Investigation of a Liquid Crystal Dispersed in an Ionic Polymeric Membrane

J. A. Ratto,[†] S. Ristori,[‡] F. Volino,[§] and M. Pineri

Department de Recherche Fondamentale, SESAM/PCM Centre d'Etudes Nucleaires de Grenoble, 85X 38041 Grenoble Cedex, France

M. Thomas and M. Escoubes

Universite Claude Bernard, Lyon I 43 Bd du 11/11/1918, 69622 Villeurbanne Cedex, France

R. B. Blumstein*

Polymer Science Program, Department of Chemistry, University of Massachusetts Lowell, Lowell, Massachusetts 01854

Novel polymer/liquid crystal composite membranes consisting of a sulfonic perfluorinated ionomer, Nafion, and nematic liquid crystal (LC) 4-cyano-4′-n-hexylbiphenyl (6CB) are prepared by swelling methods. They contain from 0 to 35% (w/w) of 6CB and have a thickness of 150 μm. Membrane morphology, phase behavior of the LC component and its response to magnetic and electric fields are investigated by differential scanning calorimetry, scanning electron microscopy, and proton and fluorine nuclear magnetic resonance (NMR). The LC component appears as phase-separated droplets in the size range 0.2–0.6 μm. The nematic–isotropic transition temperature is the same as that of the bulk 6CB for high concentrations of 6CB and slightly less for low concentrations. NMR results indicate that 6CB and water (the latter found in the hydrophilic cluster regions) are located in different domains. Although the magnetic field (2.2 T) of the spectrometer fails to orient the LC component (suggesting strong anchoring of the nematic director on the droplet surface), nematic order parameter and director configuration within the LC droplets can be extracted from the NMR data. The order parameter of 6CB increases with the LC concentration and approaches that of bulk 6CB. Fluorine NMR suggests that the polymer matrix's mobility is not appreciably affected by the presence of the liquid crystal. Preliminary oxygen and nitrogen permeation experiments show extremely high flux rates in membranes containing from 28 to 35% 6CB. The permeation coefficient jumps by some 5 orders of magnitude at the crystal–nematic transition and retains this high value upon cooling and thermal cycling. However, no permselectivity is achieved, and further studies incorporating oxygen transporters are required.

Introduction

Composite membranes containing nematic liquid crystals (LC) have been first described in a series of papers published by Kajiyama and co-workers.[1–7] The LC component may undergo reversible phase transitions from crystal to nematic (K–N) or nematic to isotropic (N–I)

phase, thus allowing thermal control of permeation properties. Solvent cast membranes composed of polycarbonate (PC) and the nematic LC n-4-(ethoxybenzylidene)-4′-butylaniline (EBBA) or poly(vinyl chloride) (PVC) and nematic 4-cyano-4′-pentylbiphenyl (5CB) were investigated, among others.[3,4] For high-LC contents, the nematic component was found to form a co-continuous phase within a three-dimensional spongy network of polymer fibrils. The LC may therefore function as a low-viscosity diffusing or transferring phase for penetrants. Permeation coefficients (Pe) and permselectivity of oxygen to nitrogen were measured for a PVC/EBBA membrane containing 60 wt % EBBA as well as a ternary membrane incorporating perfluorotributylamine (PFTA) acting as an oxygen carrier. In both cases the value of Pe jumps by a factor of 20–30 in the vicinity of T_{K-N} and the permselectivity displays a maximum in this temperature range. Permselectivity is significantly enhanced upon addition of PFTA.[7]

Permeation properties of polymer–LC composite membranes may be further modulated, at least in principle, upon application of an external field which may macroscopically align the nematic component. Nematic liquid

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A Liquid Crystal

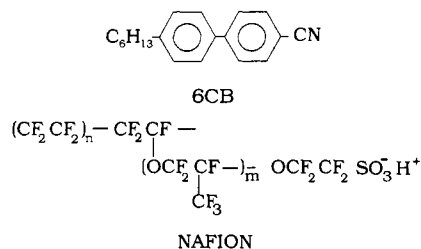*Chem. Mater., Vol. 5, No. 10, 1993* 1571

Figure 1. Structure of 6CB and Nafion.

crystals belonging to the cyanobiphenyl series are particularly suited for this type of study since the dipole moment of the cyano group lies along the long molecular axis. The local nematic directors, which are randomly oriented throughout the membrane in the quiescent state, may thus be preferentially aligned in the direction of an applied electric field. Permeation of a hydrocarbon gas was indeed increased depending on the magnitude of the applied voltage in a composite membrane of PC/5CB.[7]

There is no investigation to our knowledge of a composite membrane that combines an ionomer and a LC and we present here results from such a study. When LC droplets are confined to restricted space, as is the case in these composite membranes, their response to an external electric or magnetic field is determined by the interplay of factors such as droplet size and shape, strength of applied field, elastic deformation of the LC, and surface forces which all contribute to the director configuration within the droplet. In polymer-dispersed liquid-crystal (PDLC) systems developed for electrooptical applications, birefringent LC microdroplets dispersed in the polymer matrix are confined to cavities of micron or submicron size. The nematic droplet structures in PDLCs and their response to applied fields have been investigated by a number of authors.[8-14] The resulting models may be used for interpretation of our results, as discussed below.

