Study on the Spin Probe Added Polymeric Dense Membranes by ^{13}C Solid-State Nuclear Magnetic Resonance Spectroscopy

D. Rana, T. Matsuura, K. C. Khulbe, C. Feng

Industrial Membrane Research Institute, Department of Chemical Engineering, University of Ottawa, Ottawa, Ontario, K1N 6N5, Canada

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ABSTRACT: Dense cellulose acetate, CA, and poly(2,6-dimethyl-1,4-phenylene oxide), PPO, membranes were prepared with and without blending a spin probe, TEMPO free radical, and their ^{13}C solid-state cross-polarization magic angle spinning nuclear magnetic resonance, CPMAS NMR, spectra were taken. It was observed that there was no effect of blending TEMPO on the CPMAS NMR spectra of CA and PPO membranes. It was concluded that there was no chemical or physical interaction between the polymeric material and TEMPO. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 99: 3062–3069, 2006

Key words: TEMPO free radical; ^{13}C solid-state CPMAS NMR; cellulose acetate; poly(2,6-dimethyl-1,4-phenylene oxide); dense polymeric membrane

INTRODUCTION

Spin labeling techniques have been used widely for the structural determination of biological membranes as well as synthetic membranes.[1–4] The micellar packing and hydrophobicity of micro-heterogeneous systems such as membranes, vesicles, and micelles could be determined by nuclear magnetic resonance (NMR) spectroscopy, using a spin probe.[3] Recently, it was reported that chitosan based polymeric surfactants increased the rigidity of the membrane structure when compared with that of the conventional low molecular weight surfactants, as studied by spin probe techniques.[4] It is well known that NMR spectroscopy is used for polymer blend miscibility at the molecular level. The interactions between the spin probe and other components have been indicated by the changes in the line shapes and/or frequency of the resonance signals of the pure components. A strong interaction results in large chemical shift changes and a weak interaction in small chemical shift changes.[5–7] Recently, the ^{13}C cross-polarization magic angle spinning (CPMAS) NMR technique was used for the molecular mobility behavior of polymer chains and degree of interaction in heterogeneous polymers.[5] The ^{13}C-NMR in solution state was also used together with a spin probe, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) free radical, to study the extent of interaction between TEMPO and small organic molecules.[8] For example, the NO group of TEMPO formed complexes with phenolic OH group through intermolecular hydrogen bond. As the concentration of TEMPO increased, the ^{13}C contact shifts increased linearly due to the electron–donor/acceptor type π stacking interaction.[8] Using NMR spectroscopy studies, a broad range of pore sizes at the coating surface could be analyzed and, unlike conventional mercury porosimetry method, the sample did not need to be dried.[9]

Since the discovery of the asymmetric cellulose acetate (CA) membrane for seawater desalination by Loeb and Sourirajan, a number of materials have been tested as candidate materials for reverse osmosis (RO) membranes, but still CA membranes are widely popular.[10] Many discussions have been made on the mechanism of RO transport, where the state of water in the membrane seems to play an important role in the membrane. Considering the affinity of the constituent groups in CA to water, the acetyl groups are of hydrophobic nature whereas the hydroxyl groups, which may form hydrogen bonds with water, constitute the hydrophilic sites of the membrane. The state of water in CA has been presented as ordered or structured or ice-like by several researchers.[11–13] It is thought that CA membranes, quasi-crystalline structures, exclude ions in a similar mechanism as ice does, and the hydrogen bonding between water and CA is on average weaker than in liquid water. The presence

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Correspondence to: T. Matsuura (matsuura@eng.uottawa.ca).

