

Influence of Novel Surface Modifying Macromolecules and Coagulation Media on the Gas Permeation Properties of Different Polymeric Gas Separation Membranes

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ABSTRACT: Integrally skinned asymmetric membranes for the separation of O₂ and N₂ were fabricated by the phase inversion technique from polysulfone, polyetherimide, and polyimide. Two types of surface modifying macromolecules (SMMs) including hydrophilic SMM (LSMM) and charged SMM (cSMM) were synthesized and blended with the casting solution to modify the membrane surface. The cast film was then immersed in the first coagulant alcohol (methanol, ethanol, or isopropanol) for a predetermined period, before being immersed in the second coagulant (water). The SMMs used in these experiments were laboratory synthesized by the two-step process of polyurethane prepolymer synthesis and end capping, before being characterized by differential scanning calorimetry. Their molec-

ular structure was determined from the molecular weight obtained by gel permeation chromatography. The membranes were characterized by contact angle measurement and O₂ and N₂ gas permeation performance. Attempts were made to interpret the gas permeation data by delayed demixing affected by solubility parameters of polymer, solvent, and nonsolvent. Furthermore, the permeation performance of cSMM membranes was interpreted by the solvation of the charged sulfonate groups present in cSMM. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 2300–2310, 2012

Key words: surface modifying macromolecules; wet–wet phase inversion method; gas separation membranes; polysulfone; polyetherimide; polyimide

INTRODUCTION

The wet–wet process is a variation of phase inversion, in which incompatibility is introduced to the polymer solution by immersion of the nascent membrane into a nonsolvent coagulation medium that usually consists of water or an aqueous solution.¹ Precipitation occurs through the exchange of solvent and nonsolvent leading to formation of asymmetric membranes. Many variables are involved in the phase inversion technique. Among those, the composition of polymer solution, immersion time in coagulation medium, nature and temperature of coagulation medium, and heat treatment temperature are considered as the primary factors affecting the performance of the membrane. Depending on the combination of variables, membranes with different polymeric materials and different pore sizes can be

prepared. Most commercially available membranes for different purposes such as ultrafiltration (UF), reverse osmosis (RO), pervaporation (PV), gas separation are obtained from this versatile technique allowing all kinds of morphologies to be formed. It is evident that the type of coagulation medium (water or organic compound) can similarly have dramatic effects on the structure and separation performances^{2–8} of the resulting membrane. Some attempts were made to investigate the effect of coagulation baths on structure and performance of asymmetric membranes. Hao and Wang⁹ studied the influence of different organic coagulation media on the structure and gas permeation properties of cellulose acetate (CA) membranes. They reported that the polymer solution system CA-acetone-methanol is quite suitable to prepare integrally skinned asymmetric CA membranes for gas separation with sufficiently high selectivity. They also validated their experimental data by calculating the ternary phase diagram of polymer-solvent-nonsolvent. In another study, Fan et al.¹⁰ studied the effect of coagulation media on membrane formation and vapor permeation performance of novel aromatic polyamide membranes. They found that the diffusivity of coagulation medium ranks in the following order: water >

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methanol > ethanol > *n*-propanol. Despite the advantages of phase inversion technique in preparing asymmetric membranes for gas separation, even small numbers of pinholes in the skin layer caused the feed gas leak, lowering the selectivity of the membrane. To overcome this drawback, different solutions were proposed by membraneologists over decades. Henis and Tripodi¹¹ covered the defective pores of asymmetric membranes by coating a relatively thick silicone rubber layer on a skin selective layer to plug the pinholes. Although, Henis and Tripodi's method was successfully applied to fabricate high selectivity membranes, the method requires post coagulation processing step, increasing membrane fabrication costs. To overcome this shortcoming, phase inversion of the polymer blends containing novel surface modifying macromolecules (SMMs) was proposed. The migration of surface active additive from a polymer solution during the casting stage or the early stage of coagulation is used in this method for the modification of membrane surfaces.^{12–14}

Over the past decades, many attempts have been made toward the development of methods based on the surface migration or surface segregation of SMMs due to the thermodynamic incompatibility between polymers. It is a well known fact that when the polymer system is equilibrated in air, the polymer having the lowest surface energy will concentrate at the air interface and reduce the system's interfacial tension as a consequence. For example, Suk et al.¹⁵ synthesized a SMM from a prepolymer with hydrophobic dimethylsiloxane as its soft segment. Together with the fluorohydrocarbon end-capping group, their SMM exhibited high hydrophobicity that facilitated its migration when blended in polyethersulfone (PES) solution. The scanning electron microscopy (SEM) image revealed that, in fact, the surface segregation of the SMM layer did occur. Contact angle and X-ray photoelectron spectroscopy (XPS) measurements also confirmed that the major component of the surface layer was the SMM. On the basis of this fundamental concept, SMMs have been developed aiming at enhancing surface hydrophobicity or -philicity and chemical resistivity of membranes. SMMs migrate to the membrane surface during casting and early stage of coagulation and provide internal pore channels of the membrane as well as skin layer with a high degree of surface coverage, resulting in improvement of permeability and selectivity of the membranes. SMMs are specifically engineered and synthesized from a prepolymer containing a soft and a hard segment in its structure and end-capped with hydrophobic, hydrophilic, or charged functional groups. SMMs could be synthesized with different combinations and stoichiometries of reagents. Applications have been found in

many processes such as PV, UF, membrane distillation, and fuel cell.^{16–18}

In our earlier work,¹⁹ we have proven that SMMs, when blended in the casting dope, indeed migrate to the top surface of the cast film during the film casting procedure or in early stage of solvent-nonsolvent exchange in the coagulation bath thus affecting the phase inversion process. It has also been proven by the cross-sectional images presented in our earlier work¹⁹ that an integrally skinned asymmetric membrane could indeed be fabricated by the phase inversion technique we adopted. The discussions were hence made based on the SMM surface migration and its effect on the skin-layer formation in the phase inversion process. It was found that the addition of hydrophobic SMM into the casting dope of polysulfone (PSf) makes the miscibility gap narrower and thus enhances the instantaneous demixing in the isopropyl alcohol coagulation bath, leading to higher permeance and lower selectivity. Charged SMMs on the other hand make the miscibility gap wider and thus enhances the delayed demixing, leading to lower permeance, and higher selectivity.

