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L. Lecamp[a]; B. Youssef[a]; P. Lebaudy[b]; C. Bunel[a]
[a] Laboratoire de Matériaux Macromoléculaires INSA de ROUEN Place Emile Blondel, Mont-Saint-Aignan Cédex, France [b] Laboratoire d'Etude et de Caractérisation des Composés Amorphes et des Polymères UFR des Sciences et Techniques, Université de Rouen, Mont-Saint-Aignan Cédex, France

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CATIONIC PHOTOCROSSLINKABLE POLYDIMETHYLSILOXANE. III. SYNTHESIS AND PHOTOCROSSLINKING OF POLYDIMETHYLSILOXANE BEARING OXETANE GROUPS

L. Lecamp,[1] B. Youssef,[1] P. Lebaudy,[2] and C. Bunel[1]*
[1]Laboratoire de Matériaux Macromoléculaires
INSA de ROUEN
Place Emile Blondel
76131 Mont-Saint-Aignan Cédex, France

[2]Laboratoire d'Etude et de Caractérisation
des Composés Amorphes et des Polymères
UFR des Sciences et Techniques
Université de Rouen
Place Emile Blondel
76821 Mont-Saint-Aignan Cédex, France

ABSTRACT

From 3-hydroxymethyl-3-methyl oxetane, we synthesized three oxetane monomers with allylic, diethoxysilane or triethoxysilane functions. These monomers allowed us to prepare different polydimethylsiloxanes bearing oxetane groups by two routes. One is hydrosilylation of allylic monomer on hydrogeno polydimethylsiloxane, with different percentages of Si-H bonds. The second route is a condensation of α,ω-dihydroxy polydimethylsiloxane with di and tri ethoxysilane monomers. By using a photocalorimeter, we studied the kinetic of cationic photopolymerization of a polydimethylsiloxane bearing 7.4% oxetane functions. Influence of temperature in the range 35 to 125°C showed a maximum conversion for 80°C due to an increase in transfer and termination reactions.

INTRODUCTION

Cationic photocrosslinking of polydimethylsiloxanes showed great development over the last few years, especially with regard to radical photocrosslinking, and that is due to the properties of resulting materials [1] on one hand, and to the development of cationic photoinitiators [2] on the other hand. Nevertheless, in most cases, the research was turned to epoxy cyclohexyl [3-5] or vinyl ether [6, 7] as photocrosslinking groups. However, more recently, other polymerizable functions were grafted onto polysiloxanes by different routes: for example, pyranic group by Goldschmidt [8]; allyloxy and propenyloxy by Waker Chimie [9, 10] whose photocrosslinking has something in common with vinyl ether.

It is noteworthy that a cationic polymerizable monomer must satisfy many criterions. One of them is its basicity with regard to the initiator acidity. Several monomers meet this requirement, and in this work our choice relates to oxetane cycle. This molecule and its derivatives, such as dimethyloxetane [11], 3,3-bis(chloromethyl)oxetane [12] and 3,3-bis(trimethylsilyloxy)oxetane [13], have already been studied as homopolymers or copolymers essentially by cationic route [14] with other cyclic ethers (mainly THF). Although ring strain of oxetane is lower than oxirane (107 against 114 KJ. mol^{-1}) [15], oxetane basicity is higher (pKb = 7.4 against 3.1) [16]. Experimentally, it was observed that difunctional oxetanes are generally more reactive than their structurally similar epoxide counterparts in photoinitiated cationic polymerization [17]. Moreover, for mono-, bi- and trifunctional oxetanes, sulfonium salts are very efficient, and the shrinkage during polymerization was much lower than for vinyl monomers [18]. Thus, it seems interesting to evaluate the photocrosslinking reactivity of oxetane cycle with cationic photoinitiator when these functions are grafted onto polysiloxane backbone.

EXPERIMENTAL

Materials

Allyl chloride, 3-hydroxymethyl-3-methyl oxetane, tetrabutylammonium hydro-gen sulfate, dibutyltin dilaurate, hexachloro platinic acid were purchased from Aldrich Co.,methyl diethoxy silane, triethoxy silane, poly (dimethyl-co-methylhydro) siloxane **5** (% SiH = 3.25; $\overline{Mn}$ = 16700) from Interchim, and poly(dimethyl-co-methylhydro) siloxane **6** (% SiH = 8.5; $\overline{Mn}$ = 3500), α,ω-dihydroxy polydimethyl-siloxane **4** ($\overline{Mn}$ = 680) from Rhône-Poulenc. All the products and usual solvents (hexane, isopropanol, dichloromethane, toluene) were used without further purification.

Synthesis of Silane Monomers

Preparation of 3-Allyloxymethyl-3-methyl Oxetane (1)

25g (0.245 mole) of 3-hydroxymethyl-3-methyl oxetane, 5.1g (0.015 mol) of tetrabutyl ammonium hydrogen sulfate, 81.4g (1 mol) of allyl chloride and 100 mL of NaOH (50%) were charged into a reaction flask equipped with a mechanical stirrer (800 rpm). The mixture was maintained at 42°C for 4 hours. After cooling, the solution was diluted with 150 mL of dichloromethane and washed several times with water. The organic layer was dried over anhydrous $Mg\ SO_4$. The drying salt was then filtered off and the solvent was removed under reduced pressure. The product was distilled at 40°C under 0.1 mm Hg. Yield: 85%.

Analysis: Calcd. for $C_8H_{14}O_2$: C, 67.57%; H, 9.92%. Found: C, 67.61%; H, 9.85%.

Preparation of Diethoxy-methyl-[(3-methyl oxetane-3-yl)-methyloxypropyl] Silane (2)

14.9g (0.105 mol) of **1** in 30 mL of hexane and 15 μL of H_2PtCl_6 in isopropanol (1/1; w/v) were introduced in a 100 mL flask equipped with a dropping funnel and a condenser topped by an expansion vessel. The mixture was allowed to reach 70°C and 14.1g (0.105 mol) of diethoxy methyl silane in 15 mL of hexane was added dropwise. After 4 hours, the product was isolated by distillation at 76°C under 0.1 mm Hg. Yield: 80%.

Analysis: Calculated for $C_{13}H_{28}O_4Si$: C, 56.48%; H, 10.21%. Found: C, 56.53; H, 10.16%.

Preparation of [(3-Methyl oxetane-3-yl)-methyloxypropyl]-triethoxy Silane (3)

The reaction was carried out by using the procedure mentioned above with 17.2g (0.105 mol) of triethoxy silane . The product was distilled at 82°C under 0.1 mm Hg. Yield: 85%.

