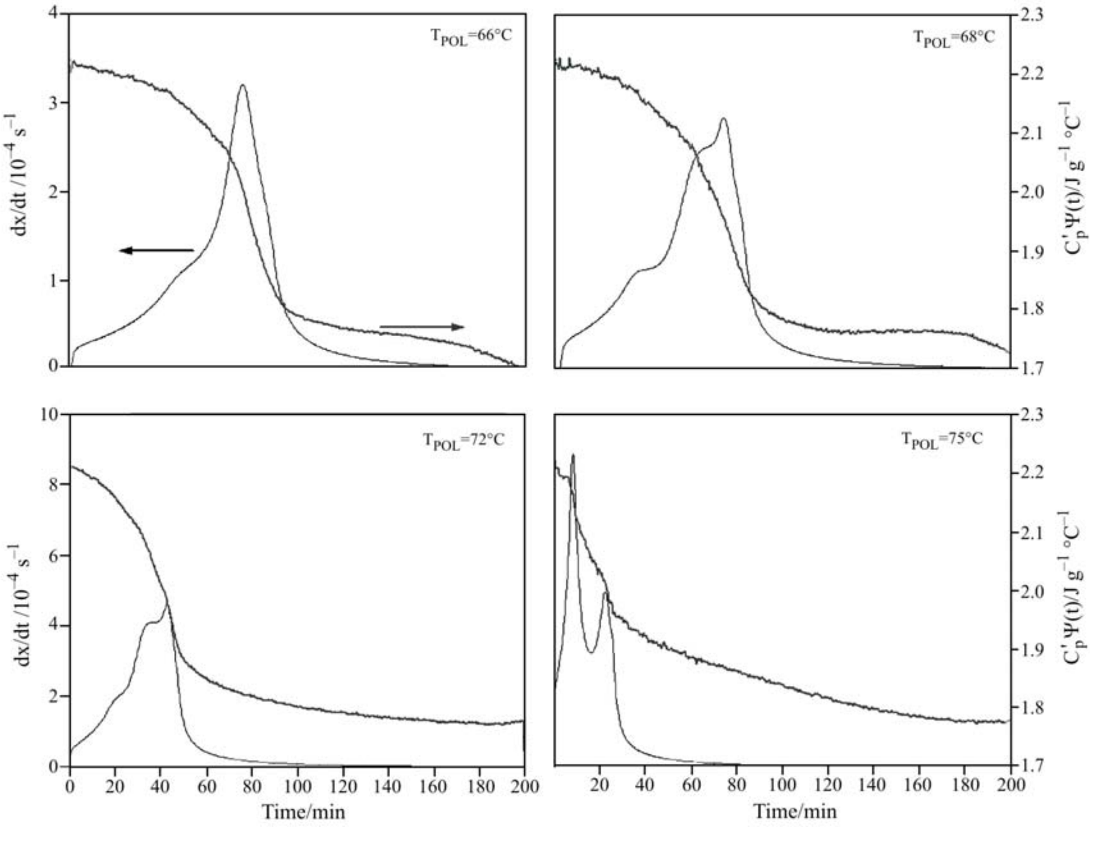

**Fig. 5** Conversion rate (left axis) and storage heat capacity (right axis) *vs*. polymerization time for isothermal polymerization at different temperatures

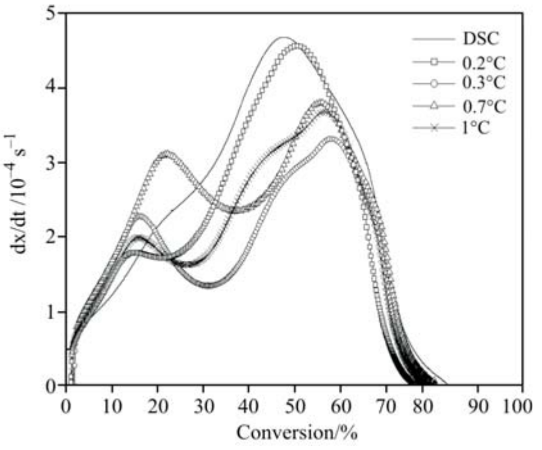

**Fig. 6** Influence of the modulation amplitude on the conversion rate plot. Samples sealed in nitrogen atmosphere

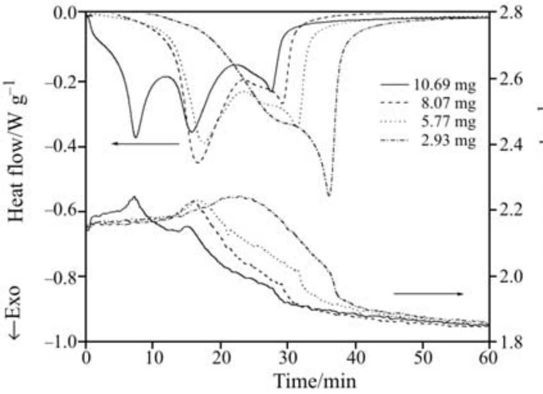

**Fig. 8** Normalized average heat flow (left axis) and storage heat capacity (right axis) for samples sealed in air atmosphere and polymerized at 85°C

