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Study of the structure of asymmetric cellulose acetate membranes for reverse osmosis using electron spin resonance (ESR) method

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Abstract

Electron spin resonance (ESR) technique was used to study the structure of the skin layer of asymmetric cellulose acetate membranes for reverse osmosis. TEMPO (2,2,6,6-tetramethyl-1-piperridinyloxy-free radical) was used as a spin probe that was brought into the membranes either by reverse osmosis experiments with feed solutions involving TEMPO, or by blending TEMPO into casting solutions. It was found that the mobility of TEMPO in the asymmetric membrane shrunk at 90°C was the same as TEMPO in a dense homogeneous membrane prepared from the same casting solution as that used for the preparation of the asymmetric membranes. On the other hand, TEMPO was more mobile in the asymmetric membranes when they were shrunk at lower temperatures and less mobile in a dense homogeneous membrane when the latter is prepared from a casting solution without pore former (magnesium perchlorate and water). Reverse osmosis experiments were also performed using feed aqueous solutions of sodium chloride and/or TEMPO. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Electron spin resonance; Cellulose acetate membrane; Pores in the membrane

1. Introduction

Although many discussions have been made on the mechanism of reverse osmosis transport [1–8] it remains as an unanswered question. Among many mechanisms proposed, the solution-diffusion model is currently most widely accepted. According to the latter model, the skin layer of an asymmetric reverse osmosis membrane is considered to be a homogeneous dense layer of polymer. The transport of a permeant occurs by sorption, diffusion and desorption of the permeant into, through and out of the skin layer. When the transport occurs by a convective flow through pores, the skin layer is thought to be defective. Without pores, the skin layer is considered perfect. According to Lonsdale [9] the structure of a perfect skin layer is the same as that of a homogeneous film which is prepared by complete evaporation of solvent after casting a polymeric solution into a film.

The preparation of an asymmetric cellulose acetate membrane, on the other hand, is based, in most cases, on the dry–wet phase inversion process. Solvent is partially evaporated from the cast solution film before the film is immersed into a coagulation bath. Often, a nonsolvent is added to the polymeric solution as a pore-former. A wide spectrum of pore sizes, from nanofiltration to microfiltration membranes, can be achieved by proper adjustment of membrane preparation conditions. A reverse osmosis membrane is prepared, according to the Loeb–Sourirajan method [10], by the heat-treatment of a nanofiltration membrane in a hot water bath. Adjusting the temperature of the hot water bath the degree of shrinkage of pores can be controlled. The higher the temperature, the pores become smaller. Ultimately, at some temperature above 80°C a reverse osmosis membrane of the highest salt rejection is obtained. According to the solution-diffusion approach, the skin layer of such a reverse osmosis membrane is dense and perfectly pore-free. The pores that existed in the nanofiltration membrane have disappeared completely as a result of heat treatment. The removal of pores by heat treatment is therefore called annealing.

An attempt was made by Kulkarni et al. [11,12] to know if the skin layer of an asymmetric cellulose acetate membrane is indeed pore-free. They have detected, by small angle neutron scattering, channels through which transport of water was taking place. Apparently, those are

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the remnant of pores of the nanofiltration membrane from which the reverse osmosis membrane was prepared.

It may be too simplistic to view the skin layer of asymmetric cellulose acetate membrane as dense homogeneous layer. The polymers of the skin layer are rather structured with different local polymer densities. (There are ample evidences for the presence of heterogeneity even in a so-called dense homogeneous film that is prepared by complete evaporation of solvent from a cast polymer solution film.) The transport of water should take place through channels that are formed within such structured polymers. These channels are of molecular dimensions and, however small they are, they can be called *pores*. Recognising the presence of o polymer aggregates that are observable under an electron microscope as spherical nodules, two types of pores in skin layer of asymmetric cellulose acetate membranes were proposed [10]. One is called 'network pores'. They are pores that may have been originated from the segmental level packing defects trapped in a polymer matrix. Unlike closely packed polymer matrix, these defects can be readily water-swollen. The other is called 'aggregate pores', which are originated from spaces of lower density between the polymer aggregates. These spaces can also be readily water swollen. The aggregate pores seem to be larger than the network pores.

