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Effects of Shear Rate on Morphology and Gas Separation Performance as Asymetric Polysulfone Membranes

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Asymmetric polysulfone flat sheet membranes have been produced by a dry/wet casting technique. The membranes were produced at different shear rate. Gas permeation properties were examined using pure hydrogen and nitrogen as test gases. Infrared dichroism was detected in all samples, the extent being greater in the high shear membranes. This suggests that the polymer molecules become aligned under high shear. Gas separation tests showed that the higher shear membranes exhibited greater selectivity (H_2/N_2). Some of the membrane selectivities even surpass the intrinsic selectivity of the membrane polymer. Increasing shear rate during casting had decreased skin layer thickness and thus increased pressure-normalized flux. High-shear casting also enhances the molecular orientation in skin layer and, in turn, heighten selectivity of membrane. Therefore, correlation of rheological aspects with primary phase inversion parameters provides a potential platform to develop high performance asymmetric polysulfone membranes for gas separation.

Key words: asymmetric membranes, gas separation, rheology, molecular orientation, super-selective, polysulfone

INTRODUCTION

Research is ongoing to enhance the pressure-normalized flux and selectivity of asymmetric polymeric gas separation membranes. Previously research into membrane production focused on the nature of polymer precipitation (Pinnau and Koros, 1993; Termonia, 1995) allowing membrane to be produced with impressive gas separation performances (van't Hof et al., 1992; Pesek and Koros, 1993). To achieve this a thin and effectively undamaged active layer is required and a number of fabrication techniques, which control the conditions of phase inversion in various ways, have been employed (Pesek and Koros, 1993; Sharpe et al., 1999; Ismail et al., 1999).

Development of integrally skinned asymmetric membranes by Loeb and Sourirajan in 1960's was a major breakthrough in membrane technology (Paul and Yampol' skii, 1994). An integrally-skinned asymmetric membrane consists of a very thin and dense skin layer overlaying on a thick and highly porous sub-layer, which is normally formed by phase inversion process (Bungay, 1986; Wang and Minhas, 1991). Previously research into membrane formation has focused on the phase inversion process parameters, which generally influenced the general morphology of the membranes, such the skin layer thickness and surface porosity. These parameters eventually the determining factors for membrane separation performance. In addition to phase inversion, it has also been recognized that

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molecular orientation will affect membrane selectivity and that orientation can be brought about by altering the rheological conditions during fabrication. Shear during casting and spinning has been shown to affect the permeation performance of polyulfone membranes and this has attributed to molecular orientation in the active layer.

Molecular orientation in membranes can now be directly measured by spectroscopic techniques. Planed polarized infrared spectroscopy has been used recently to confirm the presence of shear rate induced molecular orientation in gas separation and reverse osmosis membranes. For polysulfone hollow fibers and flat sheet membranes, increased shear were reported to elevate membrane selectivity beyond the intrinsic value of the polymer.

Phase inversion usually involves casting a shear-thinning and viscoelastic solution during which shear is subjected prior to a rapid coagulation. Shear-thinning properties of polymer solution is often suggesting a progressive alignment of polymer molecules under shear in flow direction. As a result, shear-induced molecular orientation induces favorable effects on membrane properties (Ismail et al., 1997). During casting a shear thinning and viscoelastic solution, polymer molecules are maintained in an oriented (partially) conformation by castline deformation. After casting, polymer molecules would relax to some preferred state. However, they recover only a portion of their total deformation. The as-cast membrane is then going through forced-convective evaporation. Dry phase separation progresses instantaneously and limits conformational and configurational rearrangement especially in nascent skin region. Polymeric material has no chance of relaxing and therefore shear-induced molecular orientation will be frozen into nascent skin layer of membrane. As a result, the nascent skin layer with sufficiently rigid structures form a well-defined skin layer with enhanced molecular orientation Permeability and selectivity of membrane are found to increase with increasing shear; some selectivity even surpass the generally recognized intrinsic selectivity (Ismail and Yean, 2002).