^1H NMR (360 MHz, $CDCl_3$) δ (ppm): 1.82 (t, 9H, $C\underline{H}_3CH_2O$); 3.70 (q, 6H, $CH_3C\underline{H}_2O$); 0.62 (m, 2H, - $C\underline{H}_2Si$); 1.65 (m, 2H, $CH_2C\underline{H}_2CH$; 3.39 (t, 2H, $\text{-O-}C\underline{H}_2CH_2$); 3.43 (s, 2H, $\text{-}C\underline{H}_2\text{-O-}CH_2CH_2$); 1.26 (s, 3H, $C\underline{H}_3\text{-C-}$); 4.35 (2d, 4H, $\text{-}C\underline{H}_2\text{-}$ oxetane).

^{13}C NMR (90.5 MHz, $CDCl_3$) δ (ppm): 18.2 ($\underline{C}H_3CH_2O$); 58.2 ($CH_3\underline{C}H_2O$); 6.4 (- $\underline{C}H_2Si$); 22.6 ($CH_2\underline{C}H_2CH$; 73.1 ($\text{-O-}\underline{C}H_2CH$; 75.5 ($\text{-}\underline{C}H_2\text{-O-}CH_2CH_2$); 21.3 ($\underline{C}H_3\text{-C-}$; 80.2 ($\text{-}\underline{C}H_2\text{-}$ oxetane; 39.9 (-$\underline{C}$- oxetane).

Analysis: Calcd. for $C_{14}H_{30}O_5Si$: C, 54.87%; H, 9.87%. Found: C, 54.91%; H, 9.81%.

Polydimethyl Siloxane Grafted Oxetane Moieties

Polycondensation of α,ω-Dihydroxy Polydimethylsiloxane (4) with Diethoxy-methyl-[(3-methyl oxetane-3-yl)-methyloxypropyl] Silane (2)

10.2g (15 mmol) of **4** and 3.1g (11.2 mmol) of **2** with small amount of dibutyltin dilaurate were introduced into a 100 mL round-bottomed flask with magnetic stirrer. The mixture was maintained at 80°C for 30 hours under 20 mm Hg to eliminate ethanol generated by the reaction. Unreacted products were ultimately removed under 0.01 mm Hg at 120°C.

Polycondensation of α,ω-Dihydroxy Polydimethylsiloxane (4) with [(3-Methyl oxetane-3-yl)-methyloxypropyl]-triethoxy Silane (3)

20g (29.4 mmol) of **4** and 7.6g (24.8 mmol) of **3** with a small amount of dibutyltin dilaurate were introduced into a 100 mL flask with magnetic stirrer. The reaction was carried out at 80°C for 18 hours and under 20 mm Hg to remove ethanol.

Hydrosilylation of Poly(dimethyl-co-methylhydro) Siloxane (5) with 3-Allyloxy-ethyl-3-methyl Oxetane (1)

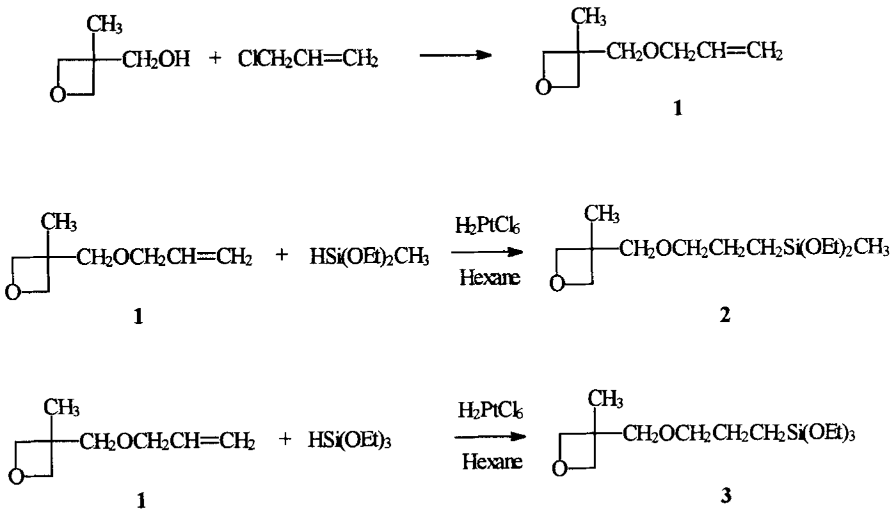
10g of **5** (% SiH = 3.25; $\overline{Mn}$ = 16700), 2g (14.1 mmol) of **2**, 10 mL of toluene and 10 μL of catalytic solution of H_2PtCl_6/isopropanol (1/1; w/v) were introduced into a 50 mL flask equipped with a magnetic stirrer. The mixture was heated up to 80°C and maintained at this temperature for 5 hours. After cooling, toluene was removed by distillation and the product was allowed to stand 30 minutes in boiling diethyl ether in the presence of charcoal. After filtration and elimination of diethyl ether, we obtained a colorless product with quantitative yield. SEC measurement exhibited an increase of $\overline{Mn}$ ($\overline{Mn}$ = 21200).

Hydrosilylation of Poly(dimethyl-co-methylhydro) Siloxane (6) with 3-Allyloxy-methyl-3-methyl Oxetane (1)

The procedure is the same as above using 20 g of **6** (% SiH = 8.5; $\overline{Mn}$ = 3500). Quantitative yield was obtained with a resulting $\overline{Mn}$ = 4000.

Measurement

IR spectroscopies were carried out with a Nicolet 510 M IR/FT. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM 360. Average molecular weights were



SCHEME 1

computed from chromatograms obtained by using a Waters 510 Gel Permeation Chromatograph with polystyrene standards. The apparatus was equipped with five μstyragel columns: 100, 500, 10^3, 10^4, 10^5 Å, working in toluene. The detection being done by a R 401 Waters refractometric detector. Viscosimetric measurements were performed on a Carri-med CSL 100 rheometer. Photocrosslinking was carried out with a photocalorimeter constituted of a DSC 7 Perkin Elmer topped with a mercury-vapor lamp (100 W). The samples were placed in aluminum pans and allowed to equilibrate for 15 minutes at experimental temperature under nitrogen. The samples were then irradiated by opening the shutter, and the course of the exothermic photopolymerization was followed by recording heat flow versus irradiation time. The light flux used in this study was 250 mW/cm^2.

