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## Photoreactivity Of Epoxy Resins

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### ABSTRACT

Work had been done to establish the photoreactivity of epoxy resins with respect to the chemical structure of their monomers. Two epoxy monomers had been chosen, both having two epoxy functional groups at each terminal ends. The difference between these two epoxy monomers being the length separating the two functional groups called the "space" group. Results show that the photochemical reactivity is influenced by the chemical structures of monomers, and thus their physical-chemical properties.

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### KEYWORDS

Epoxies;  
Photopolymerization;  
Kinetics;  
Reactivity;  
Photocalorimetry.

### INTRODUCTION

#### General description of the work

Ultraviolet(UV) radiation is currently a popular choice amongst polymer chemist to initiate polymerization reactions. This is due principally to two reasons, the first being the rapidity of UV photopolymerization and the second being the absence of polluting solvents in the reaction medium. However, there exist several problems, in particular the presence of residual functions in the 3D matrice, volume shrinkage during polymerization, and the differing parameters of monomers reactivity.

For this preliminary work, we chose to treat the problem of monomer's reactivity with respect of its chemical function. The epoxy function was chosen, and the parameter of functionality was our main consider-

ation. The aim is to find a relationship between the functionality or the chemical structure to the reactivity of the epoxy. We chose to use the cationic polymerization technique in this current work, which is the most suitable protocol for epoxy functions.

The paper will describe the subject, the problems and some backgrounds of photopolymerization. It will then be followed by an explanation of the methods used in the course of the research. The results obtained will be presented in the subsequent section followed by the attempt to rationalise the results.

#### Photopolymerisable formulation

The two elements susceptible to react under a UV radiation are:

1. The photoinitiator
2. The monomers or oligomers

## Cationic photoinitiators and photopolymerizable formulation

Cationic photoinitiators are less used in the industry due to its later discovery compared to its radical cousin. Other reason being the limited number of monomers (epoxy, vinyl ethers) which are reactive by the cationic route available in the market.

There are generally two types of cationic photoinitiators, those who generate Brønsted's acid, and those who produce Lewis's acid. The former consist mainly of sulfonium and iodonium salts discovered by James Crivello and his collaborators in general electric<sup>[1-3]</sup>. They are thermally stable (300 to 350°C), and absorb essentially in far UV region (250-300nm). A mechanism proposed by Dektar and Hacker<sup>[4]</sup>, shows us that a radical and a cation were released by the sulfonium salt photoinitiator upon irradiation.

The metallic counter ion plays a very important role in the process of acid formation. The process of photolysis is much faster if the nucleophilicity of the counter ion is weaker. General electric, Ciba-Geigy, Dow chemicals (former union carbide), Cray valley and Rhodia Silicones S.A. are the principal producers of cationic photoinitiators in the market.

Photopolymerizable formulations which are sensitive to a cationic mechanisms include generally chemicals based on epoxy resins. Nevertheless recent advances in the field produce formulations which are based on vinyl ethers. The main advantage of using the latter formulation is the lower viscosity.

## Cationic polymerization

The main difference between a cationic and a radical polymerization is the presence of a cationic species associated with its counter ion during the propagation of the polymerization. Consequently, the kinetics of the cationic polymerization is heavily influenced by the counter ion, or more precisely the solvation effects of the counter ion.

Another interesting difference between the two types of polymerization is that cationic polymerization is not inhibited by the presence of oxygen. On the other hand, the presence of water has a more significant effect on the reactivity of a cationic polymerization. In trace amounts (ppm), H<sub>2</sub>O accelerates the reaction rate due to active species solvation. Larger quantity of wa-

ter will in turns promotes termination reactions.

The propagating species in a cationic polymerization is the carbocation<sup>[5-7]</sup>. The reactivity of the carbocation depends on the nature of the substituents, and the solvent present. Transfer reactions are quite common in cationic polymerization which limits the degree of polymerization. Examples of transfer reactions include transfers to monomers, intramolecular cyclization, intermolecular cyclization and chain hydrogen abstraction. Termination processes are complicated in cationic polymerization. They could either be due to the combination of the terminal chain with the counter ion which is favoured at a high temperature, or the desactivation by a hydrogen donor such as H<sub>2</sub>O or MeOH.

