

Photopolymerization using photolabile amine catalysts

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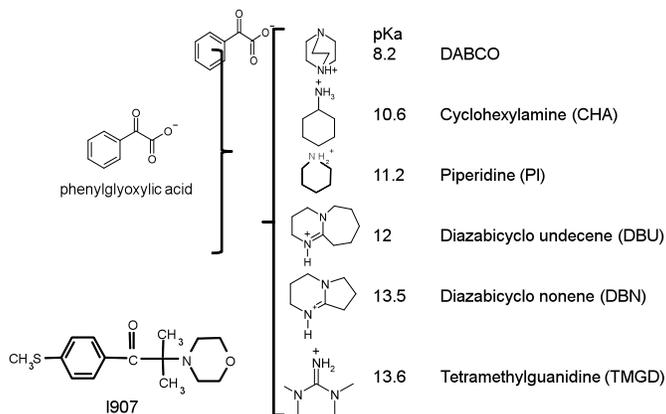
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Introduction.

Photopolymerization represents nowadays a widely used technology in many different industrial fields. Free radical polymerization is undoubtedly the leading technology and cationic photopolymerization has also attracted great interest. By contrast, use of photobase generators has received considerably less attention and, in most cases, photobase generators release weakly basic aliphatic amines under irradiation leading to strong limitations in their use [1-2]. In this paper, new series of photobase generators (PBG) was investigated which release different amines with different pKa. Base catalyzed epoxide photopolymerization, anionic photopolymerization of acrylates, polythiourethane formation and hybrid sol-gel process were investigated [3].

Materials.

The compounds used in this work are shown in Scheme 1. The PBG are quaternary ammonium salts of phenylglyoxylic acid. The synthesis was based on a procedure reported elsewhere [3]. All the synthesized PBG are compared to Irgacure 907, a free radical photoinitiator which is known to produce free weak base in the absence of radical quencher [4].



Scheme 1. Compounds used in this study.

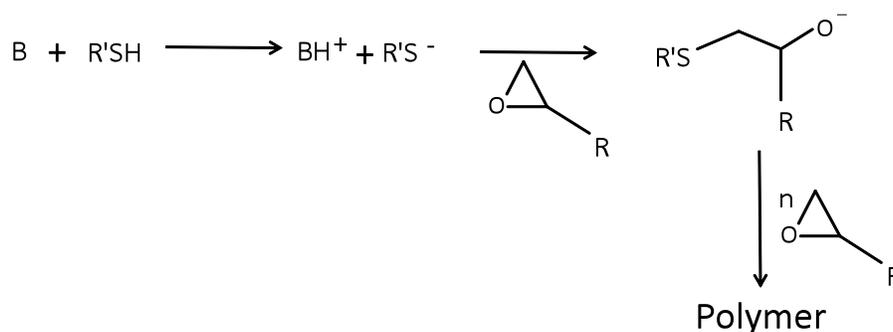
Real-time Fourier transform infrared spectroscopy (RT-FTIR) studies were conducted to monitor epoxy, alkoxy silane, mercaptan and isocyanate conversion using a Vertex 70 FTIR spectrometer (Bruker Optik) [3]. The degree of conversion C is directly related to the decrease of the peak area A corresponding to the reactive functions, and was calculated according to:

$$C(\%) = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

where A_0 and A_t were the area of the IR absorption peak of the sample before exposure and at a given exposure time t , respectively.

Base catalyzed epoxide photopolymerization.

The photopolymerization of epoxides by using the photobase generators has been extensively studied. This process suffers from the low reactivity of the bases generated and often requires a post-baking to ensure complete polymerization. Addition of thiol leads to an increase of the conversion [5]. This improvement is attributed to the formation of thiolate anion by reaction of the thiol with the photogenerated base (Scheme 2).



Scheme 2. Mechanism of the thiol-promoted epoxide photopolymerization.

It can be seen on Figure 1 that the addition of 8wt% of glycol dimercaptopropionate to the epoxide resin (Epalloy 5000) allows an efficient conversion of the epoxide reactive groups. This shows that the photopolymerization of epoxide can be operated using a photobase generator instead of the well-known cationic photoinitiators.