We describe the novel system ionomer-nematic LC, composed of Nafion and 4-cyano-4'-n-hexylbiphenyl (6CB), hereafter called NAF6CB. The ionomer is a poly(tetrafluoroethylene) with sulfonic acid pendant groups bound to the perfluorinated backbone by fluoroether side chains (see Figure 1). Nafion was chosen for this study because of its exceptional chemical, thermal, mechanical, and transport properties.[15] Its morphology is characterized by microphase separation between the hydrophobic fluorocarbon matrix and hydrophilic ionic domains (clusters). The latter are approximately 5 nm in size and are connected by short channels of 1-nm diameter.[15] This cluster-channel structure offers good pathways for diffusion of gases or ions. When Nafion is swollen in water, the latter is confined to the structure of the clusters which percolate forming a continuous diffusive phase that may lead to permselectivity.[16] On the other hand, membranes swollen in organic solvents such as methanol or ethanol may

present two diffusion pathways, through the ionic clusters and through the solvent phase acting as a plasticizer for the hydrophobic matrix.[17,18]

In this paper, we present results on the methods for preparation of defect-free membranes, their morphology and response to magnetic and electric fields as well as thermal transitions and orientational order of the LC component. The data are based on scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and NMR experiments. Preliminary results on permeation by oxygen and nitrogen as a function of temperature to follow the gas flux in the solid, LC, and isotropic phases of the 6CB are reported.

Experimental Section

Materials and Sample Preparation. 4-Cyano-4'-n-hexylbiphenyl (6CB) was supplied by BDH Chemical Co. Ltd. and has the following transition temperatures (in °C): K–14.5–N–28.5–I. Nafion, with an equivalent weight of 1100 (0.741 mequiv/g of dry polymer), was supplied by the E. I. DuPont de Nemours Co. in the H+ form. The structures are found in Figure 1. The films were soaked in a boiling nitric acid/distilled water solution and then were dried for 12 h at 95 °C. The Nafion films were then swollen in dimethylformamide (DMF) at 130 °C and were immersed in solutions of 6CB/DMF for several minutes. The 6CB/DMF solution concentrations varied in order to obtain membranes with different amounts of 6CB ranging between 6 and 35% (w/w). The samples were placed in large volumes of a nonsolvent, water, where the membrane immediately turned white indicating that the 6CB had been precipitated. The membranes were dried for one hour at approximately 100 °C with hot air. The LC content in the membrane was determined by weighing the dry membranes before and after adding the LC. Elemental analysis was also used to confirm the amount of 6CB in the membrane.

All membranes had a thickness between 150 and 200 μm.

Methods. The permeation cell containing two compartments separated by the membrane was initially evacuated to desorb any gas molecules from the membrane. The following conditions were used for all experiments: a dynamic vacuum of 10^{-6} Torr, a static vacuum of 0.01 Torr/h, a membrane area of 13 cm², and a pressure of 3 bar. Experiments were performed with nitrogen and oxygen gases in the temperature range 0–40 °C. At each temperature, the membrane remained under vacuum in the cell for approximately 15 h until equilibrium was established.

The permeation coefficients were calculated from the slope of the time–pressure curve in the steady state obeyed by Ficks law.[19] Pe is calculated from the formula

$$Pe = \frac{dP_2}{dt}\frac{V}{A}\frac{22\,400}{R}\frac{l}{P_1 - P_2} \qquad (1)$$

where P_2 is the downstream pressure, P_1 is the upstream pressure, V is the volume downstream (cm³) in the constant volume compartment, A is the area of the membrane (cm²), R is the constant of a perfect gas (6323 cm³ cmHg/mol K), and l is the thickness of the membrane. The permeation coefficient, Pe, is expressed as cm³$_{gas}$ STP cm/cm² cmHg s. Permselectivity of oxygen to nitrogen was estimated by the following equation:

$$\alpha = Pe(O_2)/Pe(N_2) \qquad (2)$$

where α is the separation factor.

