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Synthesis and photoinitiated polymerization of a new urethane acrylate monomer: influence of polymerization temperature

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Abstract

The synthesis of a new urethane acrylate monomer (UAM) from hexamethylene diisocyanate trimer (HDT) and 2-hydroxyethyl methacrylate was performed by classical condensation. Physicochemical and thermal characterization of UAM was investigated ($\overline{M}_n = 1480 \text{ g mol}^{-1}$; $T_g = -38^\circ\text{C}$) and no secondary reactions were observed. The photoinitiated polymerization of UAM with 2,2-dimethyl-2-hydroxy acetophenone (Darocur 1173) as radical photoinitiator was studied by using thermal photocalorimetry at different temperatures. Photoinitiator concentration (0.15% w/w) and light intensity (2.7 mW cm^{-2}) were kept constant. The maximum conversion was obtained at 70°C . Above this temperature, thermal polymerization interfered with the photocalorimetric measurements. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polyurethane acrylate (PUA) resins are often used, in the liquid state, as precursor to produce three-dimensional networks, which gives as a final product a high-performance material in terms of hardness, flexibility and abrasive resistance [1]. This behaviour is in keeping with the material requirements for various industrial sectors such as automobile, aeronautic, composite devices or coating [2].

It is known that polyurethane derivatives are obtained by the reaction of a polyol with a diisocyanate, whereas PUA resins are generally prepared by a

two-step synthesis [3]. An excess of diisocyanate can first react with a polyol, and only then with a hydroxy-terminated acrylate [4]. In another procedure described by Nocii et al. [5], a diisocyanate in excess first reacts with a monoalcohol acrylate and then with the polyol. Finally, as recently described by Chen et al. [6] and Schapman et al. [7], a one-step synthesis can also be performed by exothermic control or by using 2-methyl-2-propenoyl isocyanate (MAI).

The influence of the diisocyanates on the mechanical and thermal properties of PU has been studied by Li et al. [8]. They showed that PU from *m*-tetramethyl-xylene diisocyanate (*m*TMXDI) exhibits a low modulus and low elongation compared to that of toluene diisocyanate (TDI) or isophorone diisocyanate (IPDI). In the same way, PU acrylate networks obtained with

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methane diphenyl diisocyanate (MDI) show lower values of modulus and elongation than those prepared with IPDI [1]. For photopolymerized films, Chiang et al. [9] have observed that the mechanical performances decrease in the sequence MDI, TDI, CMDI (4,4'-methylene bis cyclohexyl isocyanate). For these last systems, the three-dimensional network can be obtained by a classical thermal curing reaction and also by a photochemical way directly from the liquid mixture. Thus, PUA resins exhibit the advantage of being free isocyanate and, therefore, limits the environmental and human health problems generally associated with PU.

On the other hand, isophorone diisocyanate (IPDI) trimer mixed with glycidol [10,11] or (meth)-acrylate linked to an alcohol function [12] allows the production of isocyanurate PU epoxide or acrylic resins which exhibit very good thermal properties. In a similar way, a film showing very good resistance to oil and water is obtained by mixing fluorinated alcoholic acrylates linked to alcohol functions and hexamethylene diisocyanate (HMDI) trimer [13–15]. Finally, the use of pure hexamethylene diisocyanate trimer (HDT) with hydroxy acrylate and the copolymerization with styrenic or acrylic monomers was recently patented (Rhône Poulenc, France) showing that such PUA resins are promising materials [16].

This paper deals with the synthesis of a new polyurethane methacrylate resin based on HDT and 2-hydroxyethyl methacrylate. The photocuring of this monomer, without reactive diluent, has been examined in the presence of 2,2-dimethyl-2-hydroxyacetophenone. Intrinsic thermal and mechanical properties of the resulting cross-linked resin have been investigated.

2. Experimental

2.1. Materials

The reagents were purchased from Aldrich except for hexamethylene diisocyanate trimer (HDT) which was supplied by Rhône Poulenc ($\eta=2400 \text{ mPa s}^{-1}$ and $\text{NCO}=22\%$). All products were used without further purification.