## METHODS

### Products

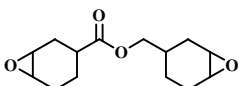
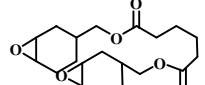
Two bifunctional epoxy monomers are used in this investigation (Figure 1). They are furnished by Dow chemicals (Union carbide) under the trade name of Cyracure®.

The properties of these two monomers are summarized in TABLE 1.

**TABLE 1: Typical properties of the monomers cyracure® UVR-6105 and UVR-6128**

Product	UVR-6105	UVR-6128
Epoxy equivalent weight	130-135	190-210
Molecular weight	252	366
Viscosity at 25°C, cP	220-250	550-750

The photoinitiator (PI) Cyracure® UVI-6974 (Figure 2) is largely studied in our laboratory<sup>[8-10]</sup> due to its high reactivity in cationic formulations, and we choose to use it in this work as well. This PI consist of a mixture of dihexafluoroantimonate of S,S,S',S'-tetraphenylthiobis (4,1-phenylene) disulfonium and

	UVR-6110	UVR-6218
Structure		
Epoxy equivalent	3-4-epoxycyclohexyl methyl-3-4-epoxycyclohexyl hexylcarboxylate	Bis-(3,4-epoxy cyclohexyl) adipate
Boiling point °C	131-143	190-210
weight MW	262-286	380-420

**Figure 1 : Chemical structures of epoxies used Cyracure® UVR-6110 and Cyracure® UVR-6218**

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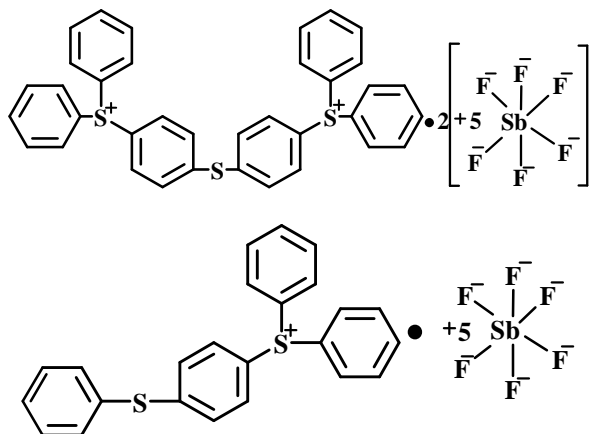


Figure 2 : Chemical structures of Cyracure® UVI-6974 used : mixed triarylsulfonium hexafluoroantimonate salts

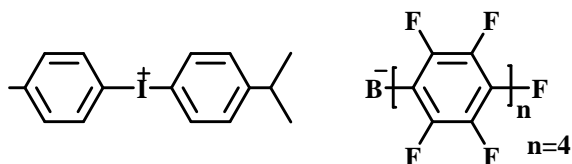


Figure 3 : Photoinitiator silcolease® UV Cata 211

hexafluoroantimonate of diphenyl (4-phenylthiophenyl) sulfonium (CAS no. 89452-32-9 and 71449-78-0) at 50% by weight in the carbonates of propylene. Another important PI used is the UV Cata 211 (Figure 3) from rhone-poulenc. It contains tetrakis (pentafluorophenyl) borate of 4-methylphenyl)phenyl iodonium (CAS no.

178233-72-2) mixed with 20% of 2-propanol (CAS no. 67-63-0).

## Analytical methods

A differential photocalorimetry (DPC) is used to study the kinetics of our system. A photocalorimetry consists of a differential scanning calorimetry (DSC) unit coupled with an insulation unit (USHIO high pressure mercury vapour lamp, USH-200DP). The DSC unit is the DuPont model "930" which is entirely computerized. Figure 4 shows a schematically drawn DPC machine.

