

Poly(vinylidene fluoride) membranes prepared via nonsolvent induced phase separation combined with the gelation



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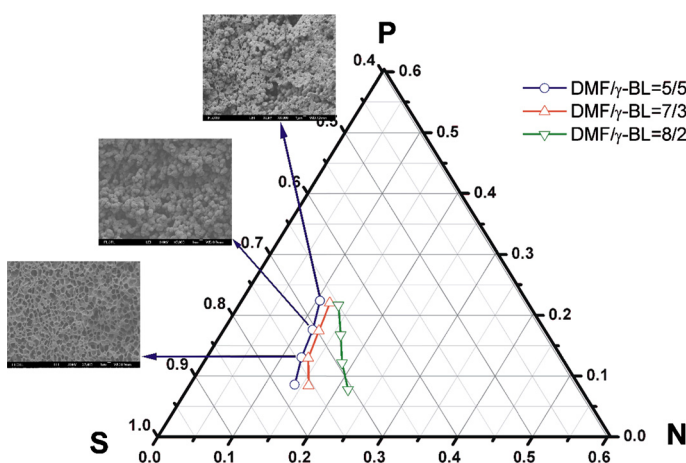
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HIGHLIGHTS

- We study the mechanism of the membrane formation via NIPS combined with gelation.
- γ -Butyrolactone (γ -BL) improves the thermodynamic stability of the dope solution.
- Liquid–liquid phase separation occurs before gelation at a low PVDF concentration.
- Changing DMF/ γ -BL ratio can tailor the membrane avoiding the finger-like structure.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 16 February 2015

Received in revised form 2 April 2015

Accepted 6 April 2015

Available online 15 April 2015

Keywords:

Poly(vinylidene fluoride) (PVDF)

Membrane

Phase separation

Gelation

ABSTRACT

In this work, we employed the nonsolvent induced phase separation (NIPS) combined with the gelation method to prepare poly(vinylidene fluoride) (PVDF) membranes. The mixture of N,N-dimethylformamide (DMF) and γ -Butyrolactone (γ -BL) was used as a solvent, and water was used as a nonsolvent. Membrane changed from a cellular to spherulitic morphologies simply by varying the mass ratio of DMF/ γ -BL and the PVDF concentration. On quenching the casting solution (with 15 wt% PVDF concentration) in the water bath, the membrane had a uniformly cellular morphology, which resulted from a typical liquid–liquid (L–L) phase separation. At higher PVDF concentrations (≥ 20 wt%), membranes presented a spherulitic structure, arising from a solid–liquid (S–L) phase separation. The crystallization behavior and crystalline form of the PVDF membrane were identified by different scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR), respectively. For the 15 wt%-PVDF membrane gained from the mixed solvent with a mass ratio of DMF/ γ -BL = 8/2, the highest tensile strength (7.3 MPa) and elongation at break (223%) was obtained.

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1. Introduction

Among the membrane materials, poly(vinylidene fluoride) (PVDF), a semi-crystalline polymer with excellent physical and chemical properties and a good thermal stability, has attracted much attention [1]. Commonly, PVDF membranes are prepared by nonsolvent induced phase separation (NIPS) and thermally induced phase separation (TIPS) methods. In the former, various parameters determined the membrane structure, such as the dope compositions, additives, coagulation medium and bath temperature, solvent power [2–4]. This method usually produces asymmetric membranes with a finger-like structure in the skin layers near the surface that contacted with the nonsolvent. The TIPS as a widely used method is gaining much interest for the advantages over the conventional membrane preparation technique [5,6]. In the TIPS, the phase separation occurs through cooling or quenching of the homogeneous polymer solution from a high temperature. During the TIPS, the liquid–liquid (L-L) phase separation, solid–liquid (S-L) phase separation, or combination of both these two separations, followed by a polymer crystallization, offers a great flexibility in controlling the microscopic morphology of polymeric membranes [5–9]. In the membrane preparation by TIPS, selecting a proper solvent is one of the keys to controlling the pore structure. Till now, a bicontinuous structure only forms in the diphenyl ketone (DPK) and diphenyl carbonate (DPC) diluted system, resulting from a wide L-L phase separation [10,11]. In most diluted systems, a spherulitic structure always forms in the condition that the S-L phase separation occurs prior to the L-L phase separation [12]. In order to obtain the bicontinuous structure resulting from the L-L phase separation, mixed solvents are applied, such as dibutyl phthalate (DBP)/dioctyl phthalate (DOP) [13,14], DPK/1,2-propylene glycol (PG) [15], DBP/di(2-ethylhexyl) phthalate (DEHP) [16], Propylene carbonate/ γ -BL [17]. Matsuyama prepared poly(methyl methacrylate) (PMMA) membrane in the combined use of TIPS and NIPS. In that work, the membrane structure was controlled by the non-solvent type [18]. Li et al. [19] used the mixture of DBP and N,N-dimethylacetamide (DMAc) to prepared PVDF membrane. The DBP content in the mixed solvent, and the temperature of the coagulation bath could control the membrane morphologies. However, the mechanism of the membrane formation is still vague.