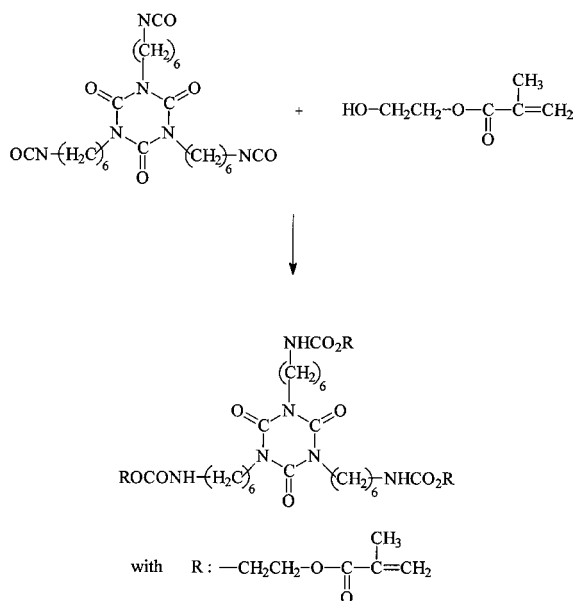
The photoinitiator 2,2-dimethyl-2-hydroxyacetophenone was dissolved in the oligomer under stirring at room temperature (0.15% w/w).

2.2. Synthesis of the monomer

A 10.1-g sample of HDT (2.004×10^{-2} mol) and 5 cm^3 of CCl_4 were placed in a 50-cm^3 three-necked flask equipped with a condenser, a dropping funnel and a device for nitrogen flow. Thereafter, 7.815 g of 2-hydroxyethyl methacrylate (6.012×10^{-2} mol) and 0.02 g of dibutyl tin dilaurate as catalyst were added to the initial mixture. The solution was stirred at room temperature for 20 min. After evaporation of the solvent under vacuum (1 mm Hg at 40°C) until constant weight was reached, the monomer was obtained in quantitative yield.

2.3. Methods

IR spectroscopies were carried out with a FT-IR Perkin–Elmer spectrophotometer. The band positions are given in cm^{-1} . ^1H NMR spectra were recorded on a Bruker AM 200 instrument using deuterated chloroform as solvent. The average molecular weight was computed from chromatograms obtained by using a Waters 510 gel permeation chromatograph (GPC) with polystyrene standards. The apparatus was equipped with three columns (100, 100, 500 \AA), working in toluene. A R401 Waters refractometric detector was used.



Scheme 1.

Calorimetric experiments were performed with a Perkin–Elmer DSC-7 calorimeter. The heat flow was followed with a heating rate of 20°C/min under nitrogen atmosphere. The sample weight was about 20 mg. Calibration was achieved with indium as reference material.

The radical photopolymerization of the monomer was followed using a DSC-7 differential scanning calorimeter topped by a irradiation unit (100 W Hg lamp) with two quartz windows; more details are described elsewhere [17]. Heat flow data vs. time was recorded isothermally during the polymerization reaction. Before irradiation, each sample was placed

in the sample cell for 5 min under nitrogen atmosphere (≤ 5 ppm O_2) to remove residual oxygen and to allow temperature stabilization. The sample was irradiated for 7 min under inert atmosphere (N_2) leading to the first curve. To remove the shift in the baseline due to difference in heat flow between the sample and the reference, further irradiation was performed when initial baseline was reached and led to a second curve. The final thermogram was obtained by subtracting the second curve from the first one. Photoinitiator concentration and light intensity, which have an influence on the final conversion, were kept constant throughout the experiment (0.15% w/w and 2.7 mW cm^{-2} ,