This work is another attempt to know more about of the skin layer of a reverse osmosis membrane. In particular, it is attempted to know if the skin layer is indeed the same as the dense film prepared by complete evaporation of solvent from a cast solution film. For this purpose, electron spin resonance (ESR) method is applied. By the above method one is able to know the degree in freedom of motion of spin probes in a given environment by analysing ESR signals obtained when the spin probes are brought into a magnetic field; i.e. the signal will consist of symmetric peaks when the spin probes are freely mobile, while asymmetricity of the peak shape will increase as motion of the spin probes becomes more restricted. In this work, spin probes are incorporated into membranes in the two ways. In one, spin probes are brought into the skin layer of a reverse osmosis membrane under a reverse osmosis condition, where an aqueous solution of the spin probe is used as feed. In the second, spin probes are incorporated into a dense film by dissolving the spin probes into the polymeric solution from which the film is cast. Then, both the asymmetric membrane and the homogeneous film are subjected to ESR analysis. If the structures of the skin layer and the homogeneous film are the same and if the transport takes place only through the dense polymer matrix of the membrane (or film) the spin probe should give the same signal in both cases.

2. Experimental

A series of asymmetric membranes were prepared from solution (A) of the following composition.

Solution (A): Cellulose acetate (Eastman 398-3), 17.00 wt%; magnesium perchlorate, 1.45 wt%; water, 12.35 wt%; acetone 83.00 wt%.

The polymer solution, the temperature of which was kept at 4–10°C, was cast on a glass plate to a thickness of 0.33 mm. The solvent was evaporated at room temperature for 1 min before the cast film was immersed, together with the glass plate, to ice cold water (4°C). The membrane was kept in ice-cold water for at least 2 h. The membrane was then shrunk in a hot water bath at different temperatures (60, 70, 75, 80, 85, 90°C) for 10 min prior to the use for reverse osmosis experiments. Membranes so prepared are coded as A-Asym-60-60, A-Asym-60-70, A-Asym-60-75, A-Asym-60-80, A-Asym-60-85 and CA-Asym-60-90. The first code indicates the type of the solution. The second code indicates that the membrane is asymmetric. The third and fourth codes indicate the evaporation period (s) and the shrinkage temperature (°C), respectively.

Solution (A) was also used to prepare a dense film, except a small quantity (0.01 wt% of the solution) of 2,2,6,6,-tetramethyl-1-piperridinyloxy free radical (TEMPO) was added to the solution. After the film was cast on a smooth glass plate to a thickness of 0.25 mm, the solvent was evaporated at room temperature for three days. This film is coded as A-dense. The second code indicates that the membrane is a dense film.

Polymer solution (B) of the following composition was used to prepare another dense homogeneous membrane.

Solution (B): Cellulose acetate, 17 wt%; acetone, 83 wt%.

A small quantity (0.01 wt% of the solution) of TEMPO was added to the solution. After the polymer solution was cast on a smooth glass plate to a thickness of 0.33 mm, the solvent was evaporated at room temperature for three days. This film is coded as B-dense.

It should be noted that the polymer solution used for the preparation of asymmetric membranes did not include TEMPO, while those used for the preparation of dense films included TEMPO. It should also be noted that the asymmetric membranes were wet, while dense films were dry.

2.1. Reverse osmosis experiments

The reverse osmosis experiments were carried out using a conventional static cell with an effective membrane area of 13.3 cm^2. The details of the experimental procedure are given elsewhere [13]. Membranes were pressurized in the test cell at 600 psi g for at least 4 h before they were subjected to reverse osmosis experiments. All reverse osmosis experiments were carried out at the operating pressure of 500 psi g and at room temperature. An aqueous sodium chloride solution (0.1 wt%), an aqueous TEMPO solution (0.05 wt%) and an aqueous solution of the mixture of sodium chloride and TEMPO (0.1 and 0.05 wt%, respectively) were used as feed solutions. In each experiment, pure water permeation rate (PWP), in the absence of the solute, product permeation rate (PR), in the presence of the solute, and the solute separation (defined as solute separation = (solute concentration in feed − solute concentration in permeate)/(solute concentration in feed)) were determined. Sodium chloride concentrations were determined by conductometry and TEMPO concentrations were determined by ESR technique [13].