RESULTS AND DISCUSSION

We synthesized polydimethylsiloxanes bearing oxetane groups linked by Si-C bond to prevent hydrolysis. Initially, two types of compounds were prepared from 3-hydroxymethyl-3-methyl oxetane: first, an allylic derivative in order to modify hydrogeno polydimethylsiloxanes by hydrosilylation; second, ethoxy silane monomers which can be copolycondensed with α,β-dihydroxy polydimethylsiloxane.

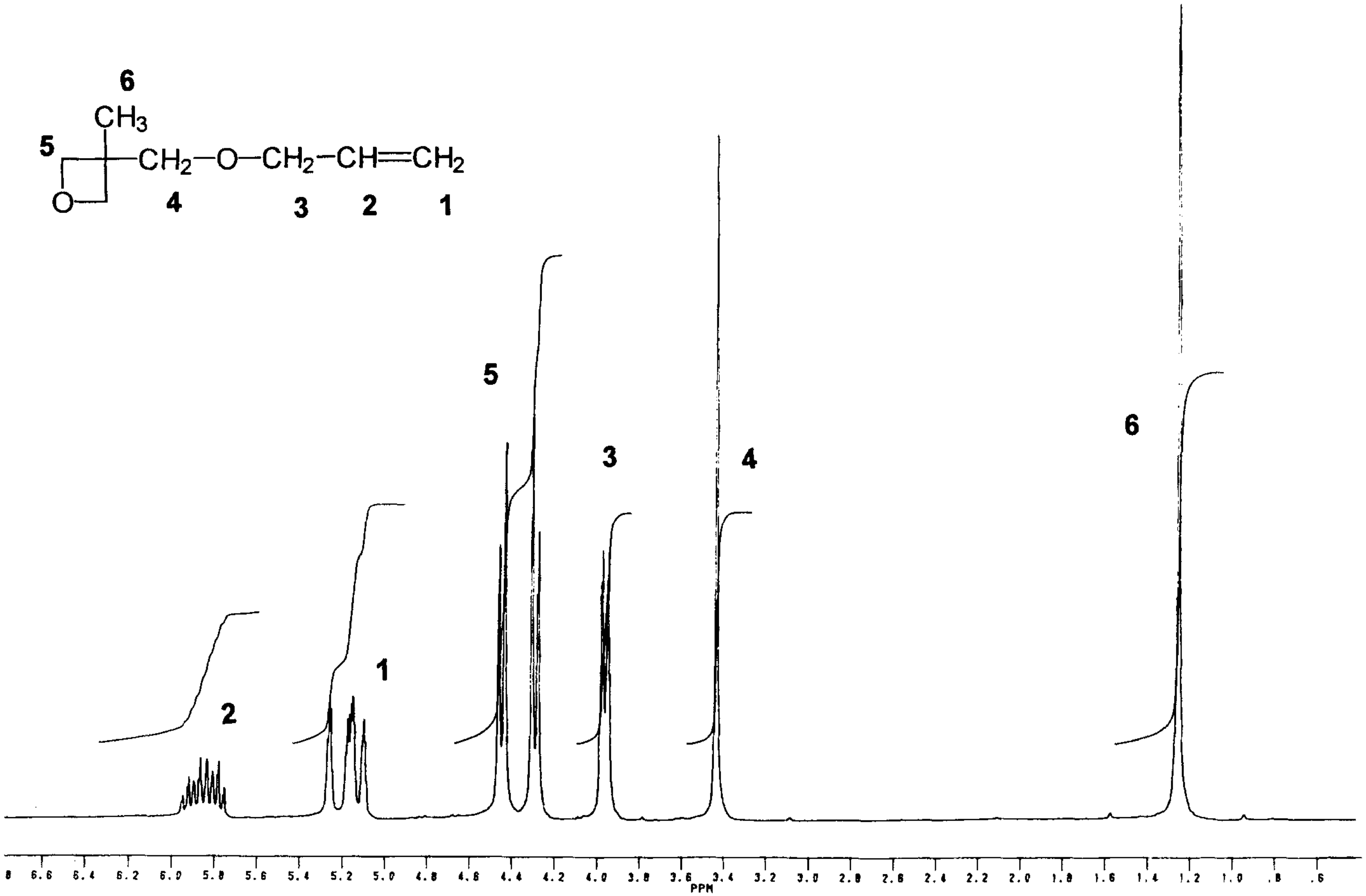


Figure 1. ^{1}H NMR spectrum of 3-allyloxymethyl-3-methyl oxetane.

3-Allyloxymethyl-3-methyl Oxetane (1)

Phase transfer reaction [19] between allyl chloride and 3-hydroxymethyl-3-methyl oxetane (Scheme 1) leads to **1** with 85% yield. ^{1}H NMR spectrum in $CDCl_3$ (Figure1) agrees with expected structure. On FTIR spectrum, one can readily identify oxetane absorption at 980 cm^{-1} and lack of OH stretching at 3300 cm^{-1}.

Di and Triethoxy Silane Monomers (2 and 3)

Hydrosilylation of diethoxy methyl silane and triethoxy methyl silane with **1** in the presence of hexachloro platinic acid in hexane leads to monomers **2** and **3** (Scheme 1). ^{1}H and ^{13}C NMR spectra agree with expected structures (e. g. Figures 2 and 3 for monomer **2**). For example, ^{29}Si NMR spectrum of **2** shows the complete vanishing of the peak at -16 ppm corresponding to Si-H bond, and the appearance of -4.8 ppm peak characteristic of the new silicium structure. FTIR spectra also strenghthened the persistence of oxetane cycle at 980 cm^{-1}.

α,ω-Dihydroxy PolydimEthylsiloxane (4) Modifications

In order to obtain a product of moderate viscosity able to be spread out on support, an α,ω-dihydroxy polydimethylsiloxane (**4**) of low molecular weight ($\overline{Mn}$ = 680) was used in excess with regards to silane comonomers. Polycondensation of diethoxy-methyl-[(3-methyl oxetane-3-yl)-methyloxypropyl] silane (**2**) or [(3-methyl oxetane-3-yl)-methyloxypropyl]-triethoxy silane (**3**) with α,ω-dihydroxy polydimethylsiloxane (**4**) was carried out with dibutyltin dilaurate (DBTL) as catalyst according to Scheme 2.

