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Effects of vitrification on the isothermal polymerization of acrylate blends under radiation

Summary — The radiation-induced polymerization of some acrylate oligomers was investigated by means of FT-IR spectroscopy applied to films of various thickness that were cured under isothermal conditions. Different types of oligomers, one polyethyleneglycol diacrylate (PEGDA), one polyurethane triacrylate (PURTA), and one epoxy diacrylate derived from bis-phenol A (EPDA) were selected for their contrasting networks properties, with a low, intermediate, and high T_g of the radiation-cured materials, respectively. In order to gain a deeper insight into the effect of gradual vitrification on the reactivity of the polymerizable systems, the conversion — dose profiles of the epoxy diacrylate were recorded at various temperatures. The dependence of the limiting conversion on the polymerization temperature was examined under various experimental conditions and compared with the conversion — T_g relation, which was deduced from dynamic thermo-mechanical analysis. The correlation between resulting T_g measured in the samples at maximal conversion for each curing temperature was shown to be slightly deviating from linearity. A phenomenological model of the reaction kinetics was shown to depict satisfactorily the observed photopolymerization profiles. From the well-determined T_g — conversion relation, a semi-mechanistic kinetic model taking into account the gradual vitrification of the network can be foreseen.

Key words: di- and triacrylates, radiation curing, polymerization kinetics, effect of vitrification, phenomenological kinetic model.

The radiation curing of acrylate blends is now a mature technology finding numerous industrial applications in the fields of graphic arts, coatings, paints, adhesives and composite materials [1]. Radiation-induced polymerizations are generally conducted under anisothermal conditions. From among of the many factors influencing the temperature of the materials under curing the following are worth to be mentioned: radiation source, type of polymerization process, monomer content and geometrical characteristics of the samples. The absorption of radiative energy as well as the strong exothermicity of the polymerization can produce strong temperature rise during the fast UV-curing of coatings [2]. In the frame of our program on the electron beam (EB) induced polymerization of acrylate compositions for high performance fiber-reinforced composites, we are currently developing the models that describe satisfactorily the relationship between process conditions, the monomer conversion (*G*) and glass transition temperature (T_g) of the material being cured [3].

Not only is the T_g value a physical property of central importance for the resulting structural materials, it is a feature of the reacting system that is gradually changing upon crosslinking polymerization [4]. The non trivial chain kinetics involves various mechanistic steps and rate constants that are affected first by gelation, and then by vitrification, apart from the additional influence of local fields of temperature and of radiation intensity [5].

The present investigation was thus carried out to determine the influence of the operating temperature on the ultimate conversion reached by various oligomer samples submitted to isothermal polymerization under radiation.

EXPERIMENTAL

Materials

The oligomers used in this study, a polyethylene glycol ($\overline{DP}_n$ = 10) diacrylate [PEGDA — Formula (I)], an aliphatic polyether-urethane triacrylate [PURTA — For-

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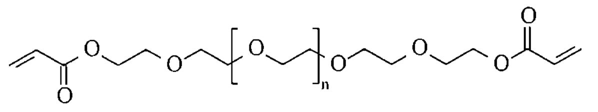

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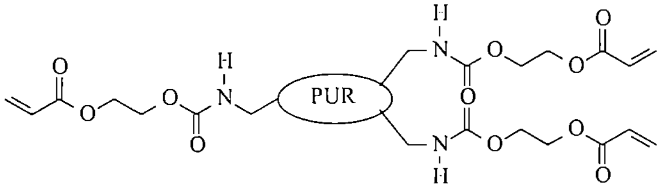

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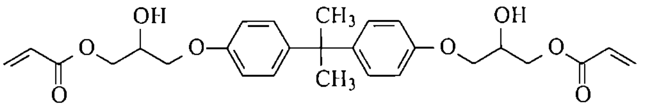

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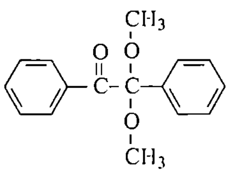

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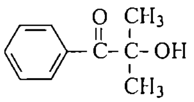

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mula (II)] and bisphenol A epoxydiacrylate [EPDA — Formula (III)] were commercial samples from UCB Radcure, having a number-average molecular weight of 600, 2000 and 5000 g · mol^{-1}, respectively. The photoinitiators for UV-induced polymerizations were 2-hydroxy-2-methyl-1-phenyl-propan-1-one [Darocur 1173 — Formula (IV)] and 2,2-dimethoxy-1,2-diphenylethan-1-one [Irgacure 651 — Formula (V)], used as received (Ciba Specialities, Switzerland).

Radiation treatment

The electron accelerator used for EB-curing of thin films was CB 150 ElectroCurtain generator (Energy Sciences Inc.), operating at 175 kV. The samples, coated on a flat substrate, were deoxygenated in the entrance airlock by a nitrogen flow and then exposed to the ionizing radiation under a stream of gaseous nitrogen (O_2 level below 180 ppm). Thick samples were cured by EB with the industrial processor (CIRCE II, 10 MeV and 20 kW) at EADS-ST Facility (Saint Médard en Jalles, France). Radiation doses were controlled by cellulose triacetate dosimetry (Nissin-High Voltage Co., Japan).