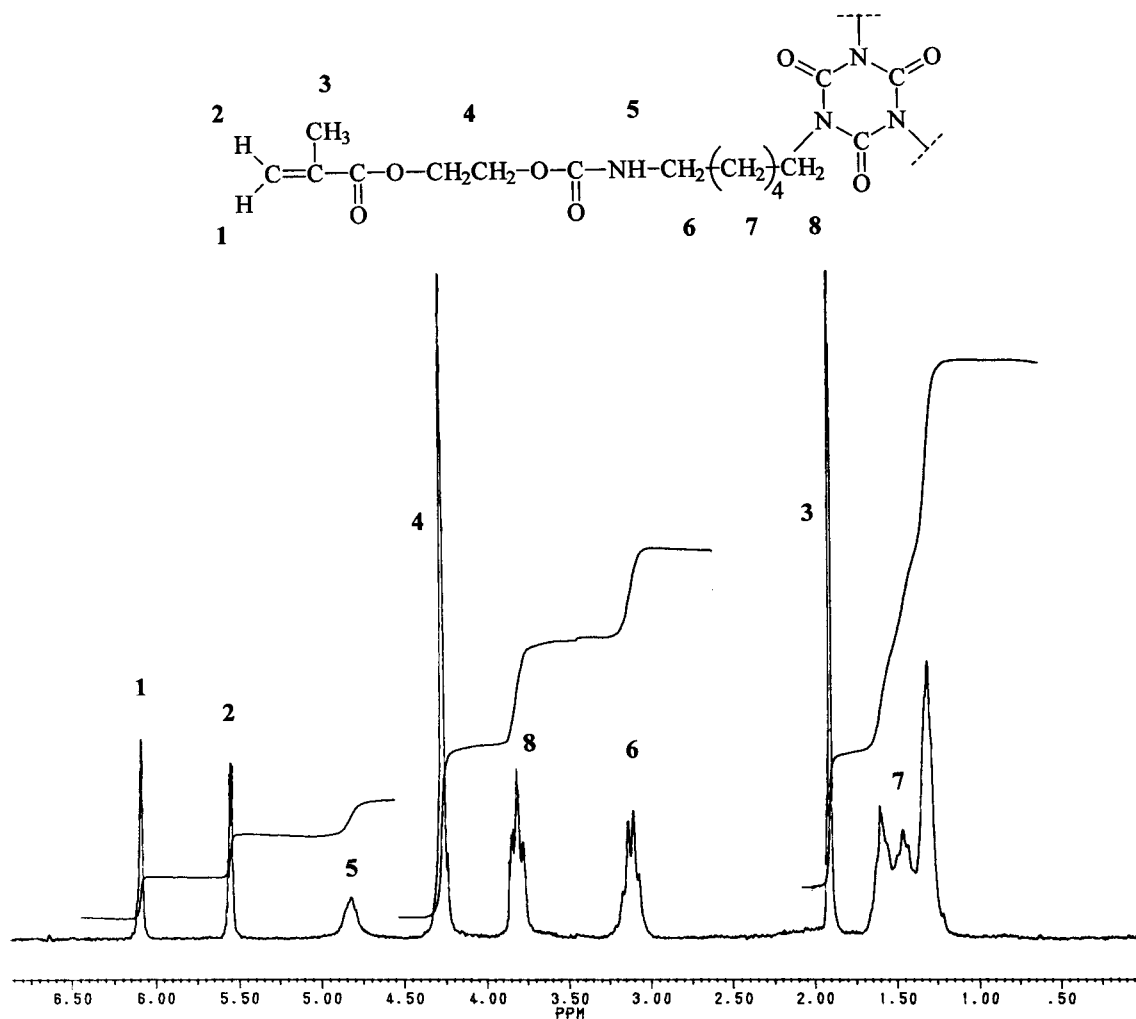


Fig. 1. ^1H NMR spectrum of the urethane acrylate monomer.

respectively). About 20 mg of the mixture were laid down over a polyethylene film (0.1 mm) covering the bottom of the DSC aluminium pan. Indeed, without the PE film, a hemispherical drop was obtained and optical disturbances confused the experimental data. It is noteworthy that the presence of PE film did not modify our measurements [18]. Experiments were carried out three times for each isothermal temperature (T_i). The reported results are the average of the collected data for each isotherm.

Polymer thermal stability was checked by thermogravimetric analysis (TGA-7 Perkin–Elmer) coupled with a spectrophotometer FT-IR Perkin–Elmer. Experiments were carried out under N_2 atmosphere. Sample weight was about 20 mg. The 50–700°C range was scanned at a heating rate of 20°C/min. For each weight loss, a characteristic temperature (T_m) was determined from the minimum of the peak observed on the derived curve.

Photocross-linked samples were analyzed by dynamic mechanical analysis (DMA-7 Perkin–Elmer) in the compression mode between two parallel plates with a 1-mm diameter probe at 1 Hz, at a heating rate of 10°C/min. The dynamic and static forces applied

were 1200 and 1400 mN, respectively. The α transition, which can be understood as the mechanical manifestation of the glass-transition phenomenon, was characterized by the T_α temperature taken at the maximum of the peak of the $\tan(\delta)=f(T)$ curve.