The objective of this study is to further extend the earlier work. Instead of isopropanol alone, three different alcohols, i.e., methanol, ethanol, and isopropanol are used as the coagulation media. Polysulfone (PSf), polyetherimide (PEI), and polyimide (PI) are used for polymeric material. Moreover, hydrophobic SMM (nSMM) is replaced by hydrophilic SMM (LSMM) in this work since blending of the former SMM was found to promote the formation of pinholes. Thus, the effects of coagulants, polymers, and SMMs on the phase inversion process and the performance of the resulting membranes on the separation of O₂ and N₂ are studied.

EXPERIMENTAL

Materials

Chemicals used in this study are listed in Table I. All polymers were dried in an air circulating oven at 80°C overnight before being used. The chemical structure of all polymers is given in Figure 1. 1-Methyl-2-pyrrolidinone (NMP) was used as the solvent. Methanol (MeOH), ethanol (EtOH), and isopropanol (IPA) were purchased from Sigma-Aldrich Chemical Co., St. Louis, MO as the nonsolvent in the first coagulation bath. Deionized water (DI) was used as the nonsolvent in the second coagulation bath.

SMMs synthesis

The synthesis of SMMs was carried out by two-step condensation polymerization process. Two types of SMMs were prepared in this study:

TABLE I
Description of Chemicals

Material descriptions	CAS number	Source	Specifications
PSf (Udel-3500, pellet)	25135-51-7	Amoco Performance Products Inc., Atlanta, GA	Mw: 37 kD; PDI: 2.11; Tg: 184.2°C; SG: 1.24
PEI (Ultem 1000, natural pellet)	61128-46-9	General Electric Co., Pittsfield, MA	SG: 1.27; Mw: 15 kD; Tg: 212.7°C
PI (Matrimid 5218, amorphous yellow powder)	62929-02-6	Huntsman Advanced Materials Americas Inc., Woodlands, TX	SG: 1.2; Tg: 280°C

- LSMM (hydrophilic SMM) was synthesized according to the method reported by Rana et al.²⁰ The urethane prepolymer was formed from the reaction of methylene bis-*p*-phenyl isocyanate (MDI) with poly(propylene glycol) (PPG) having average molecular weight of 425 Da in *N,N*-dimethylacetamide (DMAc) solvent. LSMM was synthesized by end-capping the urethane prepolymer with poly(ethylene glycol) (PEG) having average molecular weight of 600 Da. The chemical formula of LSMM is also given in Figure 1.
- The details of cSMM (charged SMM) synthesis are given in Bolong et al.²¹ Briefly, the initial step involved the reaction of MDI with PPG in a common solvent of DMAc, which resulted in a solution of prepolymer that contained ure-

thane linkage. More specifically, the prepolymer is a segment-blocked urethane oligomer having both ends capped with isocyanate. The reaction was then terminated by the addition of hydroxybenzene sulfonate (HBS), resulting in a solution of cSMM. The chemical formula of cSMM is also given in Figure 1.

SMMs characterization

Glass transition temperature (T_g) was measured by differential scanning calorimeter (DSC Q1000, TA Instruments, New Castle, DE). Around 5 mg of polymer sample was placed into an aluminum pan and was heated to 260°C at a rate of 10°C/min and maintained there for 10 min. Then, the polymer was

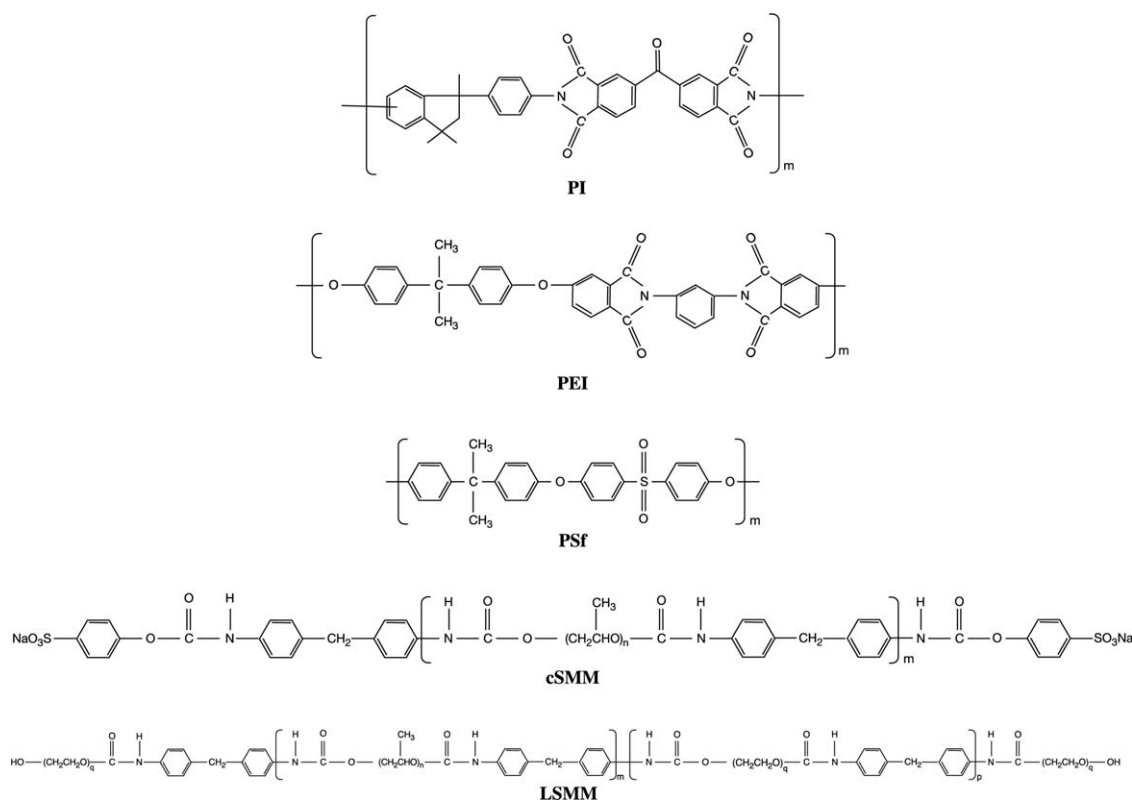


Figure 1 Chemical structure of SMMs and base polymers.