2.2. ESR experiments

ESR measurements were made with X-band Bruker 200 DC spectrometer. The wet membrane sample (area 1 cm × 0.5 cm) was fixed in the tissue cell supplied by Willmad Glass, NJ, USA. Typical parameters involved in the ESR experiments are as follows: modulation amplitude, 1 G; time constant, 50 ms; scan width, 200 G; power, 20 mW; scan center, 3400 G.

All measurements were performed at room temperature. Membranes were washed with distilled water to remove last traces of feed solutions from the surface, when they were subjected to ESR experiments after being used in reverse osmosis experiments.

3. Results and discussion

3.1. Reverse osmosis experiments

Reverse osmosis experiments were carried out with membranes A-Asym-60-60, A-Asym-60-70, A-Asym-60-75, A-Asym-60-80, A-Asym-60-85 and CA-Asym-60-90 and the results given in Figs. 1–3. Note that the shrinkage temperature was the variable in these experiments. Fig. 1 shows that PR decreased with an increase in shrinkage temperature. Fig. 2 shows that sodium chloride separation increased with an increase in shrinkage temperature. A sodium chloride separation of 95 wt% was achieved when the shrinkage temperature was 90°C. These experimental results confirm those obtained earlier [10]. Fig. 3 shows that TEMPO separation also increased with an increase in shrinkage temperature. The reverse osmosis separations of free radicals from their solutions were reported earlier by Chan et al. [14,15]. Fig. 3 also shows that a slight increase in TEMPO separation was observed in the presence of sodium chloride in the solution.

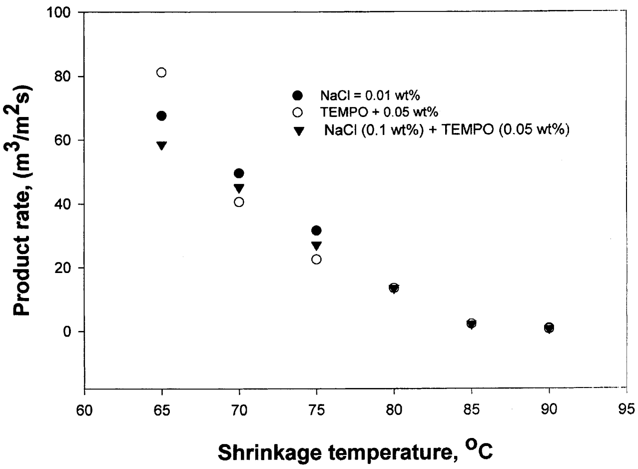

Fig. 1. Product rate obtained from reverse osmosis experiments versus shrinkage temperature. Reverse osmosis conditions: operating pressure, 500 psi g; temperature, room.

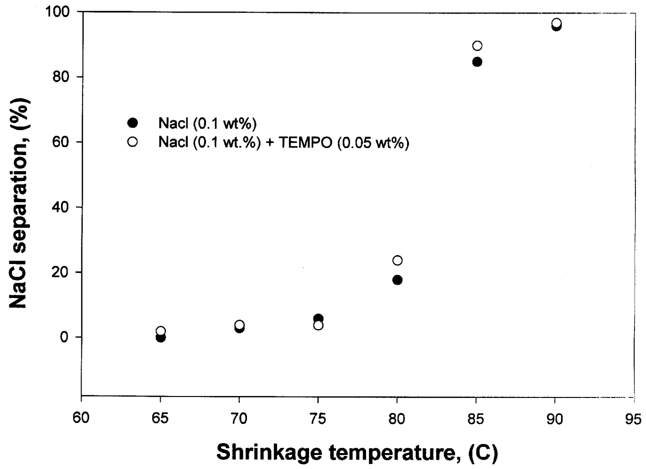

Fig. 2. Sodium chloride separation versus shrinkage temperature. Reverse osmosis conditions, same as Fig. 1.