The lack of reactivity of the second ethoxy group of monomer **2** led only to partially modified oligomers (**7**). The condensation with monomer **3** gave best results (**8**) with an important increase of the viscosity (η = 2840 cSt). For **8**, an average molecular weight $\overline{Mn}$ = 5000 was determined by SEC. Integration of ethoxy group versus of propyloxy methyl oxetane one from ^{1}H NMR spectrum (Figure 4) attests to the presence of one ethoxy per oxetane group. The good solubility of the polymer in many organic solvents strenghthens the assumption that the third ethoxy group is a lot less reactive than the first two groups and a linear chain is mainly obtained. In our experimental conditions (29.4 mmol of **4** and 24.8 mmol of **3**), theoretical calculation leads to an $\overline{X_n}$ of 11.8 if we assume that only two ethoxy groups quantitatively react. This assumption corresponds also to a polymer **8** terminated by **4** which is the diol in excess. From Figure 4, the integration ratio of any protons of ethoxy-[(3-methyl oxetane-3-yl)-methyloxypropyl] silane group and CH_3 (0.01 ppm) of PDMS sequence, allowed

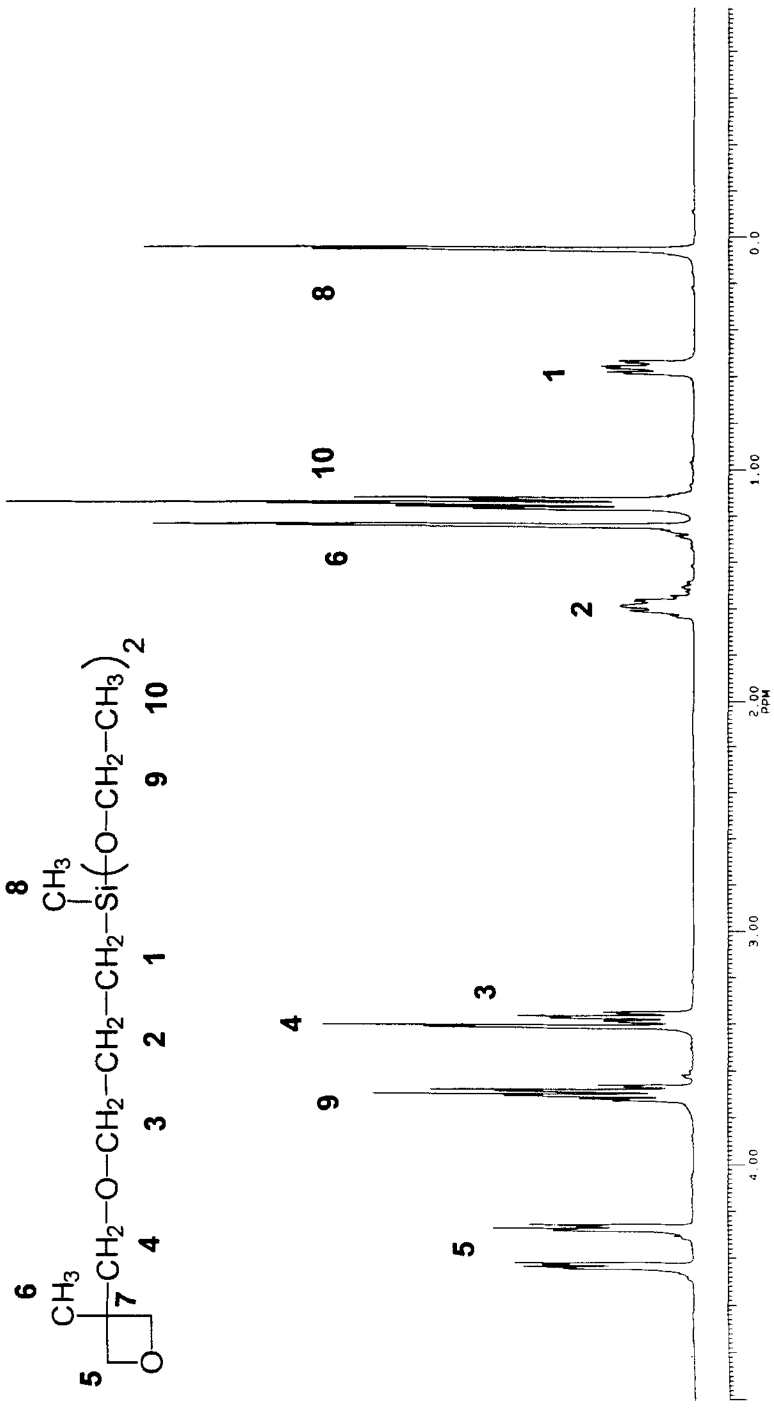


Figure 2. ^{1}H NMR spectrum of diethoxy-methyl-[(3-methyl oxetane-3-yl)-methyloxypropyl] silane.

