Microporous PVDF membrane formation by immersion precipitation from water/TEP/PVDF system

Dar-Jong Lin, Cheng-Liang Chang, Tzung-Chin Chen, Liao-Ping Cheng*

Dept. Chemical Engineering, Tamkang University, Taipei, Taiwan, ROC 25137
Tel. +886 (2) 26215656 ext. 2614; Fax +886 (2) 26209887; e-mail: lpcheng@mail.tku.edu.tw

Received 30 January 2002; accepted 6 March 2002

Abstract

For membranes synthesized from crystalline polymers by phase inversion method, crystallization can sometimes dominate the precipitation process to form a membrane characterized by the so-called particulate structure. Such is the case for PVDF membranes prepared by immersion-precipitation from water/triethylphosphate solutions. The structure of the membrane formed from this system was studied; in particular, the nano-scale fine structure of the crystallites, which form the matrix of the membrane. The phase diagram of the water/TEP/PVDF was determined using the cloud point method. Membranes were observed using LVSEM at low voltage (e.g., 1 KV) and high magnifications (e.g., 100 KX) to reveal the fine structure of the membranes.

Keywords: PVDF membrane; Crystallization; Morphology

1. Introduction

Isothermal immersion-precipitation is a process widely used to synthesize porous polymeric membranes. In this process, a dope composed of polymer, solvent and additives is immersed in a nonsolvent coagulation bath to induce precipitation by means of liquid-liquid demixing and/or crystallization [1–9]. In fact, for membranes synthesized from crystalline polymers, various studies have pointed out that the structure of the formed membrane was dictated by the sequence of these phase separation events. The formed membranes often exhibit characteristics from both types of phase separations. In general, liquid-liquid demixing process engenders cellular pores whereas crystallization forms interlinked crystalline particles. Thus, by manipulating the precipitation parameters, such as...
dope and bath compositions, precipitation temperature, types of additives, etc., the relative rate and extents of these two phase separation processes can be adjusted to produce a wide variety of morphologies that represent different combinations of these phase separation processes. At one extreme, the formed membrane comprises a tight skin and a porous sublayer that is dominated by cellular pores and/or macro-voids. This is the case when precipitation is carried out in a harsh nonsolvent bath leading to a rapid or even immediate precipitation. At the other extreme, when precipitation is carried out in a soft nonsolvent bath, mass exchange is slow, such that crystallization commences much earlier than liquid-liquid demixing. The result is a porous structure composed of arrays of inter-linked crystalline particles.

In the present research, poly(vinylidene fluoride) membranes with either asymmetric or skin-less structure were prepared by isothermal immersion precipitation from water/triethyl phosphate/poly(vinylidene fluoride) system. The phase diagram, including the crystallization-induced gelation line and the liquid-liquid demixing line, was determined at 25°C. Based on the latter, bath and dope compositions were selected to prepare membranes by isothermal immersion-precipitation method. The nanoscale fine structures of the membranes were revealed by high resolution LVSEM imaging.

2. Methods

2.1. Material

Poly(vinylidene fluoride) (Hylar 5000 HP, Ausimont USA, Inc. specific gravity = 1.75, melt viscosity = 18.7 kpoise) is a semi-crystalline polymer. Terpolymer of vinylidene fluoride, hexafluoropropylene, and tetrafluoro-ethylene (Kynar 9301, VDF/HFP/TFE = 60/20/20, intrinsic viscosity = 0.4 dL/g, Mn = 79,200 g/mole) is largely amorphous and is supplied free of charge by Elf Atochem Inc. Triethylphosphate (TEP, Acros, reagent grade, d = 0.944 g/ml) and water (distilled and de-ionized) were used as the solvent and the non-solvent for the polymers, respectively. All materials were used as received.

2.2 Gelation and liquid-liquid demixing boundaries

The gelation phase boundary at 25°C for the water/TEP/PVDF system was determined by the widely used ‘cloud point’ method [6,8]. The terpolymer (Kynar 9301) is largely amorphous, and hence was used to determine the liquid–liquid demixing boundary. The procedures can be found in the literature [8].

2.3. Membrane preparation

PVDF membranes were made by the isothermal immersion-precipitation method. An appropriate amount of the dope was dispersed uniformly on a glass plate (ca. 200 µm thick) and then immersed immediately into a coagulation bath to induce precipitation. The coagulation bath consisted of pure water or TEP/water solutions. The formed membrane was washed in a series of nonsolvents and then dried under press between sheets of filter papers at 45°C. Morphologies of the membranes were observed using LVSEM (Leo, 1530) at low voltage (e.g., 1 KV) and high magnifications (e.g., 100000 X). Uncoated samples were used to avoid artefacts caused by improper metal-coating.