TABLE II
Composition of Casting Solutions

Base polymer	Base polymer (wt %)	DMAc (wt %)	LSMM (wt %)	cSMM (wt %)
PSf	25	75	–	–
PSf	25	73.5	1.5	–
PSf	25	73.5	–	1.5
PEI	25	75	–	–
PEI	25	73.5	1.5	–
PEI	25	73.5	–	1.5
PI	25	75	–	–
PI	25	73.5	1.5	–
PI	25	73.5	–	1.5

cooled to -50°C at the same rate of $10^{\circ}\text{C}/\text{min}$. The T_g value was recorded at the onset and mid-point of corresponding heat capacity transition. Other characterization techniques include elemental analysis and gel permeation chromatography, differential scanning calorimetry (DSC), and Fourier transform infrared spectroscopy (FTIR) as have been previously reported in detail.^{17,20,21}

Membrane preparation and characterization

The casting solutions for the control membranes (without SMM addition) were 25 wt % polymer (PSf, PEI, or PI) solutions in NMP. The required amount of polymer was added to the solvent and the mixture was gently stirred at 100°C for 4 h in a rotator until the solution became homogeneous.

The casting solutions containing each of the SMMs were prepared by adding 1.5 wt % of the SMM to the polymer solution for the control membrane. A total of nine types of solutions were produced, the compositions of which are shown in Table II.

The solutions were cast over a glass plate using a casting bar with a 0.25 mm gap. Immediately after casting, the cast film together with the glass plate was immersed into the first coagulation bath (methanol, ethanol, or isopropanol) and kept there for a predetermined period of 10, 30, 60, and 90 s. to form the skin layer. Then, the cast film and the glass plate were together immersed in a water bath (second coagulation bath) to complete the solvent/nonsolvent exchange process. The membrane was peeled off the glass plate and was kept in fresh water for three days before being dried at ambient temperature for 3 days.

Static contact angle measurements

The static contact angle (SCA) measurement of the membrane surface was done using a VCA Optima Surface Analysis System (AST Products, Billerica, MA). The sample was fixed on a slide glass, and then a drop of liquid was placed on the sample sur-

face using a micro-syringe (Hamilton Company, Reno, NV). The SCAs were measured at 10 different spots on each membrane coupon. The values were averaged and the standard deviation was calculated and recorded.

Gas permeation measurements

Gas permeation tests were performed using pure nitrogen (N_2) and pure oxygen (O_2) as test gases using a constant pressure (CP) system consisting of three parallel cells. A circular membrane sample with an effective permeation area of 10.2 cm^2 was placed at the bottom of the cell over a paper filter on top of a porous metal disk. The seal was made by a 2 mm wide and 0.2 mm high semicircular metal ring that was machined on the upstream side of the cell and a flat metal surface on the downstream parts of the cell. To prevent a potential damage to the membrane by the edge of the sealing ring, the feed (upstream) side of the membrane was laminated with a paraffin film ring. Feed pressure was set at 105 psig ($\sim 120\text{ psia}$; 0.83 MPa) while the permeate side was maintained at atmospheric pressure. Experiments were carried out at ambient temperature. The gas permeation rate was measured by a soap bubble flow meter. Each experiment was carried out in triplicate to ensure reproducibility and the average of the results was reported.

Theory

The permeance (P/l) defined as pressure-normalized flux, is calculated by:

$$\left(\frac{P}{l}\right) = \frac{Q_p}{A\Delta p} \times 10^6 = \frac{F}{\Delta p} \times 10^6 \quad (1)$$

where (P/l) is the permeance, GPU (gas permeation unit = 10^{-6} cm^3 (STP)/ $\text{cm}^2/\text{s cm Hg}$), Q_p is the permeation rate, cm^3 (STP)/s, A is the permeation area of the membrane, cm^2 , Δp is the pressure difference across the membrane, cm Hg, and F is the permeation flux, cm^3 (STP)/ cm^2/s .

The ideal separation factor (hereafter called ideal selectivity) of gas i over gas j (α_{ij}°) is calculated as follows:

$$\alpha_{ij}^{\circ} = \frac{(P/l)_i}{(P/l)_j} \quad (2)$$

The permeance and the ideal selectivity were calculated using eqs. (1) and (2). Each experiment was triplicated to ensure reproducibility. The results were averaged and the standard deviations were calculated and recorded.

TABLE III
Structural Details of the SMMs and Their Solubility Parameters

SMM	n ^a	m ^a	p ^a	q ^a	Solubility parameter [(cal/cm ³) ^{1/2}] ^b
LSMM	7.02	24.59	12.29	13.23	10.01
cSMM	7.02	8.99	–	–	10.74

^a m, n, p, and q are the number of repeating units in the polymer structure as specified in Figure 1.

^b appendix, TABLE AI and TABLE AII.

RESULTS AND DISCUSSION

SMMs characterization

Glass transition temperatures (T_g s) of cSMM at the onset and the mid-point were -18.3°C , and -11.6°C , respectively. The T_g s of LSMM at the onset and the mid point were 8.15°C , and 18.28°C , respectively.

The structural parameters of the SMMs were previously determined and reported.^{17,20,21} The n , m , and p values, referring to the repeating units in the polymer structure as specified in Figure 1, for LSMM, and cSMM are summarized in Table III.^{17,20,21} The solubility parameters of the SMMs were calculated by applying the additivity rule for the structural components of each SMM.²² The detailed calculations are described in the Appendix, TABLE AI and TABLE AII.

Static contact angle characteristics

The SCA results are summarized in Table IV. The decrease in SCA values from the control membrane to SMM incorporated membranes was statistically significant. However, the difference between the two SMMs was statistically insignificant. In other words, adding both SMMs made the surface of the membranes more hydrophilic. This observation suggests that SMMs impose their intrinsic characteristics to the membrane by migrating to the surface during either casting or coagulation process.