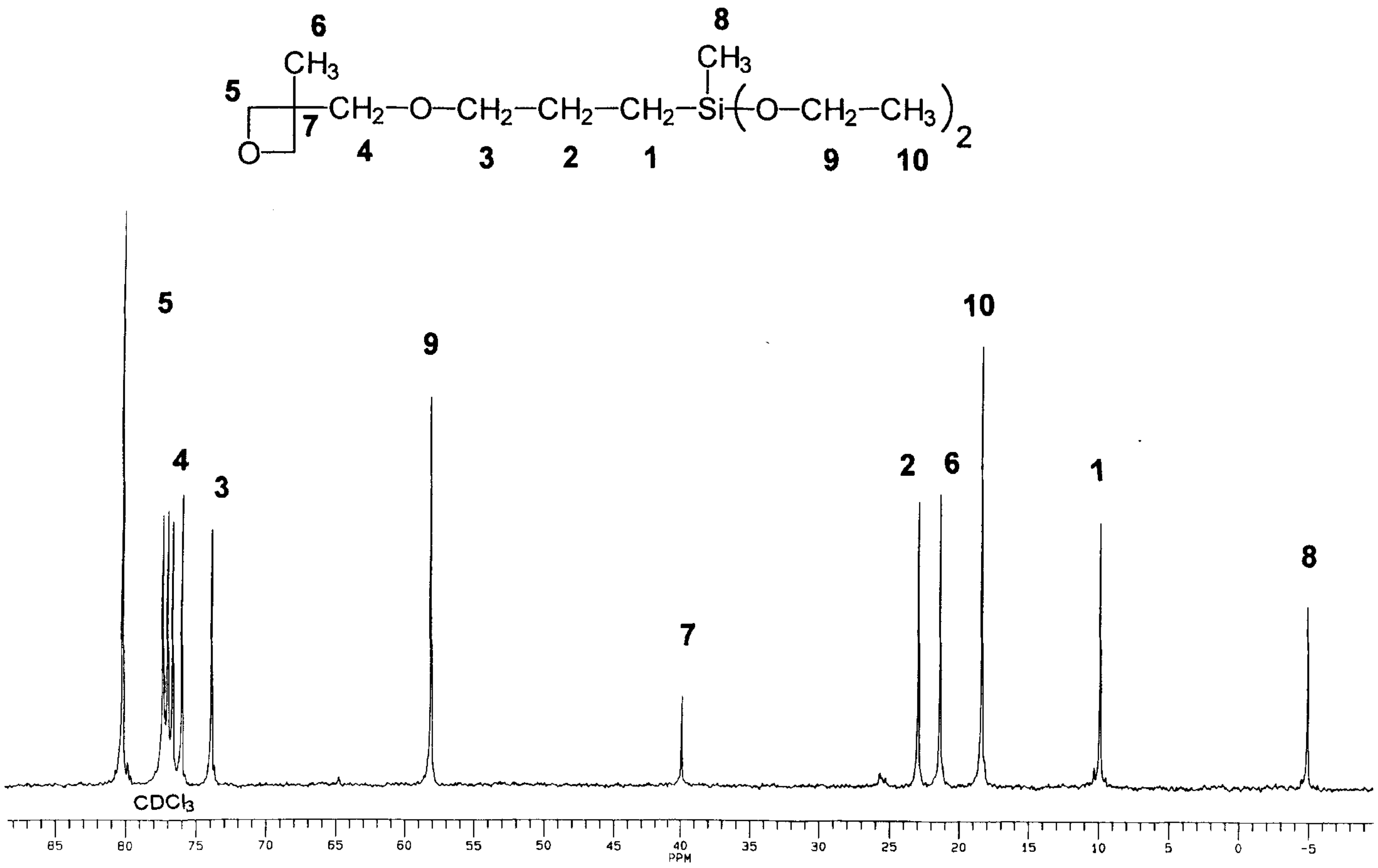
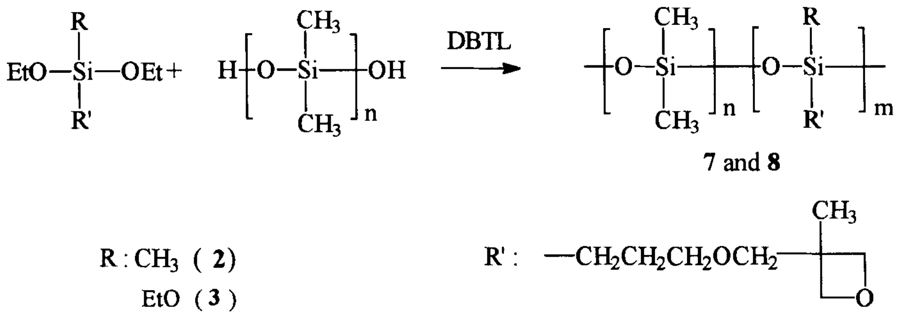


Figure 3. ^{13}C NMR spectrum of diethoxy-methyl-[(3-methyl oxetane-3-yl)-methyloxypropyl] silane.



SCHEME 2

us to estimate an average $\overline{X_n}$ of 11 ($\overline{Mn}$ = 5240) in agreement with SEC measurement and theoretical calculation. Oxetane cycle was also identified by FTIR at 980 cm^{-1}.

Hydrosilylation of Hydrogeno Polydimethylsiloxanes (5 and 6)

Direct hydrosilylation of polydimethylsiloxane bearing Si-H bonds is an usual method to graft allylic ether [20]. In this work, two hydrogeno polymers were used with different SiH contents to give polymers **9** and **10**. The general synthesis is briefly depicted on Scheme 3.

The different percentages given by the supplier were 3.25% (η = 250 cSt) and 8.5% (η = 160 cSt). ^1H NMR spectra of modified polymers **9** and **10** (e.g. Figure 5 for **9**) show clearly the appearance of new protons close to silicium (1, 2 and 3) corresponding to the vanishing of allylic protons at 5.2 and 5.8 ppm. The same observations can be done from ^{13}C NMR spectra (e.g. Figure 6 for **9**).

FTIR allows us to follow the disappearance of Si-H band at 2155 cm^{-1} during the reaction and clearly shows a quantitative modification. Oxetane band at 980 cm^{-1} is also noticed. Thus, by comparison of CH_2 oxetane with overall CH_3-Si integrations in ^1H NMR spectra, we can recompute experimental amounts of SiH of 3% for **9** and 7.4% for **10,** that is to say, slightly lower than the supplier's.

Concurrently, the increase in initial polysiloxanes viscosity (η_i to η) also attests the hydrosilylation (Table1).

In Table 1, we have also reported polymer **8** obtained by condensation which is surprisingly very viscous. In fact, the case of **8** is more complicated than **9** and **10** (hydroxy terminated, presence of ethoxy group, 10% modification). We can first noticed that η_i increases 1.6 times between **9** and **10,** whereas molecular weight