sealed in air atmosphere with samples sealed in nitrogen atmosphere. Figure 7 shows the delaying effect of oxygen in the polymerization process at 70°C by keeping all the other experimental conditions constant. The effect of oxygen inhibition on polymerization is clearly shown by the shift of the peak to higher times for the air sealed TEGDMA sample.

On the other hand, the curve becomes more complex, with several exotherms, and the evolution of the heat capacity during polymerization in the air-sealed samples presents a clear maximum before vitrification, as shown in Fig. 8.

Additionally, the influence of sample mass was studied in a number of air-sealed samples with masses ranging from 2 to 23 mg and modulation amplitude 1°C. Significant changes in the evolution of the conversion rate and heat capacity were found when changing the sample mass, as shown in Fig. 8. Variations in the amount of monomer introduced in the sample pan (always a hermetic 30-microlitre pan) may cause two effects: one of them is to change the amount of oxygen contained in the reaction volume, and the specific surface of monomer exposed to the air inside the sample pan; and the other is to change the amount of heat that must be released from the reacting mixture to the DSC block. An increase in the mass of the reacting mixture may produce an increase in the local temperature as compared to the temperature measured by the instrument due to the thermal resistance of the sample holder. This increase in the local temperature can speed up the reaction. To check the relative influence of both effects a number of samples with masses varying between 6 and 18 mg were sealed in nitrogen atmosphere and polymerized at 75°C. The heat flow profiles are shown in Fig. 9.

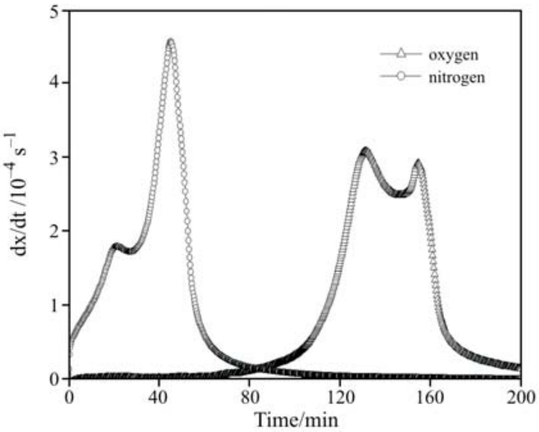

**Fig. 7** Comparison of the conversion rate *vs*. time for samples polymerized in oxygen and nitrogen atmosphere, and measured under the same conditions (temperature of polymerization of 70°C, amplitude and period of modulation of 1°C and 24 s)

The presence of double peaks in the conversion rate *vs.* time or conversion in the polymerization at the highest temperature, 75°C, in nitrogen-sealed samples can be explained by the Trommsdorff–Norrish effect. The absence of reaction inhibitors (except for the oxygen that could be solved in the monomer) makes the conversion rate increase rapidly at the first instants of the reaction. The conversion rate value is the result of the balance between initiation, propagation and termination reactions that take place simultaneously. The rate of each reaction changes as polymerization progresses due to the reduction in the amount of monomer and initiator and to the change in mobility due to the increase in the viscosity of the reacting mixture of the different species involved in the reaction. The first peak can be explained by the decrease in the amount of available monomer and initiator molecules. If the influence of the termination reactions on the conversion rate were not significant with respect to that of the initiation and propagation mechanisms, as has been pointed in some works [28, 33], the conversion rate would continue decreasing until the final stop of the reaction by vitrification. But the presence of the second peak means that the termination reactions play an important role in the conversion rate at this temperature.

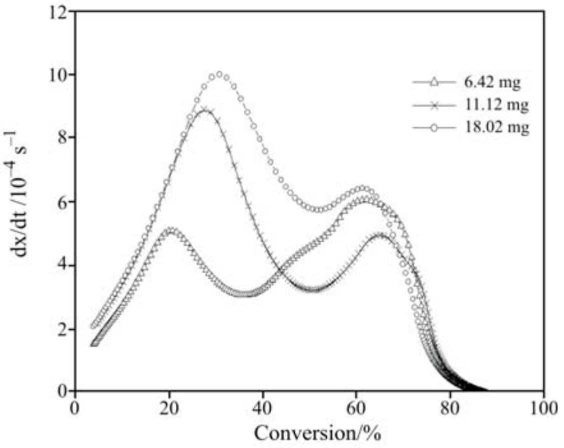

**Fig. 9** Influence of sample mass on the polymerization kinetics at 75°C (amplitude and period of modulation of 1°C and 24 s) of samples sealed in nitrogen atmosphere. The sample mass is indicated in the picture

The increase in the viscosity and the network connectivity cause the termination mechanisms involving radicals linked to the growing network to become diffusion controlled. The rate of the termination reactions rapidly decreases and the reaction self-accelerates. The second maximum would be due again to a decrease in the amount of the remaining unreacted monomer, and finally, after 27 min, vitrification takes place and the conversion rate rapidly decreases.