TABLE IV
SCA data of Control Membranes and Membranes Containing SMMs

Membrane	Average contact angle ($^\circ$)	Standard deviation ($^\circ$)
PSf	70.03	2.31
PSf-LSMM	66.28	1.42
PSf-cSMM	65.44	2.05
PEI	65.2	1.76
PEI-LSMM	56.47	2.89
PEI-cSMM	60.26	1.78
PI	70.54	3.37
PI-LSMM	63.01	1.68
PI-cSMM	63.32	2.54

Gas permeation results

Effect of coagulant and immersion time on the membrane performance

Figure 2 shows oxygen permeance and oxygen/nitrogen ideal selectivity for PSf membranes versus immersion time in the three different alcohols used

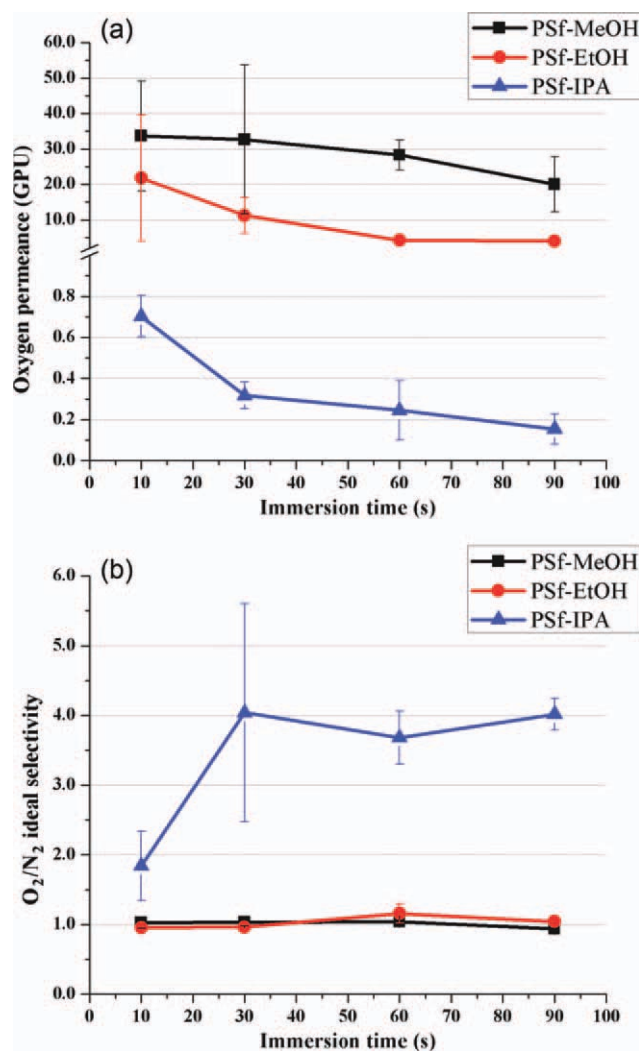


Figure 2 Oxygen permeance (a) and O_2/N_2 permeance ratio (b) of the PSf membranes immersing in methanol, ethanol, and isopropanol coagulation baths. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

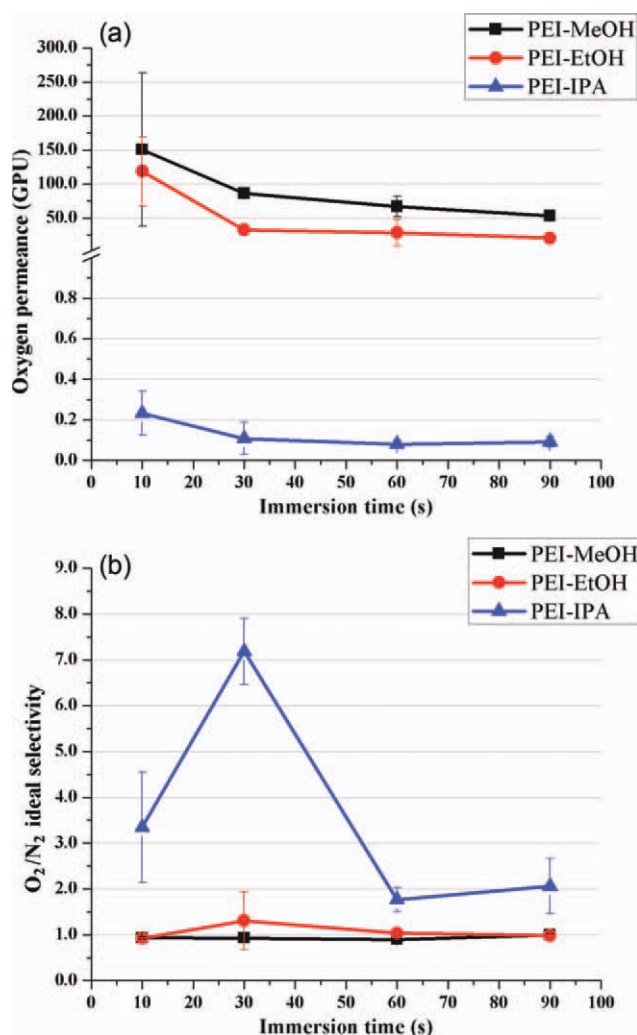


Figure 3 Oxygen permeance (a) and O_2/N_2 permeance ratio (b) of the PEI membranes immersing in methanol, ethanol, and isopropanol coagulation bathes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

for the coagulants. It is obvious, from the figure that the oxygen permeance was the largest for coagulant methanol, followed by ethanol and isopropanol. In particular, isopropanol showed an order of magnitude lower oxygen permeance. The oxygen permeance through all membranes decreased with an increase in the immersion time, indicating the formation of thicker and/or denser skin layer.

The selectivities were, on the other hand, nearly equal to unity for PSf-methanol and PSf-ethanol membranes, meaning that these membranes contained large and/or defective pores in their skin layers. The ideal selectivities of the membranes prepared using isopropanol as coagulant were above unity and reached ~ 4.0 for immersion times of 30 s or longer.

Figure 3 shows similar results for the control PEI membranes. Similar trends as for PSf membranes

were observed. That is, the membranes prepared using MeOH and EtOH showed higher permeances but no selectivity between O_2 and N_2 . The membrane prepared using IPA as coagulant, on the other hand, demonstrated low permeance but considerable ideal selectivity. The highest ideal selectivity was 7 at 30 s immersion time for the latter membrane.

Figure 4 shows the results for PI control membranes. The same trends were observed as for the PSf and PEI membranes. The maximum selectivity values (5.0–5.5) were achieved for isopropanol coagulant membrane at immersion times of 30 and 60 s.

A comparison of the three types of membranes indicated that those prepared using IPA demonstrated low permeances, in the range of 1–2 GPU, but acceptable ideal selectivities in the range of 4–7. The best ideal selectivity was demonstrated by PEI membrane immersed in IPA for 30 s.