UV-initiated polymerizations were performed with fluorescent tubes emitting at 254 nm, 312 nm or 350 nm, with an intensity of 1 mW · cm^{-2} measured at a distance of 15 cm away from the tubes. For short exposures, the irradiations were controlled by means of an electronic shutter. Thin resin samples (*ca.* 10 µm) were prepared by sandwiching a liquid film of a selected oligomer blend between two 40 µm-thick PE-LD films. Thicker samples were prepared in molds shaped to form 1 mm-thick plate of dimensions 5×40 mm. The samples to be polymerized were placed in Linkam LTS350 temperature-controlled stage adapted with a transparent glass cover and with gaseous nitrogen flow.

The experimental set-up with Linkam stage allows us to conduct the photopolymerizations at low temperature, at least down to -150 °C. We have examined, under such conditions, the photopolymerization of PEGDA, which is known to form rubber-like networks, with typical T_g = -40 °C, but subjected to some variations depending on the length of the polyether chain between two acrylate functions [6].

EPDA was polymerized in various sample forms to examine the effect of curing temperature T_{polym} on maximal acrylate conversion. Ten µm-thick resin layers sandwiched between PE-LD films or between NaCl plates were subjected to 312 nm photopolymerization under strict isothermal conditions. Another series was prepared by curing of 1 mm-thick bars, sandwiched between transparent glass plates, with 350 nm light. The conversion was monitored by direct transmission infrared analysis in the case of thin samples, whereas powdered samples obtained from the thicker UV-cured bars were analyzed in the form of KBr pellets (see next paragraph).

Methods

Spectroscopic characterization

Infrared spectra were recorded with Perkin-Elmer FT-IR System-2000 model with a conventional TGS detector and under dry air purging. Analyses were performed in the transmission mode, on NaCl plate coated with *ca.* 10 µm-thick films of the acrylate formulation (EB irradiation), or placed between PE-LD films in a sample holder (UV-curing of thin films). For 1 mm-thick UV-cured samples, 2 wt. % powder dispersions in KBr pellets were prepared, by compression, for transmission analysis.

Photocalorimetric measurements

DSC calorimeter used to record overall polymerization enthalpy of acrylate oligomers was equipped with a mercury lamp (UNIPAN, model 610M, Poland). All measurements were performed under argon atmosphere. Sample weight was equal to 20 mg. UV light was filtered in order to irradiate selectively in the wavelength range of 340—360 nm. The UV intensity at the sample surface was determined by a radiometer RM-21 (Dr. Groebel, Germany) as 0.014 mW · cm^{-2}.

Viscoelastic characteristics

Viscoelastic measurements yielding the storage shear modulus (*E'*) and mechanical loss tangent (tg δ) were performed using Rheometrics RSA viscoelastometer. Experiments were carried out in a dual cantilever mode at a frequency of 1 Hz, at temperature ranging from 20 to 200 °C with a programmed heating rate of 3 °C · min^{-1}.

RESULTS AND DISCUSSION

Nonisothermal radiation-induced polymerization

High-energy electrons accelerated by 10 MeV generator penetrate organic materials over a typical depth of 3 to 4 cm, making possible to cure the fiber-reinforced composite matrices by free radical or by cationic polymerization [7]. In typical industrial conditions, the process starts at room temperature, hence the name "cold polymerization" has coined for this novel curing method. The polymerization generally proceeds within the treated object in the absence of external thermal regulation. As a consequence of the conversion of deposited energy into heat and of the strongly exothermal nature of polymerization of acrylate, strong variations of temperatures can be expected, particularly when large parts are treated with high dose radiations.

To illustrate the large thermal effects caused by the sudden polymerization upon application of 50 kGy EB-dose to an epoxy-acrylate sample (EPDA), a series of thermocouples was placed in parallelepiped aluminum container filled with about 125 g of the diluted EPDA resin. 10 MeV and 20 kW electron beam was directed to the sample, as shown in Fig. 1. and the deposited energy was vanishing before total penetration along the long axis of the parallelepiped.

The plots in Fig. 2 indicate the temperature changes recorded from 7 thermocouples placed along one of the main diagonals of the sample. The sharp rise is essentially due to the strong exothermic effect assigned to acrylate monomers polymerization (*ca.* 330 kJ · mol^{-1}), initiated instantaneously or after a short induction period, owing to the high concentration of free radicals readily produced by the high energy beam. Clearly, the thermocouples numbered 4 and 5, placed in the front half part of the sample are submitted to the highest temperature, since they are located in a zone combining a maximal energy deposition and lower heat dissipation. In the back part of the sample, the lower energy deposition and smaller thermal effects produce a partially cured material with gel properties. The end of 150 s-long irradiation is evidenced by the break in the temperature line indicating the start point of sample cooling, as soon as the pulsed beam stops and the conversion of absorbed radiation into thermal energy does not overwhelm heat dissipation to the surrounding medium.

