Tuning Substructure and Properties of Supported Asymmetric Triblock Terpolymer Membranes

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Abstract

Asymmetric poly(isoprene-*b*-styrene-*b*-4-vinylpyridine) (ISV) block copolymer membranes fabricated via self-assembly and non-solvent induced phase separation (SNIPS) process have drawn significant attention due to the simple processing method and the generation of high-quality isoporous ultrafiltration membranes. With the present study on SNIPS membrane substructure, we systematically varied membrane casting parameters to tune the cross-sectional morphologies of SNIPS membranes while simultaneously preserving top surface structure. Parameters such as polymer concentration, evaporation time, solvent ratio, and coagulation bath temperature were investigated to control transformation of commonly produced sponge-like cross-sectional morphologies into more open and permeable finger-like substructures. Membranes with sponge-like and finger-like substructures were then integrated onto nylon supports for enhanced mechanical properties. Hydraulic permeability tests at various pH conditions gave distinct open-state flux values for SNIPS membranes with different sublayer

morphologies, while maintaining pH responsive functionality resulting from the poly(4-vinylpyridine) block.

1. Introduction

Polymeric membranes have widely been used in filtration fields because of their plentiful materials choices, robust mechanical properties, and compatibility with various fabrication techniques such as track-etching, lithography, and solvent based methods.¹

Among these methods, membranes generated through non-solvent induced phase separation (NIPS) attract great interest due to the simple fabrication procedure and accessibility to a range of pore sizes under various casting conditions. The polymer, commonly a homopolymer (e.g. polysulfone²), is dissolved into a good solvent, casted on a substrate and immersed into a coagulation bath. As phase inversion occurs with the exchange of solvent and non-solvent (coagulant), membranes are formed by precipitation of the polymer. One of the most useful properties of NIPS membranes is the ability to tailor pore size with casting solution compositions and membrane casting conditions.³ There are generally two types of cross-sectional membrane morphologies obtained through varying system conditions: 1) dense, sponge-like and 2) open, finger-like structures. Sponge-like and finger-like membranes are used as reverse osmosis and ultrafiltration membranes, respectively, due to their pore size distribution. Although widely used in industry, NIPS membranes are limited due to the trade-off between selectivity and permeability⁴. Membranes with a sponge-like cross section usually have low permeability but are more pressure resistant due to their dense structure. On the other hand, finger-like membranes have high permeability yet low selectivity with respect to solute rejection due to a wide pore size distribution.

Advancing the field from conventional NIPS membranes, Peinemann *et al.*⁵ first reported and demonstrated the fabrication of poly(styrene-*b*-4-vinylpyridine) (PS-*b*-P4VP or SV) diblock copolymer derived asymmetric membranes. Block copolymers are an attractive material for the fabrication of membranes due to their ability to self-assemble into well-ordered structures. PS-*b*-P4VP derived membranes were generated through a hybrid process of block copolymer self-assembly and NIPS (SNIPS)⁶. Membranes were prepared by 1) dissolving the polymer into an appropriate solvent system, 2) casting a thin film with a doctor blade, 3) solvent evaporation for a specified amount of time to allow block copolymer self assembly, and 4) immersion into a non-solvent (water) bath to induce precipitation of the polymer and kinetically trap the structure in a thermally non-equilibrium state. The resultant membranes were characterized by a disordered graded macroporous substructure beneath an ordered selective skin layer. Since then, Phillip *et al.*⁷ applied the hybrid SNIPS process to a triblock terpolymer, poly(isoprene-*b*-styrene-*b*-4-vinylpyridine) (PI-*b*-PS-*b*-P4VP or ISV) because of the inherent mechanical stability associated with the addition of the rubbery PI block. Membranes made from this triblock terpolymer had triple the toughness compared to its diblock counterpart.

The asymmetry of the SNIPS membranes eliminates the trade-off of permselectivity by enabling selectivity, attributed to the isoporous skin layer, and permeability, associated with the macroporous substructure. Numerous studies have been reported on the tunability of the isoporous self-assembled selective layer. Nunes *et al.* studied the effect of different solvent system compositions⁸, and metal-complexation^{9,10} on their PS-*b*-P4VP system. Pendergast *et al.*¹¹ investigated various parameters including varying polymer concentration, compositions of volatile to less volatile solvent mixtures, and evaporation times on their ISV polymer system.