A Perkin-Elmer differential scanning calorimeter 2-C with a TADS-3600 Data Station was used to determine the transition

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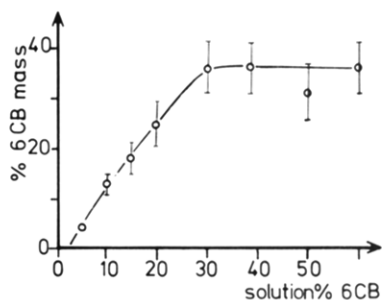
Figure 2. Concentration of 6CB in membranes vs concentration of 6CB in 6CB/DMF solution. The points represent average values from three to four measurements.

temperatures and enthalpies of the 6CB. Each sample (8–20 mg) was run under nitrogen atmosphere at a scanning rate of 10 °C/min in a temperature range of –40 to 100 °C. An indium sample was used for the temperature calibration.

Scanning electron microscopy (SEM) was performed to investigate the morphology of the surfaces and cross sectional areas of the membranes with a JEOL J5M 840A instrument. Samples were prepared by fracturing the samples in liquid nitrogen and coating them with gold.

Wide-line ^{1}H and ^{19}F NMR experiments were performed on Nafion, 6CB, and the composite membranes with varying compositions of 6CB as a function of temperature with a Bruker CXP 90 MHz spectrometer. The temperature was controlled with a VT B 1000 variable temperature accessory and a Rhaubus cooling unit with the temperature accuracy of ±0.5 °C. The samples were placed in NMR tubes as single rectangular strips (8 × 3 mm) positioned in a piece of teflon parallel and/or perpendicular to the magnetic field. The samples were first equilibrated for 20 min at 58 °C in the isotropic phase of 6CB and spectra were recorded upon cooling to 10 °C in steps of 1 or 2 °C. Several proton NMR experiments were performed in the isotropic phase at 34 °C. Spectra were obtained after drying the samples at 45 °C under vacuum and then after adding D_2O to the samples. ^{19}F NMR experiments were performed using a frequency of 84.8 MHz, an external standard of $CFCl_3$, and the same procedure as for ^{1}H NMR.

Magnetic and electric field experiments were performed simultaneously. An electric field was obtained throughout the entire strip of the membrane by coating it with gold and attaching copper wire to each end. The sample was then placed in the NMR tube and the wires were connected to a Variac. NMR spectra were recorded in the nematic phase at various voltages (25–250 V) with a maximum electric field of 500 V/cm.

Results and Discussion

Membranes have been prepared by solution and swelling methods, but only the latter are considered here (methods for reconstructing membranes from solution in DMF and for incorporating silver as a potential oxygen carrier are described in ref 20). The concentration of the 6CB in the membranes is a function of two factors: (1) the amount of swelling of the Nafion, which was dependent upon the temperature of DMF, and (2) the concentration of 6CB in the 6CB/DMF bath. The maximum swelling temperature is set at 130 °C to ensure that the LC will penetrate into the film while maintaining good mechanical properties of Nafion after the film is dried. Although highly concentrated solutions of 6CB/DMF were utilized for preparing membranes, Figure 2 shows that a maximum of 35% of 6CB (w/w) can be dispersed in the Nafion. Visual observations indicates that our preparation method con-
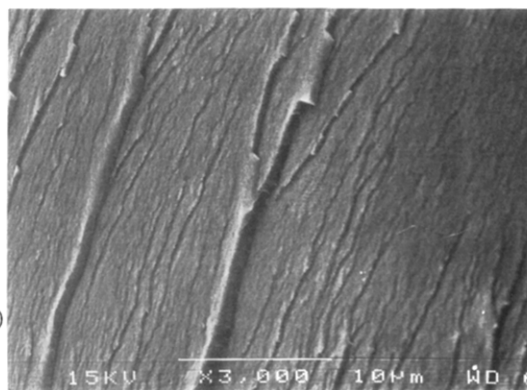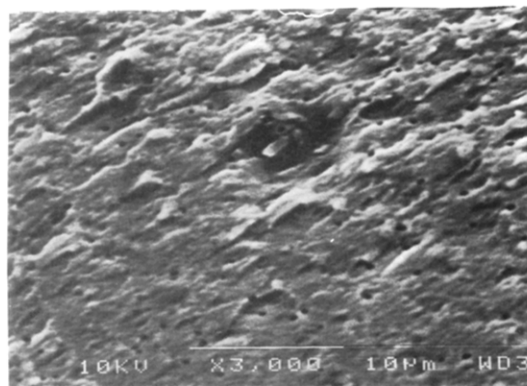
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Figure 3. SEM photograph of the (a) treated Nafion/H^{+} and (b) Nafion/H^{+}. Treated Nafion was swollen in DMF as described in the experimental section. Magnification: ×3000.