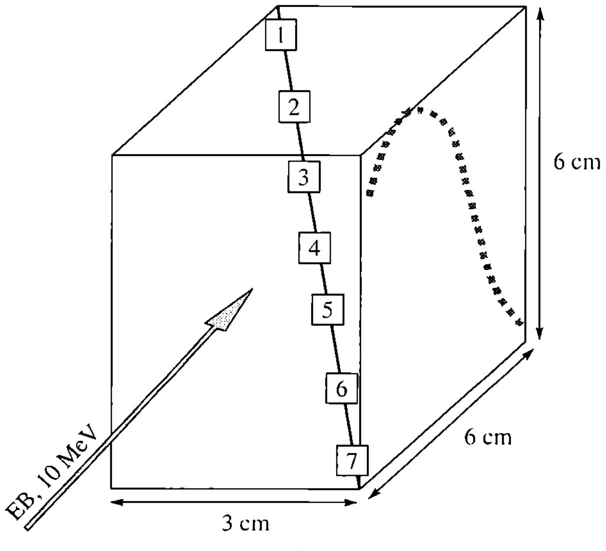

Fig. 1. Position of thermocouples in the sample of 125 g EPDA resin submitted to 50 kGy EB-irradiation dotted line indicating the dose energy deposition profile; 1—7 series of thermocouples

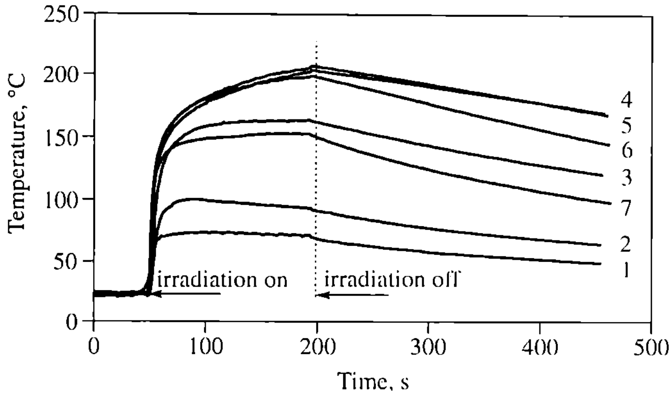

Fig. 2. Variations of thermocouple (1—7) temperature in the sample from Fig. 1

Obviously, the complex kinetics taking place in such conditions cannot be analyzed without a previous detailed study of the influence of the main parameters and variables of the system. We consequently developed a specific methodology based on discontinuous FT-IR measurements for monitoring the direct chemical effect of incremental EB (or UV) irradiation on monomer conversion. The method consists in the reconstruction of the progress of monomer conversion, in thin films, as a function of cumulated dose increments, applied under various well-defined conditions [8]. Application of fractionated dose is a simple way for minimizing thermal effects that may be detrimental to pertinent kinetic analysis. We have conducted the simulations corresponding to the sequential application of EB dose increments during a period of a given duration, followed by long rest periods allowing the sample to equilibrate with the reference temperature (20 °C) reaching [9]. For fractionated treatments at high dose rate ($\dot{D}$ = 110 kGy · s^{-1}), the first dose increment of 10 kGy follows the curve simulated for continuous irradiation beyond the point where maximal temperature is reached (Fig. 3 — lines *a*, *a'*). Limitation of the temperature increase would require

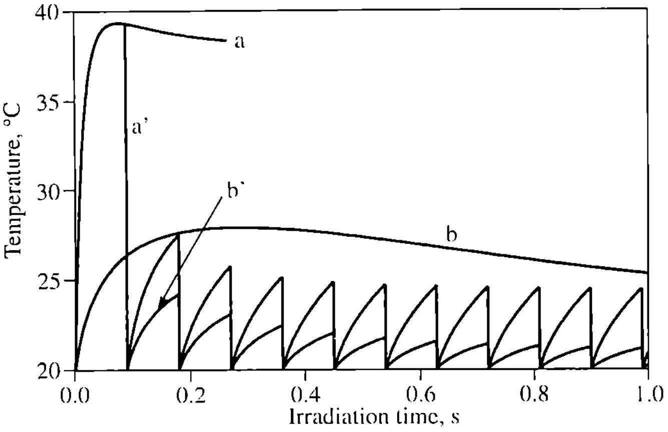

Fig. 3. Simulation of temperature vs. irradiation time variations at mid thickness of 10 μm-thick film for continuous (a and b) or incremental (a' and b') application of the radiation dose rate $\dot{D}$*: a, a' — 110 kGy · s*$^{-1}$*; b, b' — 19 kGy · s*$^{-1}$ *(*ΔH_0 *= 300 J · g*$^{-1}$*)*

exposure times shorter than 20 ms that are unrealistic when we use the lab accelerator for kinetic investigations. However, applying 1.7 kGy increments by processing at lower dose rate (19 kGy · s^{-1}), limits the temperature variation to $\Delta T \approx 6$ °C at the end of the first dose application. The temperature rise then decreases and finally does not exceed 2 °C, after the fifth application of the same dose increment (Fig. 3 — lines *b, b'*). On the basis of these numerical simulations, pertinent processing parameters can be recommended for considering that polymerization takes place under isothermal conditions.

Kinetic profiles obtained by discontinuous irradiation

Applying a small dose at a time, we have obtained informative polymerization profiles by monitoring discontinuously the sample after each incremental irradiation, using FT-IR spectroscopy. The continuous curves drawn from the experimental points seem to overlap fairly, thus indicating that, at constant dose rate, the cumulating effect of a small dose added to the preceding effects gives the same result as a single dose whatever the value of the dose increment is (single dose or cumulated exposure).