Dorin *et al.* explored the effect of block copolymer molar mass¹² and the use of small angle x-ray scattering (SAXS)⁶ as a screening tool to predict the top surface structure.

In contrast to the past focus on the top separation layer, few studies report on the investigation of parameters controlling the substructure. Current literature details various block copolymer membrane systems with sponge-like^{5,7,12-15}, comblike¹⁵ and fingerlike^{15,16} morphologies. The current study focuses on the investigation of parameters affecting the substructure to enable its tunability which in turn controls membrane performance (i.e. permeability) without disrupting the self-assembly of the top surface selective layer.

To that end we systematically study several key factors in order to tune the substructure of ISV SNIPS membranes from sponge-like to finger-like. Parameters such as polymer concentration, evaporation time, solvent system, and coagulation bath temperature are shown to affect the substructure morphology. Tunability between sponge-like and finger-like substructures is achieved while preserving the isoporous skin layer responsible for membrane selectivity, regardless of substructure morphology. Hydraulic permeability tests at various pH conditions demonstrate the substructure's influence on permeability while leaving pH responsive behavior, associated with the P4VP block^{17,18}, unperturbed. Additionally, ISV membranes with both types of substructures are integrated onto nylon supports to further improve mechanical stability.

2. Experimental

2.1 Polymer synthesis

Four triblock terpolymers, poly(isoprene-*b*-styrene-*b*-4-vinylpyridine) (PI-*b*-PS-*b*-P4VP, ISV) were synthesized via sequential anionic polymerization as previously detailed by Phillip *et al.*⁷. ISV terpolymer characteristics were determined by a combination of gel permeation

chromatography (GPC) and ^1H NMR. The experimentally determined molar mass (M_n), volume fractions of each block (f) and polydispersity index (PDI) of each triblock terpolymer are listed in Table 1.

Table 1. Summary of ISV terpolymer characteristics.

Polymer	M_n (kg/mol)	f_{PI}	f_{PS}	f_{P4VP}	PDI
ISV115	115	0.26	0.62	0.12	1.16
ISV117	117	0.29	0.59	0.12	1.13
ISV118	118	0.23	0.66	0.11	1.12
ISV139	139	0.26	0.61	0.13	1.16

*Number average molar mass (M_n), volume fraction (f) and polydispersity index (PDI).

2.2 Membrane fabrication

ISV terpolymers were dissolved in a binary solvent system of 1,4-dioxane (DOX) and tetrahydrofuran (THF) in the appropriate ratios (by weight) and concentrations (see results and discussion section). Utilizing the SNIPS process to prepare membranes, the following steps were taken: 1) the casting solution was pipetted onto a substrate, 2) a thin film was casted with a doctor blade, 3) evaporation of the solvent system for a specified amount of time, and 4) immersion into a coagulation bath. The resultant membranes were dried at ambient conditions before further characterization.

2.3 Scanning Electron Microscopy (SEM)

ISV membranes were sputter coated with gold-palladium for 6-7 s prior to SEM imaging using a Denton Vacuum Desk II. SEM micrographs were acquired using a Tescan Mira3 field emission scanning electron microscope (FE-SEM)

2.4 Membrane performance tests

For permeability tests and to evaluate the pH-responsive nature of the ISV membranes, neat and supported membrane films were evaluated in a stirred cell (Amicon 8010, Millipore, Co.) with a volume of 10 mL with an active area of 4.1 cm². Three data points were averaged to estimate the permeability under varying pH conditions. pH buffers of sodium acetate and acetic acid were prepared for pH values ranging from 3 to 6. pH buffers of imidazole and hydrochloric acid were prepared for pH values ranging from 7 to 8. The buffer solutions were tested with a pH probe before conducting performance tests.

2.5 Viscosity tests

The rheological properties of all solutions were measured by a Discovery Hybrid Rheometer (DHR-3) with a 40 mm 2.0° cone plate configuration at room temperature.

2.6 Solubility parameters calculation

Hansen solubility parameters (δ_d , δ_p , δ_h) of water, DOX and THF were obtained from literature³. Equation (1) was used to calculate solubility parameters (δ_d , δ_p , δ_h) of solvent mixtures:

$$\delta_{i,S} = \frac{\sum_j (X_j V_j \delta_{i,j})}{\sum_j (X_j V_j)} \quad (1)$$

where X_j , V_j and $\delta_{i,j}$ denote the mole fraction, molar volume and solubility parameter of a specific component j in the mixture, respectively.

