SOLUTION CHARACTERISTICS AND MEMBRANE FORMATION OF PARTIALLY IMIDIZED POLY(AMIC ACID)

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ABSTRACT

The imidization effect of a poly(amic acid) dope solution on membrane formation has been investigated. Poly(amic acid) solution in N-methyl-2-pyrrolidione has been thermally imidized at 120℃ with different curing time and its degree of imidization was determined by infrared spectroscopy. The solution properties have been studied as a function of concentration and curing time by dynamic light scattering. The quality of a solvent was changed from good to poor with increasing imidization of poly(amic acid). The reduced polymer-solvent interaction diminishes the membrane formation time. The morphology of a membrane was able to be controlled by the characteristics of dope solution.

INTRODUCTION

Asymmetric membranes are commonly prepared by the phase inversion. Since, polyimide, in particular, made of pyromellitic dianhydride (PMDA) and oxygen dianiline (ODA) is insoluble in conventional organic solvents, its asymmetric membrane can not be made directly by the phase inversion technique. However once insoluble asymmetric membranes are prepared, there are wide potential usage to apply the membranes in various fields specially dealing with organic solvents. Therefore, it is an interesting challenge to make insoluble polyimide asymmetric membranes.

In this study, we have focused on a polyimide precursor; poly(amic acid) which is soluble in N-methyl-2-pyrrolidione (NMP). The poly(amic acid) solution in NMP can be converted to asymmetric membranes by phase inversion and the subsequent imidization can yield insoluble polyimide asymmetric membranes. Poly(amic acid) undergoes a slow phase inversion, that is not appropriate for the practical production of membranes. Therefore the rate of the phase inversion should be increased. Poly(amic acid) was partially imidized in order to reduce the interaction between the polymer and water and to enhance the rate of phse inversion. When poly(amic acid) is partially imidized, its interaction with solvent and nonsolvent, and consequent solution characteristics will be changed. The imidization effects of poly(amic acid) on solution characteristics as well as on membrane morphology have been investigated. The degree of imidization of dope poly(amic acid) solution in NMP, which was determined by infrared (IR) spectroscopy, was controlled by curing temperature and time. Partially imidized poly(amic acid) solutions were characterized by dynamic light scattering. Asymmetric membranes were then prepared by the phase inversion in a nonslovent of water. The membrane morphology was correlated with the characteristics of the dope solution.

RESULTS AND DISCUSSION

The degree of imidization was calculated from the absorbance ratio of the imide band at 1380 cm^{-1} to the reference band at 1500 cm^{-1}. The choice of bands was carried out on the basis of the report that imide band near 1380 cm^{-1} shows very little effect from anisotropy. Poly(amic acid) was partially imidized in solution state at 120°C for 0 to 75 minutes. Heating over 75 minutes resulted in precipitation of polymer. Degree of imidization clearly increases with curing time and poly(amic acid) starts to precipitate at over 17% of thermal imidization .

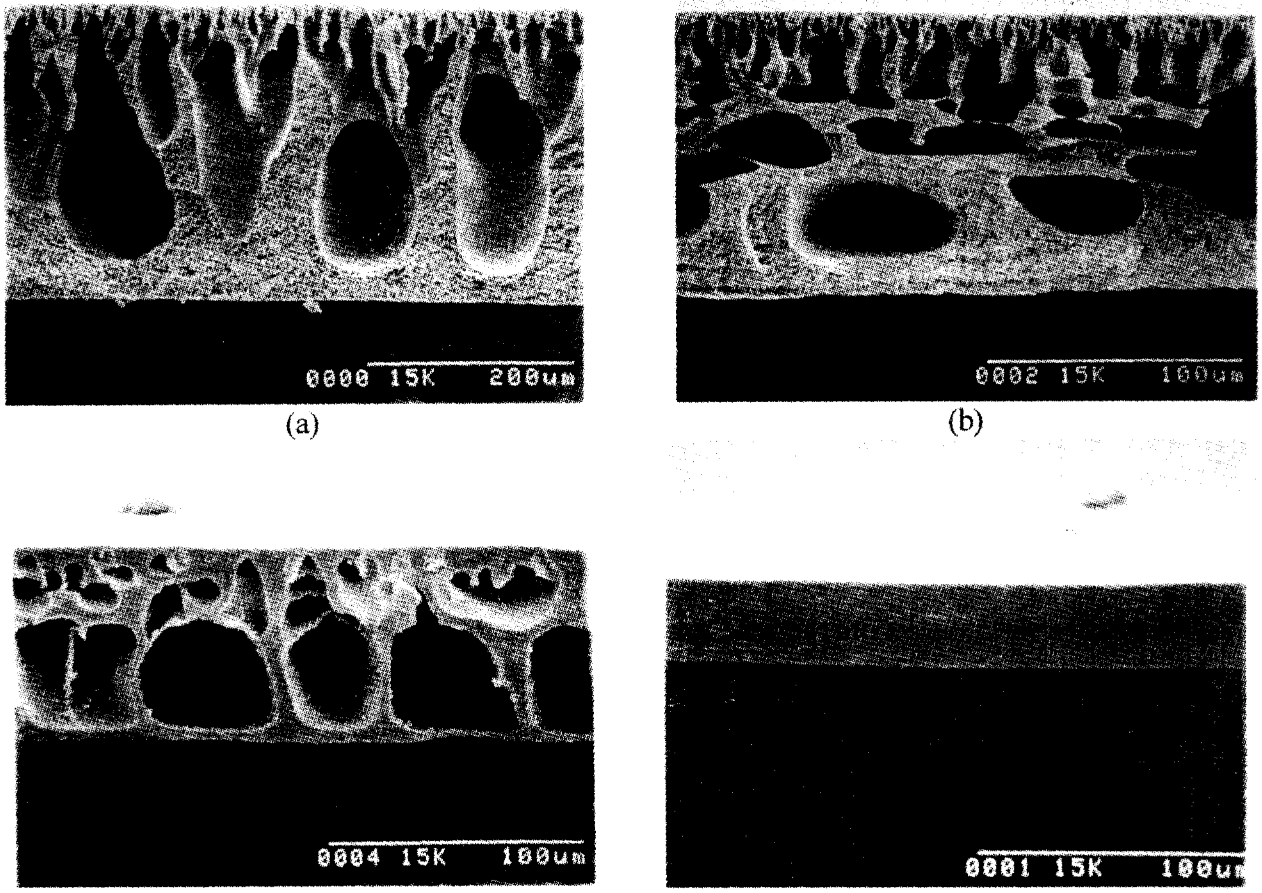
The distributions of decay rate, Γ for all samples were calculated from the autocorrelation functions measured by DLS. A single relaxation mode is found in partially imidized solutions. The contribution of the fast mode has been dispersed with curing time. The fast mode is attributed to the cooperative motion of polymer segments while two relaxation modes are found in the sample cured for 75 minutes. This transition of Γ distribution from unimodal to bimodal was reported in the change of solvent quality from good to poor [1].