The kinetic calculations done with the DPC is based on the Sestak and Berggren<sup>[11]</sup> equation :

$$R_T = \left( \frac{d\alpha}{dt} \right)_{t,T} = k(T) \alpha^m (1-\alpha)^n (-\ln[1-\alpha])^p \quad (1)$$

where  $\alpha$  is the degree of monomer conversion,  $k$  is the rate coefficient,  $m$  is the order of the initiation reaction,  $n$  is the order of propagation reaction and  $p$  is the order of termination reaction.

In order to simplify equation (1), we choose to consider the outset of the polymerization process. In so doing, the value of  $p$  in equation 1 can be taken as 0. Therefore, we will obtain a simpler autocatalytic kinetic model which gives us an equation of rate of the form :

$$R_{(T)} = \left( \frac{d\alpha}{dt} \right)_{t,T} = k_{(T)} \alpha^m (1-\alpha)^n \quad (2)$$

Finally, if the reaction follow an  $n^{\text{th}}$  order kinetics,

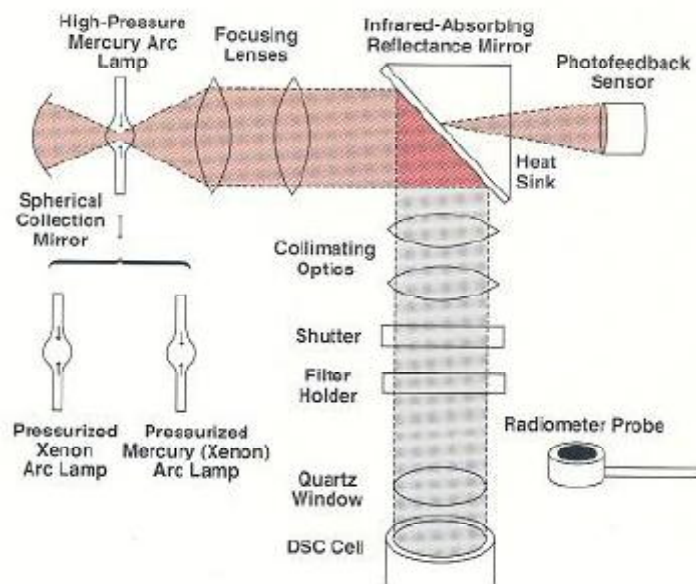
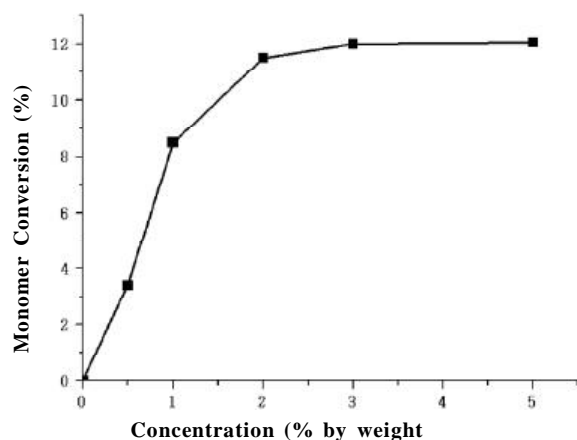
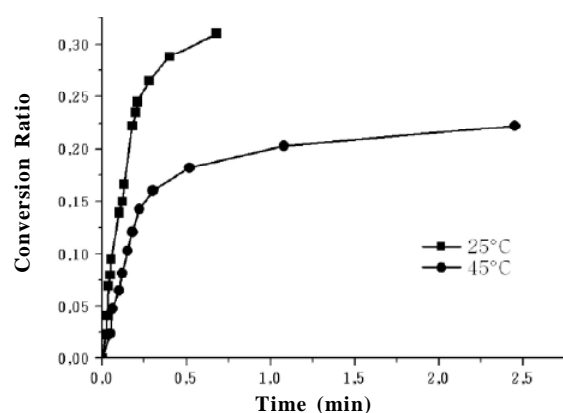