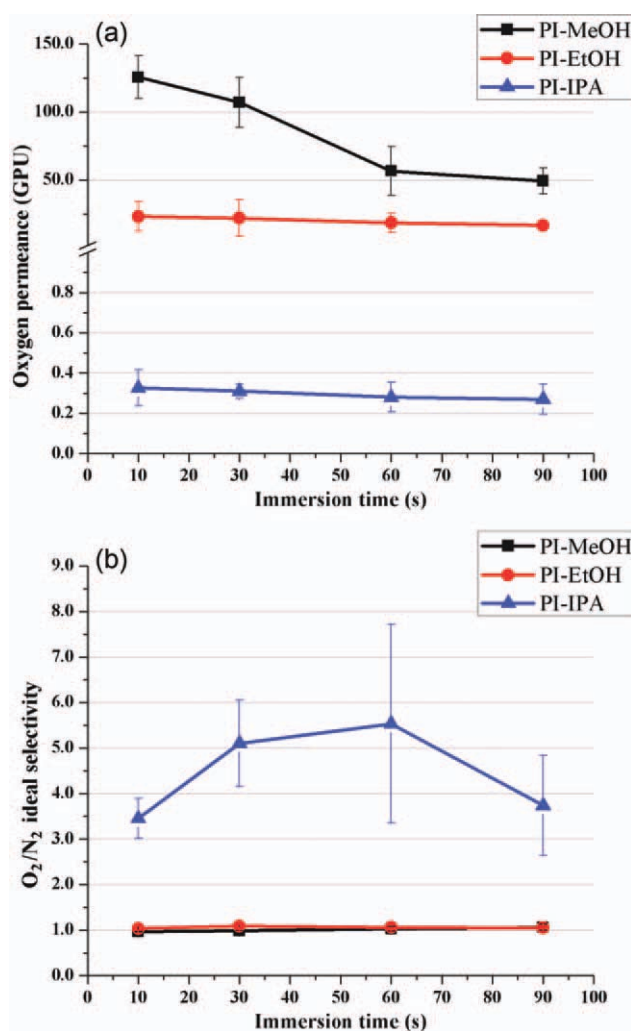


Figure 4 Oxygen permeance (a) and O_2/N_2 permeance ratio (b) of the PI membranes immersing in methanol, ethanol, and isopropanol coagulation bathes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

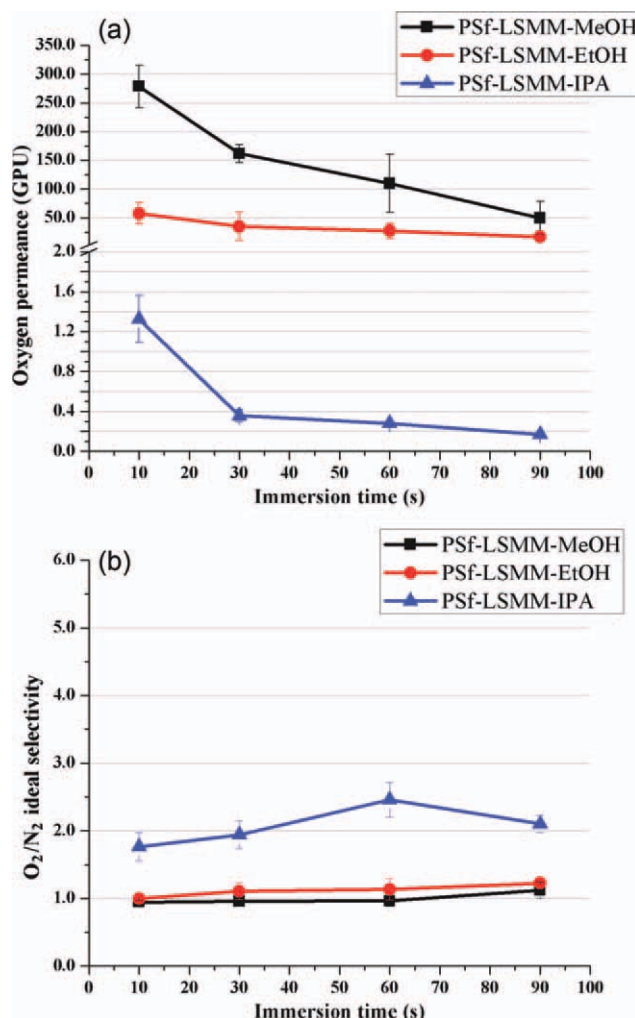


Figure 5 Oxygen permeance (a) and O₂/N₂ permeance ratio (b) of the PSf membranes with LSMM blending immersing in methanol, ethanol, and isopropanol coagulation baths. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

Effect of LSMM inclusion

Figures 5–7 show the performance of the membranes including LSMM. In general, while higher permeances were observed compared with the control membranes, the ideal selectivities remained the same or declined. The permeances of the membranes prepared using MeOH and EtOH as the coagulants were in the range of 40–700 GPU. These membranes demonstrated no selectivity between O₂ and N₂. On the other hand, all three membranes prepared using IPA as coagulant had low permeances in the range of 0.2–1.4 GPU. The ideal selectivities of these membranes were greater than unity, reaching 2.5 for PSf-LSMM-IPA membrane. The effect of immersion time was negligible if any, as the ideal selectivity of the latter membrane remained almost the same at different immersion times.

Effect of cSMM inclusion

Figures 8–10 show the performance of the membranes incorporating cSMM. All the membranes immersed in MeOH and EtOH showed high permeances and no selectivity between O₂ and N₂. On the contrary, the membranes that were immersed in IPA showed high ideal selectivities. An important observation was that the ideal selectivities for the three polymers showed increasing trends with immersion time. The ideal selectivities were greater than those of the control membranes as well as the LSMM-incorporated membranes. The highest ideal selectivity was observed at 90 s immersion time, which was around 7–8 for the three polymers.