The diffusion coefficients, D, of pristine poly(amic acid) and partially imidized poly(amic acid) solutions were obtained by linear regression from the plot of Γ versus q^2, where q is the scattering vector. When the polymer concentration, c, is much smaller than the overlap concentration, c*, D depends upon c as follows, $D = D_o (1 + k_D c)$, where D_o is the diffusion coefficient of the polymer at infinite dilution and k_D is the diffusional second virial coefficient. The obtained D values are plotted against the polymer concentration and their relationship is linear. k_D and D_o were obtained from the slope and the intercept at $c = 0$ of the curves, respectively. It is clear that the imidization of poly(amic acid) yields a progressive decrease in the k_D values representing solvent quality changes from good to poor. D_o is related to the medium viscosity, η_s, and hydrodynamic radius, R_h by the Stokes-Einstein equation; $D_o = kT/6\pi\eta_\sigma R_h$. R_h values decreased significantly first 30 minutes of curing, and then fluctuated. This fluctuation might come from the fact that R_h values were calculated under the assumption that the solvent viscosity remains constant. Moreover, it is worth noting that the presence of the slow mode greatly affects the accuracy with which R_h corresponding to the fast mode can be determined. In spite of possibility of uncertainty, it is interesting that R_h of imidized polymer decreased half of the one of pristine poly(amic acid). This could mean that polymer coils are getting tighter with curing time since the solvent quality is getting poorer with curing time and/or poly(amic acid) underwent rather dramatic changes in molecular weight. It is known that prolonged heating in the range from 100 to 150℃ can result in irreversible deterioration of films, since carboxycarboamide groups regenerate anhydride and amine moieties. The chains would be broken at these points and their molecular weights would be reduced. The possibility of molecular weight change during the solution imidization has been examined by gel permeation chromatography, and there was no significant molecular weight loss upon imidization.

The origin of slow mode is not known, but seeing the solvent quality change with curing, it is clear that the increasing amount of imide blocks in poly(amic acid) backbone reduces the interaction between the polymer and the solvent that leads for the polymer to be insoluble in NMP. Therefore aggregates would be formed. Since it is known that crosslinking does not take place below 300℃, it is reasonable to identify the slow mode as aggregates instead of gelation precursor. This heterogeneity of the dope solution would affect the membrane morphology as reported elsewhere [2].

The cross-sections of membranes prepared from poly(amic acid) solutions of different degree of imidization are shown in Figure 1. Large macrovoids are observed in the membrane obtained from the pristine poly(amic acid) solution. The total thickness of the membranes decreased with the imidization of dope polymer solution. The portion of macrovoids in the membrane cross-section increases with curing time until 60 minutes, but macrovoids were completely disappeared in the membranes obtained from the solution imidized for 75 minutes.

It is generally known that the phase inversion occurs slowly when the interaction between polymer and nonsolvent is strong [3]. The amount of hydrophilic moiety in the poly(amic acid) backbone decreases with increasing degree of imidization. Thus the interaction between polymer and nonsolvent becomes weaker. The reduced polymer-solvent interaction also plays a significant role in increasing the rate of phase inversion. Therefore the phase inversion becomes faster with the imidization of poly(amic acid) dope solution due to the reduced interactions between polymer and solvent as well as nonsolvent. The phase separation of partially imidized poly(amic acid) solution (imidized for 30 minutes) occurs faster than that of pristine poly(amic acid) while the both cases follow instantaneous demixing process. It is well known that the macrovoid formation is preferred and that porous membranes are obtained when the phase inversion follows the instantaneous demixing.



(a) (b) (c) (d)

Figure 1. Cross-section of membranes made from poly(amic acid) solutions imidized for (a) 0, (b) 30, (c) 60 and (d) 75 minutes at 120℃.

On the other hand, the membrane prepared from the dope solution cured for 75 minutes looks like symmetric without macrovoids and optically transparent which is unlike general opaque membranes obtained via the phase inversion technique. It could be thought that the interaction between polymer and solvent gets weaker, and the polymer solution reaches to the phase inversion onset with curing. Therefore a cast solution film simply inverted the phase to the final membrane at the moment of immersion into a nonsolvent.

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