Therefore, this study was carried out to investigate effects of casting shear rate on asymmetric polysulfone membrane structures and separation performances for hydrogen/nitrogen separation. In this paper, pneumatically controlled casting system has been used to generate greater shear, which overcome the limitation of the conventional casting knife.

Flat sheet membranes were cast at different shear rate using our newly developed pneumatically controlled casting system. This is done in an attempt to induce greater shear thus greater molecular orientation, which would in turn significantly alter the separation characteristics of the membranes. The molecular orientation within the membranes was examined by observing dichroism in the i.r. spectrum. The combined effect of phase inversion parameters and rheological conditions during membrane production is a unique approach in membrane research.

EXPERIMENTAL

Materials

The dope used in the current study consisted of polysulfone ((Udel-P1700, weight-average molecular weight 35 400)) supplied by Amoco Chemicals. The solvents used to prepare casting solutions were analytical grade of *N,N*-dimethylacetamide (DMAc), tetrahydrofuran (THF) and ethanol (EtOH) at appropriators specific composition, whereas tap water was used as the coagulation medium.

Membrance Casting

The asymmetric polysulfone membrane (casting solutions used in the current study consisted of 22wt.% PSF, 31.8wt.% DMAc, 31.8wt.% THF and 14.4wt.% EtOH) were produced by a dry/wet casting technique using pneumatically-controlled casting machine. The membranes were cast onto a glass plate at ambient temperature with a casting knife notch setting of 150mm. The membranes were cast at various casting speed and hence various shear rate ($152.4s^{-1}$ to $381s^{-1}$). An inert nitrogen gas stream was blown across the as-cast membrane surface for about 12s to induce forced-convective evaporation prior to immersion into an aqueous bath and remained there for 1 day. The membranes were then solvent-exchanged with methanol for about 2 hours before being finally air-dried for 1 day.

Gas Permeation

The pressure-normalized fluxes of the

membranes were measured by fixing a circular membrane sample (13.5cm^2) into a permeation cell. Pure hydrogen and nitrogen were used as test gases and the pressure-normalized flux measured at ambient temperature and at a pressure drop of 1 bar. Volumetric flowrates of permeate were measured by a soap bubble flow meter. Pressure-normalized flux and selectivity can be calculated by

$$\left(\frac{P}{l}\right)_i = \frac{Q_i}{A\Delta p} \qquad (1)$$

where A is the membrane surface area, Q is volumetric permeate flow rate and Dp is pressure difference.

Membrane selectivity, a, with respect to any two gases, i and j, is the ratio of pressure-normalized fluxes.

$$\alpha_{ij} = P_i / P_j = (P/l)_i / (P/l)_j \qquad (2)$$

Scanning Electron Microscopy (SEM)

Membrane samples were fractured cryogenically in liquid nitrogen and then deposited with gold in a sputter coater (Biorad Polaron Divison). After that, the samples were imaged and photographed by employing a scanning electron microscope (Philips SEMEDAX; XL40; PW6822/10) with potentials of 10 kV in achieving magnification ranging from 500x to 5000x.

Plane Polarized IR Spectroscopy

Plane polarized i.r. radiation has been recognized as a good probe of molecular orientation, because of the preferred orientation of specific functional groups can be determined. This technique can reveal anisotropy on the molecular level within the membrane sample. Pronounced infrared dichroism (the difference in absorption between parallel and perpendicular polarized light). The IR spectra were recorded on a Nicolet Magna-IR 560 spectrometer. Spectra of asymmetric membranes were obtained from samples about 5 cm^2. The samples were mounted at the sample position with the outer skin surface facing the infrared beam and were rotated according to the shear direction (either vertical or horizontal). Thus, linear dichroism spectra were obtained by straightforward subtraction of perpendicular-polarized spectrum from parallel-polarized spectrum.