Figure 4 : Photocalorimetry DPC



**Figure 5 :** The reactivity of the monomer-photoinitiator mixture with different concentrations of PI Cyracure UVI-6974



**Figure 6 :** Temperature effect on monomers conversion of Cyracure® UVR-6105 resin

the general equation of rate will be :

$$R_{(T)} = \left( \frac{d\alpha}{dt} \right)_{t,T} = k_{(T)}(1-\alpha)^n \quad (3)$$

With,

$$k_{(T)} = Z \exp \left( \frac{E}{RT} \right) \quad (4)$$

and, Z-collisions factor, E-activation energy ( $\text{Jmol}^{-1}$ , R-ideal gas constant ( $8.31 \text{ Jmol}^{-1}\text{K}^{-1}$ )), T-temperature (K). The monomer conversion of the polymerization reaction or the extent of polymer branching is given as :

$$a = \frac{\Delta H_{\text{exp}}}{\Delta H_T} \quad (5)$$

where,  $\Delta H_{\text{exp}}$ -experimental enthalpy of reaction ( $\text{Jg}^{-1}$ ) and  $\Delta H_T$ -theoretical enthalpy ( $\text{Jg}^{-1}$ ).

The theoretical enthalpy can be calculated by using equation (6) :

$$\Delta H_T = \left( \frac{\Delta H_{Tf}}{M} \right) f \quad (6)$$

with, f-the functionality of the monomer used,  $\Delta H_{Tf}$ -theoretical enthalpy of one reacted function ( $\text{J/mol}$ ), M-molar mass of the monomer (g). For the function of epoxy, the  $\Delta H_{Tf}=22.6 \text{ kcal/mol}^{[12]}$ .

The calculation of the energy of activation is done using the conventional Arrhenius method.

## RESULTS

### The effect of concentration

Mixtures of Cyracure® UVR-1605 and Cyracure® UVI-6974 are prepared with different concentrations of the photoinitiator. These concentrations range from 0.5% to 5% by weight and their reactivity measured at a temperature of  $25^\circ\text{C}$  is shown in figure 5. As we can see from figure 5, the reactivity of the mixture reach a plateau at concentrations between 2% to 5%. We then choose to work at a concentration of 3% for the rest of our experiments.

### The reactivity of epoxies

We also study the effect of temperature on the reactivity of our epoxies. The results which we obtained could be explained in two main fronts. We first discuss the general effect.

**Figure 5 :** The reactivity of the monomer-photoinitiator mixture with different concentrations of PI of increasing temperature on the reactivity of the monomers, and then we compare the differences of reactivity between Cyracure® UVR-6105 and Cyracure®UVR-6128.

By observing figures 6 and 8, we could say that the conversion of monomers decreases when the temperature increases and that the rate of conversion is higher for Cyracure® UVR-6105 compared to Cyracure® UVR-6128 at a same temperature. And if we were to look at the rate of reactions (Figures 7 and 9), we could observe the same pattern with the rate of reaction being inversely proportional to temperature and that Cyracure® UVR-6105 is a more reactive monomer than Cyracure® UVR-6128. This remark then brings us to the next section, which compare the reactivity of the two monomers by calculating their activation energy via the Arrhenius plot shown in figures 10 and 11.

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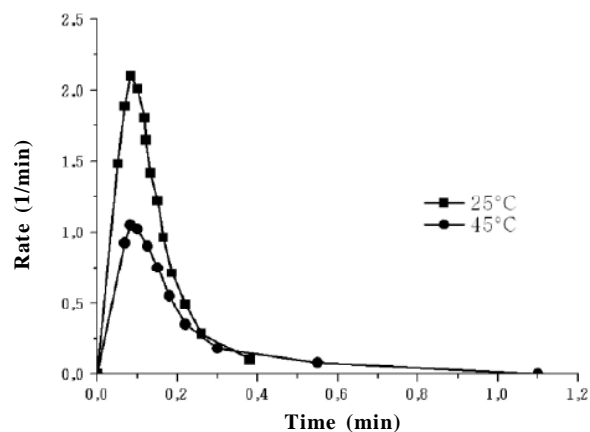