We have performed a comparative study of two different prepolymers diluted with multifunctional monomers. The kinetic profiles recorded along the EB irradiation of PURTA and of EPDA are shown in the Fig. 4.

Under similar processing conditions, the higher reactivity of PURTA blend is clearly evidenced, with a maximum conversion degree exceeding 0.9, that is reached after treatment with 20 kGy dose. The initial part of the kinetic profile of EPDA blend also reveals a steep change of conversion after application of the very first dose increments, but, once a conversion degree of 0.2 is reached, the profile is strongly flattened down. It is instructive to compare the acrylate content within the two blends submitted to similar irradiation treatments. The acrylate concentration $[C{=}C]_0$ is 6 mol · kg^{-1} and 3.5 mol · kg^{-1} in the unreacted EPDA and PURTA blends, respectively. This means that at a 60 kGy dose, the poorly reactive EPDA sample still contains larger amount of potentially reactive monomer functions than PURTA sample at the very beginning of the irradiation.

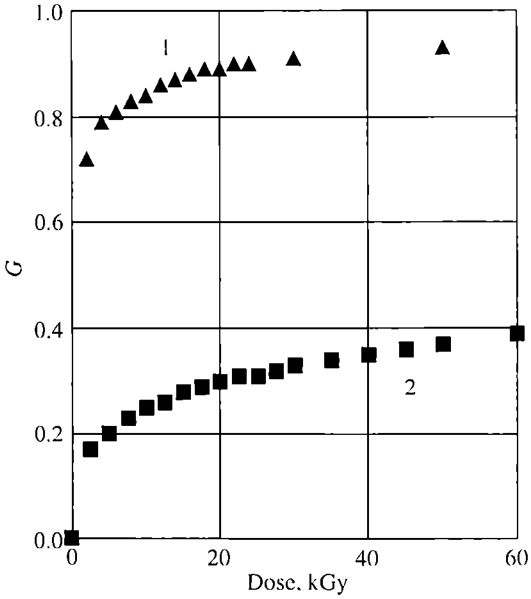

Fig. 4. Conversion (G) vs. dose profiles for diluted PURTA (1) and diluted EPDA (2) samples submitted to small increments of EB-dose so as to minimize thermal effects

The cured materials present large differences in physical properties. Soft films with T_g ranging from 45 to 50 °C are obtained from similar diluted PURTA formulations [10], whereas epoxyacrylates are used for structural composite materials with high T_g matrix [4]. We can therefore conclude about a strong effect of vitrification that restricts the mobility of active centers and monomers within EPDA blend treated with EB at room temperature.

The curves typically exhibit two remarkable domains: a steep initial slope for liquid state polymerization that proceeds readily but under the control of the initiation and the propagation of the system being investigated, and at the high dose region, a monotone and smooth dependence upon exposure to radiation that is controlled by the residual mobility. The existence of distinct kinetic regimes stresses the interest of correlating of the kinetic profile of the polymerization with the changes of network physical properties. A detailed study of dose rate effects indeed showed that the initial polymerization rate [11], $(R_p)_{t=0}$, deduced from these plots exhibited a linear dependence with the square root of the dose rate, in good agreement with the usual kinetic model for free radical polymerization [12] that is initially governed by relation (1).

$$R_p = \frac{k_p R_{init}}{2\sqrt{k_t}}[C{=}C] \rightarrow \frac{k_p}{2\sqrt{k_t}}[C{=}C]\left(\dot{D}\right)^{0.5} \quad (1)$$

where: R_{init} — *initiation rate,* k_p — *propagation rate constant,* k_t — *termination rate constant, [C=C] — double bounds concentration.*

Deviations from this law are observed as soon as the initial slope weakens as a consequence of mobility restriction. From the lines drawn at the high dose range, one obtains unambiguously a first order dependence of the polymerization rate on $\dot{D}$. This situation corresponds to a chain process with monomolecular termination as expected in a vitrified medium [13, 14].

Isothermal photopolymerization

Real time infrared spectroscopy [15] and photocalorimetry [16] are powerful tools for studying the polymerization kinetics of UV-curable monomer blends. However none of these techniques allow to obtain, from the same sample, some information about the degree of polymerization and network properties.

For this reason, we have developed a methodology to elaborate the samples by slow photopolymerization under strictly isothermal conditions. By using small initiator contents (up to 1wt. %) and photo-excitation in a spectral range where the initiator shows low absorption coefficient (close or above glass cut-off wavelength), the heat flux liberated by the sample is limited and samples of thickness of a few millimeters can be cured without significant gradient of light absorption. The sample can be submitted to dynamical mechanical analysis (DMA) for network characterization and to FT-IR for determination of residual acrylate concentration.