RESULTS AND DISCUSSION

Effect of shear on membrane performance

In polarized reflection i.r. studies of the membranes, i.r. dichroism was detected in all samples, the extent being greater in the high shear membranes. These results can be related to the rheological properties of the casting solutions. Since the dope used is shear thinning and exhibited viscoelastic by virtue of Troutan Rations suggesting that the polymer molecules become more aligned at greater shear (Shilton et al., 1997; Ismail et al., 1999). According to experimental data shown in Table 1 and Figure 1, the critical shear rate was determined to be around 381.0s^{-1}. In region prior to the critical point, increasing shear rate enhance molecular orientation and free

Table 1. Permeability and selectivity of membrane with different shear rate

Shear Rate, $\dot{\gamma}$ (s^{-1})	Permeability, P/l (GPU)		Selectivity, $\alpha_{H2/N2}$
	H_2	N_2	
152.4	12.13	0.55	22.81
190.5	15.99	0.57	27.69
254.0	21.71	0.58	37.14
381.0	30.41	0.76	41.80
762.0	22.42	0.97	27.16

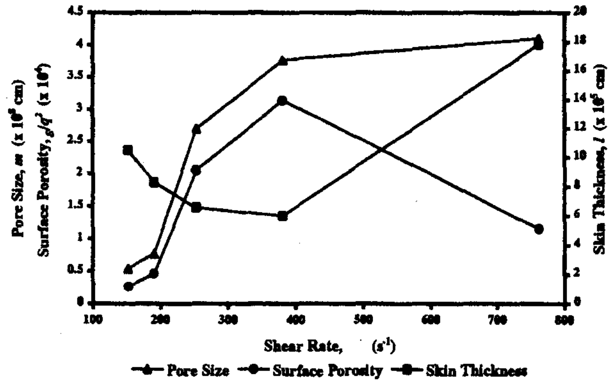


Figure 1. Apparent skin thickness, mean pore size and surface porosity of membrane with different shear rate

volume in skin layer and, in turn, improving selectivity of asymmetric membrane while maintaining sufficient permeability (Ismail et al., 1997; Shilton et al., 1994; Shilton et al., 1997).