Figure 7 : Temperature effect on the rate of reaction of Cyracure® UVR-6105 resin

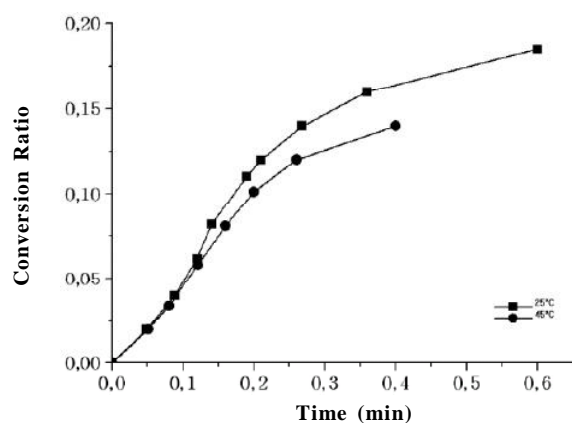


Figure 8 : Temperature effect on monomers conversion of Cyracure® UVR-6128 resin

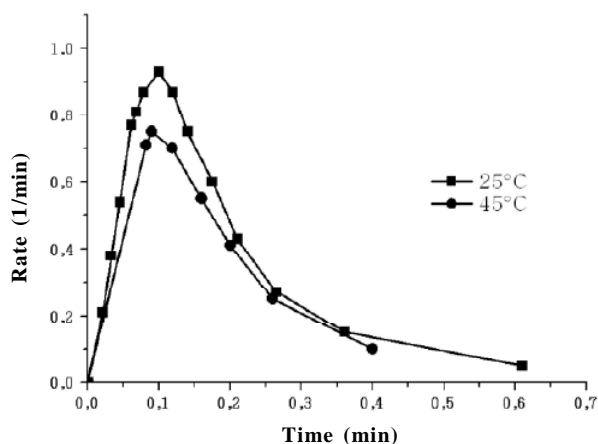


Figure 9 : Temperature effect on the rate of reaction of Cyracure® UVR-6128 resin

Upon simple calculations, we've found that the activation energy of Cyracure® UVR-6105 to be  $5.39 \pm$   $\text{kJmol}^{-1}$  and that of Cyracure® UVR-6128 to be  $9.43$

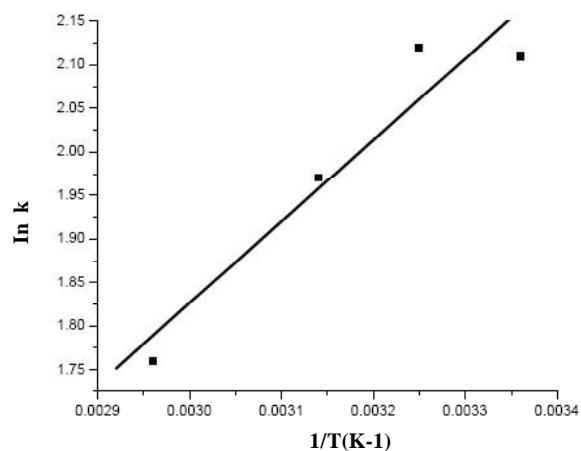


Figure 11: Arrhenius plot of Cyracure® UVR-6128 resin

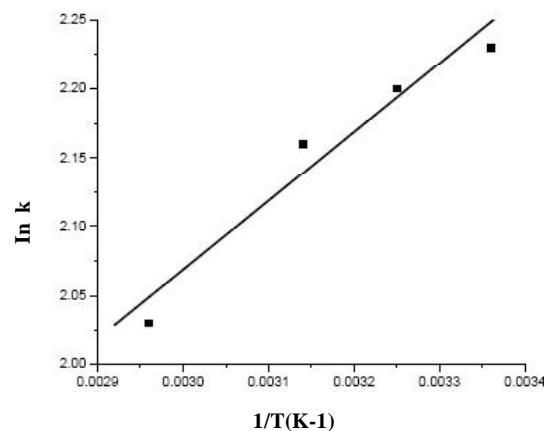


Figure 10 : Arrhenius plot of Cyracure® UVR-6105 resin

$\pm 1.48 \text{ kJmol}^{-1}$ .

