

## Elaboration of a stimuli sensitive poly(2-phenoxy ethyl acrylate) crosslinked network UVcured– Swelling characterization in isotropic solvents

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**Abstract**— In this work we present a study of a UV photo-polymerized crosslinked poly (2-phenoxy ethyl acrylate) network (poly(PEA)). The phase properties and the swelling (or deswelling) behaviour of poly(PEA) network in isotropic solvent, were investigated as a function of temperature, nature of solvent and cross-linking density. We also see the influence of chemical structure of initial components, by considering the copolymerization rate (PEA with LA (lauryl acrylate)). The experimental phase diagram of the system poly(PEA) network/solvent, can be determined from the results of the swelling study.

**Keywords:** UV Photo-polymerization, crosslinked poly (PEA) network, swelling, experimental phase diagram, copolymerization.

### I. INTRODUCTION

The interest in the behaviour of polymer networks swollen in a solvent (that called polymer gels) has grown significantly over the past decades [1-5]. The impetus for the rapid scientific development in this field was the first experimental observation of the phenomenon of gel collapse by T. Tanaka in 1978 [6]. This phenomenon consists of a sharp decrease in the volume of the gel by several orders of magnitude in response to a small variation in the external parameters. There are many different stimuli to modulate the response of polymer systems. Chemical stimuli, such as pH, ionic factors and chemical agents, will change the interactions between polymer chains or between polymer chains and solvents at the molecular level. The physical stimuli, such as temperature, electric or magnetic fields, and mechanical stress, will affect the level of various energy sources and alter molecular interactions at critical onset points [7]. These responses of polymer systems have many potential uses in various fields of biotechnology [8], medicine [9-11] and robotics [12-13], and their practical applications will be further extended if their chemical structures can be controlled [14]. We earlier [15]

presented a fundamental study on the swelling properties of some acrylic polymer networks (poly (Abu), poly (EHA)) in isotropic solvents (methanol, toluene, etc...). In this paper we extend the study for the poly (PEA) network to other parameters like temperature, chemical structure of components and effect of copolymerization. The cross-linked polymer was obtained by the UV-curing of initial solutions containing reactive monomer, a cross-linker and a photo initiator. We study their dynamic swelling behaviour in four solvents at different temperature and we see the effect of the degree of cross-linking and the chemical structure of initial component (copolymerization) on swelling behaviour. The analysis of the results of swelling makes it possible to obtain useful information of the phase properties of the system polymer network/solvent.

### II-MATERIALS AND METHODS

#### 1-Materials

The acrylic monomers used for this study are 2-Phenoxy Ethyl Acrylate (PEA) and Lauryl Acrylate (LA) (from Aldrich). The cross-linking agent is: 1,6-Hexane Diol Di-Acrylate (HDDA) (supplied by Cray Valley, France). The photo-polymerization agent used is: 2-hydroxy-2-methyl-1-phenyl-propane-1 (Darocur 1173, from Ciba-Geigy). Isotropic solvents are employed as received. The chemical structures of the different components are given in Figure 1.

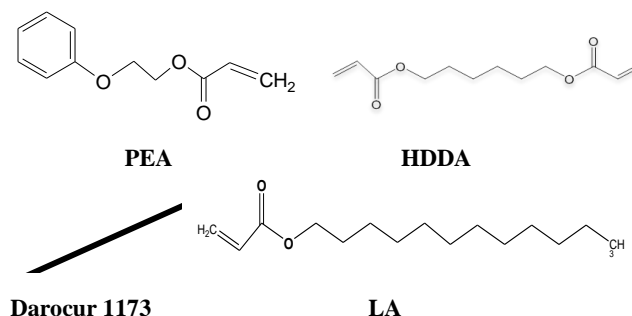


Fig1 Chemical structures of the components of the initial mixtures  
 2- Polymer networks synthesis