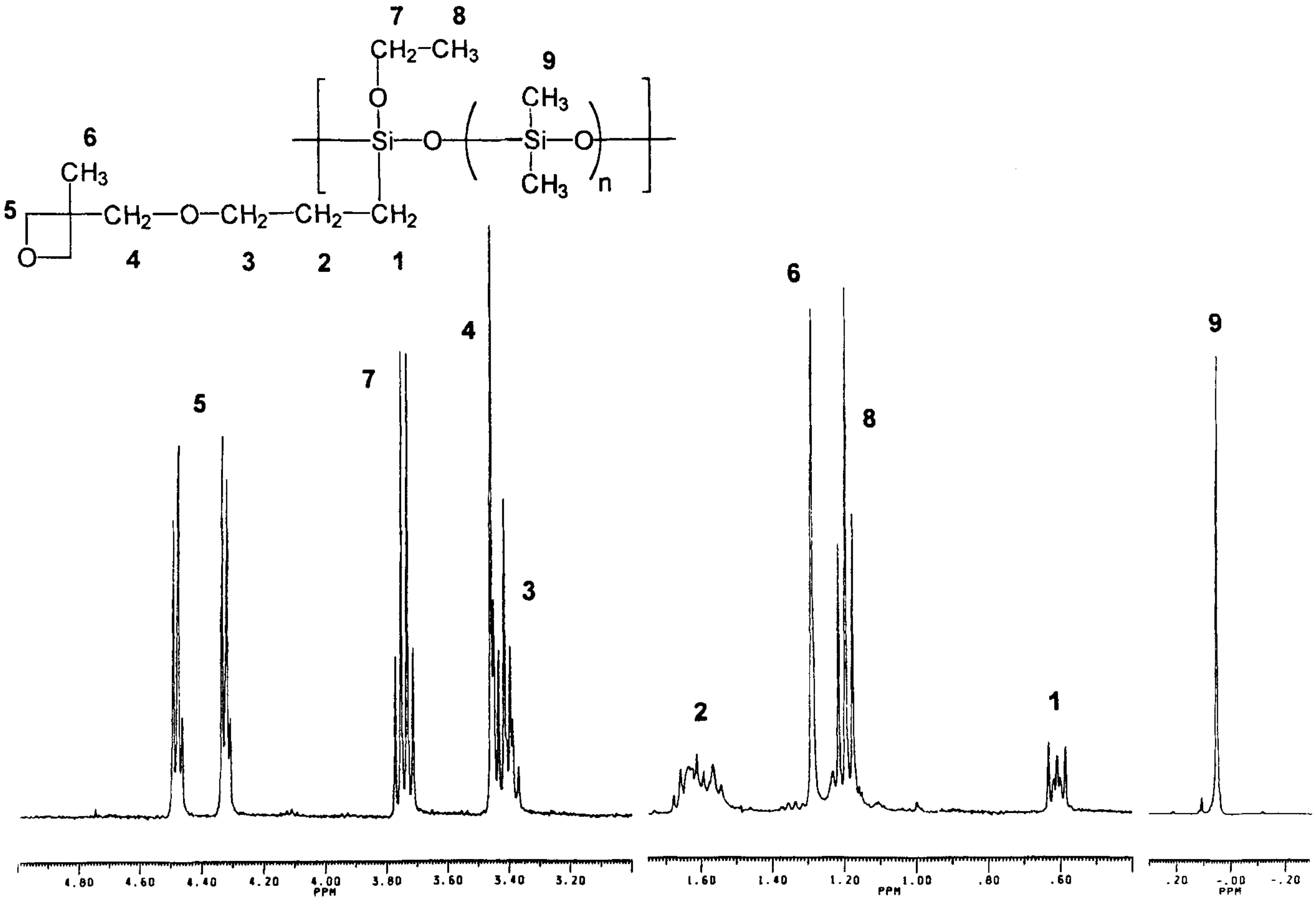
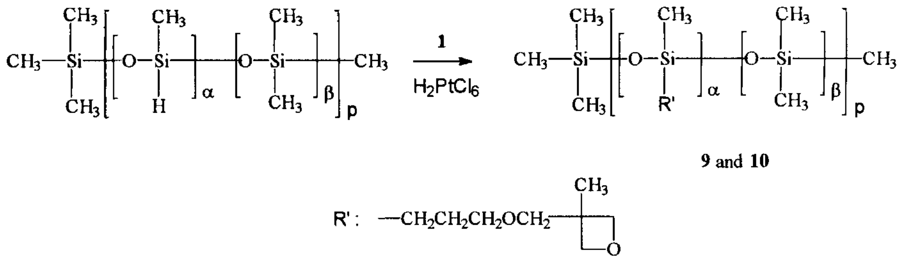


Figure 4. ^{1}H NMR spectrum of (**8**) : modified polydimethylsiloxane (**4**) by polycondensation with [(3-methyl oxetane-3-yl)-methyloxypropyl]-triethoxy silane (**3**).



SCHEME 3

increases 3.6 times. Thus, the low difference between molecular weight of **8** and **10** cannot explain the one of η which is 6.3 times higher. Nevertheless, between 3% and 7.4% modification η increases respectively 1.4 and 2.8 times for **9** and **10**. Thus, if we assume that the variation of η is linear versus the percentage of modification, we can first expect a relative increase of 1.4 times in the viscosity of **8** (10%) with regard to **10** (7.4%). Another difference comes from endcapped group. In fact, **10** is methyl endcapped whereas **8** is hydroxy endcapped. We can estimate the effect of hydroxy by comparing these polymers with well-known PDMS and α,ω-dihydroxy PDMS of equivalent molecular weight where η of the latter is 2 times larger. Finally, to justify the higher value observed for **8**, one can only assume now that the substitution of 10% methyl by ethoxy group enlarge η about 2 times. This last remark would seem to indicate a great influence of ethoxy group on viscosity. Unfortunately, we have no other experimental results to support this assumption.

Photocrosslinking of 10

For its low molecular weight, viscosity lower than **8** and modification ratio higher than **9**, a kinetic study of photocrosslinking was carried out on **10**. For this purpose, we used triarylsulfonium hexafluoroantimonate (Φ_3S^+,SbF_6^-), commercialized in propylene carbonate solution (Cyracure UVI 6974) as photoinitiator (1% w/w in polymer), previously dissolved in toluene (25/75 w/w) because of its low solubility in polysiloxanes. Kinetic measurements were made after solvent evaporation and were carried out by using a Perkin-Elmer DSC-7 differential scanning calorimeter equipped with 100W Hg lamp. Experiments were conducted isothermally on polymer-photoinitiator mixture samples of about 2mg. Thermogram treatments were published elsewhere [21, 22].

The influence of temperature on initial rate (Figure7) and polymerization enthalpy, in the range 35°C to 125°C, is given in Figures 8-10.