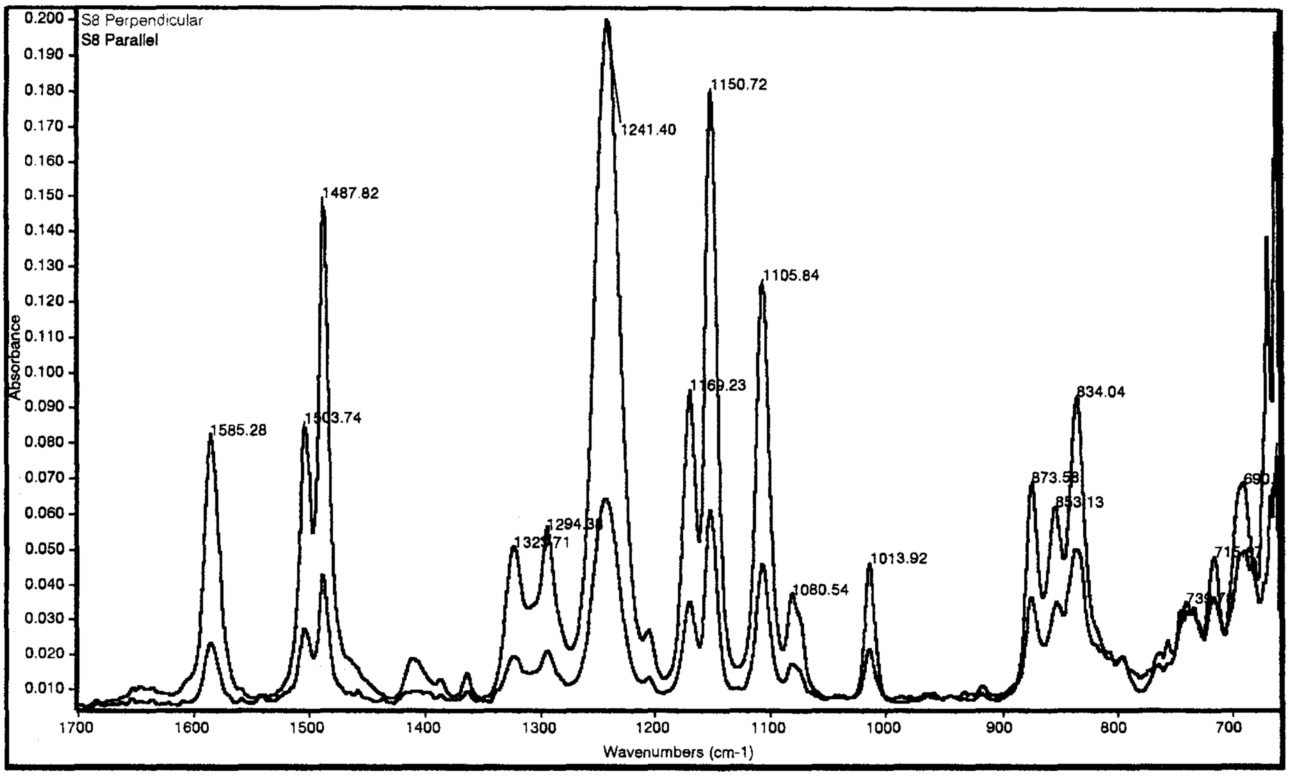
Since the solution used in this study was shear-thinning, when shear rate reached beyond the critical point, a severe decrease in solution viscosity occurred presumably due to chain entanglement losses in solution. In this case, membrane might undergo an early demixing and precipitation to result in a porous and highly oriented skin layer (Sharpe et al., 1999; Chung et al., 2000). Furthermore, casting membrane at an extremely high shear (over the critical shear rate) pulled molecular chains or phase-separated domains apart and began to create slight imperfections (defects) in skin layer (Sharpe et al., 1999). As shown in Figure 1, casting polysulfone membrane at the highest shear rate (762.0s^{-1}) caused an abrupt deterioration in selectivity of hydrogen/nitrogen and a disproportionately increase in pressure-normalized flux of nitrogen (slow gas). However, there was a decrease in pressure-normalized flux of hydrogen (fast gas) through polysulfone membrane cast at the highest shear rate (762.0s^{-1}), because shear-induced pore deformation had transformed big pores originally for Poiseuille flow to small pores suitable for Knudsen flow (Wang and Chung, 2001). Most of defective area in asymmetric membrane cast at the critical shear rate was occupied by pores for Knudsen flow. Thus, transmission of fast gas through membrane would be affected. Another possible explanation was based on substructure resistance, as proposed by Pinnau and Koros (Pinnau and Koros, 1991).

Molecular orientation, which is mechanically induced on asymmetric membrane by varying shear rate experienced during casting, can be directly measured using diffuse reflectance infrared Fourier transform spectroscopy. A preferential alignment of randomly coiled chain molecules in anisotropic sample leads to a difference in absorption of plane-polarized infrared spectra between parallel and perpendicular directions. This phenomenon is known as linear dichroism. As shown in Figure 2, polysulfone membranes produced by high-shear casting (762s^{-1}) showed a pronounced positive linear dichroism, indicating that polymer backbone aligned in shear direction. On contrary, polysulfone membranes produced by low-shear casting (152.4s^{-1}) were dichroic in opposite sense (Figure 3). Contrast distinctions between polysulfone membranes suggested that molecular orientation in skin layer was enhanced by increasing shear during casting, which had a favorable effect on membrane selectivity (Shilton et al., 1997).

