

Effect of Ethylene Glycol Monobutyl Ether on Skin Layer Formation Kinetics of Asymmetric Membranes

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ABSTRACT: The present work was concerned with skin layer formation kinetics of Polyethersulfone with Cardo (PES-C) asymmetric membranes by the phase inversion method. Gelation process was observed using an online optical microscope-CCD camera experimental system, the result indicated that a single linear correlation between square value of precipitation front move (X^2) and time (t) did not exist for the whole gelation process, which was different from the traditional conclusion. The effect of Ethylene glycol monobutyl ether (EGME) on skin layer gelation process was investigated, and the skin layer formation kinetics equation was determined, which could be described with gelation rate constant equation. The gelation rate constant

decreased with the increase of concentration of EGME. EGME concentrations affected the viscous flow activation energy, and the increase of viscous flow activation energy led to the decrease of gelation rate. The change trend of the gelation rate was exactly the same as that of the flux. The results helped to understand the asymmetric membrane skin layer formation process better, which was important for controlling the membrane separation properties and designing the membranes for a specific application. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2392–2396, 2009

Key words: formation kinetics; skin layer; asymmetric membrane; effect of EGME; wet phase inversion

INTRODUCTION

Asymmetric polymer membranes have numerous applications, such as food, chemical processing, wastewater handling, drug delivery medium, artificial human organs etc., because of their high efficiency and energy conservation. Phase-inversion method is often used for preparing asymmetric membranes.^{1,2} In the phase-inversion process, the exchange of solvent and non-solvent between casting solution and the coagulation bath includes a kinetics process.³ To get a membrane with good penetration property, an additive is usually added to the casting solution. It is presented that addition of additive has an effect on thermodynamic and kinetic process in the membrane formation and thereby affects the membrane structure and properties,⁴ many investigators attempt to elucidate the effect of addition on the membrane-forming mechanism.

It is important for exploring the membrane formation mechanisms with the help of membrane formation kinetics. The experimental techniques investigate the kinetics of membrane formation are light transmittance measurement and optical microscopy,^{5–8} are reported to be used to investigate the kinetics of membrane formation up to present. The two experimental techniques

are not real time processing system and precipitation process can not be described continuously. Time and the precipitation move are measured by manual operation. Time distance of data adopting is about several seconds or several minutes, which is too slow to obtain precipitation data in the skin layer stage. Usually a skin layer is as thin as several microns or even less than 1 μm . Thus the formation of the skin layer is very fast (within several seconds or even less than 1 s) and is difficult to be observed.⁹ Several research studies have measured the rate of precipitation of asymmetric membrane solutions.^{10–15} But the effect of EGME on skin layer formation kinetics has not still been studied.

PES-C membranes were prepared via phase inversion process with *N*-Methyl-2-Pyrrolidone dimethylacetamide (DMAc) as a solvent and Ethylene glycol monobutyl ether (EGME) as an additive. PES-C is a newly developed engineering thermoplastic and membrane material with a high glass transition temperature ($T_g = 255^\circ\text{C}$), and it shows excellent comprehensive properties and outstanding thermal stability, and it has been widely identified as a high-performance polymer. A new optical microscope-CCD camera experimental system was used to observe the formation rate of skin layer. In comparison with the previous methods, this new approach is capable of describing membrane formation intuitively, and the gelation process of skin layer stage can be observed clearly. An attempt is made to present a quantitative description of the effect of EGME on skin layer formation kinetics

