

Molecular orientation and the performance of synthetic polymeric membranes for gas separation

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Asymmetric polysulfone and polyacrylonitrile flat sheet membranes have been produced by a simple dry-wet casting technique. Both membrane types were cast at low and high shear rate. Molecular orientation in the membranes was determined using polarized reflection i.r. spectroscopy. Gas permeation properties were examined using carbon dioxide and methane as test gases. I.r. dichroism was detected in all samples, the extent being greater in the high shear membranes for both polysulfone and polyacrylonitrile. The effects, however, were more intense in the polyacrylonitrile samples. Gas permeation tests showed that for both polymer types, the high shear membranes exhibited greater selectivity (CO_2/CH_4). Selectivities were greater and permeabilities lower for the polysulfone samples. The results show (i) that polarized reflection i.r. spectroscopy can be used to determine—at least qualitatively—the degree of molecular orientation in sheared polymers, (ii) that molecular orientation is enhanced by shear during casting, and (iii) that this has a favourable effect on membrane selectivity. In the examples chosen molecular orientation was more pronounced in the polyacrylonitrile membranes, but with these the potential for high selectivity was thwarted by the poor intrinsic permeability of the polymer which causes flow through pores or imperfections to dominate. © 1997 Elsevier Science Ltd.

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INTRODUCTION

In order to improve fundamental knowledge of membrane manufacture and performance, the effect of spinning rheology on the permeation characteristics of gas separation hollow fibre membranes was studied¹: the rates of shear and elongation experienced during spinning were found to influence membrane permeability and selectivity. A further modelling study suggested that shear and elongation affect the selectivity of the solid polymer in the membrane by altering molecular orientation². In this paper, we seek to confirm these proposed rheological effects by using polarized reflection i.r. spectroscopy to determine molecular orientation in the active layer of the membrane.

Research into membrane production has focused on the nature of polymer precipitation^{3,4} allowing membranes to be produced with impressive gas separation characteristics^{5,6}. To further advance membrane technology, structural knowledge at the molecular level is now required.

Polarized transmission i.r. spectroscopy has been used previously to study molecular orientation in thin polymer films⁷, but transmission spectroscopy is applicable only if the polymer films are sufficiently transparent in the wavelength regions of interest. Reflection i.r. spectroscopy, on the other hand, has the advantage that it can be used to study the surface layers even of opaque films. Reflection i.r. spectroscopy has been employed as a means of characterizing polymer films, and these studies have included some work with polarized i.r.⁸.

Work has been carried out to investigate post formation drawing of polythene films and the effects on molecular orientation (measured by birefringence and X-ray diffraction) and gas permeation⁹. A study has also been made of polyimide outer layer deposition in composite gas separation membranes¹⁰: the authors used non-polarized i.r. spectroscopy to analyse the polyimide polymerization mechanism using various polyamic acid precursors. They then related chemical structure to the selectivity of the prepared membranes. Their study did not involve direct measurement of molecular orientation in the membrane. To the best of our knowledge, the correlation of molecular alignment with primary fabrication conditions and performance is a novel approach in membrane research. It is hoped that such fundamental knowledge will lead to the development of tailor-made membranes.

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Flat sheet membranes were cast at different shear rates in an attempt to induce molecular anisotropy which would in turn alter the separation characteristics of the membranes. The shear rates achieved were low and narrow in range because of limitations in the casting equipment. However, flat sheets were preferred to hollow fibres at this stage because their simple geometry allowed uncomplicated development of the spectroscopic techniques. The molecular orientation within the membranes was examined by observing dichroism in the i.r. spectrum.

EXPERIMENTAL

Polymers

Two polymers were used, polysulfone (Amoco Chemicals, Udel P1700, weight-average molecular weight 35 400) and polyacrylonitrile copolymer (Courtaulds, P82, a copolymer of acrylonitrile and methyl methacrylate containing approximately 15% methyl methacrylate, weight-average molecular weight 107 500). The solvent used to prepare the casting solutions was dimethylformamide.

Membrane casting

Asymmetric polysulfone (casting solution 20% w/w) and polyacrylonitrile (casting solution 15% w/w) flat sheet membranes were produced by a simple dry-wet casting technique. The membranes were cast onto a glass plate at room temperature using a mechanically controlled spreading knife with a notch height of 150 μm . Both membrane types were cast at low and high knife speeds and hence low and high shear rates. Once cast, the nascent membranes were immediately immersed in a pure water coagulation bath at 4°C for 10 min. The membranes were then air-dried for 1 day at room temperature before being finally dried under vacuum at 70°C for 2 h.