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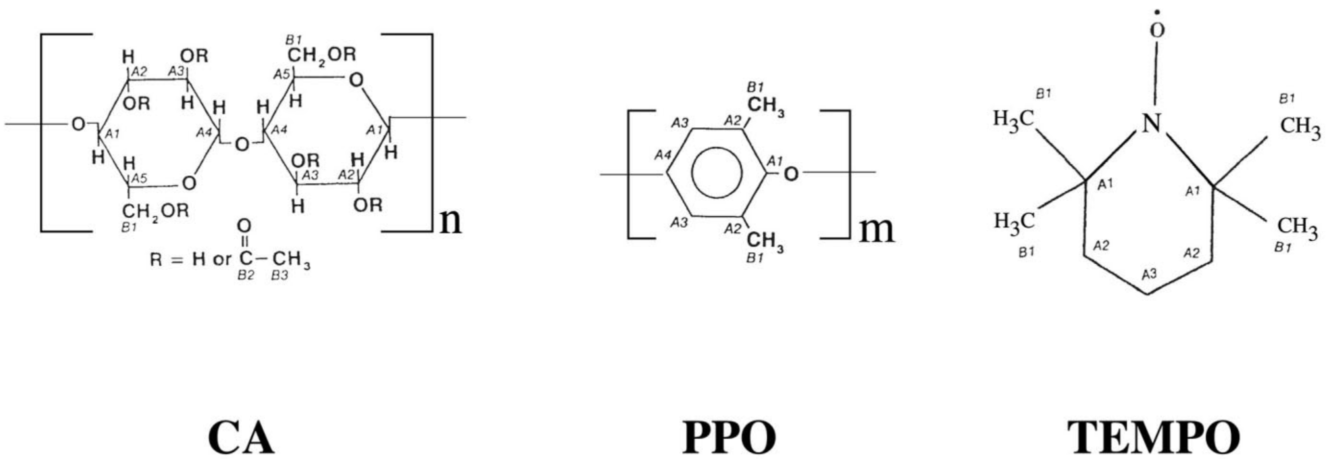


Figure 1 Chemical structure of CA, PPO, and TEMPO.

of water in four different states in the CA membrane for RO was proposed, i.e., (i) completely free water, (ii) free water interacting very weakly with CA, (iii) bound water which can contain salt, and (iv) bound water which rejects salts.[11] It was suggested that in CA membranes two types of pores are in the skin layer; one is polymer network pores, which are formed by segmental packing in the polymer matrix, and the other is polymer aggregate pores, which are formed as spaces between the polymer aggregates. The former pores are far more numerous and smaller in size than the latter ones.[14] Recently, the pore structure of the CA membranes was proven by Raman and small angle Neutron scattering (SANS) studies.[15–17] Kulkarni et al. observed from detailed SANS experiments that the pore structure in ultrafiltration (UF) membranes was well defined (10–20 °A) and also smooth, i.e., nonfractal in nature.[16,17]

The poly(2,6-dimethyl-1,4-phenylene oxide), PPO, drew attention as a fairly permeable, rather permselective, barrier polymer for gases among many aromatic polymers. PPO possesses a high glass transition temperature (T_g about 210°C), and has alternating aromatic rings and C—O linkage in the main chain. Polysulfone or bisphenol A polycarbonate, having similar structures of repeat units, do not show permeability as high as PPO possibly due to more polar groups attached to the main chain.[18]

The earlier research in this laboratory has focused on the characterization of synthetic polymeric membranes by atomic force microscopy (AFM), X-ray diffraction (XRD), electron spin resonance (ESR), and Raman spectroscopy.[19–25] The XRD analysis was made for PPO dense membranes prepared using different solvents in casting, and the results were used to explain the selectivity of CO_2/CH_4 gas separation.[20] Most recently, the dense PPO membranes were made at different evaporation temperatures ranging from 25 to 65°C and the results from the ESR and AFM experiments were correlated with permeation of CO_2, CH_4, O_2, and N_2 gases.[24] The surface morphology of water treated CA membrane was studied by AFM in terms of roughness parameter and the results elucidated the responsible water channels for the salt rejection in the RO.[25]

The aim of the present work is to investigate the possibility of studying structural changes to the membrane morphology by the NMR spin probe method. The CA and PPO polymeric materials were chosen as model systems since CA and PPO are widely used industrially for desalination and gas separation, respectively.