The performance data obtained in this work support those presented in our previous work.¹⁹ The results are also in agreement with those reported by Yamasaki et al.²³ and Lee et al.²⁴ However, the permeances obtained in the present work were lower

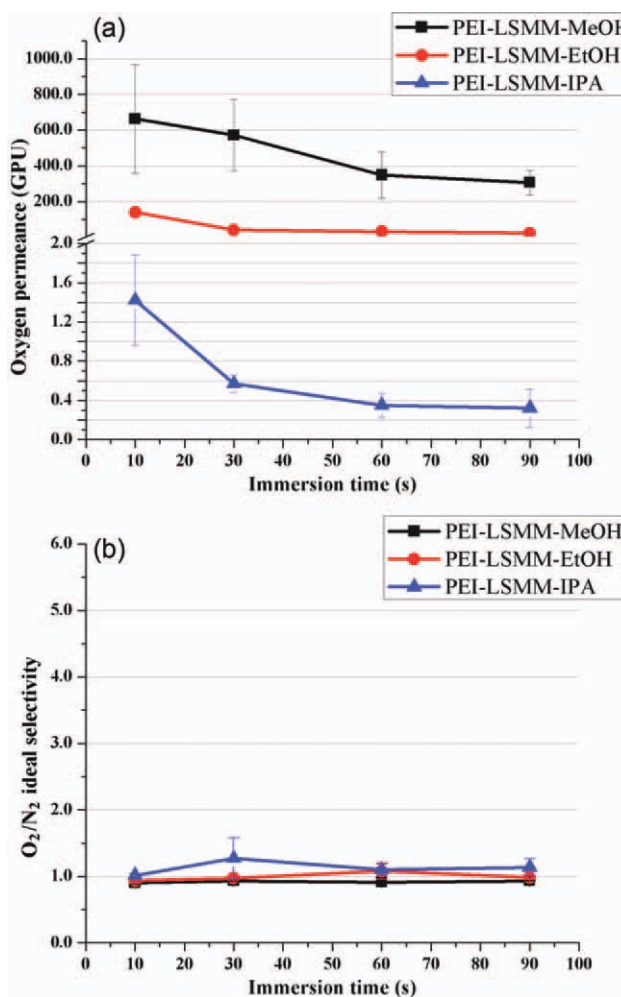


Figure 6 Oxygen permeance (a) and O₂/N₂ permeance ratio (b) of the PEI membranes with LSMM blending immersing in methanol, ethanol, and isopropanol coagulation baths. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

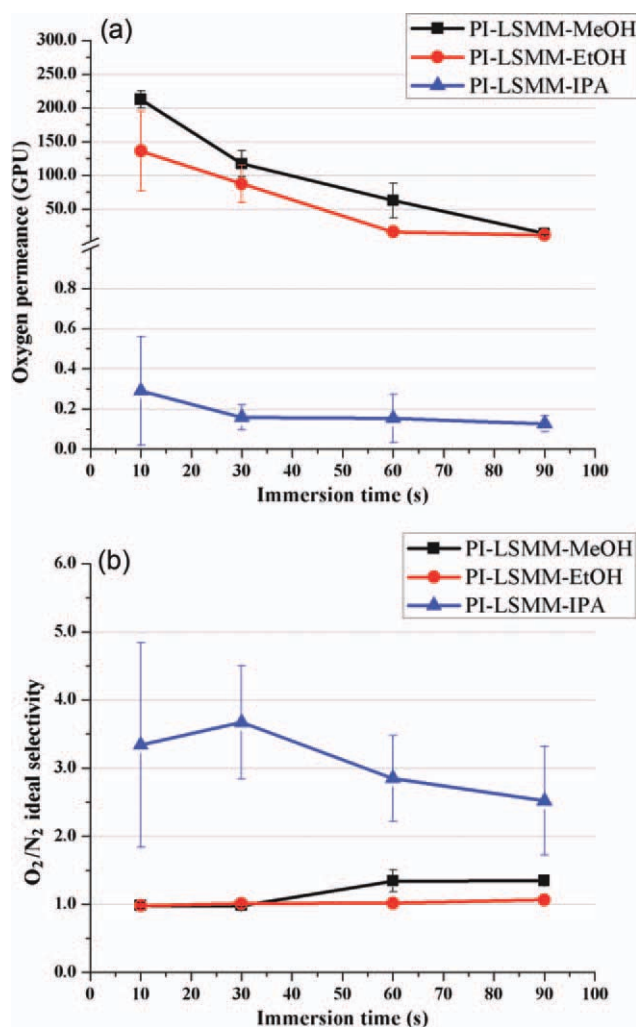


Figure 7 Oxygen permeance (a) and O₂/N₂ permeance ratio (b) of the PI membranes with LSMM blending immersing in methanol, ethanol, and isopropanol coagulation baths. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

than those reported by Lee et al.²⁴ This could be because of the formation of tighter pores underneath the skin layer imposing a greater resistance to the gas flow, or to random performance of membrane coupons.

DISCUSSION

Control membranes

According to a previous study,¹⁹ it was expected that polymer (abbreviated as P hereafter)/nonsolvent (abbreviated as N hereafter) pairs with similar solubility parameters (δ) show higher selectivity. That is, PI and MeOH ($\delta = 14.7$ and 14.5 (cal/cm³)^{1/2}, respectively), PSf and EtOH ($\delta = 12.6$ and 12.7 (cal/cm³)^{1/2}, respectively), and PEI and IPA ($\delta = 11.5$ and 11.6 (cal/cm³)^{1/2}, respectively) were expected to show acceptable ideal selectivities. However, the present

study indicated that the other factors such as diffusivity also contribute to the solvent/nonsolvent exchange. If the diffusion rate of (N) is high the time required for N to travel through the composition path on the triangular diagram is short, thus decreasing the chance of delayed demixing. Hence, alcohols of small molecular sizes such as methanol and ethanol are not suitable for delayed demixing. Use of such media as coagulant does not help formation of thick and defect free skin layer, thus resulting in membranes of low selectivities.