The solubility parameter difference (δ_{S-NS}) between solvent and non-solvent was calculated by

$$\delta_{S-NS} = \sqrt{[(\delta_{d,S} - \delta_{d,NS})^2 + (\delta_{p,S} - \delta_{p,NS})^2 + (\delta_{h,S} - \delta_{h,NS})^2]} \quad (2)$$

Both equations were obtained from the literature¹⁹.

3. Results and discussion

The formation mechanism of sponge-like and finger-like substructures in NIPS membranes has been extensively studied.^{3,19} One dominating theory in the field attributes the different substructures to the demixing rate. In this theory, upon plunging the thin film into a coagulation bath, the casting dope solution separates into two liquid phases, a polymer-rich phase and a polymer-poor phase, designated as liquid-liquid demixing. The substructure's pore sizes are largely determined by this demixing rate. If instantaneous demixing occurs, the polymer-rich phase precipitates quickly to form a solid membrane while the polymer-poor phase converts into large voids, resulting in an open, finger-like cross-sectional morphology. If demixing is delayed, polymer, solvent and non-solvent stay miscible in one phase before phase separation occurs causing a denser sponge-like structure in the final membrane. As the SNIPS process is a combination of self-assembly and NIPS, the formation mechanism of cross-sectional morphology deduced from NIPS membranes should be applicable to SNIPS membranes to tailor sublayer structure.

Among the many variables that influence the demixing rate, we investigated four parameters—casting solution concentration, evaporation time, solvent system, and coagulation bath temperature – to study their effects on the substructure of SNIPS membranes. These parameters are easily adjusted in the membrane fabrication process and include both kinetic and thermodynamic factors that influence the demixing rate.

3.1 Concentration and evaporation time dependence

ISV117 was dissolved in a solvent system of DOX/THF = 5/5 with varying polymer concentrations of 9 wt%, 10 wt% and 11 wt%. ISV117 membranes were prepared by the SNIPS process with evaporation times of 45 s and 60 s. SEM characterizations of ultrafiltration layers and cross sections are presented in Figure 1. With increasing solution concentration at a constant

evaporation time (45 s), the membrane cross section transformed from a dominantly finger-like substructure to a half finger-like, half sponge-like substructure. By increasing the evaporation time from 45 s to 60 s, membranes casted with varying concentrations all resulted in dense sponge-like substructures.

The transformation from finger-like to sponge-like morphology at higher concentrations, as well as longer evaporation times, as previously demonstrated, is due to delayed demixing.²⁰ With increasing concentration or evaporation time, the casting dope solution becomes more viscous before being plunged into the coagulation bath. This rheological hindrance reduces the solvent and non-solvent exchange rate, delaying liquid-liquid demixing, therefore resulting in denser sponge-like substructures.

In addition to the tunable sublayers, SEM images of the top surfaces of all six membranes showed similar mesopores with narrow pore size distributions (inset images in Figure 1, Figure S1 and S2 in supporting information). The ability to maintain the isoporous skin layer while changing the substructure promises high selectivity with tunable permeabilities but also distinguishes the ISV terpolymer system as a robust system for the fabrication of ultrafiltration membranes via SNIPS process.

Figure 1. Cross-sectional morphology evolution influenced by casting solution concentration and evaporation time. SEM images of cross sections and top surfaces (inset images) of SNIPS membranes cast from (a,d) 9 wt%, (b,e) 10 wt%, and (c,f) 11 wt% ISV117 solutions in DOX/THF = 5/5 at evaporation times of (a-c) 60 s and (d-f) 45 s.

