Experimental report

29/03/2017

Proposal:	**9-11-1705**	**Council:**	4/2014
Title:	Kinetic characterization of demixing processes occurring in casting solutions during manufacture of macroporous membranes (second milestone)		
Research area:	Soft condensed matter		

This proposal is a new proposal

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Samples: Cellulosenitrate/Methyleneacetat-d6/Isopropanol-d7/D2O

Instrument	Requested days	Allocated days	From	To
D11	4	2	13/11/2014	15/11/2014

Abstract:

The creation of a macroporous structure results from the induced demixing of a casting solution whether by selectively removing the solvent or by adding nonsolvents. Even if these industrial processes are nowadays performed at large scale (millions of m²/year), the basic mechanisms, that lead to membranes with well-defined pore sizes (from 30 to 200 nm) are not yet known and, hence, the technical process is far from being optimized. During our SANS measurements at ILL last summer (DIR-109), we achieved our first objective by developing an experimental setup that enables us to investigate the demixing of usual casting solution with SANS. Our results revealed us that we are dealing with much more complex systems than what we assumed. This higher complexity is due to the overlapping of two miscibility gaps which lead to interesting and so far never observed demixing phenomena. We are therefore interested in achieving our second milestone the thermodynamic and kinetic characterization of the demixing of such systems.

The use of SANS for the kinetic characterization of demixing processes occurring in casting solutions during industrial manufacture of microporous membranes (9-11-1705)

Introduction

The efficient downstream of biopharmaceuticals is strongly driven by new development in membrane technology. In this particular field, polymeric membranes are usually used for filtration and diagnostic purposes. Polymer solutions also called casting solutions involved in industrial membrane manufacture mostly consist of a polymer blend, a solvent and one or two nonsolvents. The creation of a microporous structure results from the induced demixing of a casting solution whether by selectively removing the solvent or by adding nonsolvents.

Even if these industrial processes are nowadays performed at large scale (millions of m^2/year), the kinetics of the basic mechanisms, that lead to membranes with well-defined pore sizes (from 30 to 200 nm) are not yet known and, hence, the technical process is far from being optimized. While the phase diagrams are frequently known from macroscopic experiments, no studies of the microscopic structure and its evolution during the demixing process have been reported until now. Knowledge about the type of demixing that occurs on the top side of the film and in its depth as well as the necessary time for the formation of a specified microporous structure would be a great benefit for membrane scientists.

Experimental Setup

The objective of this experiment was to characterize the kinetics of the demixing mechanisms of such quaternary systems and to understand how they may be influenced by the polymer content at the entry point in the miscibility gap and the alcohol/water ratio of the nonsolvents.

The experimental setup is the enhanced equipment from experiment DIR109 and consists of following parts:

- Temperature controlled Stirred Reactor (STR)
- Neutron transparent flow-through cell (FTC) from aluminum, enhanced to an adjustable layer thickness
- High precision and fast dosing pumps
- Tubes and storage vessels for solvent and non-solvents
- Turbidity measurement System

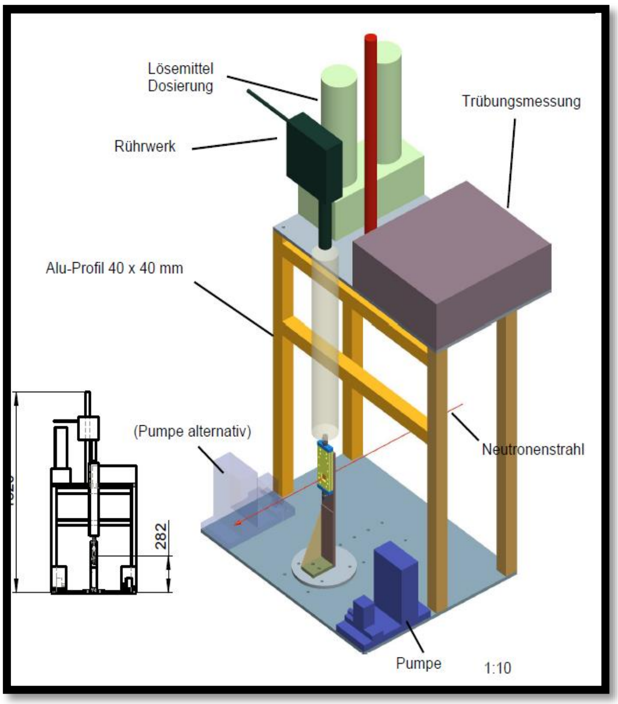

Figure 1: Enhanced SANS equipment.