Infrared analysis of PEGDA and EPDA samples

In order to validate the procedure of isothermal curing under UV radiation, we have recorded the infrared spectra of acrylate blends. The decrease in infrared absorbance at 810 cm^{-1} characteristic for vinyl groups (A^{810}), allows to perform the precise measurements from the same sample, submitted to cumulative UV irradiation in the temperature-controlled stage. For PEGDA samples (Fig. 5a), the fractional conversion of acrylate functions (*G*) is simply calculated from the absorbance ratio, as written in equation (2), since the out of plane deformation band of the acrylate does not overlap any other vibration band.

$$G = 1 - \frac{[acrylate]_t}{[acrylate]_0} = 1 - \frac{A_t^{810}}{A_0^{810}} \quad (2)$$

For EPDA samples (Fig. 5b), the presence of an aromatic absorption band at 830 cm^{-1} in the spectra requires some correction to be done, as indicated in equation (3).

$$G = 1 - \frac{A_t^{810} - 0.15A_t^{830}}{A_0^{810} - 0.15A_0^{830}} \quad (3)$$

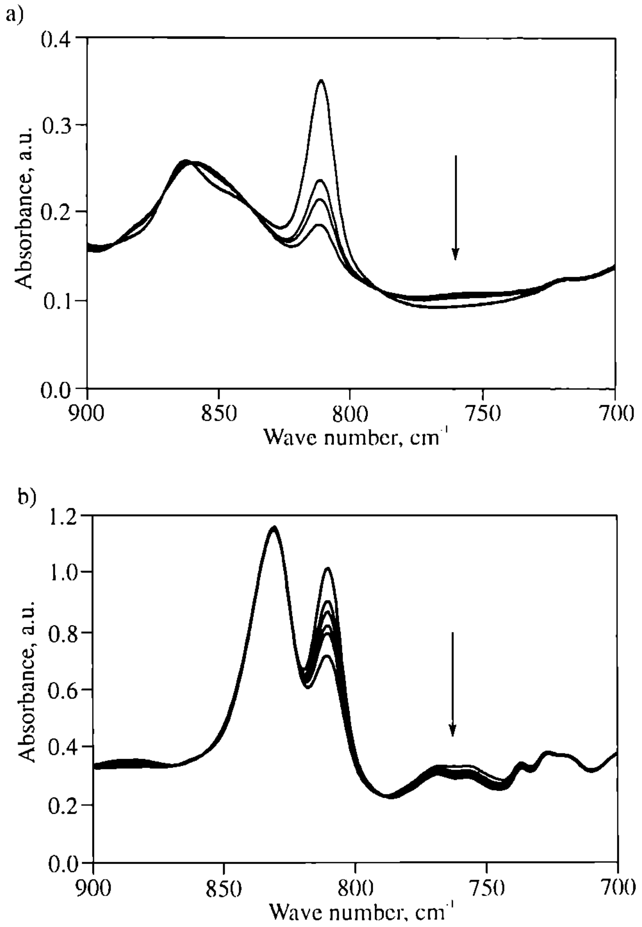

Fig. 5. FT-IR spectra of PEGDA (a) and EPDA (b) samples submitted to 312 nm irradiation as a function of time (1 wt. % of Darocur 1173, 0.5 mW · cm^{-2}); maximum irradiation time: a) — 50, b) — 1000

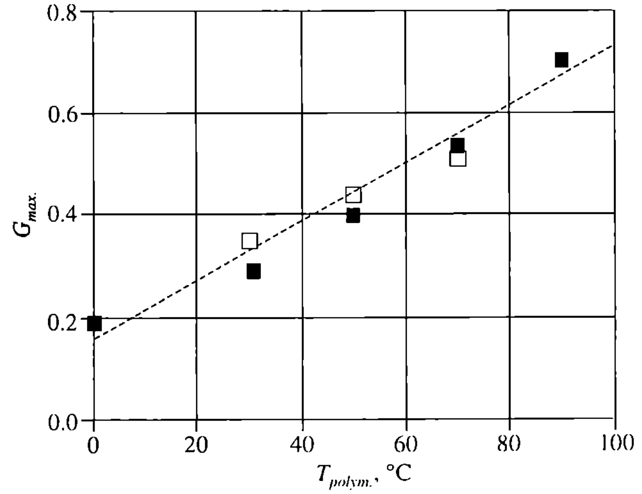

Fig. 6. Comparison of the maximal monomer conversion (G_{max}) of EPDA samples (1 wt. % of Darocur 1173) as a function of UV-curing temperature, determined by photocalorimetry (□) or by FT-IR analysis (■)

The maximal conversion (G_{max}) measured for the samples cured by a long UV-light exposure under isothermal conditions was shown to agree fairly with photo-calorimetric measurements performed at the same temperature with the same EPDA formulation (Fig. 6).

We can expect, in such monomer blends, a strong influence of gelation on the polymerization kinetics, as a consequence of Trommsdorff effect. In di- and triacrylate blends we have used for the present study, gelation occurs at low monomer conversion (typically *ca.* 10 %). We believe that the overall profiles, recorded with a discrete number points at the conversion $G > 0.1$, are affected by gel effect, with low termination efficiency. This explains the particularly high initial polymerization rates of these systems compared with their monofunctional analogues.

The kinetic profile of EPDA photopolymerization at constant temperature can be varied by changing of the nature of photo-initiator and irradiation source. At 25 °C, using Irgacure 651 with 312 nm light or Darocur 1173 with 312 and 360 nm light, we observed the curing within various timescales but with the same limiting conversion $G_{max} = 0.37 \pm 0.02$ (Fig. 7). This demonstrates that vitrification exerts its control of the progress of polymerization in the different situations, provided that thermal control is effective.