3.2 Solvent system dependence

Typically in the SNIPS process, the solvent system used for the casting solution is a mixture of two or more solvent components. At least one solvent is volatile which aids in the formation of an isoporous skin layer derived from block copolymer self-assembly. Specifically for the ISV system, a mixture of DOX and THF are used. By adjusting the solvent ratio in the casting solutions, substructure morphologies can be tuned. ISV139 was dissolved in solvent systems of

DOX/THF in ratios of 5/5, 6/4, and 7/3 at the same polymer concentration (9 wt%). Under the same casting conditions (45 s of evaporation), membranes' cross-sectional structures changed significantly. The membrane casted from DOX/THF = 5/5 system exhibited a hierarchical cross-sectional morphology (Figure 2a). Pore sizes gradually increase from the membrane's top to bottom surface. By increasing the DOX/THF ratio to 6/4, a half sponge-like and half-finger-like substructure appeared (Figure 2b). In the membrane casted from DOX/THF = 7/3 system, the finger-like morphology ran through almost the entire substructure of the membrane as indicated in Figure 2c. The SEM characterization and analysis of the respective isoporous skin layers are shown in Figures S3 and S4 again demonstrating good control over pore size distribution.

Figure 2. Solvent system influence on cross-sectional morphology. SEM images of cross sections of SNIPS membranes cast from 9 wt% ISV139 solutions with (a) DOX/THF = 5/5, (b) DOX/THF = 6/4, and (c) DOX/THF = 7/3 solvent systems at evaporation time of (a-c) 45 s.

To understand the cause of this trend, viscosities of the three casting solutions were analyzed with a rheometer under a series of shear rates. Viscosity data are shown in Figure 3. The casting solution containing DOX/THF = 7/3 has the highest viscosity while the casting solution in DOX/THF = 5/5 is the least viscous. As mentioned above, more viscous solutions usually result in delayed demixing giving denser, sponge-like structures due to rheological hindrance. From the

opposite trend seen here, viscosity is not the leading factor in determining substructure morphology in this case.

Figure 3. Viscosity of ISV139 casting solutions with DOX/THF = 5/5 (black) DOX/THF = 6/4 (red) and DOX/THF = 7/3 (blue) solvent systems.

Solvent - Non-Solvent (S-NS) affinity is another important parameter that determines the demixing rate. Calculation of S-NS affinity is detailed in the Experimental Section. A low solubility parameter difference between S-NS (δ_{S-NS}) indicates a high S-NS affinity, which favors instantaneous demixing because of the fast solvent - non-solvent exchange. Vandezande *et al.*¹⁹ varied S-NS affinities by several approaches and observed cross section morphology changes. The variation of solvent mixture ratios could also result in different S-NS affinities. Therefore, we calculated δ_{S-NS} between water and various solvents including DOX, THF and their mixtures at ratios of 5/5, 6/4, and 7/3 (Table 2). The δ_{S-NS} values in Table 2 indicate that DOX has the highest affinity with water while THF has the lowest. In the mixture systems, δ_{S-NS} decreases with increasing DOX/THF ratio. Accordingly, the affinity between solvent and

coagulant has the trend of $7/3 > 6/4 > 5/5$. Therefore, DOX/THF = 7/3 system has the highest S-NS exchange rate (i.e. instantaneous demixing) resulting in a more finger-like structure.

Another possible contribution, also studied by Vandezande *et al.*,¹⁹ is the THF ratio in the co-solvent mixture. THF has a lower boiling point as compared to DOX and tends to evaporate faster than DOX. The preferential evaporation of THF creates a concentrated polymer barrier layer which slows down the (S-NS) exchange rate. Hence, with higher THF content (DOX/THF = 5/5), the membrane presents a denser cross-sectional substructure at equivalent evaporation times. To conclude, the observed substructure morphology evolution as a function of DOX/THF solvent ratio most likely is due to a synergistic effect of both S-NS affinity and preferential evaporation of THF.

Table 2. Hansen solubility parameters (δ_d , δ_p , δ_h) of solvents and non-solvents and solubility parameter differences (δ_{S-NS}) between solvent and non-solvent

	δ_d (MPa ^{1/2})	δ_p (MPa ^{1/2})	δ_h (MPa ^{1/2})	δ_{S-NS} (MPa ^{1/2})
H ₂ O	15.5	16	42.3	0
DOX	16.8	5.7	8	35.8
THF	19	10.2	3.7	39.2
DOX/THF 7/3	17.5	7.2	6.6	36.9
DOX/THF 6/4	17.8	7.7	6.1	37.2
DOX/THF 5/5	18.0	8.1	5.7	37.5

3.3 Coagulation bath temperature dependence

In addition to changing the concentration and evaporation time, coagulation bath temperature can kinetically influence the demixing rate. In Figure 4, SNIPS membranes cast from the same solution (7 wt% ISV139, DOX/THF = 5/5) and casting conditions (45 s) were plunged into coagulation baths at room temperature (~20 °C) and at 50 °C. SEM images show a clear

transformation from predominant sponge-like to predominant finger-like substructures as coagulation bath temperature increases. SEM characterization of the isoporous skin layers is shown in Figure S5. Previously, this behavior was also reported and explained in NIPS membrane systems.²¹ At high coagulation bath temperatures, the system kinetically favors instantaneous demixing which results in larger pore sizes and, in our case, the finger-like substructure.