3. Results and discussion

3.1. Synthesis of the monomer

The monomer was synthesized by a classical condensation reaction of hexamethylene diisocyanate trimer (HDT) with 2-hydroxyethyl methacrylate (Scheme 1).

After elimination of the solvent, a colourless liquid was obtained. The end-group functionality of the acrylate monomer was determined by 1H NMR. The indexed spectrum is shown in Fig. 1. The methacryloxy group content was calculated from the integration ratio of methacryloxy protons $-OCO-C(CH_3)=CH_2$ (two singlets: 6.2 and 5.6 ppm) to middle protons of isocyanurate $-NH-CH_2-(CH_2)_4-CH_2-N=(1.2-1.8$ ppm).

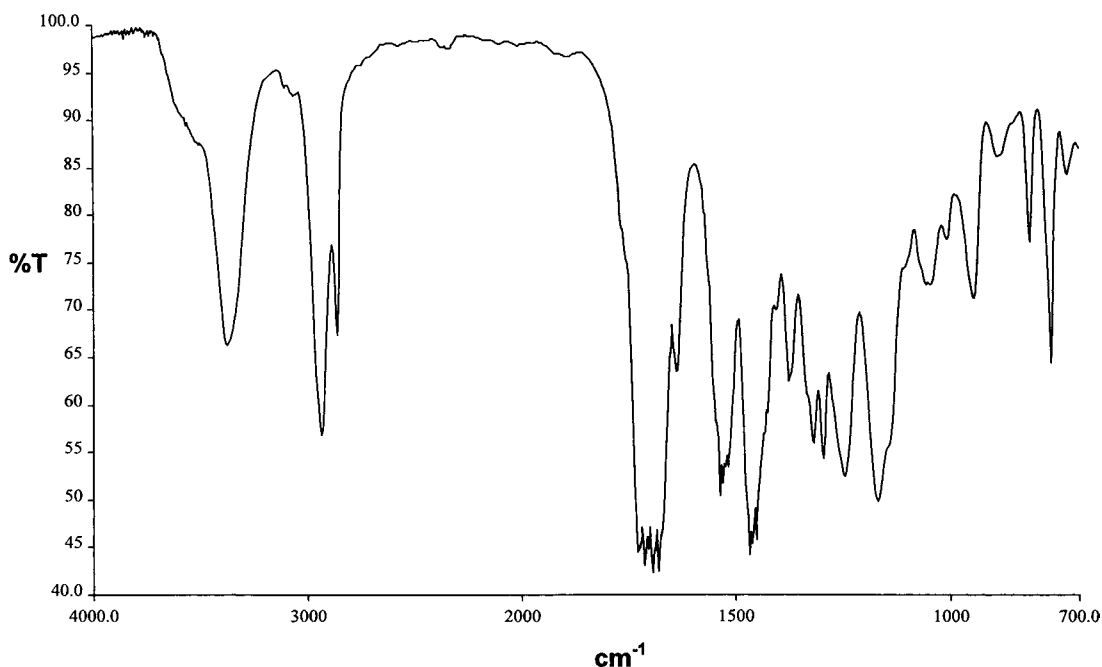


Fig. 2. FT-IR spectrum of the urethane acrylate monomer.

The FT-IR spectrum in Fig. 2 shows the existence of absorption at 3390 and 1637 cm^{-1} associated, respectively, with N–H and the C=C band at 1718 and 1689 cm^{-1} . No NCO absorption was observed at

2270 cm^{-1} which indicated that the reaction was complete. On the other hand, from SEC investigations the number-average molecular weight (\overline{M}_n) was found to be 1480 g/mol with a polydispersity of 1.1, showing