Membrane coating

The membrane sheets were coated with a highly permeable elastomeric silicone polymer (Sylgard 184, Dow Corning). The purpose of coating with silicone is to fill any surface pinholes or imperfections which render the membranes useless for gas separation. Blocking these cavities results in a decrease in permeability but improved selectivity. Coating is a standard procedure which allows the membrane to exhibit permeation properties closer to the inherent characteristics of the membrane polymer itself¹¹. The coating was applied by dipping the sheets into a 3% w/w solution of the silicone in hexane for 15 min. After coating, the membranes were placed in an oven at 60°C for 2 h to allow curing.

Polarized reflection i.r. spectroscopy

The i.r. spectra were recorded on a Bomem MB-100 Fourier transform i.r. spectrometer with a modified top plate. With this arrangement, the beam from the interferometer was focused at a point about 2.5 cm outside the instrument case and the detector was located so as to collect reflected radiation from a sample placed at or near this focus (Figure 1). Specular reflection could be avoided by having the sample plane at an angle of 2.5° or more with respect to the edge of spectrometer case, but this precaution was apparently unnecessary in our experiments. Interchangeable DTGS and MCT detectors

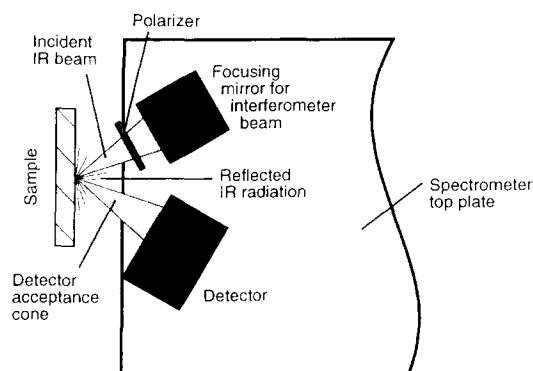


Figure 1 Top view of the modified top plate of the FT i.r. spectrometer, showing the locations of the sample and the polarizer

were available, but the results reported here were all obtained with the former and at a resolution of 4 cm^{-1} . The spectrometer was interfaced via a DSP-100 fast Fourier transform card to a Viglen 25 MHz 386SX computer with a co-processor. Spectra were acquired either with standard Bomem software or with Galactic Industries LabCalc. The use of this spectrometer to examine low-temperature matrices has been described previously¹².

The i.r. beam of the spectrometer was polarized with a SpecAc aluminium grid polarizer on a KRS-5 substrate held in a rotatable mount. The polarizer was located in the incident beam as shown in Figure 1, thus avoiding any optical components between the polarizer and sample. Spectra could be recorded with the plane of polarization at any angle to the vertical, but best results were obtained when this plane was maintained vertical and the sample itself was rotated. With this arrangement the *E*-vector of the polarized incident light remained parallel to the plane of the sample surface, and any component normal to this plane was minimized. Background spectra were recorded with a gold plated mirror located at the sample position. Experiments with the polarizer at various angles revealed that there was little or no intrinsic instrument polarization.

Spectra of polymer membranes were obtained from samples about 5 cm square. These were mounted vertically at the sample position (Figure 1) with the outer surface (i.e. the surface which had been in contact with the casting blade) facing the i.r. beam and the shear direction either vertical or horizontal. Thus for each sample, i.r. spectra were obtained with the plane of polarization parallel and perpendicular to the shear direction. It was estimated that the sample area was a spot of several mm in diameter, and precautions were taken to ensure that the same region of the membrane was sampled in each of the polarizations. In any case, consistent results were obtained in several determinations, both with different samples and with the same sample on different occasions, so there was no indication that inconsistent membrane thickness or other irregularities affected the recorded spectra.

Gas permeation

The gas permeability of the membranes was evaluated by fixing a sample into a permeation chamber, pressurizing one side and then measuring the resulting gas transmission rate. The test gases used were pure carbon dioxide and methane. The pressure difference across the

membrane modules in the tests was 1 bar. Permeability, P is given by

$$P = \frac{Q}{A\Delta p}$$

where A is membrane surface area, Q is flowrate and Δp is pressure difference.