Besides using PI Cyracure® UVI-6974, we also use another PI Silcolease® UV Cata 211. Contrary to reported high reactivity of Silcolease® UV Cata 211<sup>[13]</sup>, we've found that it has a much inferior reactivity compared to Cyracure® UVI-6974 for our two monomers. The results are summarized in TABLE 2.

## DISCUSSIONS AND CONCLUSIONS

Sulfonium salts such as Cyracure® UVI-6974 with a counter ion of  $\text{SbF}_6^-$  is a better PI with respect to the

TABLE 2 : Reactivity of various combinations of photoinitiators and monomers at  $64^\circ\text{C}$

Product	$\Delta H, \text{J.g}^{-1}$	Induction time, s	$k, \text{min}^{-1}$
UV-16974+UVR-6105	247.5	3.3	7.74
UV-16974+UVR-6128	117.2	3.1	6.07
UV Cata 211+UVR-6105	164.5	25.2	2.25
UV Cata 211+UVR-6128	109.8	28.6	1.08

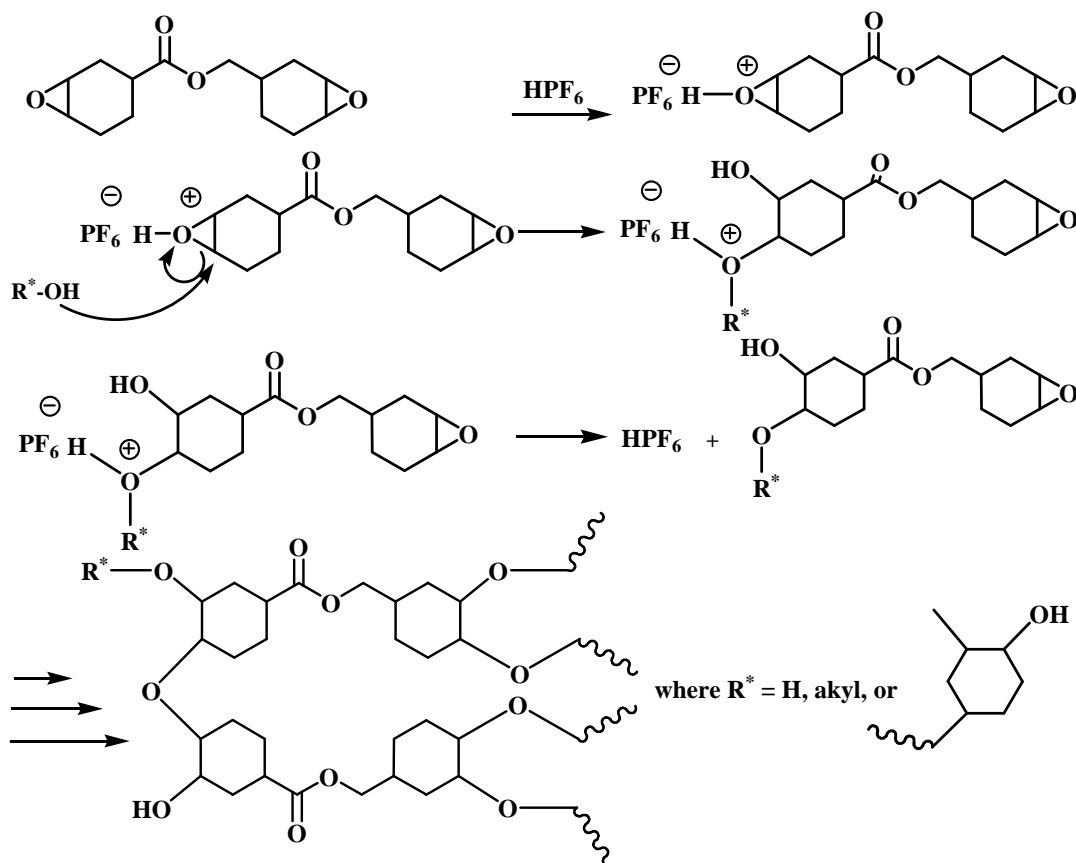


Figure 12 : Crosslinking reaction of Cyracure® UVR-6110 resin induced by photopolymerisation