EXPERIMENTAL

The spin probe used in this study was 2,2,6,6-tetramethyl-1-piperidinyloxy, TEMPO, free radical supplied by Sigma Chemical Company, St. Louis, MO and was used without further purification. Cellulose acetate (CA, 398–3) was supplied by Eastman Kodak Company, Rochester, NY and specified as: acetyl content 40% and ASTM viscosity 25. General Electric Company, GE Plastic, Selkirk, NY supplied the ultra high molecular weight poly(2,6-dimethyl-1,4-phenylene oxide), PPO, with an intrinsic viscosity of 1.5 dL/g in chloroform at 25°C. Both CA and PPO dense films were prepared by the following method. A polymer solution with a concentration of polymer 2 wt % in 1,1,2-trichloroethylene (TCE, Fisher Scientific Company, Fair Lawn, NJ) was prepared. TEMPO (1 wt % or lower with respect to polymer) was added to the above polymer solution. An aliquot of 3 mL solution was spread smoothly over a glass plate inside an O-ring made of aluminum for molding. The solvent was evaporated at room temperature for 48 h before the film was removed from the glass plate. The film was further dried in a vacuum chamber for 24 h to remove the last traces of solvent from the film.

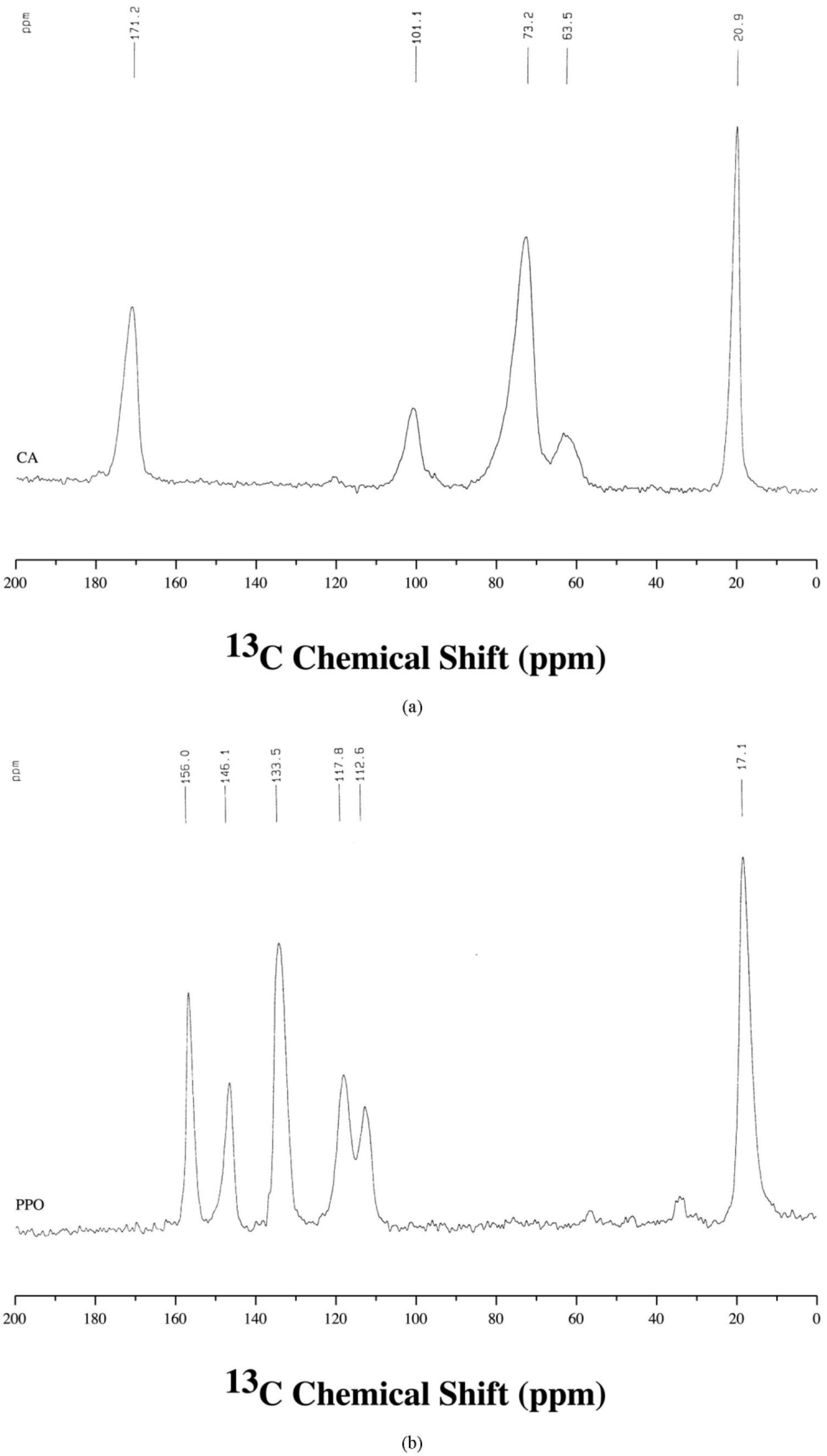
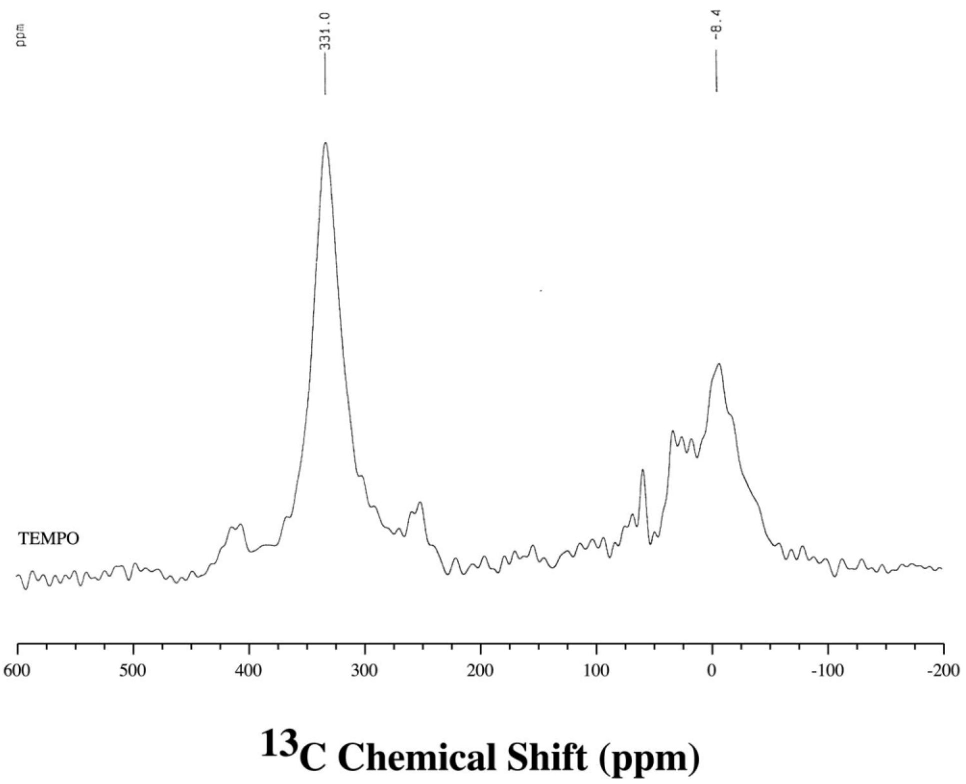


Figure 2 ^{13}C solid-state CPMAS NMR spectra of pure sample: (a) CA, (b) PPO, and (c) TEMPO.



