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# Membrane synthesis by microemulsion polymerisation stabilised by commercial non-ionic surfactants

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## Abstract

Earlier works had demonstrated that microemulsion polymerisation is a well suited technique to produce nanostructured membranes if surfmers (polymerisable surfactants) are used to stabilise the primary template (sponge phase microemulsion). Up to now, however, same hadn't been done using common surfactants. Present work aims to show this is possible if proper surfactants are selected. Specific formulation selection was done by means of phase diagram. Phase diagram was obtained by conductivity, surface tension and QELS measurements through several dilution lines. Polymerisation region was selected from phase diagram where no globular system was observed. Membranes were characterised by SEM, DSC and permeation experiments.

*Keywords:* Microemulsion polymerisation; Nanostructured membranes; Sponge phase; Methyl methacrylate; Hydroxyethyl methacrylate; Commercial surfactants

## 1. Introduction

The aim of this research is to show the possibility to produce porous membrane using the auto assembled structure formed in microemulsion (E), especially the sponge phase structure. A microemulsion is a thermodynamically stable dispersion, composed by an oil phase and a water phase stabilised by surfactants. If the oil phase is composed by monomer, one can induce the polymerisation of the oil phase leading to a porous polymer (i.e. the water phase gives the

pore). Gan studied this method to produce porous polymer and membranes [1,2]. He showed that the major problem is the auto assembled structure is not maintained during polymerisation when non polymerisable surfactants are used (i.e. SDS). He succeeds in the production of transparent membrane from the polymerisation of a E stabilised by a polymerisable surfactant. Transparent membrane indicates that membrane microstructure is still mesoscopic. Pore size of this membrane is in the nanometer range [2].

From the Gan papers, one can conclude that this way is not interesting to produce

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membranes from the industrial point of view. On one hand, the production of nano-structured membrane is only possible using a surfimer, which are not commercially available and must be synthesised. On the other hand, Gan conclude that phase transition occurs when the surfactant is not polymerisable. But on the basis of Gan's papers, he used only one or two common surfactants, like SDS. So the surfactant may be not suitable for the synthesis (does not stabilize enough the E during the reaction). This work aims to fill the gap which might be quite interesting from the industrial standpoint by selecting commercial surfactant(s) that can preserve more or less the structure of the E in order to produced nanostructured membrane.

## 2. Material and methods

### 2.1. System composition

All chemicals are commercially available products and were used without further purification.

Aqueous phase (A<sub>Ph</sub>) is comprised of hydroxyethyl methyl methacrylate (HEMA, Aldrich France) and Ammonium Persulfate (PSA, Aldrich France) aqueous solution.

Oil Phase (O<sub>Ph</sub>) consist on a blend of methyl methacrylate (MMA, Aldrich France) and ethylenglycol dimethacrylate (EGDMA, Aldrich France). EGDMA concentration is 4.0%wt of pure monomers mass. *N,N,N,N*-Tetramethylethylenediamine (TEMA, Aldrich France) is the reductor agent of redox initiator system.

Surfactant system (ST) is composed of 1/3 of full mass of: alkyl ether POE (12) (Quimidroga S.A., Spain), POE (11) synthetic primary C13/C15 alcohol (Uniqema Ltd, Netherlands) and ultrapure water.

### 2.2. Formulation and phase diagram determination

Surfactant selection is not described here because of lack of place. Phase diagram

determination was achieved by titration, surface tension and QELS measurement at 25°C. E were visually titrated with surfactant or surfactants blend. During all titration conductivity has been recorded using a conductimeter. Visual aspect of the mixture and conductivity were used to identify the two phase, emulsion and E regions. Samples micelle diameter has been measured by QELS, using a Malvern PCS 4700 to determine whether their structure is micellar or bicontinuous. Surface tension has been measured using a GBX 3S balance.