Effect of shear on membrane MORPHOLOGY

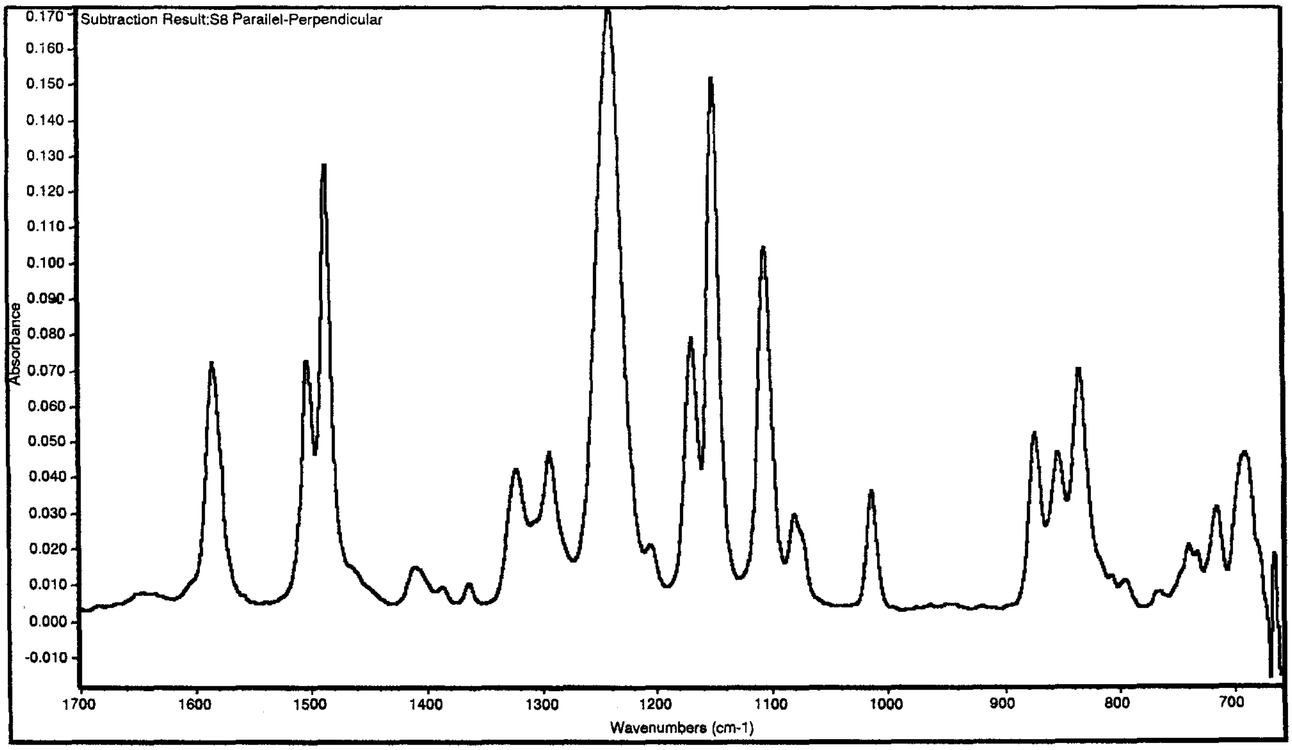
The electron micrographs of wall cross-sections of the membranes are shown in Figure 4. As depicted in Figure 4, polysulfone membranes developed in this study composed of an ultrathin, dense skin layer with a sponge-like porous substructure. As the shear rate increases during casting, there is a transformation from thick skin to thin skin. A relatively thick transition layer was observed in membrane at highest shear rate (762.0s^{-1}), resulting in relatively low membrane selectivity as shown in Table 1. At this point, we can observe that the effect of shear directly influences both membrane morphology as well as membrane performance.

In addition, there was not much difference between substructures of membrane cast with different shear rate; where uniform voids spread throughout membrane sublayer. As shown in Figure 5, no pores could be observed in membrane skin surface even at the highest magnification of scanning electron microscopy since pore size (within a few angstrom) of membrane skin layer is on borderline of equipment resolution.