When a specific nonsolvent is selected for the first coagulant, the solubility parameter rule is supposed to work, since the diffusivity is fixed. For example, when isopropanol is selected as the nonsolvent (N) the solubility parameter rule predicts the highest selectivity and lowest permeability for PEI (P) since solubility parameters of PEI and IPA [11.5 and 11.6

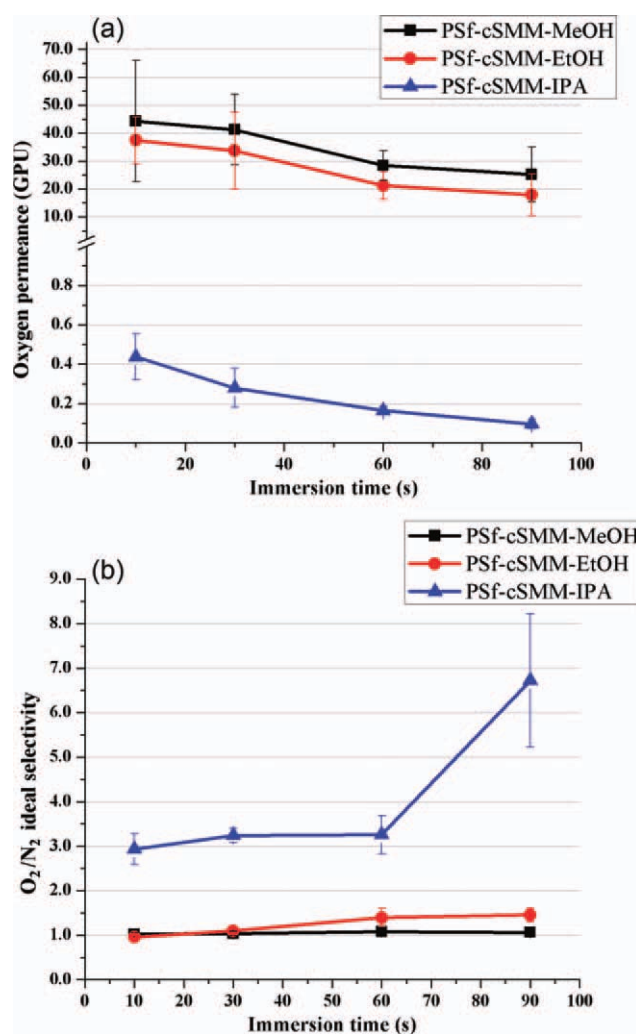


Figure 8 Oxygen permeance (a) and O₂/N₂ permeance ratio (b) of the PSf membranes with cSMM blending immersing in methanol, ethanol, and isopropanol coagulation baths. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

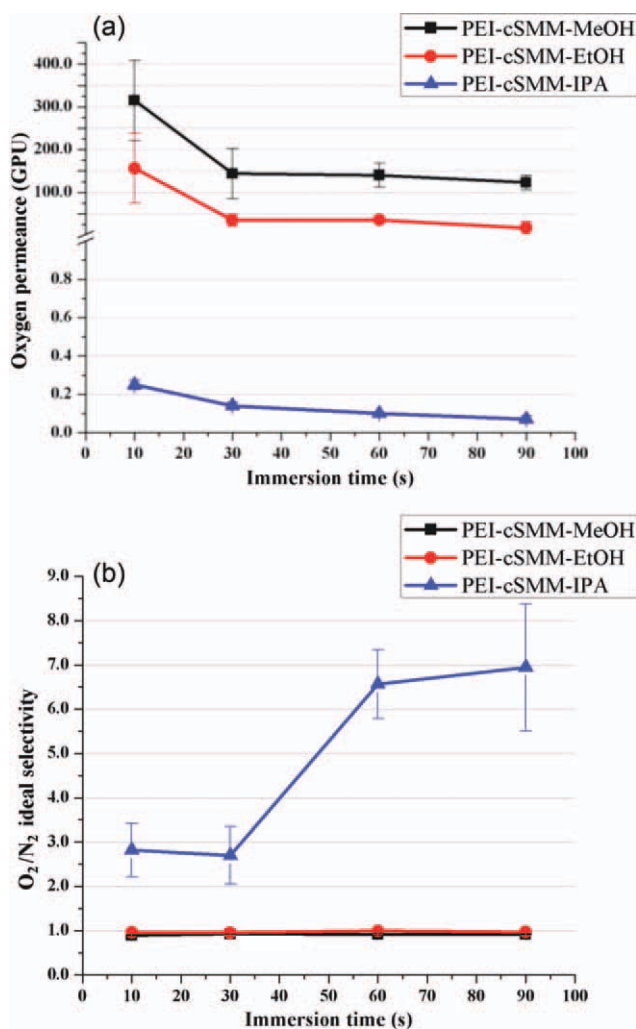


Figure 9 Oxygen permeance (a) and O₂/N₂ permeance ratio (b) of the PEI membranes with cSMM blending immersing in methanol, ethanol, and isopropanol coagulation baths. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

(cal/cm³)^{1/2}, respectively] are nearly equal. Indeed, the experimental results confirmed this prediction because PEI/IPA showed the highest maximum selectivity of 7.2 (Fig. 3). Also, PEI showed the lowest oxygen permeance in 3 out of 4 cases (10, 30, and 90 s immersion times).

LSMM incorporated membranes

In our previous work,¹⁹ we hypothesized that, for the SMM-incorporated membranes, the solubility parameter of the SMM, rather than that of the base polymer, controls the phase inversion process. This is due to the migration and accumulation of SMM at the surface of the cast polymer solution, hence at the nonsolvent/polymer solution interface, as evidenced by contact angle measurements and XPS data.

The present discussions are focused on the selectivity of membranes made by immersion in isopropanol.

The order of solubility parameters of the polymers (including LSMM) under study is as follows: LSMM (10.0) < PEI (11.5) < PSf (12.6) < PI (14.7).

On the other hand, the order of solubility parameter differences between isopropanol as nonsolvent (N) and the polymers (P) (including LSMM) is as follows: PI/IPA (3.1) > LSMM/IPA (1.6) > PSf/IPA (1.0) > PEI/IPA (0.1).

Applying the aforementioned rule that a pair of P/N with similar solubility parameters results in a membrane of higher selectivity, α the selectivity of LSMM incorporated membranes should be lower than the control PSf and PEI membranes. The experimental data indeed confirm this prediction. It was also expected that the selectivity of PI membrane would improve by incorporating LSMM. However, the results indicated that it remained the same. This is another example, that the solubility parameter