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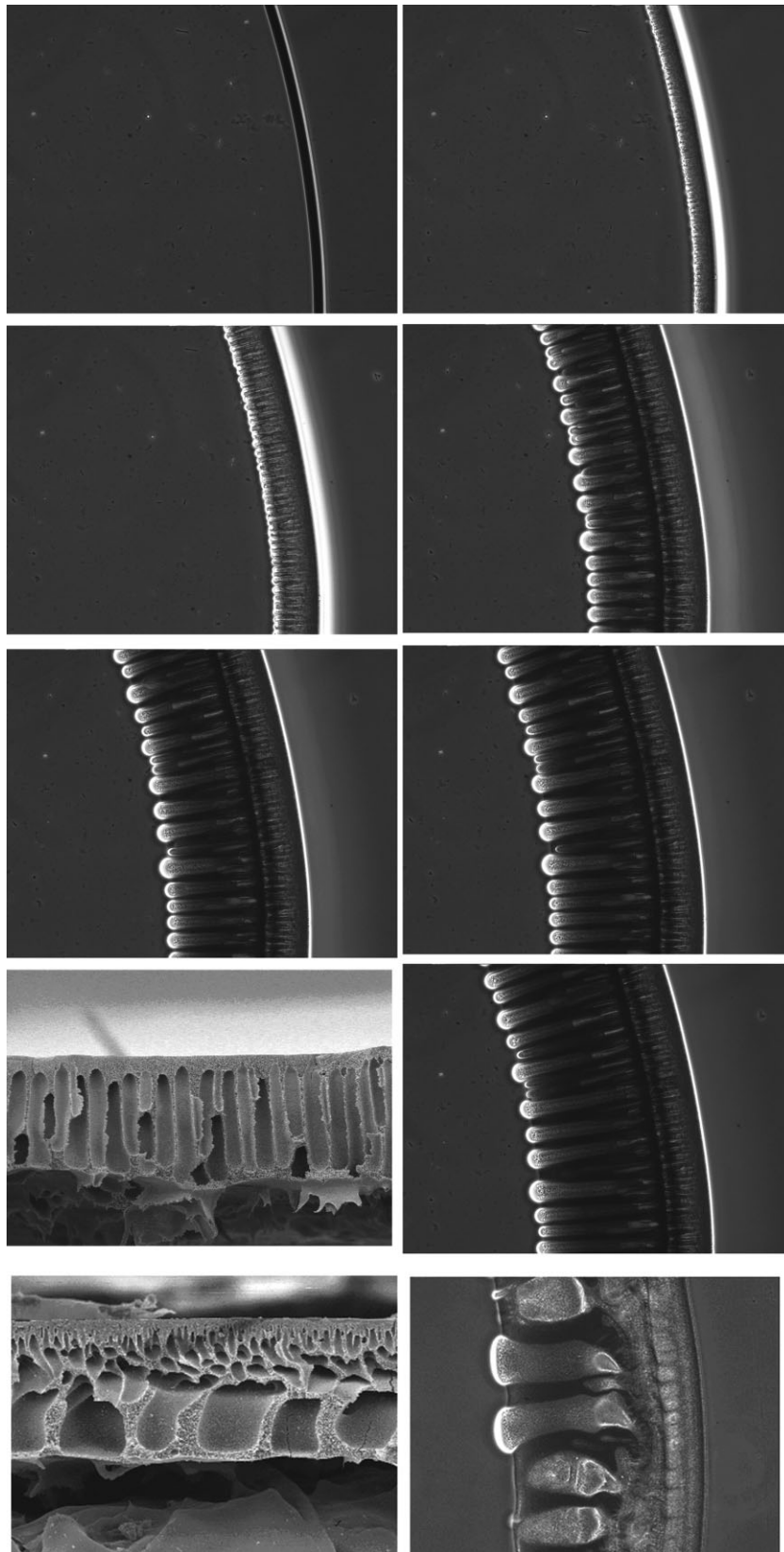


Figure 1 Comparison between SEM photo and Gelation kinetics photo. (a) The evolution of gelation kinetics photo, PES-C: 16 wt %; Solvent: DMAC/OA: 6 wt %; Gelation temperature: 60°C, t was 0, 0.5, 5, 30, 40, 60 s, respectively. (b) The left photo was SEM photo, the right one was gelation kinetics photo. PES-C: 16 wt %; Solvent: DMAC; OA: 6 wt %; Gelation temperature: 60°C. (c) The left photo was SEM photo, the right one was gelation kinetics photo. PSF: 18 wt %, Solvent: NMP, Gelation temperature: 60°C.