Membrane selectivity, Ω , with respect to any two gases, i and j , is the ratio of permeabilities

$$\Omega_j^i = \frac{P_i}{P_j}$$

RESULTS AND DISCUSSION

Polarized i.r. spectroscopy

The general technique. Plane polarized i.r. radiation is a good probe of molecular orientation, because the preferred orientations of specific functional groups can be determined. Each molecular vibration has a transition moment, which, in the simplest and most common case of a non-degenerate vibration, is a vector with a particular direction in the molecule. Excitation of the vibration by absorption of radiation of appropriate frequency (i.r. radiation) will occur with a probability which depends on the angle between the molecular transition moment vector and the E -vector of the incident radiation. Specifically, if this angle is θ , the probability of absorption is directly proportional to $\cos^2 \theta$.

The theory of spectroscopy with plane polarized radiation has been thoroughly treated by Michl and Thulstrup¹³, but only a basic and qualitative grasp of the concepts is needed to appreciate the results reported in this paper. As an example, the CN stretching mode of a nitrile such as benzonitrile (PhCN), involves a periodic elongation and contraction of the CN bond, during which the electric dipole moment of the molecule changes. The dipole moment change occurs along the direction of the CN bond, and this defines the transition moment direction for this particular vibration. In a fluid medium such as liquid PhCN or a solution of the compound, the individual molecules are constantly tumbling, and at any instant in time molecules will be present in all possible spatial orientations. The sample will thus be isotropic, and absorption of i.r. radiation of the correct frequency to excite the CN stretch will occur equally with all polarizations. If the molecules are constrained, however, such as will occur in frozen solutions, it is possible to generate an anisotropic sample, in which an excess of molecules exist in one orientation. In this case, plane polarized i.r. radiation will be absorbed more strongly when the plane of polarization (and hence the E -vector) is parallel to the preferred orientation of the CN bonds. There will thus be a difference in absorption between parallel polarized and perpendicularly polarized radiation, a phenomenon known as *linear dichroism*. In the extreme case of a single crystal of a compound, all the molecules will be aligned in a single orientation or, at most, in a few orientations with fixed geometrical relationships. The observation of linear dichroism in the vibrational spectra of a sample is thus a clear indication of molecular alignment, and in favourable cases can be related to preferred directions of specific bonds in the molecules.

Most linear dichroism measurements are made with transmitted light, but the polymer membranes which we have studied were found to be almost completely opaque to i.r. radiation in the region of interest (4000–400 cm^{-1}). For that reason it was necessary to acquire polarized i.r. spectra by reflection, and an i.r. spectrometer was modified to that end, as shown in *Figure 1*. For reflection i.r. spectra of powder samples, the variation of background reflection with wavelength is dependent on particle size^{14,15}. It is a common procedure to record the reflection i.r. spectra of dilute samples (1–5%) mixed with a non-absorbing host such as KBr of known particle-size distribution. The pure host with a similar particle-size distribution can then be used to provide a reference spectrum, thus eliminating intensity variations due only to sample reflectivity. With neat samples, such as the membranes which we have studied, it is not possible to account for wavelength dependent reflectivity in this way. Differences in background reflectivity between spectra recorded with different polarizations can be expected, and were indeed observed (see below). Rather than apply baseline flattening functions or normalizations based on selected absorptions, we have opted to derive linear dichroism spectra by straightforward subtraction of one polarized spectrum from the other. The resulting linear dichroism spectra contain, therefore, a contribution from background reflectivity as well as sample absorption. Consequently, our conclusions concerning molecular orientation are based on relative intensity differences between i.r. absorptions in the linear dichroism spectra, and not on the absolute signs of the dichroism, which with weakly polarized bands is indeterminate.