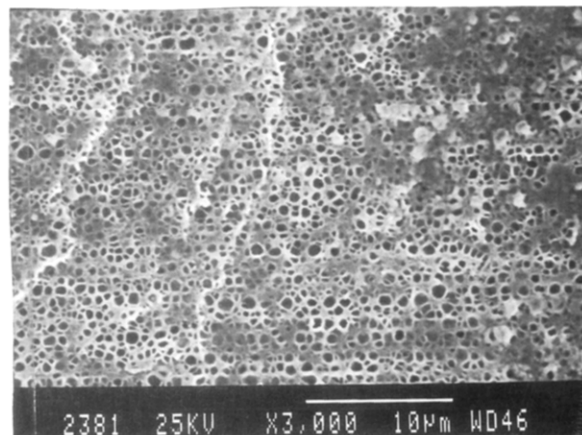**Figure 4.** SEM photograph of the NAF6CB28 membrane. Magnification: ×3000.

verts the transparent Nafion film into a white membrane after 6CB has been incorporated.

SEM photographs of untreated and treated Nafion are displayed in Figure 3. Untreated Nafion was used as received from du Pont, and the treated Nafion had been swollen in DMF, immersed in water, and dried. The untreated Nafion has a smooth surface, but the treated Nafion contains several pockets (0.5–0.6 μm). In a NAF6CB membrane, these pockets are filled with 6CB and additional 6CB microdroplets have formed as well. A SEM photograph of NAF6CB membranes containing 28% of 6CB is shown in Figure 4. In general, the size and number of droplets increase with 6CB concentration, but there is a scattered distribution of droplet diameters in the range of 0.2–0.6 μm. We speculate that 6CB may also be dispersed in smaller domains between the droplets. For concentrations of 6CB greater than 30%, there is some
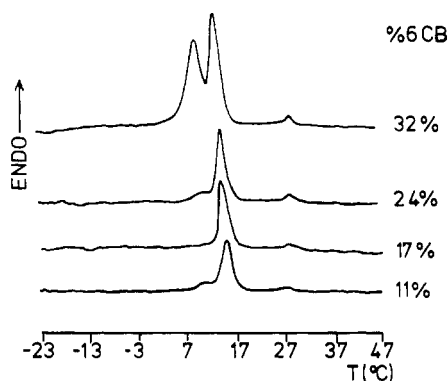
Figure 5. DSC heating scans of NAF6CB with varying concentrations of 6CB (32, 24, 17, 11%).
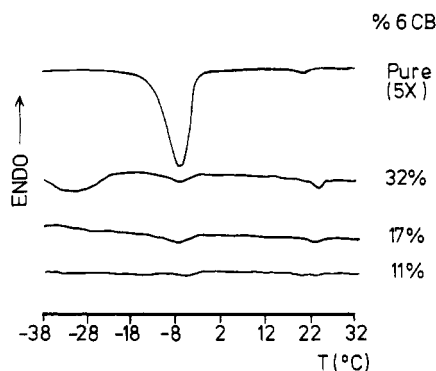

Figure 6. DSC cooling scans of pure 6CB and NAF6CB with varying concentrations of 6CB (32, 17, 11%).

difficulty to obtain a SEM as the 6CB sublimes under the beam and distorts the droplets.

The DSC scans upon heating and cooling of the pure 6CB and the composite membranes with 32, 24, 17, and 11% 6CB are shown in Figures 5 and 6. The Nafion has no thermal transitions in the temperature range used in these scans. No peaks corresponding to 6CB transitions were observed for concentrations below 11%, suggesting dispersion of 6CB into small scale domains. Upon heating, the T_{K-N} temperature transitions were independent of composition, and slightly lower than for pure 6CB. The T_{N-I} transitions decreased by 1–2 °C as the concentrations of 6CB were lowered and this trend is also observed by NMR experiments (see below). Upon cooling, again there is a slight decrease in the T_{I-N} transition and the T_{N-K} transition temperature is constant with 6CB composition.

The shapes of the DSC curves display an interesting behavior. There are crystallization peaks for the NAF6CB membranes that are not observed for the 6CB. For example, upon heating, there are two main peaks corresponding to the T_{K-N} transition, which suggests the presence of two different crystal domains. In addition, upon cooling, two crystallization peaks are observed for membranes containing more than 25% 6CB. While the values of ΔH_{N-I} vary linearly with 6CB concentration, crystallization appears to be strongly depressed upon dispersion of 6CB into the Nafion matrix. All results are reproducible for subsequent heating and cooling scans.