(c)

Figure 2 (Continued)

^{13}C solid-state cross-polarization magic angle spinning nuclear magnetic resonance (CPMAS NMR) spectra were collected on a Bruker ASX-200 NMR spectrometer at ambient temperature that was operating at 50.3 MHz for ^{13}C using a proton 90° pulse of 3.9×10^{-6} sec. The proton relaxation time for solid TEMPO was observed to be very short. As a result, both the relaxation delay and contact time in the ^{13}C CP measurements were shortened from more conventional values. The contact time used was 5×10^{-4} sec and the relaxation delay was set to 5×10^{-1} sec. Typically, 4×10^{4} transients were collected using a spectral width of 6×10^{4} Hz. Spectra were also collected using dipolar dephasing. Dephasing delays of $20-40 \times 10^{-6}$ sec were used. The ^{13}C CP spectra for the pure polymers were acquired with a 2×10^{-3} sec contact time and a 2 sec relaxation delay. The dense films were put in liquid nitrogen for 30 min and then crushed into powder mechanically, using a porcelain mortar. The powder was dried in a vacuum oven for 24 h.

RESULTS AND DISCUSSION

The chemical structures of the three materials (CA, PPO, and TEMPO) used in this study are shown in the Figure 1. The ^{13}C solid-state CPMAS NMR spectra of the pure CA, PPO, and TEMPO are depicted in Figures 2(a)–2(c). The spectrum of CA permits the following assignments as in the Figure 2(a): 171.2 ppm corresponds to the carbonyl carbons (B2); 101.1 ppm corresponds to the two carbons (A4) adjacent of ether linkage; 73.2 ppm corresponds to the two carbons (A1) adjacent of ether linkage and another three carbons (A2, A3, and A5); 63.5 ppm corresponds to the carbons (B1); and 20.9 ppm corresponds to the fast rotating methyl carbons (B3). The peak assignment of CA was done according to the literature.[26,27] The spectrum of PPO permits the following assignments as in the Figure 2(b): 156 ppm corresponds to the carbon (A4); 146.1 ppm corresponds to the carbon (A1) adjacent of ether linkage; 133.5 ppm corresponds to the two carbons (A2); 117.8 and 112.6 ppm correspond to the two carbons (A3); and 17.1 ppm corresponds to the two fast rotating methyl carbons (B1). The peak assignment of PPO was done accordingly to the literature.[28,29] The spectrum of TEMPO permits the following assignments as in the Figure 2(c): 331 ppm peak corresponds to two carbons (A1) and the four fast rotating methyl carbons (B1), and −8.4 ppm broad peak corresponds to the three carbons (A2 and A3). In the present work, the assignments of the TEMPO peaks were determined using the dipolar dephasing techniques.