Polyacrylonitrile co-polymer membranes. Reflection i.r. bands of a typical membrane formed from polyacrylonitrile co-polymer with methyl methacrylate are given in *Table 1*. The i.r. spectrum is comparatively simple. The polymer consists of a hydrocarbon backbone (CH and CH_2 groups) with pendant nitrile (CN) and ester (CO_2CH_3) groups and some residual alkene groups ($-\text{CH}=\text{CH}_2$). Band assignments which can be confidently made by reference to standard tabulations of i.r. data^{16,17} are also given in *Table 1*. *Figure 2* shows portions of plane polarized i.r. spectra of a similar membrane, formed under conditions of relatively high shear. The spectra are plotted as reflectance against wavenumber, where the reflectance is the logarithm of the intensity of reflection of the gold plated mirror used as a reference (R_0) divided by the intensity of reflection of the sample (R). It is clear that the background reflectance of the samples decreases towards lower wavenumbers and that this tendency is more pronounced when the i.r. beam is polarized perpendicularly to the shear direction. Similar wavelength dependent i.r. reflection has been noted previously for powder samples, and has been found to be very sensitive to particle size¹⁴. Despite this difference in background reflectance, it is clear that the membrane exhibits distinct linear dichroism in some of the i.r. bands, notably those at 2241 (νCN), 1728 (νCO) and 1450 cm^{-1} (δCH). The dichroism is seen very plainly in the difference spectrum (*Figure 2c*). The direction of the observed dichroism accords with expectations. The nitrile groups, for example, will be approximately perpendicular to the main polymer backbone when the polymer is elongated. Therefore, if a significant

Table 1 I.r. absorptions of a polyacrylonitrile co-polymer membrane in the 4000–400 cm⁻¹ region, obtained from reflection spectra^a

$\bar{\nu}/\text{cm}^{-1}$	Assignment	$\bar{\nu}/\text{cm}^{-1}$	Assignment
3629 <i>br, s</i>	H ₂ O	1228 <i>w</i>	
3546 <i>br, m</i>	H ₂ O	1207 <i>w</i>	
2937 <i>br, s</i>	Aliphatic $\nu\text{C-H}$	1172 <i>m</i>	$\nu\text{C-O}$ (methacrylate)
2870 <i>w</i>	Aliphatic $\nu\text{C-H}$	1110 <i>sh</i>	
2241 <i>vs</i>	$\nu\text{C}\equiv\text{N}$	1093 <i>w</i>	
1728 <i>vs</i>	$\nu\text{C=O}$ (methacrylate)	1068 <i>w</i>	
1664 <i>m</i>	$\nu\text{C=C}$	1041 <i>sh</i>	
1628 <i>w</i>		958 <i>vw</i>	
1450 <i>vs</i>	Aliphatic $\delta\text{C-H}$	834 <i>vw</i>	
1384 <i>sh</i>		762 <i>br, vw</i>	
1357 <i>m</i>		659 <i>vw</i>	
1272 <i>sh</i>		536 <i>br, w</i>	
1251 <i>w</i>			

^a Qualitative band shapes and intensities are given as *br* broad, *sh* shoulder, *vs* very strong, *s* strong, *m* medium, *w* weak, and *vw* very weak

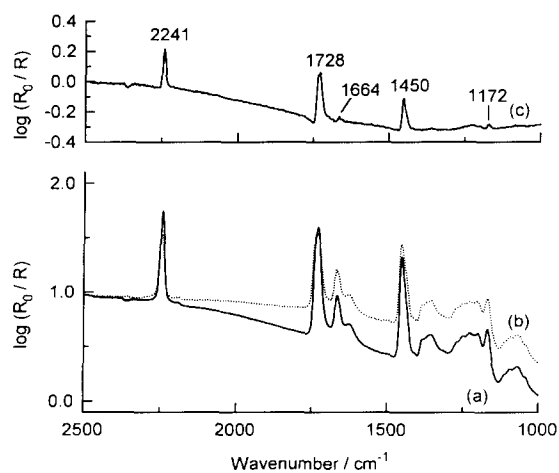


Figure 2 Polarized reflection i.r. spectra of a polyacrylonitrile co-polymer membrane formed under conditions of relatively high shear. The plane of polarization of the i.r. beam was perpendicular (a) (solid line) and parallel (b) (dotted line) to the shear direction. The difference spectrum (c) was obtained by subtracting spectrum (a) from spectrum (b)