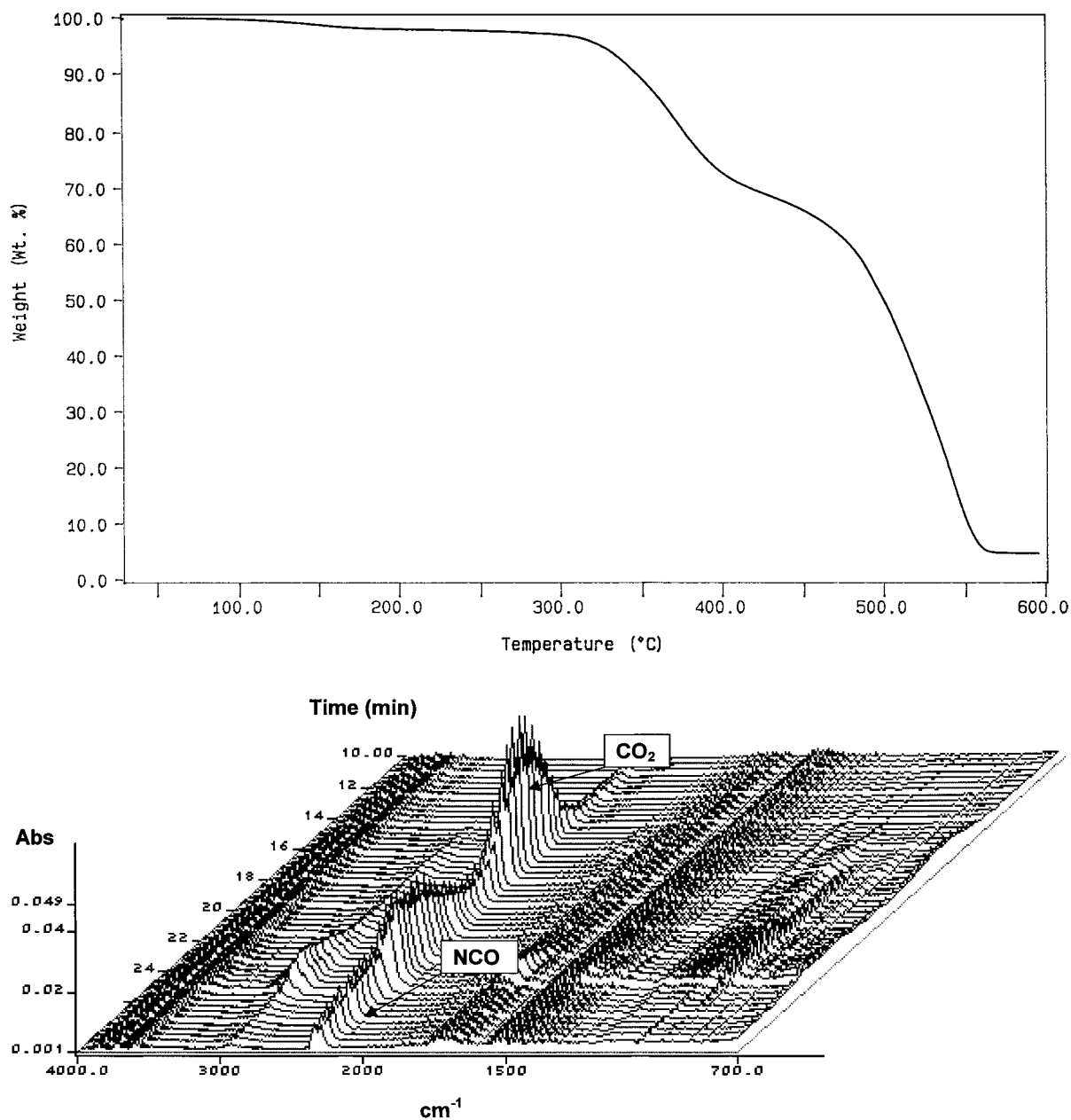


Fig. 3. Thermogravimetric analysis of the urethane acrylate monomer.

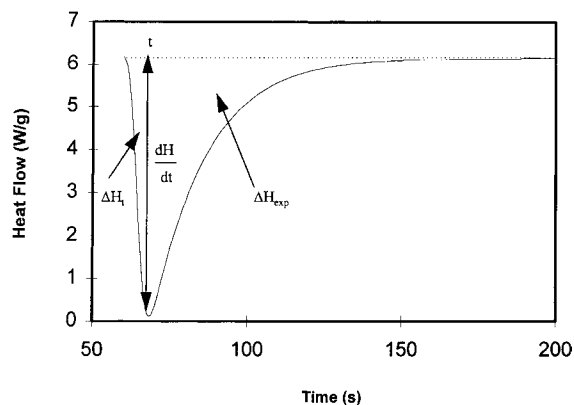


Fig. 4. Typical thermogram of photoinitiated polymerization.