Obvious transformations between sponge-like and finger-like substructures are only observed under certain casting conditions. Although, as shown in Figure S6, cross-sectional morphologies transformed to larger pore sizes with increasing bath temperature, this temperature increase cannot completely overcome the rheological hindrance due to the high concentration (9 wt%) and long evaporation time (55 s), and as a result, did not fully convert the membrane to a finger-like substructure.

Figure 4. SEM images of cross sections and bottom layer of SNIPS membranes cast from 7 wt% ISV 139 solutions in DOX/THF = 5/5 at an evaporation time of 45 s and immersed in a water coagulation bath at (a) room temperature resulting in a dense sponge-like substructure, and (b,c) 50°C resulting in an open finger-like cross section.

3.4 Membranes atop nylon support

For final use of block copolymer derived SNIPS membranes it is desirable to cast the material on supports that provide additional mechanical stability during handling and use. In the last part of this study we therefore wanted to find out whether control over sponge-like and finger-like substructures could be preserved when casting was performed in the presence of a support structure and finally how the support would influence permeability of the final assembly. To this end ISV115 and ISV118 polymer casting solutions were prepared by dissolving ISV terpolymer into a binary solvent system of DOX and THF in a 7/3 ratio (by weight). Neat and supported ISV115 membranes were cast from a 11 wt% polymer solution with an evaporation time of 30 s. Neat and supported ISV118 membranes were cast from a 11 wt% polymer solution with an evaporation time of 30s. A lower concentration neat ISV118 membrane was cast from a 9 wt% polymer solution and an evaporation time of 45s. Casting solutions were pipetted onto glass substrates to generate neat, unsupported membranes. For supported membranes, casting solutions were pipetted directly onto 0.1 or 0.2 μm nylon substrates (Sterlitech, Inc.) as it eliminates additional fabrication steps and is therefore preferred. The casting solutions were casted using a doctor blade with a height between 0.203 and 0.229 mm. The neat and supported thin films were allowed to evaporate for specified times before immersion into a coagulation bath.

The optimized casting conditions chosen for ISV115 and ISV118 membrane fabrication were based on polymer concentration, solvent ratio, and evaporation time parameters that yielded a uniform and porous top surface above the desired sponge-like or finger-like macroporous substructure. Molar mass of the ISV terpolymers is another parameter that controls substructure. An additional parameter, viscosity, was taken into consideration for the fabrication of supported ISV118 membranes as the increased viscosity of the casting solution impeded its infiltration through the nylon substrate while allowing the membrane to remain atop the nylon substrate.

Figure 5. SEM micrographs of top surfaces (top row) and cross sections (bottom row) of neat SNIPS membranes cast from (a,d) 11 wt% ISV115 at evaporation time of 30 s, membrane thickness $t \approx 26 \mu\text{m}$; (b,e) 11 wt% ISV118 at evaporation time of 30 s, $t \approx 55 \mu\text{m}$; and (c,f) 9 wt% ISV118 at evaporation time of 45s, $t \approx 48 \mu\text{m}$. In all cases DOX/THF = 7/3 was used as solvent system.

Furthermore, the trends discussed using results shown in Figure 1 for the ISV117 terpolymer are applicable to terpolymer ISV118. For example, the membrane derived from 9 wt% ISV118 with 45 s evaporation time has a finger-like substructure. By increasing the concentration (i.e. moving to 11 wt%) but lowering the evaporation time to 30s, the cross-sectional morphology stays finger-like, see Figure 5. Moreover, increasing the evaporation time to 45s for 11 wt% ISV118 leads to a transition to a sponge-like morphology (see supporting information, Figure S7), also in good agreement with results from Figure 1. While those trends are applicable over a

range of polymers, exact parameters, in particular the evaporation time, may be different for each specific terpolymer in order to tune for optimal finger-like versus sponge-like substructures as well as surface structure.