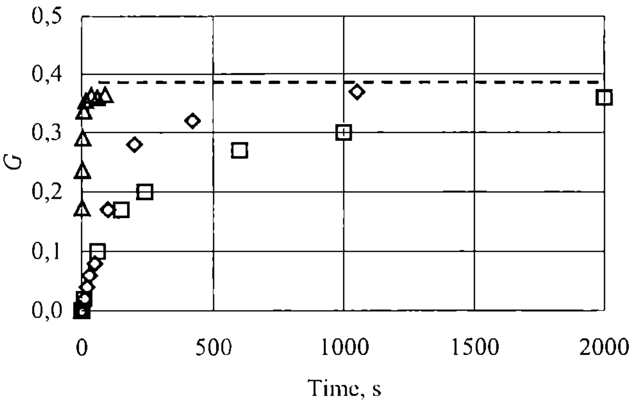

Fig. 7. Conversion (G) vs. time profiles for EPDA photopolymerization at 25 °C; Δ — 1 wt. % of Irgacure 651, 312 nm; ◇ — 1 wt. % of Darocur 1173, 312 nm; □ — 1 wt. % of Darocur 1173, 360 nm

The profiles recorded at various temperatures ranging between 10 °C and 90 °C and the same photoinitiator (Darocur 1173), are shown in Fig. 8, giving another evidence of the effect of mobility restrictions that are shifted to higher conversion levels, as curing temperature is raised.

The continuous progress of polymerization as a function of polymerization time (t) can be described by a phenomenological equation using the formalism of equation (4) [9] with adjustable parameters $c_{1\text{-}3}$:

$$G(t) = c_1 t + c_2 - \frac{1}{c_3 t + c_2^{-1}} \qquad (4)$$

which appeared to be more convenient than so-called auto-catalytic models [16]. Parameter adjustment was achieved by standard least square procedure. The best fitting parameters shown in Table 1 allow to predict satisfactorily the conversion degree of a sample submitted to the given curing conditions. It would be worth examining and quantifying the influences of initiator concentration and of light intensity on the kinetic profiles. From the data available at present, we were able to examine the influence of temperature on the initial polymerization rate [$(R_p)_0$] using Arrhenius model.

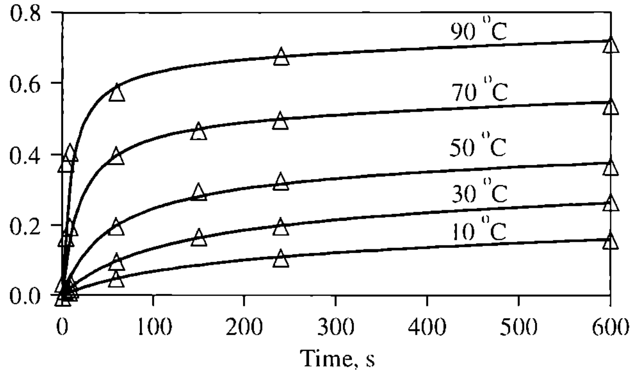

Fig. 8. Time dependence of monomer conversion (G) for EPDA oligomer (1 wt. % of Darocur 1173, 360 nm irradiation) as a function of curing temperature

Table 1. Coefficients used for modeling of the polymerization profiles in Figure 8, using equation (4)

T_{polym}, °C	$c_1 \cdot 10^5$, s^{-1}	c_2, s^{-1}	c_3, s^{-1}	Initial slope $\cdot 10^3$, s^{-1}
10	5.5	0.15	0.055	1.10
30	5.9	0.27	0.033	2.50
50	6.0	0.37	0.050	6.25
70	7.0	0.52	0.100	25.0
90	8.0	0.68	0.150	8.00

The dependence of $\ln(R_p)_0$ as a function of reciprocal temperature allowed us to determine an activation energy of 45±5 kJ · mol^{-1} that compared well with some other studies on photopolymerization kinetics [17].

At ambient temperature, a conversion degree 0.5 for PEGDA was measured after 1 s of exposure to 312 nm light, for the sample containing 1wt. % of Darocur 1173. The maximal conversion, $G_{max} = 0.9$ was obtained for exposures longer than 8 s. This behavior indeed reveals the absence of mobility restriction during the whole course of the crosslinking polymerization. By temperature decreasing we were able to reduce the efficiency of curing, but, since the measurements were performed under ambient conditions, free radicals trapped in the glassy medium as soon as produced by photolysis were shown to recover their activity upon reheating. As a consequence, the conversions measured for samples treated for 15 s at curing temperature T_{polym} lower than -40 °C were much higher than expected from the reaction in the vitrous state. The results in Fig. 9 are therefore deceptive. Conversion at low temperature is believed to be insignificant, hypothetically materialized by the dotted line in Fig. 9. The observed conversions very probably result from post-irradiation effects, involving a number of trapped free radicals. These free radicals, which are more abundant as the exposure time is increased, start the initiating of polymerization as mobility is recovered on reheating (arrows in Fig. 9). This is one evident limitation of the method, compared with *in situ* real time techniques.