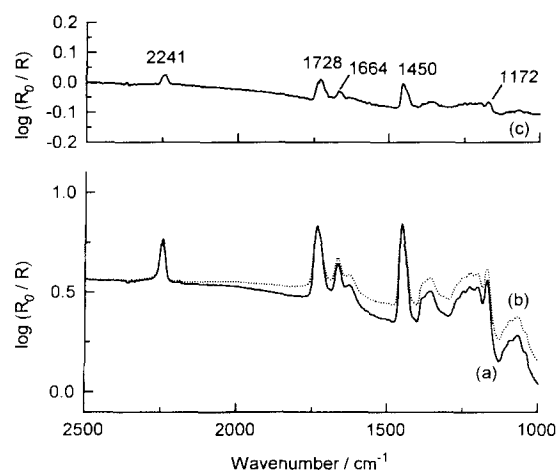


Figure 3 Polarized reflection i.r. spectra of a polyacrylonitrile co-polymer membrane formed under conditions of relatively low shear. The plane of polarization of the i.r. beam was perpendicular (a) (solid line) and parallel (b) (dotted line) to the shear direction. The difference spectrum (c) was obtained by subtracting spectrum (a) from spectrum (b)

level of molecular orientation is achieved during casting of the membrane, the nitrile groups would be expected to have a preferred orientation perpendicular to the shear direction. Thus the intensity of absorption of the nitrile stretching band (νCN) should be greater in polarization perpendicular to the shear direction than in polarization parallel to the shear direction. As *Figure 2* shows, this is indeed observed. Similar arguments can be adduced to account for the observed direction of dichroism of the carbonyl stretching band (νCO) and CH deformation band (δCH).

Figure 3 shows analogous polarized and difference i.r. spectra for a similar polyacrylonitrile co-polymer membrane cast under conditions of relatively low shear. Once again, background reflectance falls off towards lower wavenumbers as noted above. With this membrane, however, the linear dichroism is markedly less distinct. In particular, note the differences in relative intensities of the bands at 2241, 1728 and 1450 cm⁻¹ in the two difference spectra of the high shear membrane (*Figure 2c*) and the low shear membrane (*Figure 3c*). In the latter spectrum, the 2241 cm⁻¹ (νCN) band appears much lower in relative intensity, and all three bands have lower relative intensity when compared, for example, with those at 1664 and 1172 cm⁻¹. Thus the degree of linear

dichroism, especially that of the νCN band at 2241 cm⁻¹, provides the expected confirmation that a higher level of molecular orientation is achieved when the polymer membrane is cast with a higher rate of shear.

Polysulfone membranes. Reflection i.r. bands of a typical membrane formed from polysulfone are given in *Table 2*. Compared with the polyacrylonitrile co-polymer membrane, the i.r. spectrum is comparatively complicated, having many strong bands in the 'fingerprint' region of the spectrum below 1700 cm⁻¹. The polymer consists of a backbone made up of diaryl sulfone (Ar-SO₂-Ar) and diaryl ether (Ar-O-Ar) groups, and lacks easily recognized pendant functionalities. Band assignments made by reference to standard tabulations^{16,17} are given in the table. The strong absorptions due to the asymmetric (ν_{as}) and symmetric stretches (ν_s) of the sulfone group, are found at 1328 and 1157 cm⁻¹, respectively, as expected, but they lie close to other strong bands, and there will be considerable mixing of the various vibrational modes at these frequencies.

Figure 4 shows polarized reflection i.r. spectra and a difference spectrum for a polysulfone membrane cast under conditions of relatively high shear. Unlike the

Table 2 I.r. absorptions of a polysulfone membrane in the 4000–400 cm^{-1} region, obtained from reflection spectra^a