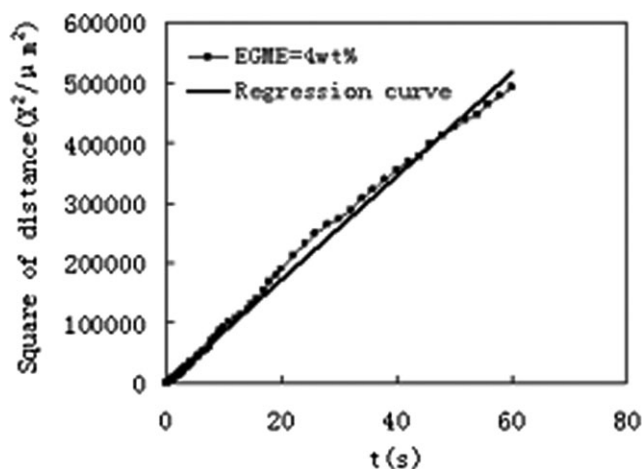


Figure 2 Variation of the square value of precipitation front move with time: PES-C: 16 wt %.

of asymmetric membranes. The results presented here may provide a better understanding formation mechanism of asymmetric membranes.

EXPERIMENTAL

Materials

PES-C ($\eta = 0.6 \text{ m}^3/\text{kg}$) was obtained from Changchun Institute of Applied Chemistry Chinese Academy of Sciences. DMAC and EGME were obtained from Xingchenweiye chemical reagent company. All the solvents in the experiment were commercial and used without further purification.

Observation of gelation process

The gelation rate of casting solution was determined by using an online optical microscope–CCD camera experimental system (OM–CC system). This system contains an Olympus IX71 optical microscope (Olympus, Japan), a Basler A101f CCD camera (Basler AG, Ahrensburg, Germany), a personal computer, and two specially designed microscope slides. The gelation process can be observed clearly, especially in skin layer stage. The magnification was from $120\times$ to $2000\times$. The images are automatically captured by the camera and stored in a computer using a high speed digital video recording software (Video Savant 4.0, Industries, Canada) and processed using an image processing software (ImageJ, National Institute of Mental Health, Bethesda, MD).

Rheological property

The casting solution viscosity was measured using a Brookfield DV-II+CP (Brookfield, USA) viscometer varied from 25°C to 65°C arranged at intervals of 5°C .

RESULTS AND DISCUSSION

Comparison OM–CC images with SEM micrographs

A drop of the casting solution was dropped between two special microscope accessories and then the precipitant (distilled water) was introduced on these accessories. When the distilled water began to touch with the casting solution, the precipitation process occurred. The whole precipitation process was observed and recorded with an optical microscope photographically and CCD camera, as showed in Figure 1(a). SEM photo were compared with the photograph taken from OM–CC in Figure 1(b,c), the membrane structure photos observed on the computer were similar as the SEM micrographs, which indicated that the membrane formation process observed with optical microscope and real membrane formation were almost uniform.

Analysis of the gelation rate curve

The relationship between X^2 and t was showed in Figure 2, From Figure 2, it could be seen that X^2 – t curve didn't present a perfect straight line of passing through the original point, which was not consistent with the commonly accepted conclusion.^{13,14} The traditional opinions considered to be a single straight linear correlation between X^2 and t in the whole gelation process.⁷

The reason is that X and t is measured by manual operation in previous study. The manual operation method usually spent about several seconds or minutes in each time distance to capture the data. The long time distance hid the true precipitation process and led to the line relationship, which could be reflected in Figure 3, when time span was 10 s, a

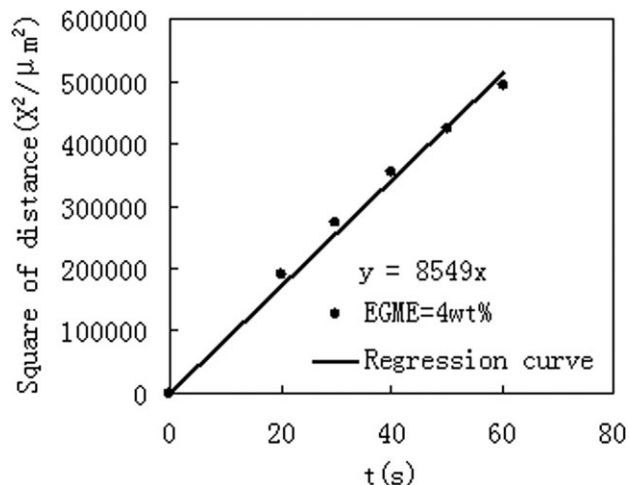


Figure 3 The square value of precipitation front move with time: PES-C: 16 wt %, when time was 20, 30, 40, 50, and 60 s.