The experiment typically starts by filling a casting solution in the STR. The latter is then hermetically closed and the solution is continuously pumped through the FTC and tempered at 23°C. Once the target temperature has been reached, one simultaneously starts the time resolved SANS measurement, the transmission measurement and the pulse-like addition of nonsolvents to demix the polymer solution. After the growth is achieved, it is possible to generate a new homogeneous solution by adding solvent or a solvent/non-solvent mixture. This new created homogeneous solution may undergo a new phase separation via addition of non-solvent. This method makes the generation of several demixing points from one starting solution possible. In view of the high incoherent cross section of hydrogen it is necessary to work with fully deuterated solvent and non-solvents.

The experiments were carried out with the casting solution shown in table 1:

Table 1: Composition of the used casting solution

Cellulose Nitrate	Acetone-d6	Methanole-d4	D_2O
1,4 %	43,1 %	44,5 %	11,4 %

Results

The enhanced equipment has been successfully tested on the D11 instrument. The aim of the new plant was to reduce the response time between the demixing of the solution and the first diffraction data. This goal could be achieved. It was possible to decrease the response time from 120 seconds to 15 seconds. Exemplary data of the measurements are shown in Figure 2. After induction of the demixing process the scattered intensity increases abruptly. There is a small growing of intensity within the first 60 second observable. However, the diffraction angle is very small. It could be concluded that even the first precipitates are bigger than the range of SANS.

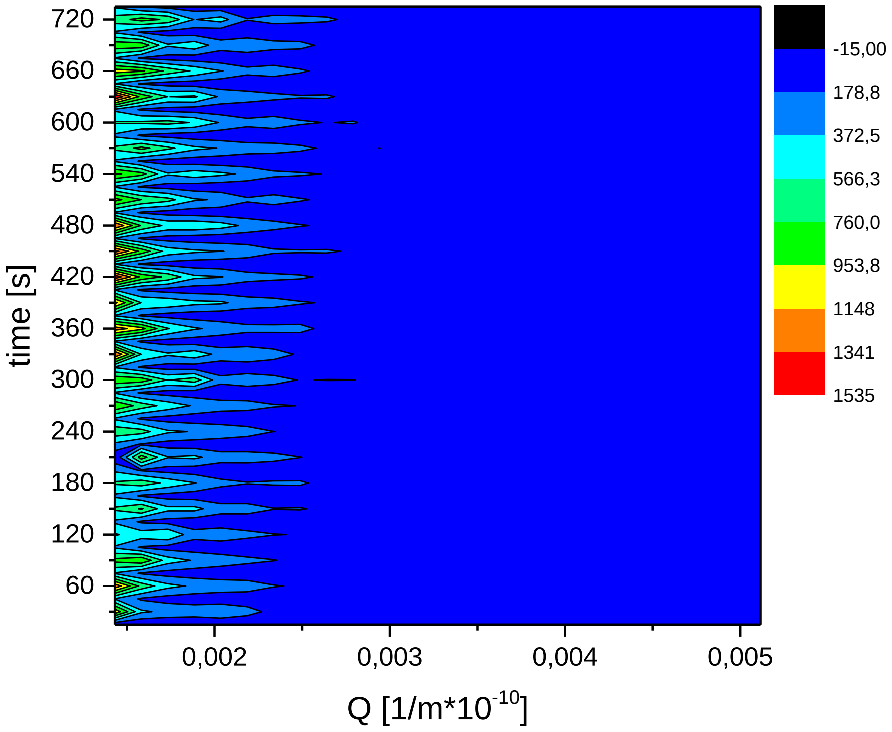

Fig. 2: Result of the SANS measurement