Casting under the aforementioned conditions for neat ISV115 and ISV118 resulted in ordered, isoporous membranes with a sponge-like and finger-like substructure, respectively, see SEM micrographs of top surfaces and cross sections depicted in Figure 5. Supported membranes were then fabricated by directly casting the ISV115 and ISV118 (both 11 wt%) thin films onto porous, nylon substrates. Figure 6a,d depicts the top surface and cross sectional image of a 0.2 μm nylon substrate with an internally inert polyester support. As demonstrated in Figure 6, the top surface, characterized by uniform pores and the respective sponge-like or finger-like cross sections were retained atop the nylon substrates. This demonstrates that membranes characterized by sponge-like and finger-like substructures can both be integrated with a support layer.

Figure 6. Membranes casted on nylon supports. SEM micrographs of top surfaces (top row) and cross sections (bottom row) of (a,d) 0.2 μm nylon support and SNIPS membranes cast from solutions in DOX/THF = 7/3 at evaporation time of 30s and concentrations of: (b, e) 11 wt% ISV115 on 0.2 μm nylon, and (c, f) 11 wt% ISV118 on 0.1 μm nylon. 0.1 and 0.2 μm nylon differ by average pore sizes and permeabilities (see supporting information, Figure S8 and S9).

Due to the pH-responsive nature of the P4VP block membrane performance was characterized by measuring the permeability at varying pH conditions^{7,9,10,14}. Permeability measurements were taken with a stirred cell on membranes with an applied N₂ gas pressure of 1-2 psi. Membrane compression is observed at higher pressures, with sponge-like substructures more pressure resistant than finger-like substructures (see supporting information Figure S10). From the results shown in Figure 7, it can be concluded that the pH-responsive nature of the ISV membranes adhered to a nylon support was preserved.

Figure 7. Performance of neat and supported ISV115 and ISV118 membranes under varying pH conditions.

As expected, in general membranes with a finger-like substructure have enhanced permeability as compared to membranes with sponge-like substructures. The difference in flux of neat membranes, see corresponding SEM micrographs in Figure 5 and permeabilities in Figure 7, is attributed to thickness and substructure differences. The 11 wt% ISV118 membrane is $\sim 10\text{ }\mu\text{m}$ thicker than a membrane from 9 wt% ISV118 resulting in lower permeability due to a longer path. The 11 wt% ISV115 (sponge-like) membrane has lower permeability relative to a membrane from 11 wt% ISV118 since sponge-like substructures (ISV115) provide more resistance to flow than finger-like channels (ISV118). However, it is important to look at the structural details of block copolymer derived SNIPS membranes casted on supports in order to fully understand the observed behavior. For example, adhering a ISV115 membrane with a sponge-like substructure to a nylon support resulted in a permeability reduction by a factor of 3.3 at neutral pH conditions. When analyzing SEMs of the cross-sectional structure of this membrane we observed the formation of a dense layer at the interface of the membrane and nylon support (see supporting information, Figures S11 and S12) not observed for the unsupported membrane and most likely responsible for this large permeability reduction. A smaller permeability reduction factor of 1.7 at similar pH conditions was found for supported finger-like ISV118 membranes. Despite the complexities of the SNIPS membrane system which are due to the multitude of parameters associated with the SNIPS process, these results suggest tunability of membrane performance as a consequence of specifics of the substructure even in the case that membrane supports are used during membrane fabrication.

4. Conclusion

In this work, we systematically demonstrated methods to tune the substructure of SNIPS membranes between sponge-like and finger-like morphologies while simultaneously leaving the

self-assembled and ordered top surface layer intact. The mechanism of substructure formation was shown to be determined by the demixing rate, which was influenced by kinetic parameters such as concentration, evaporation time, and coagulation bath temperature, as well as by thermodynamic parameters including solvent and non-solvent (S-NS) affinity. Asymmetric ISV membranes integrated with a porous nylon support for improved mechanical stability maintained isoporous ultrafiltration surface layers and simultaneously allowed control over sponge-like and finger-like substructures. Results suggest high tunability and robustness of asymmetric membrane structure for the ISV triblock terpolymer system which should enable fine tuning of structure to simultaneously maximize membrane selectivity and permeability.

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