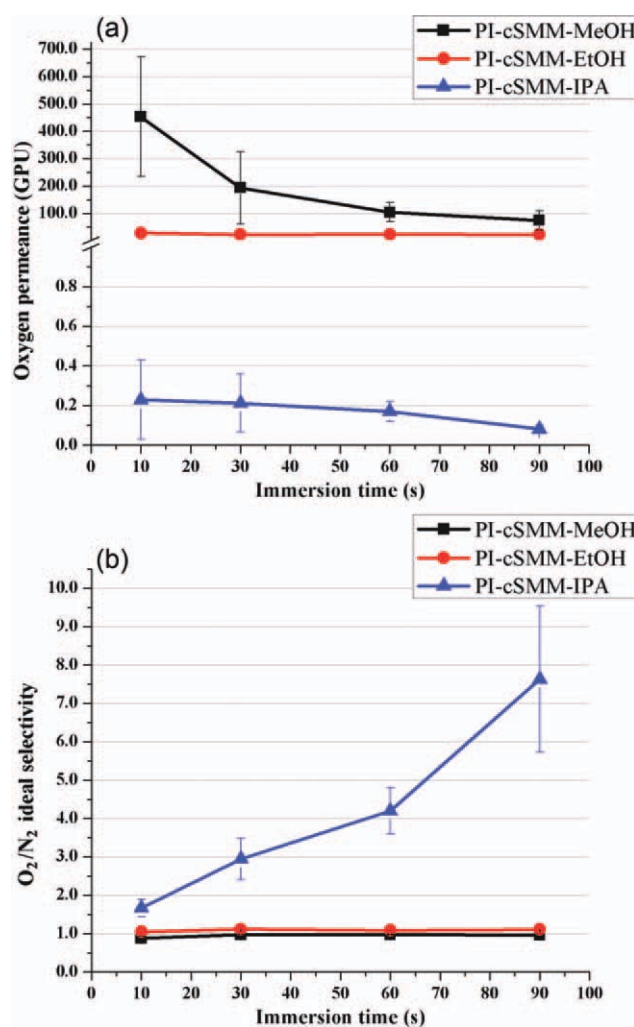


Figure 10 Oxygen permeance (a) and O₂/N₂ permeance ratio (b) of the PI membranes with cSMM blending immersing in methanol, ethanol, and isopropanol coagulation baths. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

alone cannot explain the trends observed in gas separation.

cSMM incorporated membranes

The experimental results for cSMM-incorporated membranes indicated that the selectivity improved only at longer immersion times in IPA. Since, the solubility parameters of cSMM and LSMM are comparable (10.7 and 10.0 (cal/cm^3)^{1/2}, respectively), and lower than any of the polymers, the observed tendencies cannot be explained by solubility parameter alone. It is postulated that the electric charge carried by the sulfonate ion of cSMM is also a substantial factor.

In an earlier work,²¹ it was postulated that formation of clusters of nonsolvent around the sulfonate ions leads to the formation of defective large pores. The same argument is applicable to the present study. That is, the sulfonate functional groups of cSMMs were solvated by NMP molecules before the cast film was immersed in isopropanol. These molecules formed large solvent clusters which eventually were transformed into pores. The solvation of electrolytes by NMP is highly possible due to the high dielectric constant of NMP (32.2 at 25°C). Hence, the selectivities of cSMM-incorporated membranes are low when the immersion time in isopropanol is short. As the immersion time becomes longer, S (NMP)/N (Isopropanol) exchange progresses. Because the dielectric constant of isopropanol (18.23 at 25°C) is considerably lower than that of NMP, the degree of solvation decreases, resulting in densification of SMM-covered interface. This phenomenon results in progressively increasing selectivity with immersion time. The repulsive force between negative charges of sulfonate ions decreases with a decrease in dielectric constant, which also contributes to the polymer densification. The densification effect is strongest for isopropanol among the alcohols used in the present study as nonsolvent and follows the order in their dielectric constants (all values at 25°C): methanol (33.4) > ethanol (24.3) > isopropanol (18.23).

In the present study, immersion times beyond 90 s were not investigated, but it would be beneficial to

find a maximum immersion time beyond which, the effect reverses.

CONCLUSIONS

1. An integrally skin asymmetric membrane can be made by wet-wet phase inversion process by immersing the cast polymer film into different alcohols as the first coagulant followed by immersion in water as the second coagulant.
2. Among methanol, ethanol, and isopropanol, only isopropanol leads to the formation of membranes with acceptable selectivities between oxygen and nitrogen.
3. A minimum immersion time in isopropanol required for the formation of selective control membranes was found to be 30 s.
4. Incorporation of cSMM was found to enhance the selectivity of the membranes when they were immersed in isopropanol. The ideal selectivity of the membranes was found to increase with immersion time up to 90 s.

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APPENDIX: CALCULATION OF SOLUBILITY PARAMETERS

The solubility parameter can be calculated by applying additivity rules to the structural components of the repeat unit of the macromolecule and to those of the solvent molecule, by the following equation²²:

$$\delta_{\text{sp}} = \sqrt{\frac{\sum E_{\text{coh}}}{\sum V}} \quad (\text{A1})$$

where δ_{sp} is solubility parameter, (cal/cm^3)^{1/2}, E_{coh} is heat of vaporization, cal/mol , V is molar volume, cm^3/mol .

TABLE AI
Solubility Parameter Calculation of LSMM

Structural component	OH	—C ₆ H ₄ —	—NHCOO—	—CH ₂ —	—O—	—CH ₃	>CH—
No. of repeating units	2	2*24.59+ 2*12.29	1*24.59+ 1*12.29	2*13.23+1+1*7.02* 24.59+1*24.59+2*13.23* 12.99+1*12.29+2*13.23	(7.02-1)*24.59+ (13.23-1)*12.29	1*7.02*24.59	1*7.02*24.59
E_{coh} (cal/mol)	7120	7630	6300	1180	800	1125	820
V_i (cm ³ /mol)	10	52.4	18.5	16.1	3.8	33.5	-1

$$\delta_{\text{sp}}=10.01(\text{cal}/\text{cm}^3)^{1/2}.$$

TABLE AII
Solubility Parameter Calculation of cSMM

Structural component	OH	SO ₂	—C ₆ H ₄ —	—NHCOO—	—CH ₂ —	—O—	—CH ₃	>CH—
No. of repeating units	2	2	4+2*8.99	2+2*8.99	1+1*7.02*8.99+8.99	(7.02-1)*8.99	1*7.02*8.99	1*7.02*8.99
E_{coh_i} (cal/mol)	7120	9350	7630	6300	1180	800	1125	820
V_i (cm ³ /mol)	10	23.6	52.4	18.5	16.1	3.8	33.5	-1

$$\delta_{sp}=10.74 \text{ (cal/cm}^3\text{)}^{1/2}.$$

On the basis of aforementioned equation the numerical values assigned to each structural component of each SMM are summarized below. It should be mentioned that the solubility parameters of nonsolvents and base polymer used were obtained from aforementioned reference.

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