If a DSC scan is performed after the permeation experiment, the NAF6CB membrane temperature transitions do not change, although the first T_{K-N} peak may become enhanced in some cases. All enthalpy values drop by some 10%, suggesting a loss of 6CB during the permeation experiment.
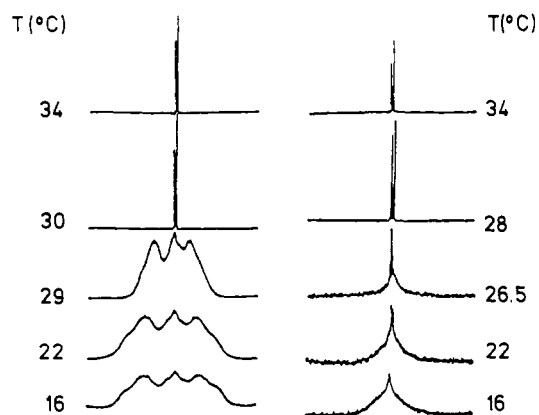

Figure 7. Typical proton NMR spectra of pure 6CB (left) and NAF6CB27 (right) as a function of temperature. Spectra are recorded on cooling. Full width 33 kHz.
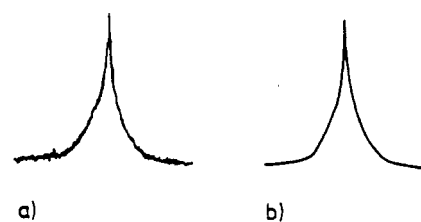

Figure 8. Proton NMR powder spectra of NAF6CB28 in the nematic phase: (a) experimental spectrum; (b) simulated spectrum.

Typical proton spectra of a pure 6CB and NAF6CB27 (27% 6CB) are shown in Figure 7 as a function of temperature. For the pure 6CB in the isotropic phase the spectra reduce to two sharp lines corresponding to the chemical shifts of the aliphatic and aromatic moieties. In the nematic phase we observe the broad spectra characteristic of a monodomain with a mean director aligned along the static magnetic field. The width is proportional to the uniaxial order parameter S_{zz}. The absolute value of the nematic order parameter was estimated from the main dipolar splitting using results for 5CB and 6CB described in refs 21 and 22. The data presented for the NAF6CB in Figure 7 are representative of all the membrane compositions. The I–N transition is characterized by a broadening of the line due to the nematic character of the phase but without macroscopic alignment. The general shape of the spectra is independent of the amount of 6CB in the membrane. From the spectra, it is observed that the T_{I-N} is exactly the same in the composite membrane as in the pure 6CB with concentraions of 6CB greater than 28% but decreases slightly for lower concentrations of 6CB, in agreement with DSC observations.

Figure 8 compares an experimental spectrum of NAF6CB28 in the nematic phase with a simulated "powder" spectrum of 6CB calculated from the monodomain spectra illustrated in Figure 7a. It is apparent that no macroscopic alignment is achieved within the membrane; the local monodomains within the individual droplets remain randomly oriented, as in the quiescent state. The value of S_{zz}, however, can be extracted from the spectrum as in the case of pure 6CB. Figure 9 illustrates the temperature dependence of the order parameter for pure 6CB and 6CB within representative membranes. The

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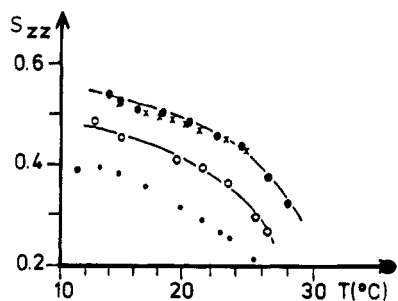
Figure 9. Temperature dependence of order parameter of 6CB and NAF6CB membranes. ●, PURE 6CB; ×, 33% 6CB; O, 26% 6CB; ·, 17% 6CB.
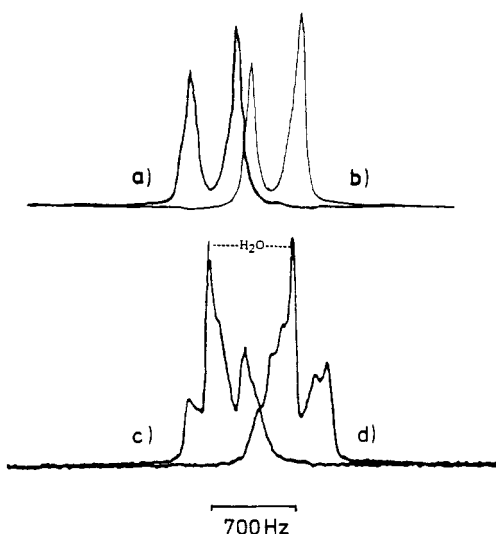

Figure 10. Proton NMR spectra in the isotropic phase at 34 °C (NAF6CB28). (a and b) "Dry" membrane (loosely bound water has been removed). (c and d) Membrane exposed to ambient humidity. Sample strip is perpendicular (a and c) or parallel (b and d) to magnetic field.

value of S_{zz} increases with increasing 6CB concentration within the membrane, approaching the value observed for bulk 6CB. Orientation of the 6CB molecules with respect to the droplet director is restricted by their interaction with the Nafion surface. Since the surface-to-volume ratio increases with the decreasing concentration of 6CB, the order parameter decreases concomitantly with droplet size.