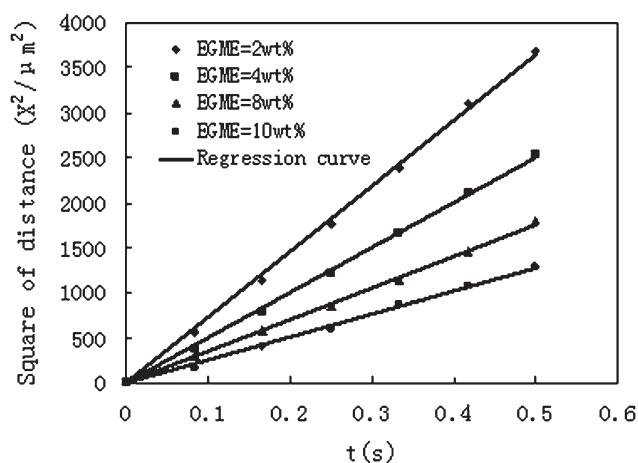


Figure 4 Variation of the square value of skin layer precipitation front move with time: PES-C: 16 wt %.

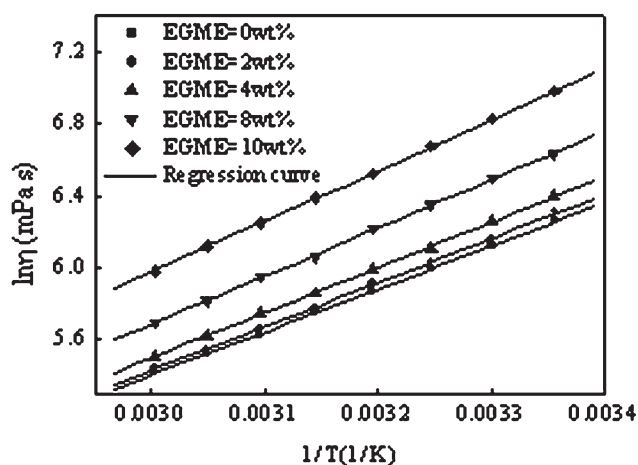


Figure 5 Relationship between viscosity of cast solution and temperature.

perfect line passing through the original point was obtained, the slope of line was 8,549.

In the membrane cross-section, three layers could be clearly distinguished as Figure 1 showed: a dense skin layer, a medium dense transition layer, a loose finger structured support layer. Because of inhomogeneity of asymmetric membrane cross-section, the resistance of exchange between solvent and gelation medium changed gradually with the increase of precipitation time and thereby gelation rate constant (slope rate) changed. The traditional method could not measure gelation process of skin layer and transition layer in time. Since the skin layer was actually taking the most important role for an asymmetric membrane, it might lead to misunderstanding for traditional method to describe the whole membrane formation process.

Effect of EGME on membrane skin layer formation kinetics

Figure 4 showed the effect of EGME on the gelation rate of skin layer, and EGME concentrations are 2, 4, 8, and 10 wt %, respectively. The result showed that X^2 increases linearly with the increase of t , gelation rate constant decreases with the increase of EGME concentration. The reason was that addition of EGME increased viscosity of casting solution, which limited

movement of macromolecular segment. Thus, the diffusion of precipitation into the casting solution became slower, which delayed the time of phase separation time and led to the decrease of gelation rate.

X^2 could be described using equations ($X^2 = kt + b$), equations were listed in Table I. X was the movement of the precipitation front, t was the gelation time, k was gelation rate constant, R was the correlation coefficient, value of R closed to 1 indicated excellent linear reliability. From Table I, it could be seen that correlation coefficients of the regression equations all presented exceeded 0.99. As shown in Table I, when EGME concentration was 4 wt %, the gelation rate constant skin layer was 5014, which was different with the gelation rate constant shown in Figure 3 (8549). The result showed that gelation rate was not same during three different layer formation processes. Since the support layer was the dominant structure from a geometric point, skin layer and transition layer only occupy a small proportion of the whole membrane thickness. Because one straight line equation could not describe the whole gelation process, the result of the gelation kinetics predicted by the line equation was incorrect. Actually, each layer should have a different gelation rate constant individually.