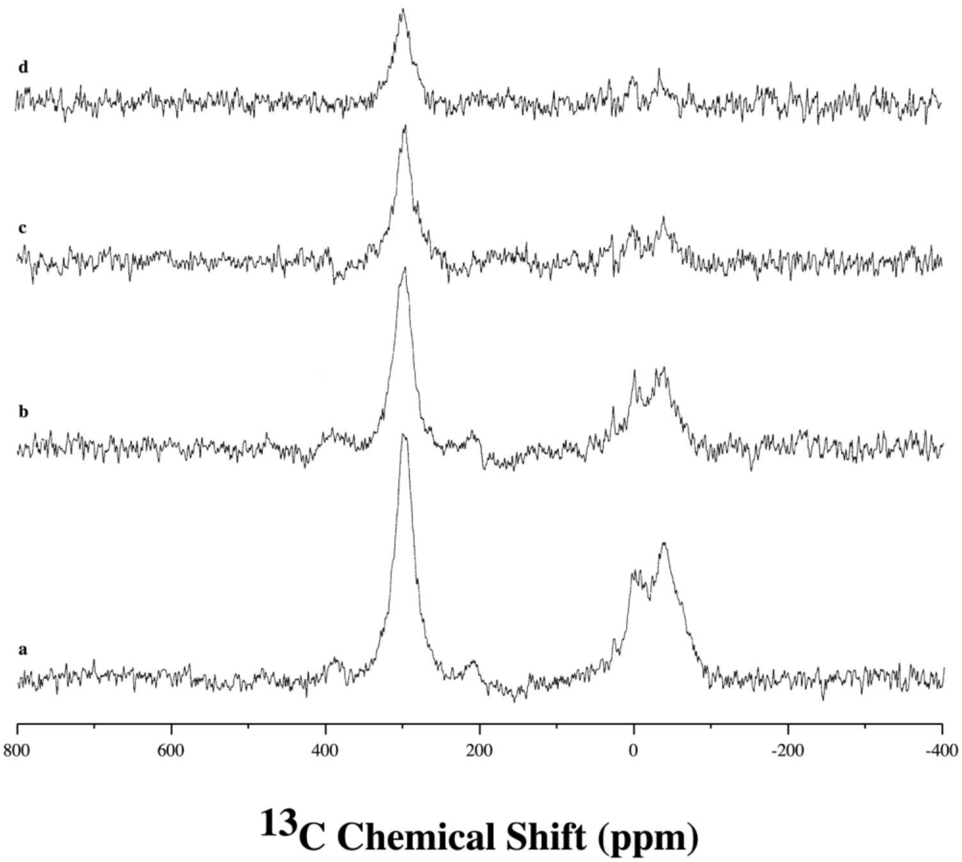


Figure 3 ^{13}C solid-state CPMAS NMR spectra of pure TEMPO at various dipolar dephasing delay time: (a) 0, (b) 20×10^{-6}, (c) 40×10^{-6}, and (d) 60×10^{-6} sec.

The ^{13}C solid-state CPMAS NMR spectrum of TEMPO consisted of two main groups of very broad resonance at 331 and −8.4 ppm. The chemical shifts are very different from those expected in diamagnetic organic solids, the discrepancy being due to the unpaired electron present. With such unusual chemical shifts, assignment of the resonance was not possible by simple inspection of the peak positions. In an attempt to assign the spectrum, a separate spectrum was measured using a dipolar dephasing delay time of 40×10^{-6} sec. The delay, in which the proton decoupler is turned off, is inserted at the end of the contact time immediately preceding data acquisition. During the delay, one expects carbon atoms with strong dipolar interactions with protons to decay significantly (often completely), while those with weak dipolar interactions will decay only slightly. By using this technique, one expects the three carbons (A2 and A3) to disappear while carbons (A1) and fast rotating methyl carbons (B1) to decay only slightly. The dipolar dephasing spectrum (with a 40×10^{-6} sec dephasing delay) shows a single broad resonance at 331 ppm. The groups of resonance at −8.4 ppm have completely disappeared. It can be concluded that the resonance at 331 ppm results from the two carbons (A1) and four methyl carbons (B1) whereas the lower frequency peaks are due to the three carbons (A2 and A3). The very large chemical shift of the methyl and carbons is the result of their close proximity to the unpaired electron. The chemical shifts of the three carbons are less perturbed, probably because of the fact that they are further away from the localized unpaired electron. The three carbon's resonance was reduced and finally disappeared with different dipolar dephasing delay time, as shown in the Figure 3. It is noted that as a paramagnetic material, the base line of TEMPO spectrum is slightly scattered.

The ^{13}C solid-state CPMAS NMR spectra of the CA with TEMPO (0.01 and 0.2 wt %) are shown in Figure 4. From the figure, it is noted that the peak positions of the blended CA are the same as the pure CA. Therefore; the TEMPO does not affect any peak positions and shapes. The ^{13}C solid-state CPMAS NMR spectra of the PPO with TEMPO (0.2 and 1 wt %) are shown in Figure 5. The peak positions of the blended PPO are also the same as pure PPO. It seems that there was no effect of blended TEMPO on the CA or PPO CPMAS NMR spectra and the peaks of TEMPO did not appear in the blended spectra. The concentration of TEMPO was very low in this study to avoid spin exchange