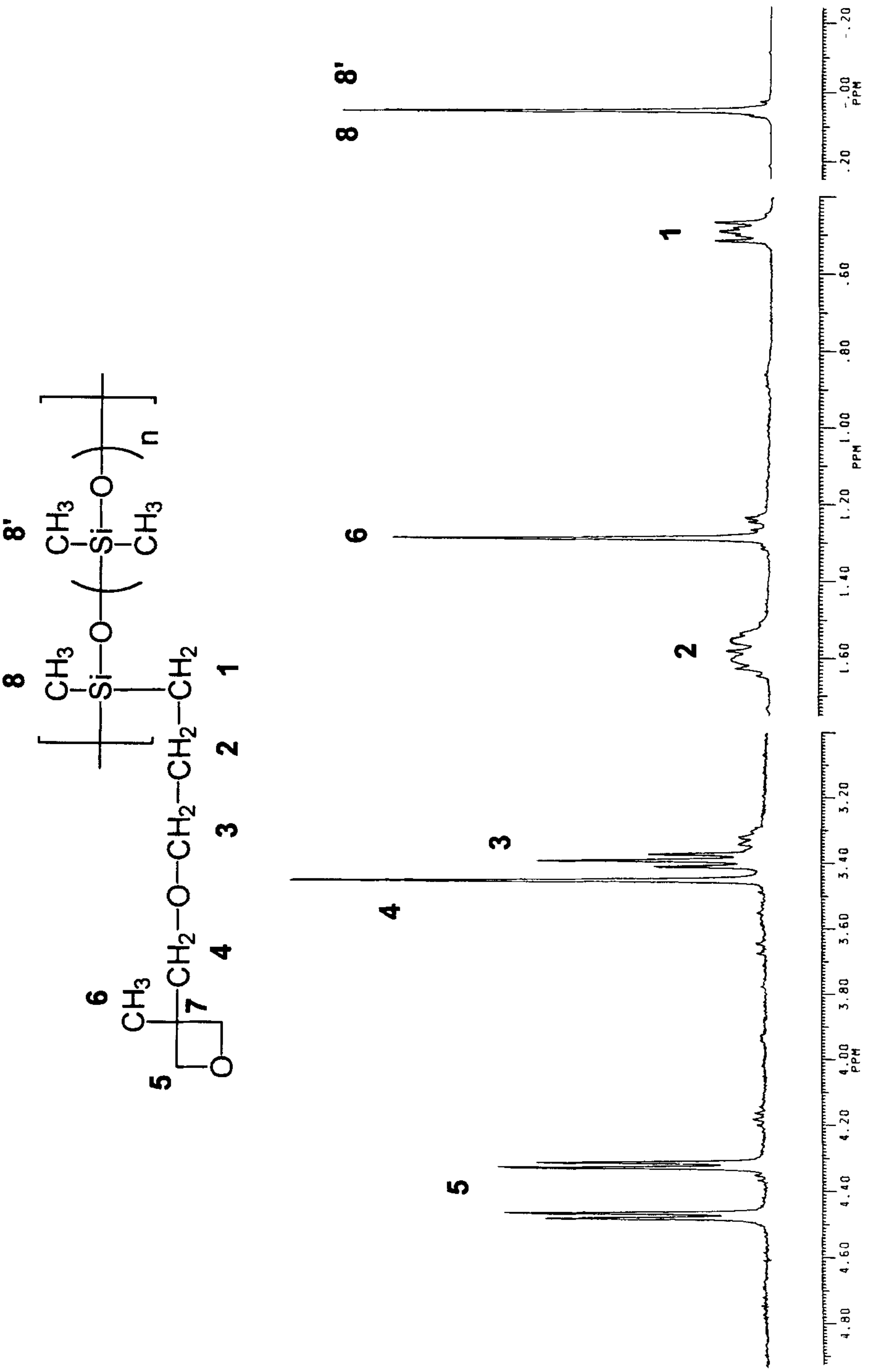


Figure 5. ^{1}H NMR spectrum of modified polydimethylsiloxane (**9**) by hydrosilylation with 3-allyloxymethyl-3-methyl oxetane.

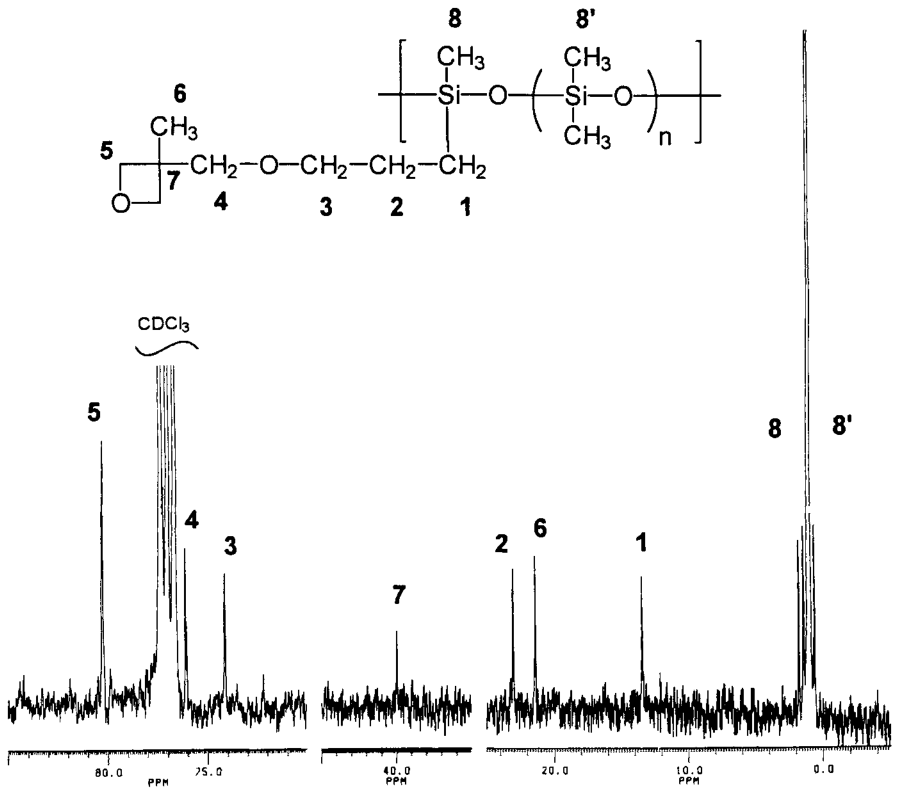


Figure 6. ^{13}C NMR spectrum of modified polydimethylsiloxane (**9**) by hydrosilylation with 3-allyloxymethyl-3-methyl oxetane.

TABLE 1: Molecular Weight and Viscosity of Polydimethylsiloxane before and after Modification.

Polymer	$\overline{M_n}$	η_i (cSt)	η (cSt)
8	5000	-	2840
9	14300	250	345
10	4000	160	450

We can notice an increase in both initial rates and ultimate enthalpies from 35°C to 80°C. If we take 81 kJ/mol. as polymerization enthalpy for oxetane [23], we obtain a $\Delta H_0 = 67.4$ J/g as theoretical enthalpy in our case. Thus, this value leads to conversions (% conversion = 100 $\Delta H/\Delta H_0$) ranging 83 to 92%. These high conversions justify the low increase observed with increasing temperature. With

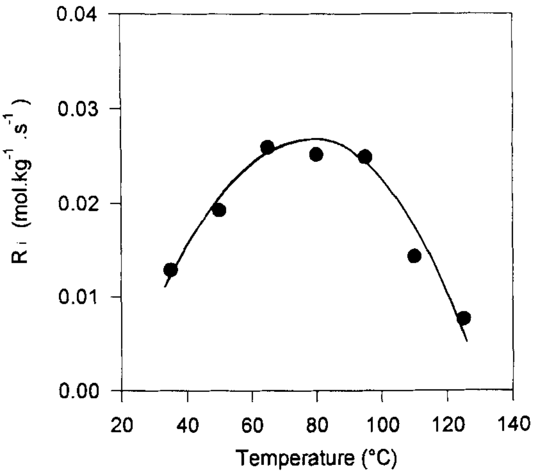


Figure 7. Initial rate versus temperature for photocrosslinking of **10**.