$\bar{\nu}/\text{cm}^{-1}$	Assignment	$\bar{\nu}/\text{cm}^{-1}$	Assignment
3656 <i>br, m</i>	H ₂ O	1259 <i>vs</i>	$\nu\text{C-O-C}$
3562 <i>br, w</i>	H ₂ O	1220 <i>m</i>	
3165 <i>vw</i>		1205 <i>w</i>	
3094 <i>w</i>		1174 <i>s</i>	
3066 <i>m</i>	Aromatic $\nu\text{C-H}$	1157 <i>s</i>	$\nu_s \text{SO}_2$
3035 <i>w</i>		1141 <i>sh</i>	
2970 <i>s</i>	Aliphatic $\nu\text{C-H}$	1112 <i>s</i>	
2933 <i>w</i>		1097 <i>sh</i>	
2910 <i>sh</i>		1080 <i>m</i>	
2871 <i>m</i>	Aliphatic $\nu\text{C-H}$	1014 <i>s</i>	
2594 <i>br, w</i>		961 <i>vw</i>	
2450 <i>br, w</i>		945 <i>vw</i>	
2410 <i>br, w</i>		918 <i>vw</i>	
2079 <i>vw</i>		977 <i>vs</i>	
2047 <i>w</i>		858 <i>s</i>	
1904 <i>m</i>	Ring combination band	838 <i>s</i>	
1776 <i>w</i>		796 <i>w</i>	
1726 <i>vw</i>		759 <i>sh</i>	
1677 <i>vs</i>		737 <i>m</i>	$\nu\text{C-S-C?}$
1593 <i>vs</i>	Aromatic $\nu\text{C=C}$	715 <i>s</i>	
1573 <i>sh</i>		695 <i>vs</i>	
1510 <i>vs</i>	Aromatic $\nu\text{C=C}$	660 <i>m</i>	
1492 <i>s</i>		636 <i>m</i>	
1477 <i>m</i>		603 <i>w</i>	
1409 <i>s</i>		572 <i>vs</i>	
1385 <i>m</i>		547 <i>w</i>	
1383 <i>m</i>		462 <i>vw</i>	
1328 <i>s</i>	$\nu_{\text{as}}\text{SO}_2$	426 <i>vw</i>	
1298 <i>s</i>		410 <i>vw</i>	
1284 <i>sh</i>			

^a Qualitative band shapes and intensities are given as *br* broad, *sh* shoulder, *vs* very strong, *s* strong, *m* medium, *w* weak, and *vw* very weak

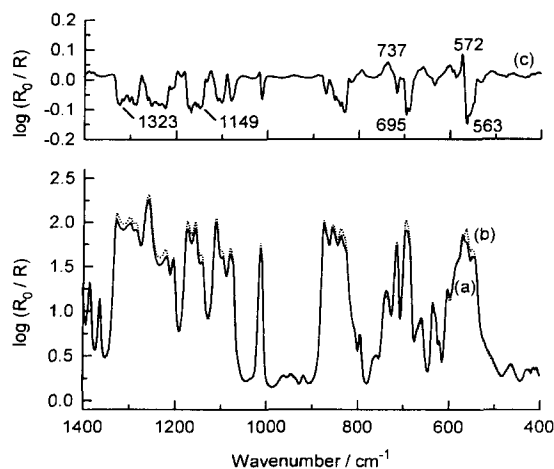


Figure 4 Polarized reflection i.r. spectra of a polysulfone membrane formed under conditions of relatively high shear. The plane of polarization of the i.r. beam was perpendicular (a) (solid line) and parallel (b) (dotted line) to the shear direction. The difference spectrum (c) was obtained by subtracting spectrum (a) from spectrum (b)

polyacrylonitrile membranes discussed above, this membrane exhibits little or no wavelength dependent variation in background reflectance, but the degree of linear dichroism is much less than was found for the polyacrylonitrile membranes. Nevertheless, as the difference spectrum shows (Figure 4c), detectable linear dichroism was observed, with some bands, e.g. those at 737 and 572 cm^{-1} , showing greater absorption with the polarization perpendicular to the shear direction, while most of the others were dichroic in the opposite sense.

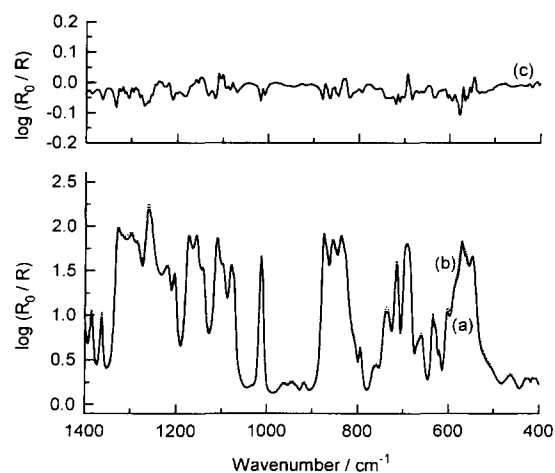


Figure 5 Polarized reflection i.r. spectra of a polysulfone membrane formed under conditions of relatively low shear. The plane of polarization of the i.r. beam was perpendicular (a) (solid line) and parallel (b) (dotted line) to the shear direction. The difference spectrum (c) was obtained by subtracting spectrum (a) from spectrum (b)

The complexity of the spectra precludes more detailed analysis.