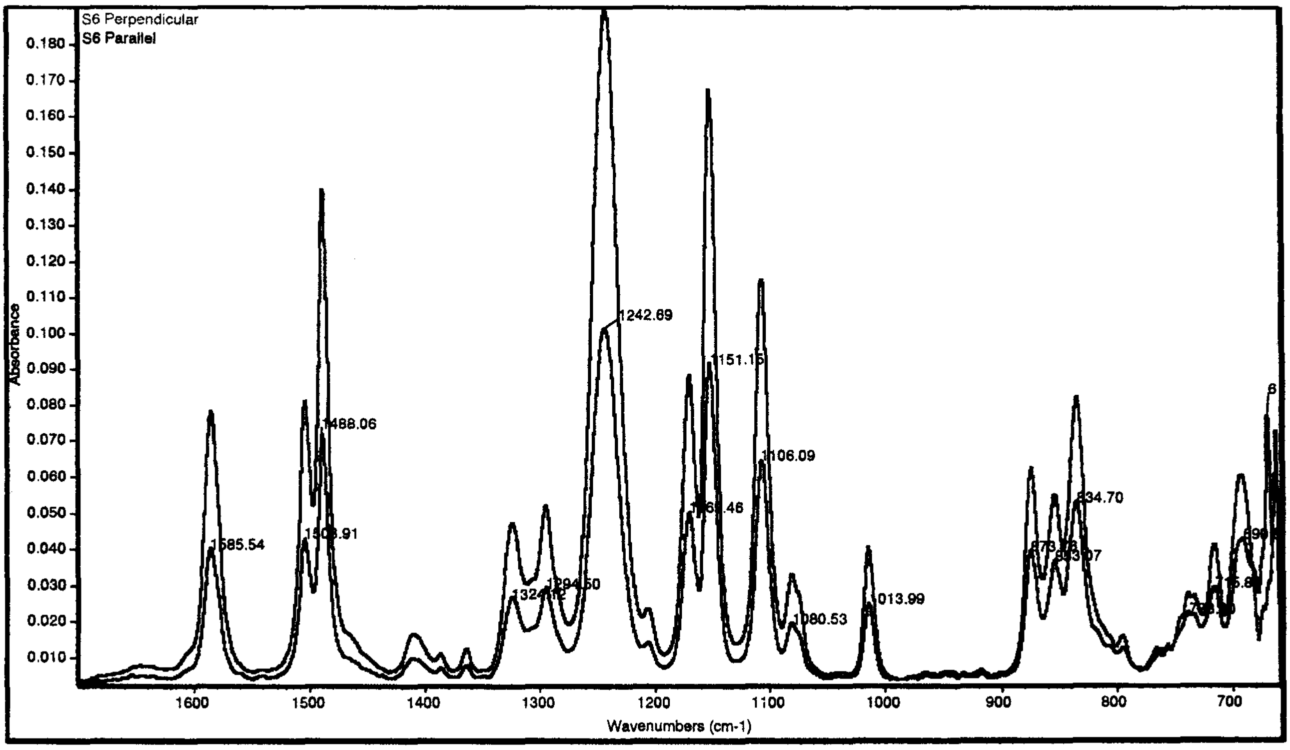


(a)

Figure 2: (a) Plane-polarized infrared spectra parallel (black line) and perpendicular (red line) to shear direction and (b) a linear dichroism spectrum for membrane cast at high shear (762.0s^{-1})