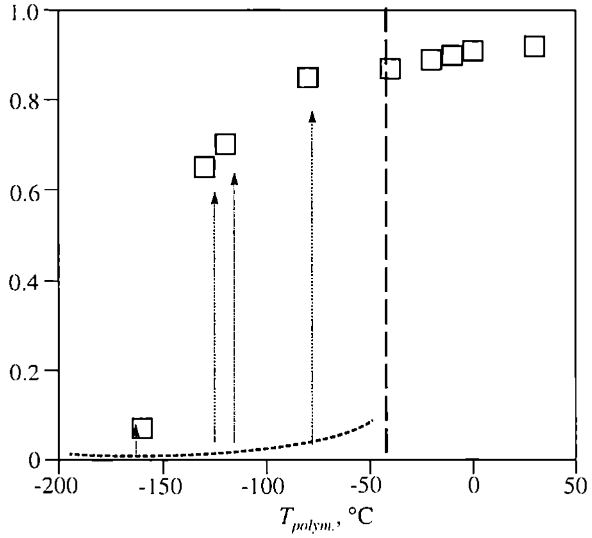

Fig. 9. Dependence of the observed maximal conversion (G_{max}) as a function of curing temperature, for PEGDA oligomer (1 wt. % of Darocur 1173, 312 nm irradiation); dotted line corresponds with real conversion reached at temperature <T_g and irradiation time 15 s, arrows — conversions reached as post-effects, vertical dashed line marks the value of T_g = -40 °C

The dependence of maximal conversion as function of curing temperature, (T_{polym}), set between 10 °C and 120 °C for EPDA is shown in Fig. 10. Independently on the photo-initiator nature and content (Darocur 1173 or Irgacure 651 from 0.25 to 1 wt. %), irradiation wavelength (312 or 360 nm) and thickness of the sample (from *ca.* 10 μm to 2 mm), we can observe a continuous variation of the limiting conversion as a function of T_{polym}. These results point out the effective control of T_{polym} under given experimental conditions.

These results encouraged us to further establish another correlation between curing temperature and EPDA network T_g at the maximal conversion for value of T_{polym}. The calorimetric determination of T_g in densely crosslinked acrylate networks is generally difficult and inaccurate. We preferred to use viscoelastometric measurements for determining the storage and loss moduli E' and E'', respectively, as well as the loss factor tg δ. The variations of this latter quantity with temperature can be used to determine on α relaxation temperature, associated with the glass transition. A typical DMA spectrum, recorded during the first thermal raising from 10 °C to 200 °C, is shown in Fig. 11. The relaxation spectrum covers a broad range of temperature, the width of tg δ peak being as large as 80 °C, which is a typical feature of this class of material [18]. We used the position of tg δ maximum to determine $T_\alpha \approx T_g$ value. Similar

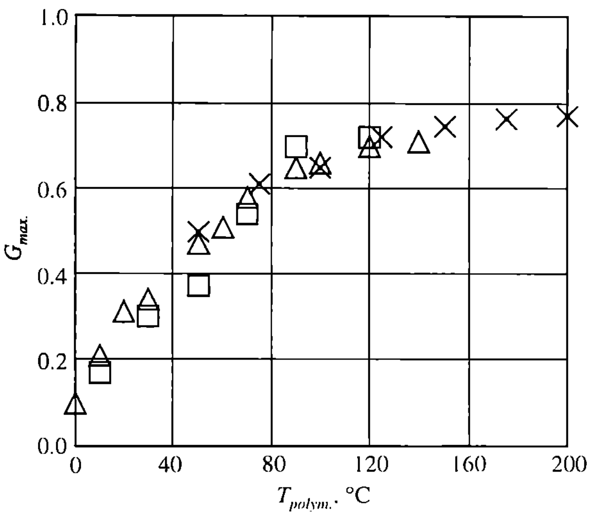

Fig. 10. Dependence of maximal conversion (G_{max}) as a function of curing temperature, for EPDA oligomer: Δ — 10 μm-thick PE-LD sandwich, 0.5 wt. % of Irgacure 651, 312 nm; □ — 10 μm-thick, NaCl plates, 1 wt. % of Darocur 1173, 312 nm; × — 1 mm-thick, glass sandwich, 0.25 wt. % of Darocur 1173, 360 nm irradiation

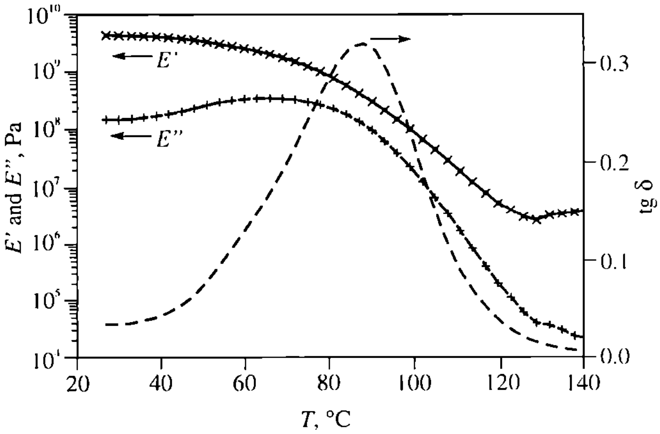

Fig. 11. Typical DMA spectra of 1 mm thick UV-cured EPDA sample (0.5 wt. % of Darocur 1173, 365 nm irradiation)

thermo-mechanical spectra were obtained from a number of other samples, prepared at various curing temperatures.