TABLE I
The Correlation Equations of Polymer Skin Layer Between the Square of Gelation Front Motion (X^2) and Gelation Time (t) with Various EGME Concentration

Concentration of EGME	Equations	R
EGME = 2 wt %	$X^2 = 7286t$	0.9982
EGME = 4 wt %	$X^2 = 5014t$	0.9979
EGME = 8 wt %	$X^2 = 3502t$	0.9983
EGME = 10 wt %	$X^2 = 2550t$	0.9956

TABLE II
Relationship Between the Viscous Flow Activation Energy and the EGME Concentration

Concentration of EGME	Arrhenius equations	Viscous flow activation energy, E_{η} (KJ/mol)
EGME = 0 wt %	$\ln(\eta) = 2393.28/T - 1.78$	19.91
EGME = 2 wt %	$\ln(\eta) = 2458.05/T - 1.95$	20.45
EGME = 4 wt %	$\ln(\eta) = 2528.00/T - 2.09$	21.03
EGME = 8 wt %	$\ln(\eta) = 2688.45/T - 2.38$	22.37
EGME = 10 wt %	$\ln(\eta) = 2837.38/T - 2.54$	23.61

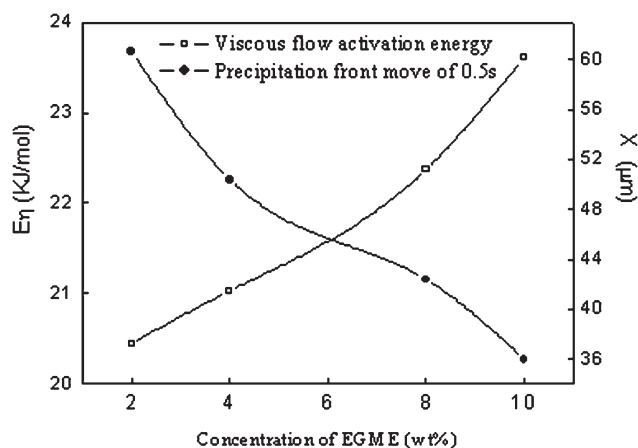


Figure 6 Relationship between the viscous flow activation energy and the gelation rate.

Relationship between viscous flow activation energy and gelation rate

The viscosity of cast solution with various EGME concentrations was measured at various temperatures. In Figure 5, the natural logarithm value of the viscosity of cast solution was plotted against the reciprocal value of the temperature. It could be concluded that a straight line was obtained at a given EGME concentration. The rheological data of the cast solution at various temperatures could be described using Arrhenius equation. Table II gave the Arrhenius equations and viscous flow activation energy at various EGME concentrations. Viscous flow activation energy increased with the increase of EGME concentrations. In Figure 6, viscous flow activation energy and precipitation front move at 0.5 s were plotted against the EGME concentration. When viscous flow activation energy was bigger, more energy was needed for the diffusivity between solvent and nonsolvent molecules. Since the diffusivity of the solvent molecules through the precipitated polymer layer strongly affected the final membrane morphology, it was possible to obtain different membrane morphology by simply controlling the EGME concentration.¹³

CONCLUSION

The effect of EGME on skin layer gelation process of asymmetric membranes had been investigated using

PES-C/EGME/DMAC cast solution. This result extended the observation to the gelation process of the skin layer, which was very important for controlling membrane characteristics and performances. The relation between X^2 and t with various EGME concentrations was determined, gelation rate constant equations of membrane skin layer formation were obtained. EGME concentration strongly affected the gelation rate of skin layer, the gelation rate constant decreased with the increase of concentration of EGME. Rheological property of the cast solution had been investigated. The results showed that the relationship between the apparent viscosity and temperature could be described with the Arrhenius equation. Further the EGME concentrations affected the viscous flow activation energy.

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