Blends of PEA/HDDA/Darocur1173 and (PEA/LA)/HDDA/Darocur1173, were prepared in different weight fractions by varying the quantity of HDDA or LA and keeping the amount of the photo initiator constant (PEA/HDDA/Darocur1173 = 99/0.5/0.5wt.%, ....), (PEA/LA/HDDA/Darocur 1173 = 94.4/5/0.1/0.5 wt.%, ....). These initial mixtures were stirred mechanically for some hours before they were cast in small flat sample holders, exhibiting a single homogeneous phase. The samples were exposed to UV radiation under nitrogen atmosphere, using Philips TL08 UV lamps exhibiting a wavelength  $\lambda=365$  nm and an intensity  $I=1.5$  mW/cm<sup>2</sup>. The exposure time was fixed at 25 minutes to achieve complete conversion of all monomers in the precursor system [15]. The samples obtained are optically transparent cross-linked polymer networks.

3-Dynamic swelling experiments

To study the dynamic swelling behaviour, a cylindrical sample was weighed and immersed in different solvent at room temperature (T=20°C). The sample was taken out at regular intervals of time, wiped with a filter paper for the removal of the free liquid on the surface and then weighted. The percentage swelling ratio (SR) was calculated from the following expression:

$$\text{Swelling ratio} = \frac{W_s - W_i}{W_i} \times 100$$

Where:  $W_s$  is the weight of the swollen network and  $W_i$  is the weight of initially dried network.

III-EXPERIMENTAL RESULTS:

Measurements of swelling kinetics are carried out on samples of polymer networks made of PolyPEA (PEA/HDDA/Darocur1173) and co-Poly(PEA/LA) (PEA/LA/HDDA/Darocur1173) in different isotropic solvents by studying the influence of the temperature of the solvent and the structure of chemical components (cross linking density/copolymerization).

A. Influence of the nature of solvent

For the purpose of observing the swelling behaviour of polymer networks in solvents, samples of polymers networks were left at ambient temperature for a sufficiently long time. It is known that swelling degree increases with time up to a certain point and then it becomes constant, see figures (2, 3). This value of maximum swelling degree is named the “equilibrium degree of swelling” (EDS).

Figure2 shows the experimental curves of the swelling kinetics of the crosslinked poly (PEA) network (with 0.1 wt.%

HDDA) at room temperature (T = 23 ° C) in organic solvents such as THF, toluene, acetone and MIBK.

Is clearly observed a significant swelling for the curve corresponding to poly (PEA) network swollen in THF. Therefore, this result shows that the sample of poly(PEA) network (crosslinked with wt.0.1% HDDA) has a high miscibility with THF molecules. In addition, in the case of acetone, the thermodynamic equilibrium (saturation value), is quickly reached indicating that this network has a low miscibility with this solvent. It may be noted that THF is a good solvent for the poly(PEA) network, while acetone and MIBK are a nearly poor solvents for the poly (PEA) network. Toluene has an intermediate degree of swelling compared to those of THF and acetone as the value of its solubility is between those of the latter two. We also observe that the toluene and MIBK swelling kinetics are slower compared to other solvents.

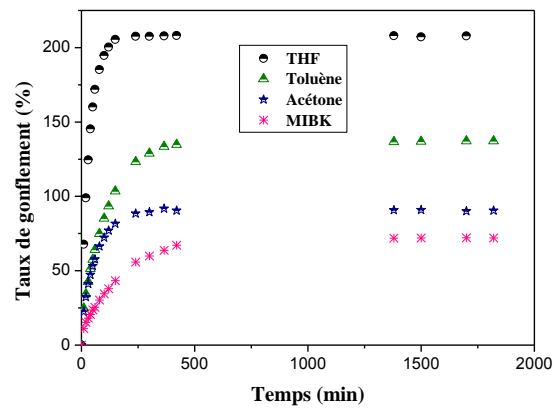


Fig 2 Swelling kinetics of Poly (PEA)/0.1wt%HDDA different solvents

B. Influence of cross linking density in the kinetic swelling

The Figure 3 shows the swelling ratio of the Poly (PEA) network with different density of cross-linking, in Toluene and MIBK at room temperature (T=20°C). It is clear that the weak cross-linked network has the most important swelling. This swelling ratio decrease with each time one increases the concentration of cross-linker agent this is due to the mobility of the polymeric chains. A high concentration impedes mobility of the polymer chains resulting in lower swelling. The results clearly show that the change in the amount of crosslinking agent HDDA (that is to say, the network architecture) in the initial mixtures, strongly influences the behavior of swelling poly (PEA) network. We can conclude that the swelling rate varies inversely proportional to the crosslink density of the network.