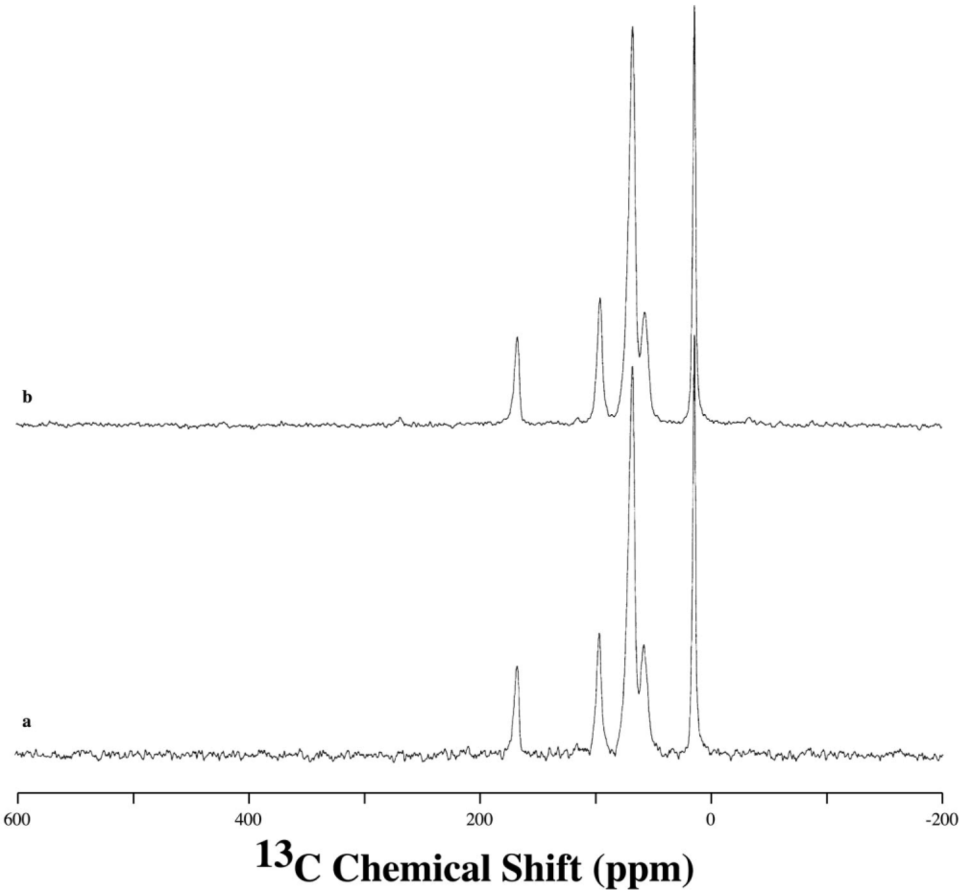


Figure 4 ^{13}C solid-state CPMAS NMR spectra of TEMPO blended CA: (a) 0.01 and (b) 0.2 wt % TEMPO.

broadening. These TEMPO peaks in the blended samples were in the noise level and CPMAS NMR could not identify them. This observation indicates that the TEMPO blended in the CA or PPO film is in the free state without interacting chemically or physically with CA or PPO within the experimental limit of the CPMAS NMR technique.

The RO and liquid chromatography (LC) separation of various free radicals in aqueous solution was studied in the CA membrane and CA packing material, respectively.[30,31] Four piperidinoxy (one is TEMPO, and the other three are substitutes of TEMPO) free radicals together with one undissociated piperidinoxy material and two dissociated piperidinoxy materials were used. The positive separation in RO experiment was observed for all the solutes, using a CA membrane. Thus, permeation of free radicals through porous CA membrane indicated the validity of the pore flow model. The LC experiments observation was as follows: the retention volumes of the free radicals are only slightly higher, those of the dissociated materials are only slightly lower and that of the undissociated is far higher than the reference standard D_2O. The LC results indicate the free radicals are weakly attracted towards the CA membrane materials.

Very recently, ESR of spin probe doped CA and PPO membranes were studied.[19–23] The structure of asymmetric and dense CA membranes was studied by adding spin probe TEMPO in the feed solution of the RO experiments and also blending in polymeric casting solutions before making the dense membranes.[21] The mobility of the TEMPO additive depended on the temperature at which the asymmetric CA membrane was shrunk. The mobility became less as the shrinkage temperature increased and became the least, and equal to that of the dense CA membrane, when the shrinkage temperature was as high as 90°C. The ESR spectra from the PPO membranes were not affected by the addition of TEMPO.[23] It was thought that as the TEMPO size was very small compared with that of the void spaces (free volume or micro-cavity) of the PPO material, the TEMPO had enough space to tumble very fast in those quite large micro-cavities. From the ESR spectra of TEMPO spin probe that was added to the PPO dense membrane, it was suggested that TEMPO in PPO membrane was more mobile than in water media.