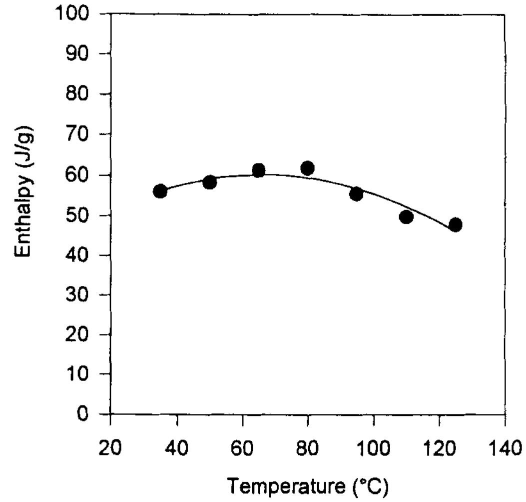


Figure 8. Ultimate enthalpy versus temperature for photocrosslinking of **10**.

regard to initial rate, if photoinitiator decomposition is independent of temperature, initiation (k_i) and propagation (k_p) constants increase with temperature and the resulting rates are enlarged.

On the contrary, for temperature higher than 80°C, both initial rates and conversions decrease. Nevertheless, enthalpy decay is very moderate (Figure10) with still 71% (48 J/g) at 125°C.

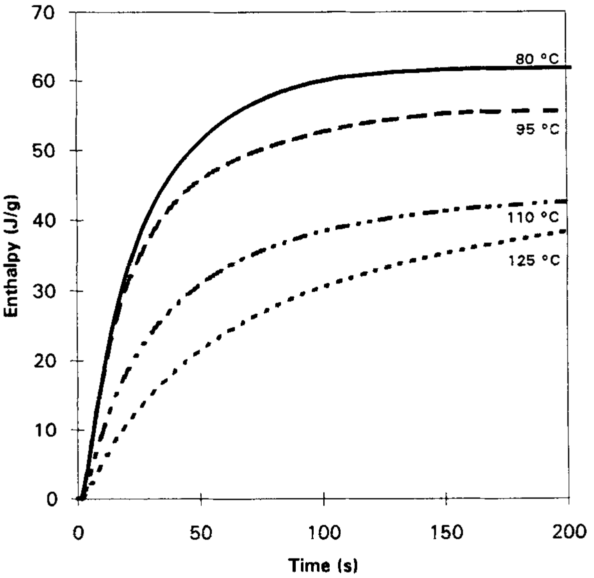


Figure 9. Enthalpy versus time in the range 80 to 125°C for photocrosslinking of **10**.

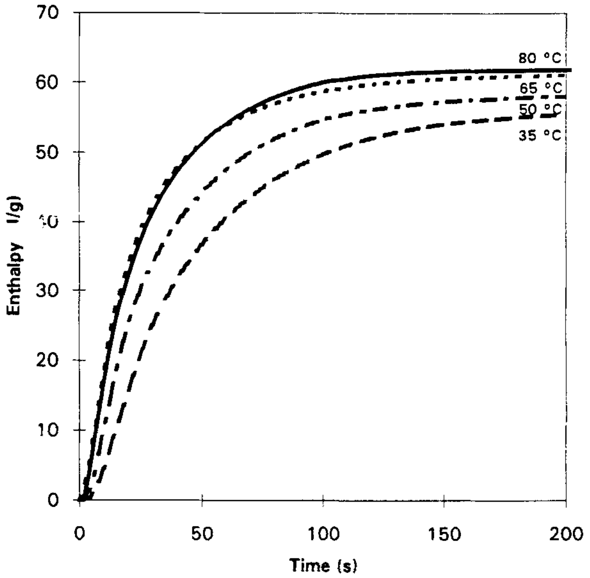


Figure 10. Enthalpy versus time in the range 35 to 80°C for photocrosslinking of **10**.

This behavior is classical in cationic ring opening polymerization where the effect of temperature on conversion and degree of polymerization is very complex. For most polymerization, increasing the temperature leads to a decrease in conversion and molecular weight due to an increase in the rates of transfer and termination reactions. For example [24], it was shown that for BF_3-H_20 polymerization of 3,3-bis (chloromethyl) oxetane, intrinsic viscosity and ultimate conversion decrease when temperature increases. The decrease in polymer molecular weight in this polymerization corresponds to an increase in termination by back-biting reaction with an increasing yield of tetramer. In our case, transfer and termination reactions are also probably the reasons for the shape of conversion curve. Another comment can be made on the relation between initial rates and ultimate conversions. As a matter of fact, in case of photoinitiated polymerization, initiation rate is very high. Thus, crosslinking system cannot be in volumic equilibrium because volume shrinkage rate is much slower than chemical reaction rate. This difference generates a temporary excess of free volume which increases the mobility of the chains and allows residual oxetanes to reach higher conversion than for system in volumic equilibrium.

Industrial Application

Modified polymers **8**, **9** and **10** were spread out and photocured on paper in order to prepare release paper. A mixture of polymer with 1% (w/w) of photoinitiator was spread out on paper, on the basis of 1 to 2 g/m2, and exposed to UV radiations (120 W/cm2 with irradiation window of 10 cm).

For polymers **8**, **9** and **10**, threshold rates to obtain a well cured coating (no smear, migration, or rub off) were respectively of 43, 8 and 15 m/min. As expected, these results emphasize that **8**, which has the highest amount of oxetane group (10%), is more reactive. Unfortunately, its too high viscosity is unfavorable to its use. Thus, polymer **10** is the most interesting of the series.

CONCLUSION

Polysiloxanes bearing oxetane functions were readily prepared in good yields from allyl ether or silane precursors by either hydrosilylation of hydrogeno polydimethylsiloxane or condensation with α,ω-dihydroxy polydimethylsiloxane. These modified polymers undergo easy and rapid UV-induced photocrosslinking using diaryliodonium salt photoinitiator. Kinetic study by using photocalometer clearly shows that the polymerization rate and conversion are dependent on the temperature with an increase up to 80°C and a moderate decrease above 80°C due to an increase in transfer and termination reactions.

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