The spectra changed depending on membrane orientation with respect to the magnetic field in both the isotropic and the nematic phase. Figure 10 illustrates spectra recorded in the isotropic phase at 34 °C. Figure 10a,b shows the spectra recorded in a dry membrane (28% 6CB) where only 6CB is visible by PMR; Figure 10c,d were recorded after exposing the membrane to ambient humidity and the spectra of water and 6CB are superposed. The sample strip is positioned either parallel (10a,c) or perpendicular(10b,d) to the magnetic field. For the dry membrane, we observe a line shift equal to 696 Hz upon changing the orientation of the membrane strip with respect to the field. For the membrane containing water a change in the lineshape of the water component is observed as well. From the shift of 696 Hz, the magnetic susceptibility χ of the composite membrane can be estimated:

$$\chi = -\Delta\nu/\nu \qquad (3)$$

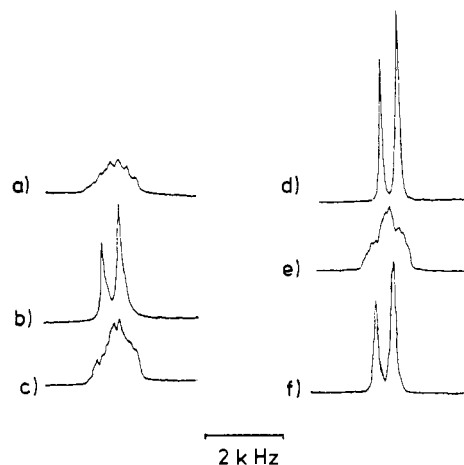This results holds because the membrane has a thickness that is very small compared to its other dimensions,

2 k Hz

Figure 11. Proton NMR spectra of NAF6CB30 at 34 °C. (a) Humid sample. (b) Dried at 50 °C under vacuum 15 h. (c) Sample 11b with D_2O added to NMR tube. (d) Sample 11c dried at 50 °C under vacuum for 15 h. (e) Sample 11d with D_2O. (f) Sample with D_2O after several weeks (following removal of bound H_2O0).

therefore making the demagnetizing field weak when the sample is parallel to the field and approximately the bulk value in the perpendicular direction. Thus, the molecules experience a diamagnetic anisotropy effect due to the macroscopic shape of the sample. The change in line shape observed for the spectrum of water suggests that water molecules experience an additional diamagnetic effect due to the shape and the size of the water domains (see below).

Figure 11a shows a representative proton spectrum of a membrane exposed to ambient humidity. We observe many superimposed absorptions over 1000 Hz, which implies that water is subjected to a large distribution of static local magnetic fields, due to its location in very small cavities that are anisotropic in shape. Figure 11b shows the proton spectrum of the same membrane following removal of loosely bound water by treatment of drying at 50 °C under vacuum for 15 h. The spectrum of 6CB, which could not be distinguished in Figure 11a, is clearly visible. Figure 11c displays the proton spectrum following immersion of the sample shown in Figure 11b in D_2O for several hours. A distribution similar to that of Figure 11a but somewhat narrower is observed, illustrating exchange between D_2O and the bound H_2O that had remained in the sample of Figure 11b (bound water line width is very broad and is not visible on the width scale of Figure 11). This process was repeated several times until there was a complete exchange of bound residual H_2O, at which point no further change in line shape was observed. Figure 11f shows that the spectrum of 6CB in the presence of D_2O is identical to that of 6CB in a dry membrane, proving that the 6CB does not experience the same static distribution of local magnetic fields as water and consequently is located in different domains. These domains are presumably much larger than that of water as illustrated on the SEM photographs.

Water in Nafion is probably located in very small domains that are approximately 10 Å in size.[23] Line-shape change with orientation of the membrane may reflect shape anisotropy of water domains and their nonuniform orientation within the membrane throughout the cluster–channel network. The 6CB domains, on the other hand,

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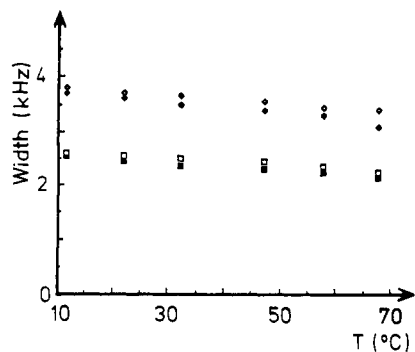(23) Volino, F.; Pineri, M.; Dianoux, A. J.; De Geyer, A. *J. Polym. Sci.: Phys. Ed.* **1982**, *20*, 482.