3. Results and discussion

3.1. Phase diagrams

The experimental phase equilibrium data at 25°C for PVDF in water/TEP solutions are presented in Fig. 1. The open circles represent the gelation compositions for PVDF in water/TEP. These measured data are largely consistent with those reported by Bottino et al. [9]. Below the gelation line is a meta-stable region where gelation will take place for a dope stand-
ing over an extended period of time. It has been shown previously for PVDF in water/DMF and 1-octanol/DMF systems using DSC and SALS techniques that this type of gelation was induced by polymer crystallization [7,8]. The filled circles (cloud point data) are measured liquid-liquid demixing compositions for the terpolymer in water/TEP solutions. As suggested by previous studies on several other semi-crystalline polymers, the binodal for the terpolymer can be used to approximate the amorphous phase behavior of the crystalline PVDF in nonsolvent/solvent solutions [7,8]. This is based on the fact that the PVDF and the terpolymer have a similar chemical structure.

3.2. Structure of the membranes

As a semi-crystalline polymer, PVDF may be precipitated either by liquid-liquid demixing and/or crystallization process during the course of the immersion-precipitation process to produce various microporous membranes. In the discussion that follows, two immersing cases, which illustrate the effects of bath composition on membrane morphology are presented. All other observable morphologies can be considered intermediate between these cases.

3.2.1. Dope ‘A’ immersed in water

As dope ‘A’ (20 wt.% PVDF in TEP, cf. Fig. 1) was immersed in pure water, polymer precipitated into a porous membrane with interesting morphological features, which are illustrated in Figs. 2–4. As shown in Fig. 2, the cross-section has an open porous structure being composed of large interconnected objects (ca. 3–5 µm) whose shapes are more or less spherical. Cellular pores and macrovoids, which are typical for polymers precipitated from harsh bath (e.g., water) are not evident here. The microscopic structure of an object is shown in Fig. 3 at a high magnification (60000 X) where in the nano-scale structure of PVDF crystallites can be seen. The crystalline identities have the shape of a ‘leaf or petal-like’ sheet whose thickness is on the order of 20 nm. Near the central region of Fig. 3, a ‘sheaf-like’ crystalline unit (sometimes called axialites or hedrites in the literature) corresponding to an intermediate stage spherulite is evident. Its stem is composed of 20 nm thick crystalline stacks, which splay out at their ends and join the other full spherulites.

All voids in the membrane are interconnected and they form numerous tortuous paths within the polymer matrix. No close pore, as is typically derived from liquid-liquid demixing, is observed in the cross section. This type of porous structure is produced when polymer crystallization occurs preceding liquid-liquid demixing and dominates the precipitation process [6–8]. After contact with the precipitation bath, the dope enters the gelation zone with respect to crystallization as a result of mass exchange between the dope and bath. Crystallization then takes place in terms of nucleation and growth to form the spherulites. During growth, impurities (solvent and nonsolvent) are expelled into the dilute phase, which eventually becomes the voids of the membrane. Certainly, liquid-liquid demixing may also happen at this stage, if the dilute phase surrounding the crystal enters the binodal caused by depletion of polymer and influx of non-
solvent from the bath. This results in the formation of large voids. The growing spherulites finally impinge on each other to form a polymer matrix. The top surface of the membrane is shown in Fig. 4. It is tight and essentially non-porous; i.e., this surface may be termed a skin. There can be observed polygonal spherulites whose surfaces break into dendritic structure. And interestingly, some nano-pores (ca. 20–40 nm) can be observed. Most of them are close and non-penetrating, and thus contribute limit-edly to the filtration flux.

3.2.2. Dope ‘A’ immersed in a soft bath

When dope A was immersed in a soft bath, the rate of precipitation slowed down considerably. For the present system, the composition of the coagulation bath influences the membrane structure most significantly on the top surface. This is demonstrated in Fig. 5, which represent the case of immersing dope ‘A’ in a 70% bath. Compared with the tight, continuous skin shown in Fig. 4, this top surface is very porous where the structure resembles its cross section, being totally open and composed of “sheaf-like” crystals. The absence of skin resulted from the initial presence of a weak interfacial gel layer that was disrupted by the growing crystalline particles. The effect of coagulation bath on the structure of the cross section is shown in Figs. 6 and 7. This cross section is rather uniform and consists of numerous small crystallites. At a high magnification (40000 X, Fig. 7), it can be seen that the small crystallites exhibit a “stick-like” feature with their ends slightly fanning out. It appears that these spherulites are at their preliminary stage. Because of the high nucleation density, these crystallites are small and cannot grow into full spherulites. This porous structure also indicates that crystallization has dominated the precipitation process where-in crystals were nucleated and grown in a similar concentration field and finally fused together to form a bi-continuous structure.
4. Conclusion

Phase equilibrium curves, binodal and crystallization line, for the water-TEP-PVDF system were measured at 25°C. Membranes were prepared by the isothermal immersion precipitation process. In contrast to ordinary nonsolvent/solvent/polymer systems where liquid-liquid demixing tends to dominate the precipitation process to yield cellular structure, crystallization appears to be relatively important for this system. Even precipitated in a harsh bath (e.g. water), the formed membrane still consists of large spherulites (characteristic of crystallization) whereas cellular pores (characteristic of liquid-liquid demixing) are not in evidence. In a soft bath, the precipitated product is a uniform membrane where-in “stick-like” crystallites interlocked into a bi-continuous structure.

Acknowledgement

The authors thank the National Science Council of Taiwan for financial support (NSC89-2216-E-032-001).

References