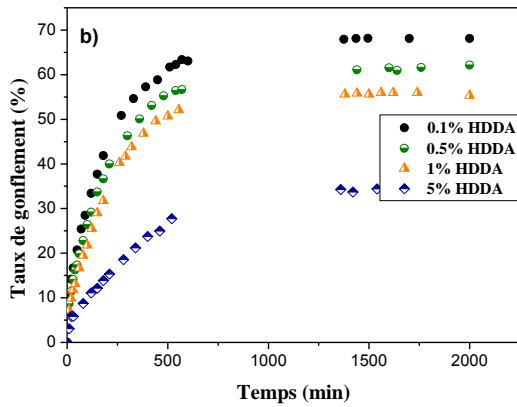
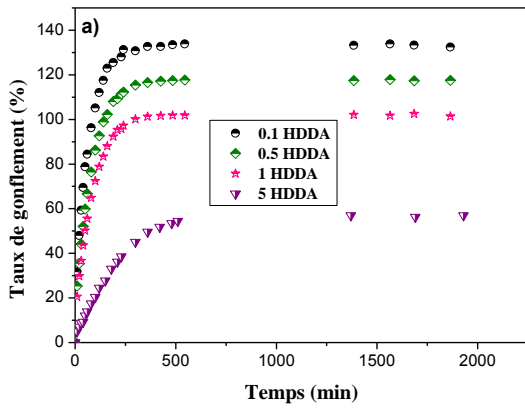


Fig 3 Kinetic swelling of poly (PEA) networks in a) toluene and b) MIBK at room temperature as a function for several concentrations of cross-linker agent (HDDA).

C. Influence of chemical structure of components in kinetic swelling

The figure 4 report the influence of chemical structure of polymers networks of poly (PEA) when we copolymerize PEA with a different rate of LA, in the swelling behaviour in two solvents (Toluene and MIBK). We can note that the swelling rate is very important in the case of copolymerization with a rate of 10 wt.% of LA. The swelling rate decreases when a rate of LA is very low. That means that the chemical structure of polymer networks influences the swelling behaviour because of interactions some chemical groups with solvent medium.

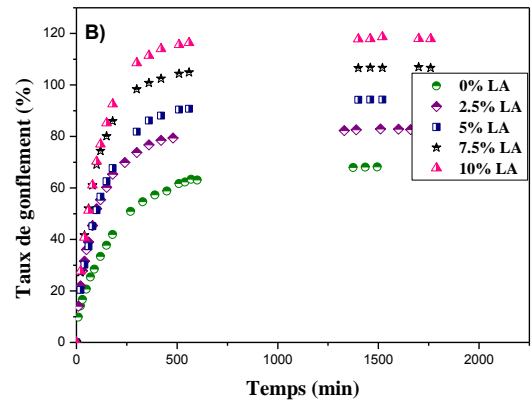
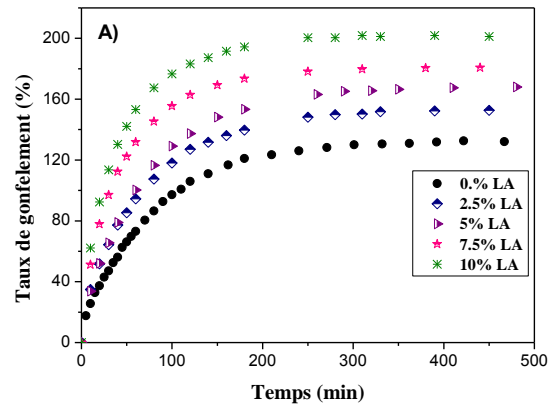


Fig 4 Swelling kinetics of Poly (PEA/0.1wt%HDDA) and copolymer with LA for different rate in A)Toluene and B) at room temperature.