As expected, the measured T_g's were shown to increase with the degree of conversion of the samples, hence with the curing temperature. The decrease in chain segment mobility when the temperature of an elastomeric polymer approaches T_g from higher temperatures T can be described by Williams—Landel—Ferry (WLF) model, as shown in equation (5):

$$\frac{\eta_T}{\eta_{T_g}} = \exp\left[\frac{C_1(T-T_g)}{C_2+(T-T_g)}\right] \qquad (5)$$

where: η_T, η_{T_g} — *polymer viscosity at temperature T and* T_g, *respectively;* C_1 *(dimensionless quantity) and* C_2 *(°C) — numerical parameters.*

In the present situation, we have to adapt the reading of this description, by considering that at a given polymerization temperature (*T*), the mobility of the chain is decreased with the progress of vitrification that gradually shifts the network T_g to higher temperature.

On the basis of a simple description of the phenomenon by considering that mobility restrictions appear at the same temperature difference between network T_g and working temperature (*T*), we could thus expect a linear correlation between the data in Fig. 12 [19]. From the cumulated results we can see from this plot that for intermediate conversion degrees, T_g obtained is very close to the curing temperature. There is, however, a deviation at low curing temperature, which seems to produce the networks showing a lightly higher T_g, whereas at higher curing temperature, the resulting network T_g is lower than expected from a linear extrapolation. The low temperature deviation is probably due to the resumption of polymerization during the first heating raising at DMA experiment. We believe that the high temperature deviation is more significant and really characteristic for the network, as produced at the end of the curing process. A deeper analysis of DMA data and of thermal dependence of the polymerization reaction is continued.

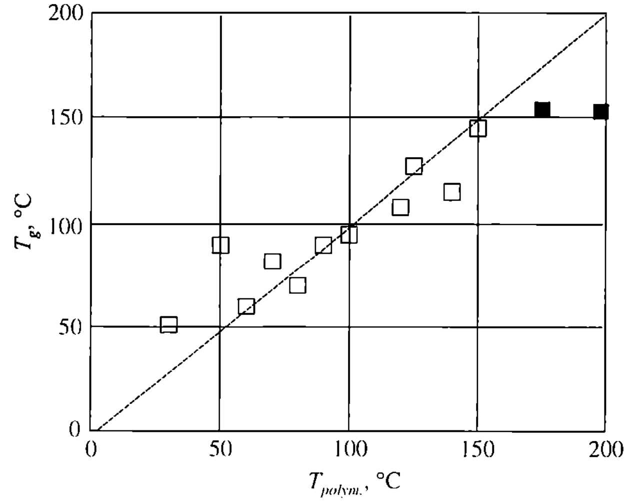

Fig. 12. Correlation between the glass transition of 1 mm-thick UV-cured EPDA samples and curing temperature (0.25 wt. % of Darocur 1173, 360 nm irradiation); □ — T_g *values roughly satisfying the linear dependence,* ■ — T_g *values not satisfying the linearity*

The relations, presented in this paper, between curing temperature and final monomer conversion provide us with valuable information to work out a model for predicting T_g value of a volume element in radiation-cured material. The kinetics of isothermal polymerization can be modeled on the basis of two extreme kinetic regimes observed in the conversion *vs.* dose plots and from the assumption that a linear combination of 2 regimes can describe satisfactorily the transition regime, as written in equation (6):

$$R_p = [M]_0(1-G)f_1k_{p,1}[M1^\bullet]_0 + f_3k_{p,3}[M3^\bullet]_0 \qquad (6)$$

where: *[M] — monomer concentration; (1 - G) — mole fraction of unreacted monomer;* $k_{p,i}$ *— propagation rate constant;* $[M_i^\bullet]_0$ *— free radical concentration at instant t in first or third regime, respectively;* f_1 *and* f_2 *— weighting factors [20].*

Diffusion controlled reactions in materials placed at temperature close to their glass transitions have their rate constants following generally a thermal dependence conveniently described by WLF equation. We now have an interesting set of data concerning EPDA to make a progress in this type of modeling, which already proved to be useful for industrial processing parameters defining [3—5].

CONCLUSIONS

The method presented in this work can be implemented to reproduce the actual polymerization profile of UV-initiated polymerization, induced by application of incremental radiation doses. The method used to monitor quantitatively the chemical and physical changes during radiation-induced polymerization is effective and well adapted to investigations of kinetic behaviors. Radiation processing is confirmed as a powerful tool for preparing densely crosslinked polymers. The established relationships between curing conditions, expressed in terms of dose, initiation rate and temperature on the one hand, and acrylate conversion and the resulting mechanical properties on the other, permit significant progress in providing with the bases for a model of the temperature and conversion profiles in space and time seen by the cured material. Models can be further developed to draw the map of resulting mechanical properties and to adjust radiation processing conditions as the functions of required use properties. Thanks to new modeling tools, faster and less expensive analysis can be done for complex geometry and material stacking, with UV, EB or X-ray curing methods.

The dependences of the polymerization rate on the composition of the reactive formulation, dose rate and temperature during the treatment are currently investigated in some details and will be described in a series of forthcoming papers. In particular, the accuracy of the conversion — dose relationship obtained under well-defined conditions authorizes to develop and to assess the models based on mechanistic considerations.

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