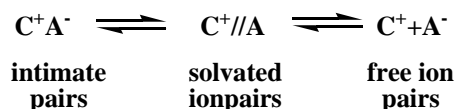


Figure 13 : Equilibrium between the carbocation and its counter ion

monomers which we employ in this study compared to the Silcolease® UV Cata 211. This lack of reactivity for the latter PI is due to the presence of isopropanol as solvent. Alcohol is an inhibitor for cationic polymerization, by quenching all the cationic species, such as proton in the reacting medium. We are planning to study the reactivity of the pure tektrakis PI in the absence of an alcohol solvent in the near future.

The mechanism of the polymerization of the epoxies using Cyracure® UVR-6105 monomer as an example is shown in figure 12. We can see from figure 12, the photoinitiator induces an polarization of the oxirane group making the oxygen atom of the epoxy group on the monomer susceptible for a nucleophilic attack from an other

protonated monomer. The ionic polymerization is then initiated, as well as the crosslinking reaction.

Kinetics studies done in this work show that the reactivity of epoxy monomers and also the rate of monomer conversion, are both inversely proportional to temperature variation. This is due to the presence of an equilibrium consisting of three ionic species; the “intimate ions” pairs, “solvated ions” and “free ions”. When the temperature is increased, the equilibrium (shown in figure 13) is shifted to the left hand side which increases the amount of “intimate ion” pairs which will in turn causes a decrease in reactivity.

Finally we look at the influence of the chemical structure of monomers with respect to the reactivity of the monomers. If we observe the structures of both Cyracure® UVR-6105 and Cyracure® UVR-6128, we realize that the latter has a higher degree of liberty due to the presence of 2 carbonyl groups, 6 methylene groups and 2 oxygens compared to Cyracure® UVR-6105. We would presume a higher reactivity of a more

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flexible molecule but our result shows the contrary. This is mainly caused by the higher viscosity of Cyracure® UVR-6128 which inhibits the free movements of reactive species such as the protons and the monomers.

The lack of reactivity of Cyracure® UVR-6128 with respect of Cyracure® UVR-6105 is postulated to be due to a low “functional group density”. Functional group density (FGD) is defined as the ratio between the molecular weight of the reacting functional group (in our present case, the epoxy functional group) and the total molecular weight of the monomer. If we do a simple calculation, the FGD of Cyracure® UVR-6105 is 0.333 (the molecular weight of an epoxy is taken as the total molecular weight of the oxygen, the two carbons and the two hydrogens) whereas it only 0.230 for the longer monomer, Cyracure® UVR-6128. A higher FGD actually translate to a higher “visibility” of the reacting group, thus more epoxies are exposed fro reaction in solutions of Cyracure® UVR-6105 compared to its larger cousin Cyracure® UVR-6128.

An other aspect to be taken into consideration is the vitrification time,  $t_v$  of photopolymerization. A longer  $t_v$  would entailsm that monomers could react before the structure vitifies. For both system studied, the  $t_v$  is very short, thus both conversion and the reactivity are reduced significantly. Currently we are using molecular dynamics simulation<sup>[14]</sup> to understand the vitrification processes, and to see whether it has a role in the overall reactivity of the monomer in questions.

To summarize this paper, we obtained cross-linked polymers using both Cyracure® UVR 6105 and Cyracure® UVR-6128 epoxy monomers with the presence of suitable photoinitiator Cyracure® UVI-6974. The polymerization is activated by UV radiation. The polymer is a hard and adhesive. The increase of temperature decreases the reactivity of our system. Furthermore the viscosity of the reacting medium plays a much more important role at the start of the polymerization reaction than the chemical structures, in determining the reactivity of polymerization process.

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