D. Swelling at different temperature:

Figure 5 shows the influence of temperature on the swelling kinetics of the system Poly (PEA) / 0.1% HDDA swollen in a)toluene and b) MIBK, we observed that temperature affects proportionately over the swelling rate to steady achievement for toluene. But its effect on the MIBK is pronounced until a certain value of temperature where the rate and the swelling kinetics become independent of it.

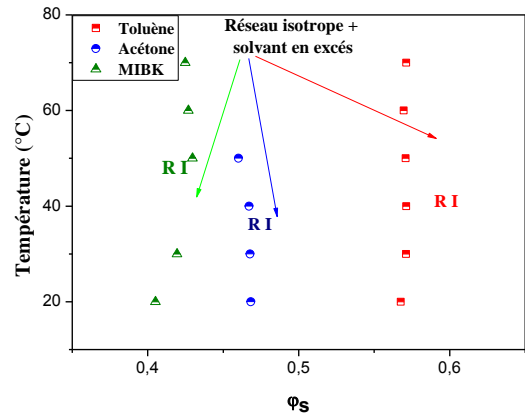
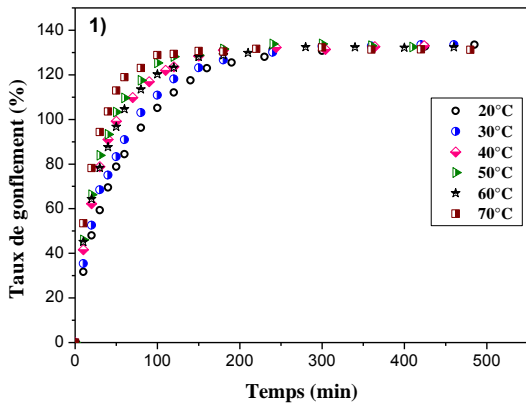


Fig6 Experimental phase diagram

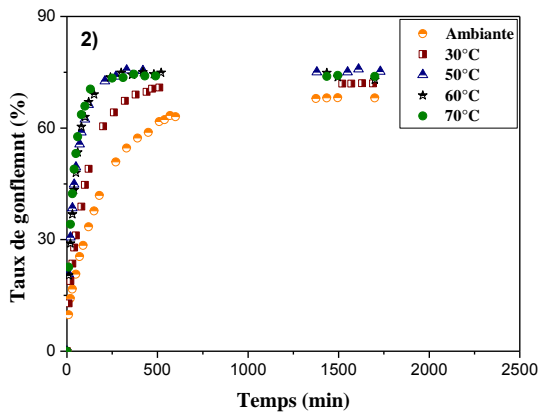


Fig5 Swelling kinetics of poly (PEA)/0.1wt%HDDA networks at different temperature in 1) toluene and 2) MIBK.

### III. PHASE DIAGRAMME EXPERIMENTAL

The experimental phase diagrams are represented in the case of thermodynamic equilibrium. Each point on the curve corresponds to the values of the plateau swelling kinetics curves. We still consider the flexible network Poly (PEA) / 0.1% HDDA swollen in different solvents.

Figure 6 illustrates the variations of the temperature as a function of the mass fraction of the solvent defined as follows:

$$\phi_s = \tau / (1 + \tau)$$

where the swelling rate  $\tau$  is given by the relationship:

$$\tau = m_{\text{solvant}} / m_{\text{polymère}}$$

### IV. CONCLUSIONS

The synthesis of polymer networks poly (PEA) and copoly (PEA/LA) by photo polymerization, and the characterisation of swelling in different solvents with temperature was the aim in this study. The swelling behaviour of polymer networks Poly (PEA) has been studied according to three parameters: temperature of medium, chemical structure and the degree of cross-linking. We found that the Influence of temperature is proportional to the kinetics of swelling.

Flexibility of the poly (PEA) depend on molecular structure: the swelling rate decreases when adding the amount of the crosslinking agent. The modification of the structure by the copolymerization of (PEA) with (LA) for different rate influences the swelling sample in the same solvents studied.

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