As temperature decreases, the conversion rate plot becomes simpler; nevertheless, between 72 and 68°C the overlapping of more than one peak is quite clear. In this temperature range, the high conversion side of the curve shows a more or less sudden slope change that can be ascribed to the onset of vitrification. For temperatures below 68°C, only one single peak can be observed.

The reason for this change in behaviour can be found in the fact that initiation and propagation reactions show higher activation energy than that of termination [25–27]. The rates of initiation and termination mechanisms become more different from each other as temperature decreases. At low temperatures the kinetics of the polymerization process is governed by the kinetics of initiation and propagation.

The plot of the real part of the complex heat capacity $C'$ *vs*. time shows the characteristic drop that can be associated with the vitrification of the system. Nevertheless there are some peculiarities in this system that requires a more detailed analysis. The lower the polymerization temperature is, the longer the time at which the $C'$ step occurs (remember Fig. 5). To characterize the position of the $C'$ step in the time axis, the time for the mid-point decrease of $C'$ in the step, $t_{mp}$, will be defined, similarly to the mid-point glass transition temperature in a DSC scan of a glass forming liquid. It is possible to calculate the conversion at that time that we call $x_{mp}$, its values are represented in Fig. 10. It is worth noting the great dependence of $x_{mp}$ with temperature. In this system the glass transition of the monomer ($T_{gM}$=–86°C) and that of the polymer network ($T_{gN}$≈156°C [34]) are quite different. When the system vitrifies during the polymerization reaction at a temperature in the order of 70°C it must consist in a polymer network with a cross-linking density below the stechiometric one, due to a number of unreacted double bonds in it and some unreacted monomer that acts as a plasticizer. The glass transition of this system is approximately the polymerization temperature, thus, around 100°C below the final glass transition temperature of the polymer network. The difference comes both by (*i*) the defect in cross-linking density and internal plasticization due to branching and (*ii*) the plasticization effect of unreacted monomer. To analyze the effect of each factor Fig. 10 shows the polymerization temperature (or the glass transition temperature of the system after vitrification during the isothermal polymerization) *vs*. the conversion. At the moment of vitrification in the reaction at 64°C the conversion of double bonds is $x$=0.51. Clearly not all the monomer is fixed to the polymer chains since in that case the system would consist in a linear polymer. But an increase in the conversion up to $x$=0.75 (conversion attained at 75°C) only increases de glass transition temperature by 15°C. If at this conversion most of the monomer is consumed, the additional cross-links produced by the reaction of the remaining double bonds in the network should account for the increase of the $T_g$ of the system from 75 to 156°C. To analyze the effect of plasticization, Fig. 10 shows a rough estimation of the conversion dependence of $T_g$, assuming that the unreacted monomer and the polymer network form a homogeneous mixture obtained using Fox equation [35].

$$\frac{1}{T_g+273.15}=\frac{x}{T_{gN}+273.15}+\frac{1-x}{T_{gM}+273.15} \tag{5}$$

The changes in the mixture composition that would produce a change in the $T_g$ of the mixture from 60 to 75°C (the temperature interval of our experiments) would be very small as shown in Fig. 10. The situation does not change significantly if one takes into account that the polymer network actually has a lower $T_g$ due to the discussed deficiency in cross-linking density. None of both effects (*i*) or (*ii*) or a combination of them satisfactory account for the experimental results. An alternative explanation is that a phase separation takes place in the system as polymerization progresses and the monomer is segregated from the growing network. Once an initiator molecule decomposes and the polymer network starts growing the local monomer/polymer ratio corresponds to the maximum swollen capacity of the polymer network that is smaller than that given by the average conversion. The local glass transition temperature in the growing network becomes higher than the reaction temperature and the heat capacity drops because of the local vitrification although a homogeneous monomer/polymer system with the composition given by the conversion at that time would have a glass transition temperature still lower than the polymerization temperature. At the moment of the drop in $C'$ the system consists of polymer network domains swollen in the amount of monomer roughly estimated by the Fox equation for a plasticized network, and domains consisting of pure unreacted monomer. The progress in the reaction follows by the opening of more initiator molecules in the monomer phase or by the diffusion of monomer into the glassy network domains. The reaction involves the incorporation of the monomeric unit to the glass and thus a transition from the liquid to the glassy state that contributes to a further decrease in the heat capacity of the system. It is interesting to note that according to this interpretation the glass transition of the monomer should be detected in the reacting system even for high conversion states, as in fact has been found by some of us using dielectric relaxation spectroscopy [36]. If after vitrification the sample is cooled to a temperature low enough to stop any further progress of the reaction and some time is allowed for the diffusion of the monomer into the polymer network, the glass transition temperature measured in a subsequent heating scan is smaller than the temperature at which the polymerization takes place, as shown in Fig. 3 for a sample polymerized at 66°C that was stored for a long time at 5°C before the DSC heating scan. This sample shows $T_g$ around 45°C. If vitrification had taken place in a homogeneous mixture during reaction, the glass transition would be equal to 66°C independently of the time delay before the DSC heating scan.