### 2.3. Polymerisation method

Polymerisation takes place under nitrogen at room temperature during 120 min and is initiated using a redox system (TEMA/PSA). Selected formulations have been prepared without adding TEMA, in order to avoid uncontrolled polymerisation. TEMA was added to the E just before the nitrogen purge. E was spread over a glass plate containing spacers and covered with another glass plate. Membrane is extracted demoulding after 24 h of extraction in a mixture of water and acetone.

### 2.4. Membrane characterization

Membranes were characterised by SEM, DSC and permeation experiments. Pure water permeability were measured using an Amicon<sup>®</sup> 8020 filtration cell with ultrapure water. MWCO are under measurement using PEG as tracers.

## 3. Results and discussion

In order to determine formulations that might produce high porous membranes with the sponge phase microstructure, phase diagram must be obtained. Results of titration, QELS and surface tension tests are presented in Fig. 1. It was considered that best area to work in is located in the A<sub>Ph</sub> rich section of the phase

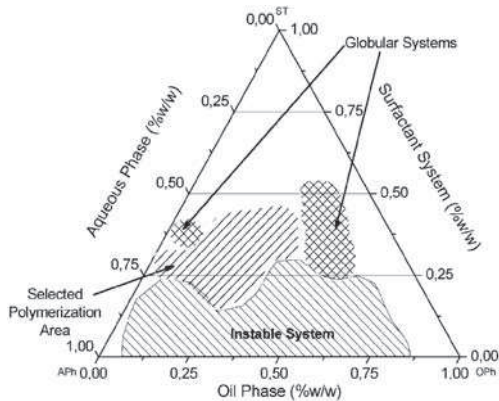


Fig. 1. Pseudo-ternary phase diagram.

diagram, attending porosities about 40%. Most phase diagram areas seem to have a microstructure other than micellar. Sponge phase is most probable microstructure at low surfactant concentration considering results not shown here.

By polymerising formulations described below, we obtained transparent membranes of  $20 \pm 10$   $\mu\text{m}$  thickness which are mechanically strong. Gan consider that E nanostructure is preserved (no phase separation nor transition

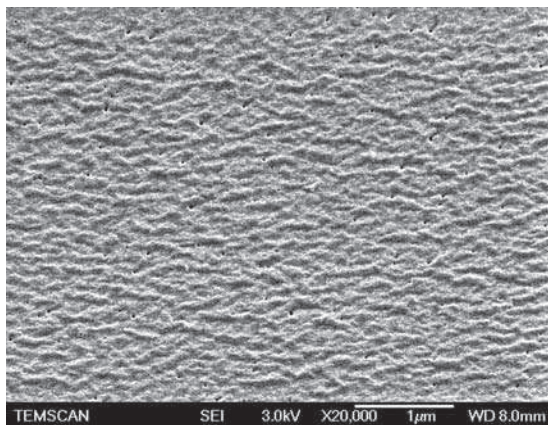


Fig. 2. Micrograph of membrane section showing a channel network oriented in the flow direction.

occurs) when a transparent material is obtained. This could be confirmed by SEM (Fig. 2) as an homogeneous channel network structure is clearly observed. No pore was observed even at the higher magnification (i.e. 20000) that can be used without affecting the membrane.

Pure water permeability are in the range of 1.2 to 4.2 L/(bar  $\text{m}^2$  h) for a membrane thickness of 20  $\mu\text{m}$ , that might be expressed related to a 1  $\mu\text{m}$  thickness membrane as 24.0–84.0 L/(bar  $\text{m}^2$  h) at 25°C. Other data on permeation measurement and on material characterisation will be presented.

#### 4. Conclusions

Microemulsion polymerisation allows flat membranes ( $20 \pm 10$   $\mu\text{m}$  thickness) synthesis using commercial non-ionic surfactants. Selecting a proper initial formulation, transparent membranes were synthesised from sponge phase microemulsions avoiding phase separation during the reaction. Membrane microstructure seems to be similar to the initial one. Synthesised membranes have permeability values around 24–84 mL/(bar  $\text{m}^2$  h) related to 1  $\mu\text{m}$  thickness membrane. This new way is very promising and will be further studied.

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