Figure 12. Fluorine NMR data for Nafion and NAF6CB26 membrane. Widths at half and quarter height vs temperature. ◆, NAF6CB $\Delta H_{1/4}$; ◇, Nafion $\Delta H_{1/4}$; ■, NAF6CB $\Delta H_{1/2}$; □, Nafion $\Delta H_{1/2}$.

do not show such anisotropy, possibly because they are located within relatively large quasispherical pools (as suggested by the SEM data).

Since 6CB could not be macroscopically oriented by the magnetic field, an electric field of 500 V/cm was applied parallel to the magnetic field in order to enhance alignment. This is approximately 10 times stronger than comonly applied in the case of PDLCs. No alignment was observed, although 6CB droplets in the Nafion membrane are of about the same size as in conventional PDLCs. This suggests that strong interactions between Nafion and 6CB anchor the nematic director on the droplet surface. The coherence length, which represents the distance over which the surface order penetrates into the droplet when the director is anchored onto the wall, appears to be equal to or larger than the droplet radius suggesting that surface effects are dominant in this system.

Moreover, from the line shape illustrated in Figures 7 and 8, one may speculate concerning the configuration of the nematic director within the droplets. The "powder" spectra of NAF6CB do not show any narrowing or orientational effects which suggests that director configuration may be bipolar; e.g., the molecules have parallel anchoring with respect to the surface of droplets (assuming that the self diffusion coefficient is not smaller than 10^{-12} m²/s).[24]

The results of ¹⁹F NMR of the Nafion and composite membranes are shown in Figure 12. The line widths at half and quarter height as a function of temperature for the Nafion and NAF6CB membrane are comparable. This demonstrates that the 6CB does not significantly increase the mobility of the host matrix.

Figure 13 illustrates the temperature dependence of Pe for two representative membranes containing 14 and 33% of 6CB. These composite membranes are designated as NAF6C14 and NAF6CB33. For Nafion itself, the value of the selectivity factor α is approximately 2 for all temperatures investigated (Table I); however, the treated swollen Nafion does not have any significant permselectivity. The value of Pe in NAF6CB14 is approximately 100 times higher than in Nafion and is roughly independent of temperature, with no discontinuity observed upon the K–N or N–I transition. This behavior is characteristic of membranes containing less than 28% 6CB. For 6CB concentrations in the range 28–35% behavior is as illustrated for NAF6CB33. Permeability below the T_{K-N} is about an order of magnitude lower than for NAF6CB14,
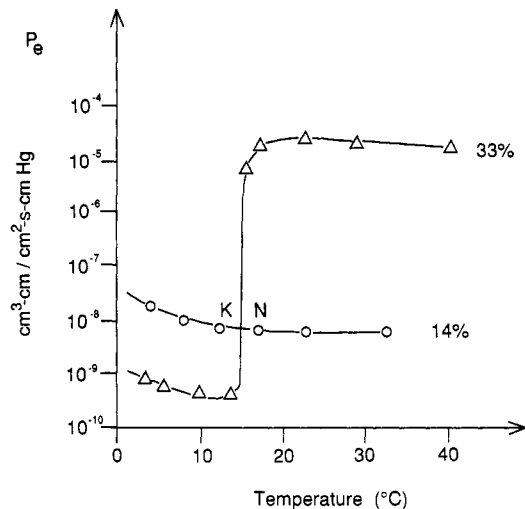

Figure 13. Pe vs temperature for NAF6CB membranes. O, 14% 6CB; Δ, 33% 6CB. Recorded on heating.

Table I. Comparison of Permeability Coefficients and Permselectivity ($Pe = cm^3\ cm/cm^2\ s\ cmHg$)[a]

membrane	$O_2 \times 10^{-10}$	$N_2 \times 10^{-10}$	α	temp (°C)	LC phase	ref
Nafion	8.8	4.3	2	30		20
Nafion/6CB						
33%	120 000	120 000	1	40	nematic	
14%	100	100	1	40	nematic	
PVC/EBBA	5.75	1.95	3	14	crystal	2
(60% EBBA)	51.9	20.6	2.5	75	nematic	2
PVC/EBBA/PTFA	10.2	2.00	5.1	14	crystal	2
	85.7	25.1	3.7	75	nematic	2

[a] EBBA = N-(4-ethoxybenzylidene)-4'-butylaniline. PFTA = perfluorotributylamine.