Another interesting feature is that $C'$ does not show a maximum before vitrification. According to the work of Wang and Johari [19] this maximum can be expected due to the mixture of monomer and polymer network. The reason why the peak is not present in our system can also be due to the existence of a phase separation that prevents the formation of a homogeneous mixture of monomer and polymer chains. Interestingly enough the peak in $C'$ appears clearly and repeatedly in the samples polymerized in aluminium pans sealed in air atmosphere. In that case the reaction is much slower than in the absence of oxygen provided the polymerization temperature is the same. There is more time for monomer to diffuse into the growing network and the segregation of the monomer can occur at longer polymerization times.

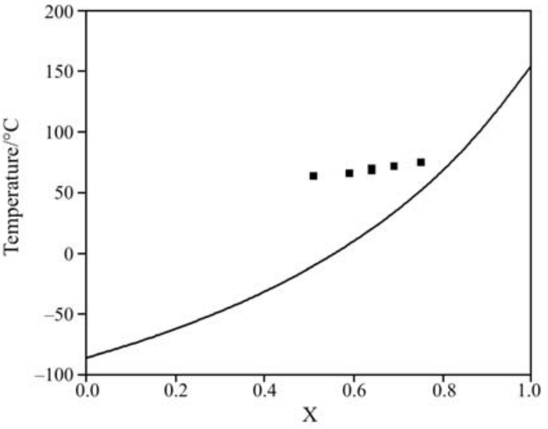

**Fig. 10** Relationship between polymerization temperature and conversion at the mid-point of the $C'$ step corresponding to vitrification. The solid line represents the glass transition temperature of a homogeneous mixture of monomer and the polymer network according to Fox equation

Oxygen is a well-known inhibitor in these reactions [7, 37, 38] that affects both initiating and propagating species in radical polymerization. In Fig. 7 the shift of the peaks in the heat flow plot to higher times can be observed for TEGDMA sealed in air atmosphere.

Two peaks are always present in the heat flow *vs.* time plot of samples sealed in air atmosphere (Fig. 9), which separate when the sample mass is increased. These can be easily related to the peaks present in the nitrogen-sealed samples. But, in addition a third peak can be observed when the mass is 10.69 mg. Recently Soulé *et al.* [31] observed a similar feature in the free radical isothermal polymerization of isobornyl methacrylate with benzoyl peroxide as initiator. A peak appears in the heat flow trace of the sample polymerized in presence of air which is not present in the case of samples sealed in nitrogen atmosphere; more experiments are necessary to clarify the origin of this peak.

## Conclusions

The shape of the heat flow or the conversion rate profile during isothermal polymerization of TEGDMA measured by TMDSC highly depends on temperature. The presence of more than one maximum in the heat flow *vs*. time curves can be caused by the gel effect. The presence of oxygen inside the DSC pan has an inhibiting effect (at the same temperature, the samples polymerized in oxygen atmosphere have a longer induction time than the samples polymerized in nitrogen atmosphere) but at the same time the shape of the heat flow profile gets affected and a new maximum appears.

The great dependence of conversion with the polymerization temperature can be explained if the growing polymer network is accompanied by a phase separation between highly cross-linked domains containing a certain amount of monomers such that their glass transition temperature equals the polymerization temperature, and another phase containing unreacted monomer.

Before vitrification, the temperature dependence of the real component of the complex heat capacity goes through a maximum in the samples sealed in air atmosphere. This was explained by Wang and Johari by the entropy of mixing of the monomer and the growing polymer network. Nevertheless, this peak is absent in samples sealed in nitrogen atmosphere. The difference between both situations may come from the phase separation mentioned in the former paragraph.

## Acknowledgements

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