Hoog et al. [20] presented new investigations of the kinetics and subsequent structure of phase in an aqueous mixture of gelatin and dextran in the presence of gelation. With their results, it is possible to control the coarseness of the phase separating system in the presence of gelation. Anderson et al. [21] also investigated the influence of the gelation of one gelatin on the phase separation and morphology of an aqueous mixture of gelatin and dextran. They found that a spinodal decomposition still occurs, but the effect of gelation is observed more strikingly in the final structures. γ -Butyrolactone (γ -BL) is one of the organic solvents for PVDF gel preparation, in which the spherulites formed [22,23]. The gelation of PVDF/ γ -BL solutions also occurs due to the crystallization, when cooling this homogenous solution at an elevated temperature. It has been demonstrated that the binodal line or liquid–liquid phase separation line is below the gelation temperature. So, the crystallization of PVDF inhibits the precise observation of the binodal line composed of cloud points [22,23]. Hong et al. [24] clarified the effects of the crystallization and phase separation on the gelation of PVDF/tetra(ethylene glycol) dimethyl ether (PVDF/TG) solution. The crystallization and the gelation rate depend on the kinetic conditions in the competition between these two processes, according to their model of gelation mechanism. In order to obtain a bicontinuous membrane structure, some researchers modified the gelation mechanism of PVDF/ γ -BL system. Cha et al. used PVDF/ γ -BL cast solution exchanging with a soft coagulant to prepare PVDF membrane via TIPS method. The membrane structure was controlled

Table 1
Solubility parameters and dipole moment of organic solvents and PVDF.

	δ_d (MPa ^{1/2})	δ_h (MPa ^{1/2})	δ_p (MPa ^{1/2})	δ_t (MPa ^{1/2})	Dipole moment (10 ⁻³⁰ C m)
DMF	17.4 ^a	13.7 ^a	11.3 ^a	24.8 ^e	12.88 ^c
γ -BL	19 ^a	16.6 ^a	7.4 ^a	25.8 ^e	13.74 ^c
PVDF	17.2 ^b	12.5 ^b	9.2 ^b	23.2 ^b	7.0 ^d

^a Ref [28].

^b Ref [29].

^c Ref [30].

^d Ref [31].

^e Ref [32].

and tailored by the composition of the coagulant [25]. Song et al. employed γ -BL/DOP as a mixed diluent to prepare PVDF membranes with a well-interconnected cellular structure through TIPS method [26]. However, there are few reports about the PVDF gelation in γ -BL during the NIPS process. As demonstrated [27], PVDF may be precipitated either by liquid–liquid phase separation or crystallization induced gelation during NIPS, which produces membranes that cover a broad spectrum of structures. So, combining NIPS with the gelation process may provide another way to control the morphology of the membrane.

In this article, mixed solvents composed of various mass ratios of γ -BL and N,N-dimethylformamide (DMF) was used, and we investigated the mechanism of the membrane formation via NIPS combined with gelation. We studied the relationship between the solubility parameter and the mechanism of the membrane formation as well. Finally, we characterized the morphology, crystallization behavior, and mechanical properties.

2. Experimental

2.1. Materials

PVDF (Kynar K-761), in powder form, was supplied by Elf Atochem of North America Inc. (USA). N, N-Dimethylformamide (DMF) was obtained from Chinasun Specialty Products Co., Ltd (Shanghai, China). γ -Butyrolactone (γ -BL) was obtained from Chinasun Specialty Products Co., Ltd (Shanghai, China). All materials were used as received. The physical constants, such as solubility parameters and dipole moment for those organic solvents and PVDF are listed in Table 1. The solubility parameter includes the total parameter δ_t , and the dispersion (δ_d), polar (δ_p) and hydrogen bonding (δ_h) parameters.

2.2. Phase diagram

It should be noted that the cloud points are represented by the gelation resulting from both liquid–liquid and solid–liquid (accompanying with crystallization) demixing of the polymer solution [33]. The cloud point observation determined the gelation phase boundary for the PVDF/mixed solvent/non-solvent system. In this work, a mixed solvent was composed of DMF and γ -BL with their mass ratios of 5/5, 7/3 and 8/2. A definite amount of PVDF was dissolved in a mixed solvent and sealed with Teflon film in a glass bottle. After the homogeneous solution had been formed, a certain quantity of nonsolvent (water) was added to this solution. The equilibrium gelation point was identified as the composition at which the homogeneous solution began to precipitate into a gel.

2.3. Membrane preparation

Membranes were prepared via NIPS combined with gelation method. Homogeneous dopes composed of PVDF and the mixed solvent (DMF/ γ -BL = 5/5, 7/3, and 8/2) in an airtight bottle at

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