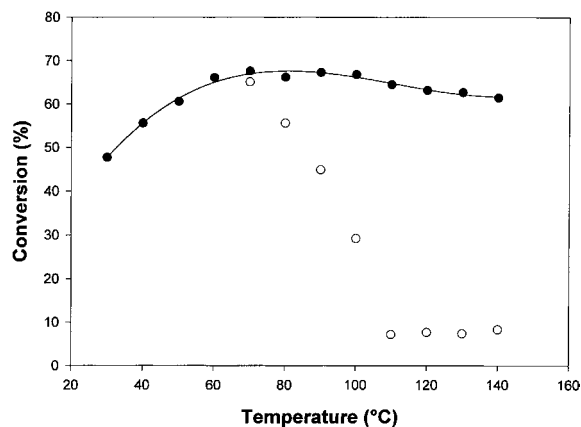


Fig. 5. Photopolymerization conversion vs. temperature after: 5 min (●) or 2 h (○) stabilization period.

that no secondary reaction had taken place. The glass-transition temperature was found to be -38°C by DSC.

In Fig. 3(a and b), the thermogravimetric and the corresponding IRFT spectra are displayed. Thermal decomposition of this material takes place in two steps under nitrogen atmosphere. The first step, from 300° to 425°C ($T_m=375^{\circ}\text{C}$), corresponds essentially to the liberation of CO_2 as shown by the FTIR spectrum. In the second ($T_m=525^{\circ}\text{C}$), only a very weak NCO peak attests the reversible cleavage of the urethane linkages at high temperatures.

3.2. Photoinitiated polymerization

Fig. 4 shows a typical enthalpic curve obtained isothermally on irradiation. For isothermal temperatures up to 70°C , the magnitude of the peak increases, whereas for higher isothermal temperatures it remained fairly constant.

The conversion, C , was calculated from the relation $C = \Delta H_t / \Delta H_0^{\text{theor}} \times 100$, where ΔH_t and $\Delta H_0^{\text{theor}}$ are the values of the enthalpy at time t and the theoretical enthalpy for complete conversion. For a methacrylate double bond, Moore [19] and Kurdikar et al. [20] have

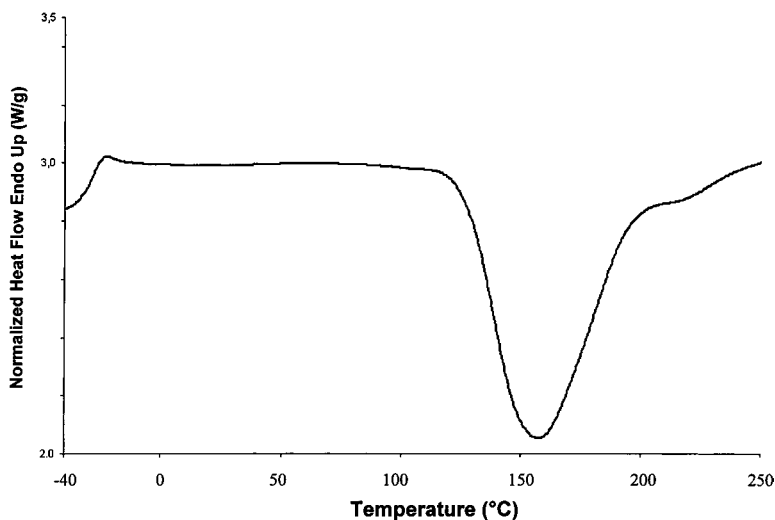


Fig. 6. Thermal polymerization of the urethane acrylate monomer.

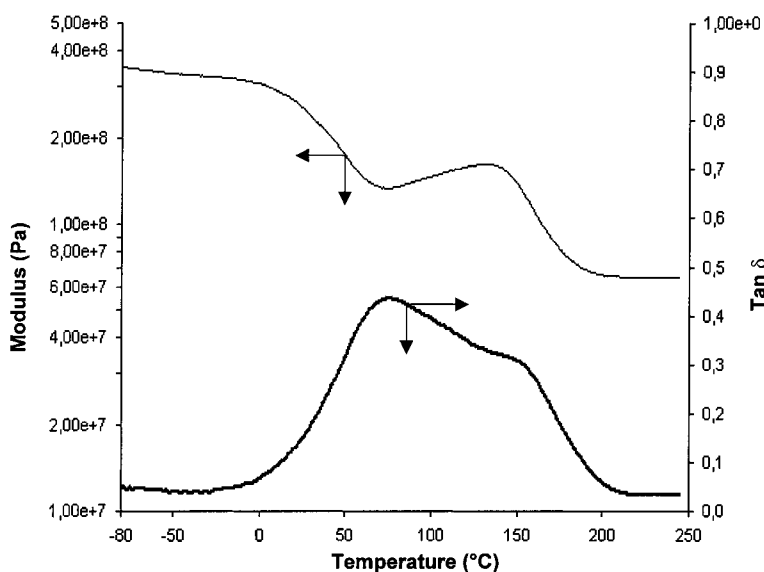


Fig. 7. Mechanical behaviour of a polymer irradiated at 30°C.