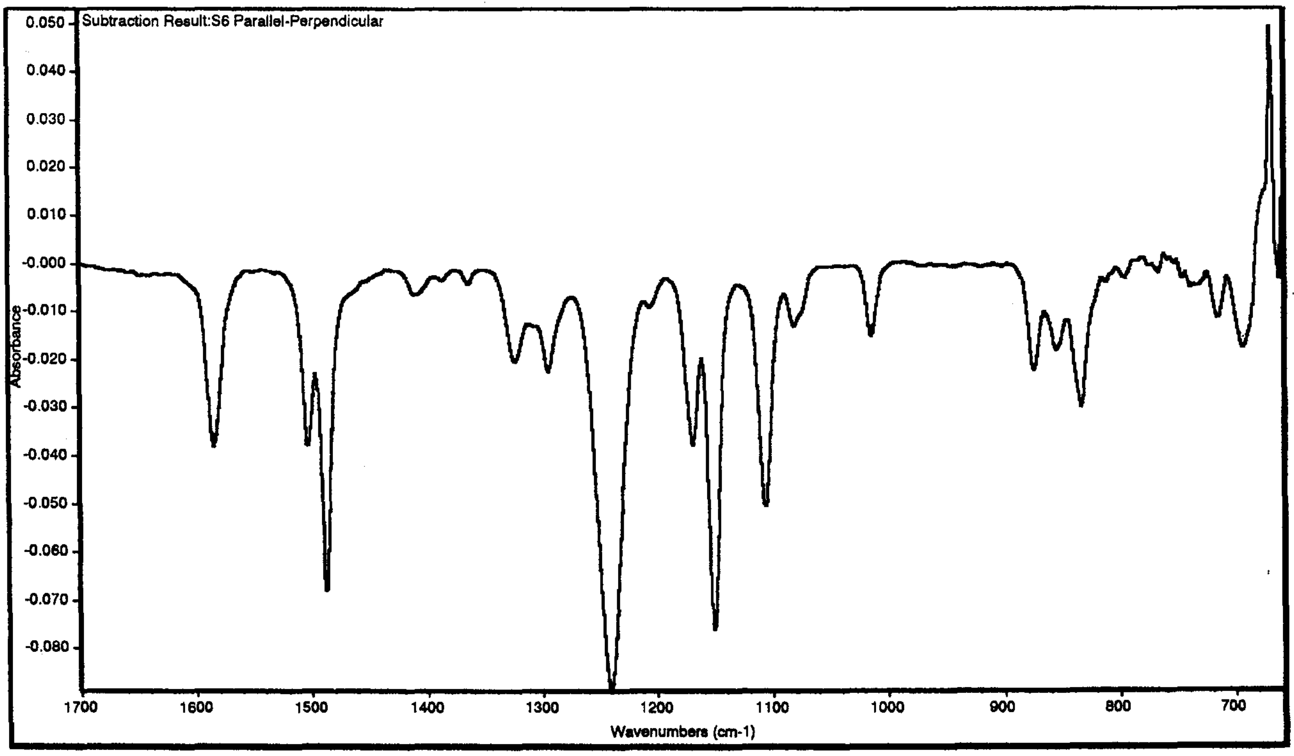


(b)

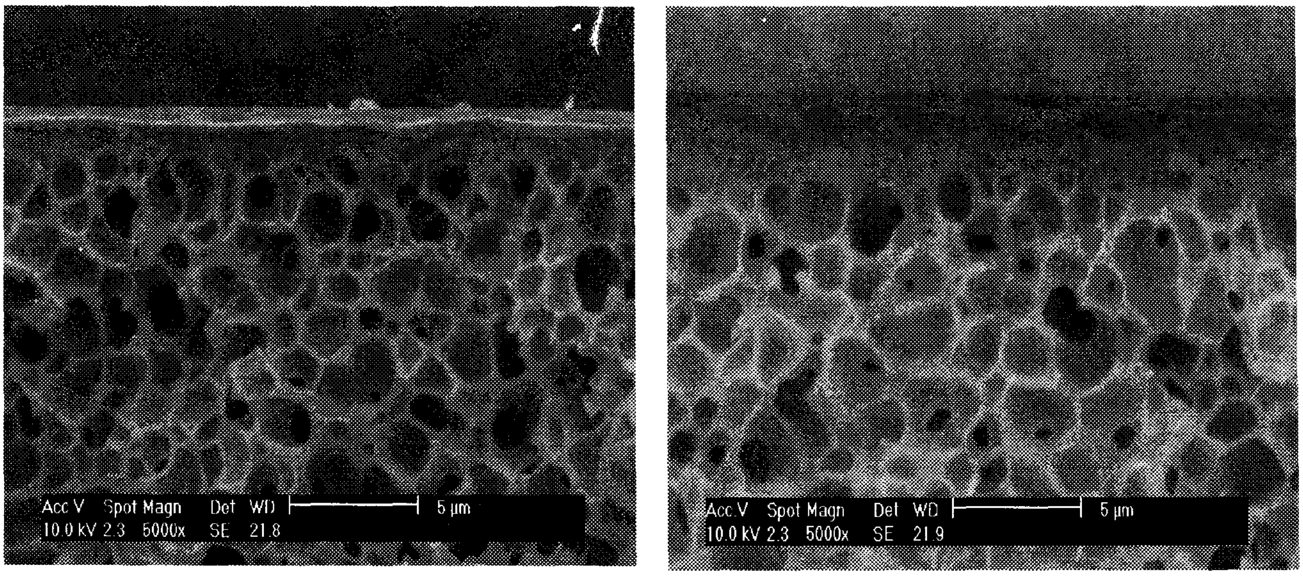


(a)