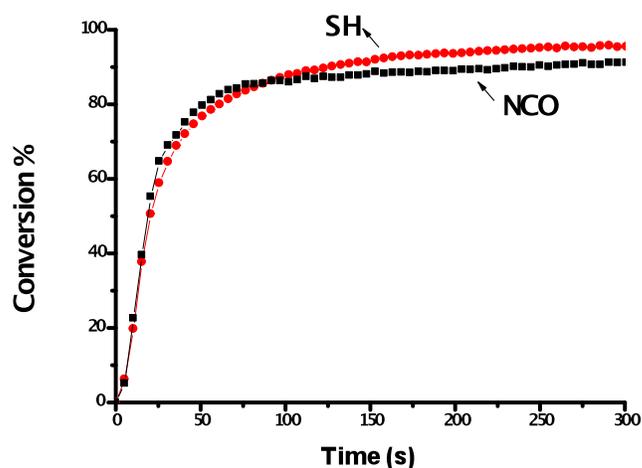
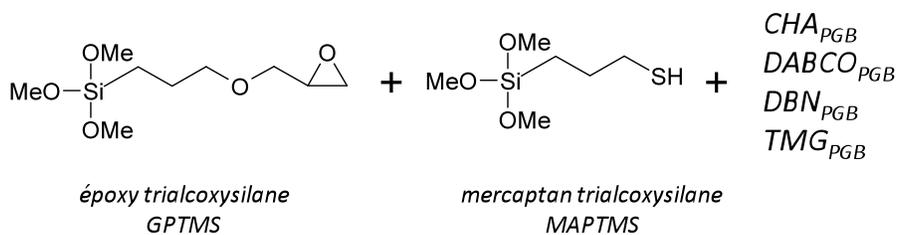


Figure 2. Conversion of isocyanate and thiol groups as catalyzed by irradiated TMG_{PBG} .

Base photocatalyzed inorganic/organic sol-gel photopolymerization.

So-gel polymerization is a very interesting process for the formation of scratch resistant coatings [6]. The compounds used are shown in Scheme 4.



Scheme 4. Compounds used for sol-gel polymerization.

It is shown in Figure 3 that an efficient conversion of epoxide occurs with TMG_{PBG} . It can be seen that epoxide functional groups react quite efficiently, in a similar way as shown above. Interestingly, the Si-O reactive groups undergo a hydrolysis reaction which is typical for the formation of silicon inorganic network.

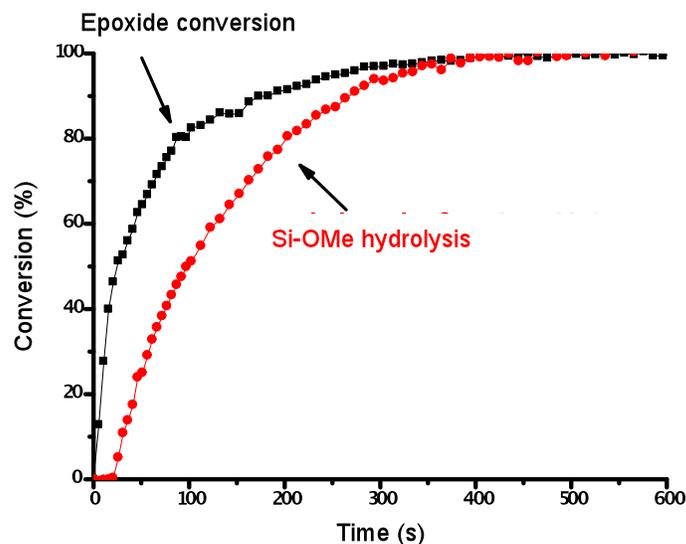


Figure 3. Inorganic/organic sol-gel catalysis by TMG_{PGB} .

Conclusion :

On the basis of different examples, it was shown that new kind of photobase generators can lead to the formation of different polymer networks such as for epoxide polymerization, polythiourethane network and sol-gel chemistry. This opens new opportunities for use in the field of UV-cured coatings.

References

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