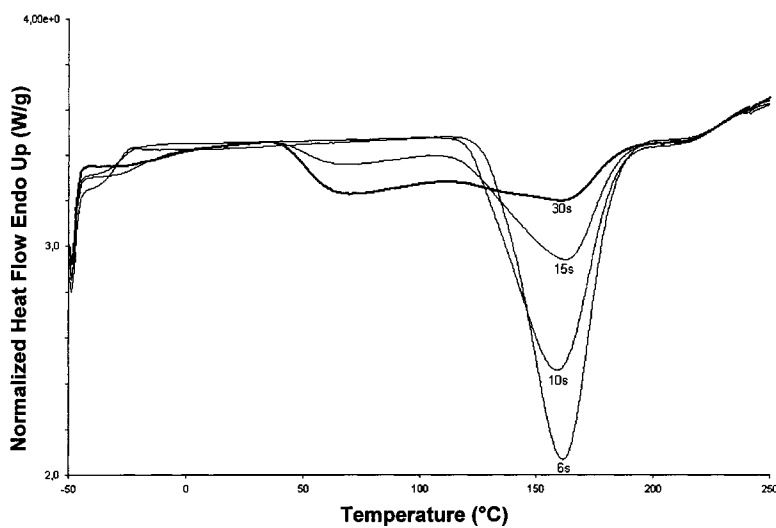


Fig. 8. Heat flow vs. temperature after different prior irradiation times.

reported a value of $\Delta H_0^{\text{theor}} = -13.1 \text{ cal/mol}$ which corresponds to $\Delta H_0^{\text{theor}} = -180 \text{ J g}^{-1}$ for our monomer. For all isothermal temperatures (T_i) investigated, variations in conversion vs. time increases drastically as soon as the irradiation is performed, to reach a plateau after $t \approx 100$. From these curves, an ultimate conversion was calculated for each T_i (Fig. 5).

We observed that C increased with T_i up to 70°C and then decreased slightly for higher isothermal temperatures probably because thermal polymerization takes place before irradiation during the 5 min of the stabilization period.

To enhance this thermal effect, the sample pan was left in the DSC furnace for 2 h under nitrogen atmos-

phere, instead of 5 min, before irradiation. The result is a drastic drop of the conversion for $T_i > 70^\circ\text{C}$ which confirms that thermal polymerization occurs during the temperature stabilization step (Fig. 5).

Finally, calorimetric measurements were carried out on the monomer without irradiation. The enthalpic curve shown in Fig. 6 clearly shows a broad exothermic peak near 150°C , with $\Delta H = -140 \text{ J/g}$, in agreement with our assumption, since only the thermal polymerization is observed by this method. Insofar as thermal polymerization occurs when the temperature increases, it is logical that experimentally the monomer thermogravimetric analysis, reported on Fig. 3, is identical to that of the cross-linked polymer.

Thus, for $T_i > 70^\circ\text{C}$, an increasing number of double bonds are consumed before irradiation and the resulting initial photopolymerization rate decreases. According to the theory of free volume [21,22], the corresponding ultimate conversion decreases too. Thus, instead of an increase in conversion, which is generally expected without thermal polymerization, in our case, the result is a more or less drop of conversion according to the length of the stabilization period.

The photopolymerized samples were then analyzed by DMA and a typical curve is reported on Fig. 7. Two

distinct steps were observed in the modulus and $\tan \delta$ curves. As soon as the α transition appears, a further polymerization reaction is revealed. In fact, the radicals produced during the irradiation period are trapped in the cross-linked structure in its vitreous state and, therefore, when T_α is exceeded during the DMA analysis the molecular mobility of the medium becomes high enough so that thermal polymerization resumes. Thus, the storage modulus increases again until the new α transition is reached.