The free volume of PPO contains a three-dimensional network of intermolecular micro-cavities as suggested by Ilinitch after detailed analysis of ^{129}Xe

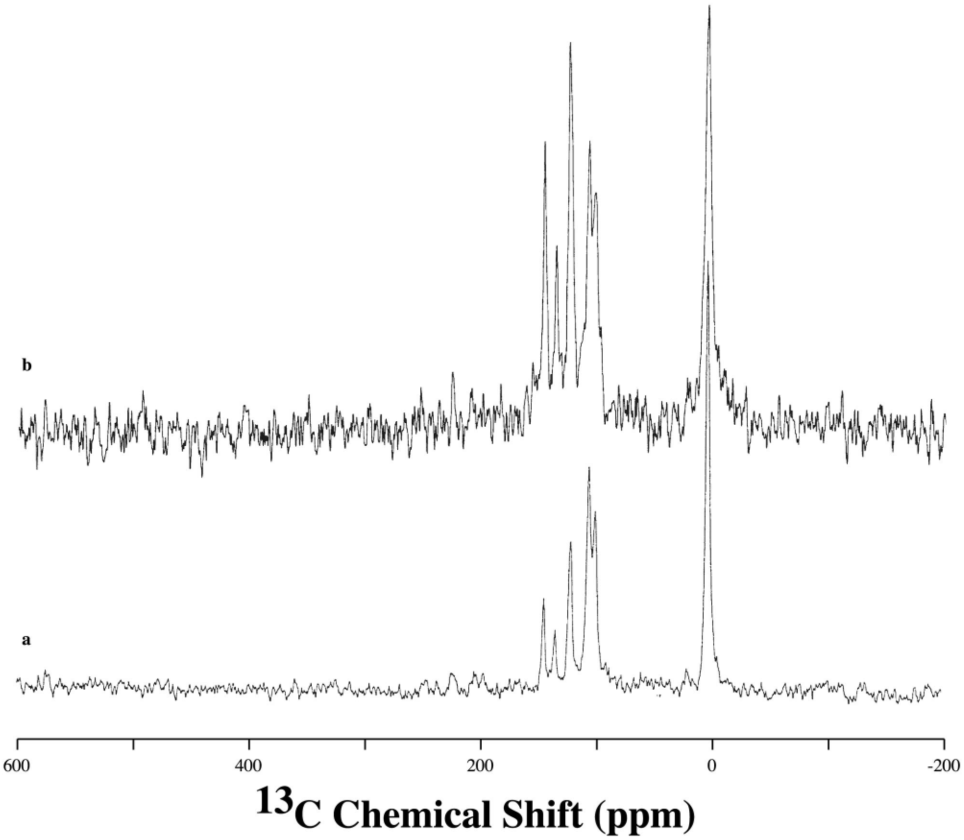


Figure 5 ^{13}C solid-state CPMAS NMR spectra of TEMPO blended PPO: (a) 0.2 and (b) 1.0 wt % TEMPO.

NMR spectra.[32] The multi-throat cavity model for intrinsic microporosity and free volume structure of PPO was adequate for representation. The effective diameter of the pore throats is in the range of ca 0.4 nm at 77 K, and increasing up to ca 0.5 nm at ambient temperature.[32] Thus, the PPO membrane behaves in a way similar to that of the solid adsorbents such as carbon molecular sieves.

CONCLUSIONS

It seems that the size of the TEMPO is small enough to move freely in the micro-cavity or free volume of the CA and PPO dense membranes. The present study proved that the TEMPO is not chemically or physically affected by the polymeric dense membrane structure of the CA or PPO.

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