Figure 5 shows analogous polarized and difference i.r. spectra for a similar polysulfone membrane cast under conditions of relatively low shear. Once again, background reflectance varies little with wavelength. As expected the linear dichroism is markedly less distinct than that shown in Figure 4. Indeed the two spectra recorded with polarizations perpendicular and parallel to the shear direction are virtually superimposable, and the difference spectrum (Figure 5c) contains only small irregular excursions above and below the zero line. Thus, although observed linear dichroism for the polysulfone membranes was much less distinct than that observed for the polyacrylonitrile membranes, a clear enhancement of molecular orientation during formation at higher shear rate was detectable.

Molecular orientation during casting

In our 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 for both polysulfone and polyacrylonitrile.

These results can be related to the rheological properties of the casting solutions. Both dopes were shear thinning¹ and exhibited viscoelasticity by virtue of Trouton Ratios¹⁸ suggesting that the polymer molecules become more aligned at greater shear. Coagulation is most rapid at the membrane surface, causing the dense active layer to form, and orientation may be 'frozen into' this region. The spectroscopic results do suggest this: the greater dichroism appears at higher shear.

The dichroic effects were more intense in the polyacrylonitrile membranes. This is not surprising since the polyacrylonitrile solutions have larger molecules, are more shear thinning and have superior viscoelasticity (exhibiting both creep relaxation and normal stress)¹ all of which suggest greater molecular alignment in these membranes. The observed direction of linear dichroism for the pendant nitrile groups accords fully with the expectation that shear will tend to align the polymer backbone in the shear direction, leaving the nitrile

Table 3 The effect of casting shear rate on the gas permeation properties of polysulfone and polyacrylonitrile flat sheet membranes

Shear rate (s ⁻¹)	Polysulfone		Polyacrylonitrile	
	356	436	632	889
Uncoated 10 ⁴ P _{CO₂} (cm ³ (STP) s ⁻¹ cm ⁻² cmHg ⁻¹)	0.2408 ± 0.0257	0.2169 ± 0.0062	–	–
Coated 10 ⁴ P _{CO₂} (cm ³ (STP) s ⁻¹ cm ⁻² cmHg ⁻¹)	0.1559 ± 0.0288	0.1673 ± 0.0344	8.736 ± 3.577	11.03 ± 3.410
Uncoated Ω _{CH₄} ^{CO₂}	2.53 ± 0.36	3.06 ± 0.13	–	–
Coated Ω _{CH₄} ^{CO₂}	3.95 ± 0.30	6.30 ± 0.66	1.82 ± 0.08	2.06 ± 0.05

groups with a preferred orientation perpendicular to this direction.

Gas permeation

The gas permeation results are shown in Table 3. The results show that for both polymer types, the high shear membranes exhibit greater selectivity (CO₂/CH₄). This can be attributed to the enhanced polymer molecule orientation at high shear. (The conditions of phase inversion were kept constant throughout and hence the general morphology of the membranes was fixed for both polymers.)

As would be expected, selectivities were greater for the polysulfone membranes. The extremely low intrinsic permeability of polyacrylonitrile¹ causes flow through minute surface pores to dominate in these membranes, even when they are coated with silicone. (Silicone penetration is insufficient to cause a significant rise in selectivity; the Knudsen diffusion through the remainder of the open pores remains dominant².) The uncoated polyacrylonitrile membranes were extremely permeable (values not quoted) suggesting a high porosity.

CONCLUSIONS

The results show that molecular orientation is enhanced by shear during casting and that this has a favourable effect on membrane selectivity. It was perhaps unfortunate that the molecular orientation seemed to be more pronounced in the polyacrylonitrile membranes where the potential for high selectivity was thwarted by the poor intrinsic permeability of the polymer. Nevertheless the utility of correlating molecular orientation, determined by polarization reflection i.r. spectroscopy, with membrane performance in gas separations has been demonstrated.

The results, although promising, should be viewed cautiously since the shear rates available in the flat sheet production were low and narrow in range. Further work

is under way to apply these techniques to hollow fibre membranes, where shear rates are far greater (10 000 s⁻¹) and the effects can be expected to be more marked. Improved phase inversion techniques will also be employed in the future to boost the general level of membrane selectivity⁶. The production of super-selective membranes with enhanced molecular orientation is pursued.

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