This phenomenon is also clearly exhibited in the following set of experiments. For a selected isothermal temperature, $T_i = 40^\circ\text{C}$, the monomer was irradiated for different times and immediately analyzed by DSC (Fig. 8). Up to 10 s, the glass-transition temperature was still clear and its value remained constant. On the other hand, the exothermic peak at 150°C , related to the number of reacting species, decreases. Beyond 10 s, a second exotherm appeared at 80°C and is attributed to trapped radicals which can react further.

The variations of the first T_α vs. time for the different T_i , and vs. T_i are displayed in Figs. 9 and 10. One can clearly observe that as T_i increases, T_α exhibits thinner peaks. T_α values increase with temperature and reach a plateau at 170°C . This last

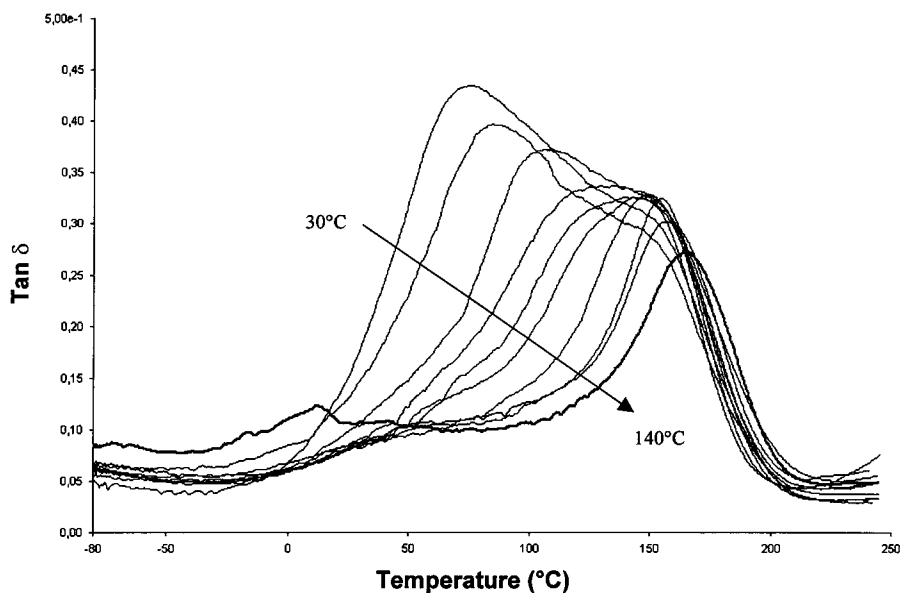


Fig. 9. Evolution of $\tan \delta$ vs. temperature for polymers irradiated at different temperatures T_i (30° , 40° , 60° , 70° , 80° , 90° , 110° , 120° , 130° , 140°C).

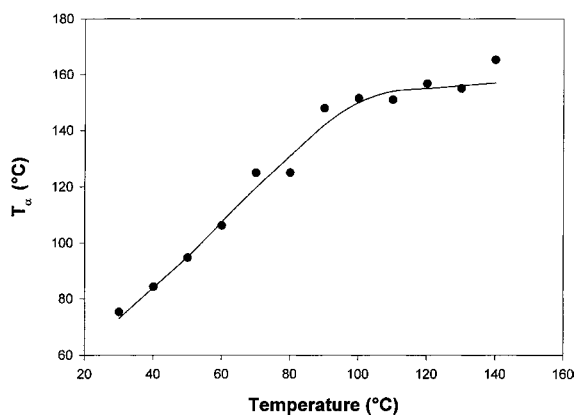


Fig. 10. Variation of T_{α} vs. irradiation temperature T_i .

observation shows that the overall conversion increases with temperature even if the experimental photopolymerization conversion decreases very slightly (Fig. 5).

4. Conclusion

In this work, we have synthesized and characterized a new urethane acrylate monomer. Photoinitiated polymerization, followed by photocalorimetry, showed maximum conversion at 70°C with a photo-initiator concentration of 0.15% (w/w) and a light intensity of 2.7 mW cm⁻². This maximum was not due to kinetic consideration but only because of thermal polymerization which occurs above this temperature and interferes with the photocalorimetric measurements. Nevertheless, from the DMA analysis, one can observe that T_{α} , and therefore T_g , always increases with temperature and corresponds to an increase in the overall conversion.

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