Figure 3: (a) Plane-polarized infrared spectra parallel (black line) and perpendicular (red line) to shear direction and (b) a linear dichroism spectrum for membrane cast at low shear (152.4s^{-1})



(b)



(a) *(b)*

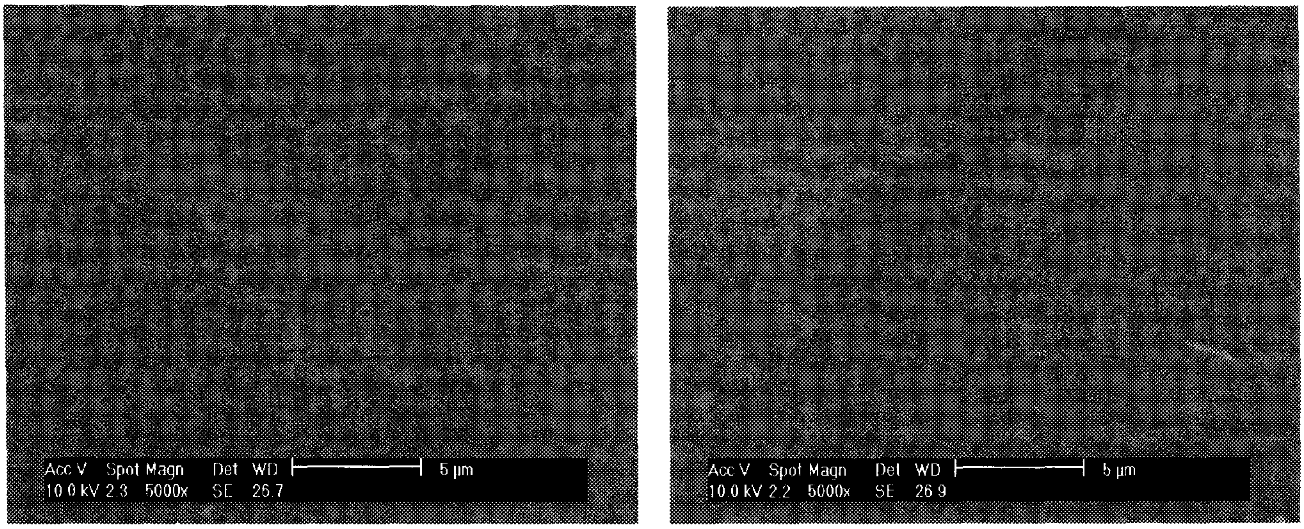
Figure 4: SEM of membrane cross-section (a: 152.4s^{-1}; b: 762.0s^{-1})

CONCLUSION

This study has indicated that the profound effects upon separation properties of asymmetric polysulfone membranes are mainly controlled by the variations in casting shear rate. Peressure-normalized fluxes of asymmetric polysulfone membrane were increased with increasing shear rate because of the reduction in skin layer thickness, while membrane selectivity were increased due to enhanced molecular orientation in skin layer. Therefore, the combine rheological conditions with the primary phase inversion parameters is proven to be the best approach in membrane research, if membrane selectivity is to be heightened beyond the recognized intrinsic value of the membrane polymer. Findings from this study can provide a potential platform to further develop high performance asymmetric membrane for gas separation.

NOMENCLATURE

A	Membrane effective surface area (m^2)
Q	Volumetric flow rate of gas i (m^3/s)
l	Membrane skin thickness (m)



(a) *(b)*

Figure 5: SEM of membrane surface at different shear rate (a: 152.4s^{-1}; b: 762.0s^{-1})

Δp	Pressure difference across membrane (Pa)
P_i	permeability coefficient for gas *i* (m^3(STP)•m/m^2•s•Pa)
$(P/l)_i$	Pressure-normalized flux or permeability for gas *i* (m^3(STP)/m^2•s•Pa)
a	Ideal separation factor or selectivity (unitless)

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