but there is a huge jump in permeability (approximately 5 orders of magnitude) at the T_{K-N}. No further increase in Pe is observed at the T_{N-I} temperature transition. This jump is much higher than observed by Kajiyama et al. at the T_{K-N} transition in PVC/EBBA membranes, as shown in Table I. Unfortunately, the NAF6CB membranes do not appear to display permselectivity with respect to oxygen, in contrast to PVC/EBBA membranes, for which a value of α equal to 2–3 was reported.[3]

An interesting observation is that the permeability coefficient for NAF6CB33 remains at this high value when the experiment is performed upon cooling. This irreversibility is still evident even after the sample has been quenched in liquid nitrogen and the permeation experiment is repeated. DSC enthalpy data for high 6CB containing membranes show that some 10% of LC is expelled after the initial permeation experiment. This expulsion of LC is also visible on the permeation cell. To ascertain that LC loss does not introduce pinhole defects within the membrane, we have measured hydraulic flux in a cell with a liquid phase on both faces of the membrane and a pressure gradient of several bars. The liquid water transport through the composite membrane is indeed very low and correlates with that of pure Nafion.[25]

Oxygen permeability coefficients in NAF6CB14 have approximately the same value as in water swollen acid Nafion and are about 6 times smaller than in Nafion swollen with ethanol.[18] The increased permeability of the membrane swollen in ethanol is attributed to a combi-

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(25) Thomas, M. Doctorate Thesis, University Claude Bernard, Lyon, France, 1989.

nation of two diffusion mechanisms, through the ionic clusters (as in the case of water) and through the organic phase (as a result of penetration of solvent into the polymer matrix).

During the prepartion of the composite membrane, some DMF swells the ionic domains until percolation occurs throughout the entire thickness, while the remaining DMF penetrates the polymer matrix. Upon exchange with water, DMF is expelled from the ionic domains and from the organic phase. The 6CB observed in the droplets precipitates upon expulsion of DMF from the polymer matrix. The relatively low permeability in NAF6CB14 may indicate lack of connectivity between the 6CB droplets, with permeation controlled by diffusion through the ionic cluster-channels pathway. This permeation mechanism would also explain why no discontinuity in the value of Pe is observed at T_{K-N} in NAF6CB14.

In the case of NAF6CB33, the 6CB expelled by the pressure gradient during the initial treatment of the membrane might form crystalline pockets which mask permeability below T_{K-N}. Above T_{K-N} permeation appears to be dominated by diffusion through the low-viscosity LC domains.

In summary, we have presented a study of phase behavior and morphology in a composite ionomer membrane containing LC droplets. Preliminary permeation experiments indicates that membranes containing between 28 and 35 wt % of 6CB display very high flux rates which are retained upon thermal cycling. Membranes containing two other cyanobiphenyls, 5CB and 7CB, have also been studied and found to display analogous permeation characteristics with a discontinuity at the T_{K-N} transitions. No selectivity between oxygen and nitrogen was observed. One should note that we have introduced silver as a potential transporter of oxygen into a membrane containing 28% 6CB without achieving significant improvement in permselectivity. Silver in Nafion has been shown to interact with the diffusive domains.[26] Results revealed

that the separation factor of oxygen to nitrogen permeability was more than 5 times higher than in pure Nafion at room temperature but decreased drastically with increasing temperature.[26] Our failure to achieve selectivity in the presence of silver added to NAF6CB28 may be understood by recalling that the dominant permeation mechanism in membranes containing between 28 and 35% 6CB appears to involve diffusion through the organic phase (6CB droplets), whereas silver is associated with the ionic diffusion pathways.

The swelling preparation method that we developed allows the 6CB as well as oxygen transporters soluble in 6CB to be easily incorporated into the Nafion, and further studies are in progress. From comparison of morphology for treated and untreated Nafion (SEM photographs in Figure 3) and loss of permselectivity upon treatment with DMF, we conclude that this preparation method changes the morphology of the Nafion and contributes to the permeation characteristics. As viewed from the SEM, the morphology of these membranes consisted of polydispersed domains and droplets of 6CB inside the NAF6CB.

Although NMR indicates that the magnetic field of the spectrometer does not orient the nematic phase inside the droplets, NMR has nonetheless been a powerful tool for this study. Nematic order and director configuration within the LC droplets were investigated. Water was found to be located in different domains than the 6CB, but it can ultimately influence the permeation characteristics of the membranes. The simulation of proton spectra illustrates that the nematic order parameter is smaller in the droplets than in the bulk phase at the same reduced temperature. Fluorine NMR experiments do not indicate any interactions of the Nafion and liquid crystal. All these results have provided some insight into the behavior of this type of novel composite membrane.

(26) Sakai, T.; Takenaka, H.; Torikai, E. *J. Membr. Sci.* **1987**, *31*, 227–234.