3.2. ESR experiments

Fig. 4 shows the ESR spectra of an aqueous solution in which both sodium chloride and TEMPO (0.1 and 0.05 wt%, respectively) were dissolved. The spectra consist of three symmetric peaks, since the NO$^{\cdot}$ radical of TEMPO is freely mobile in the solution. The ratio *b*/*a*, where *b* is the height in arbitrary unit of the middle line B, from the bottom to the top of the peak, and *a* is the height of the first line A, from the bottom to the top of the peak, is unity in this spectrum, indicating the symmetry of the spectrum. When the radical becomes less mobile, the spectra will be less symmetric and ratio will increase.

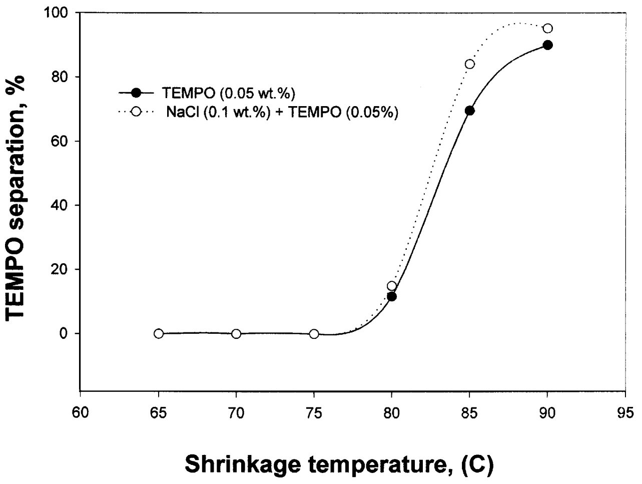

Fig. 3. TEMPO separation versus shrinkage temperature. Reverse osmosis conditions: same as Fig. 1.

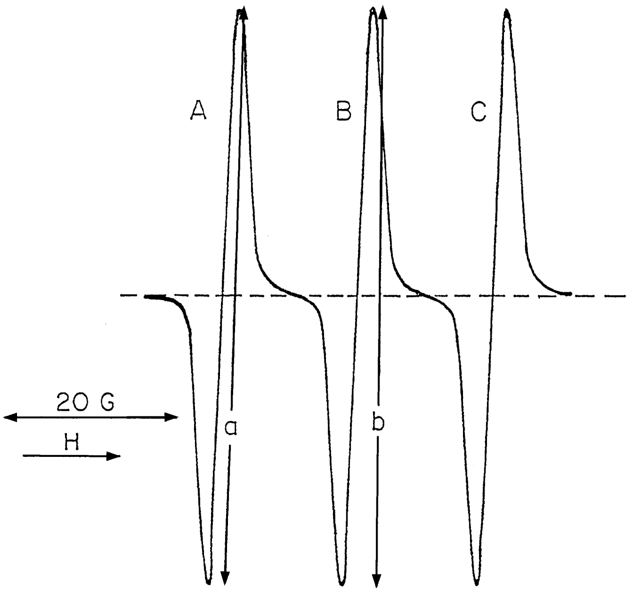

Fig. 4. Typical ESR spectra of TEMPO in an aqueous solution containing 0.1 wt% NaCl and 0.05 wt% TEMPO.

Fig. 5 shows the ESR spectra of an A-Asym-60-65 membrane when it was immersed in TEMPO solution (0.05 wt%) for 24 h and then rinsed with water to remove the residual solution from the membrane.

Both RO and UF membrane are in general asymmetric in nature, that is they consist of a thin, relatively dense film (usually referred to as the skin layer) supported by a porous sublayer. The skin layer is primarily responsible for the selectivity retaining certain materials, and allowing the passage of others, while the sublayer provides mechanical support and allows high flux of permeable substance. It contains large pores. On rinsing with water, most of the free radicals in the sublayer are washed out. The ESR spectra are therefore mainly due to remaining radicals in the skin layer. These radicals are sitting either in the pores where they have weak restriction in movement or interacting with the polymer and have more restriction in the movement.

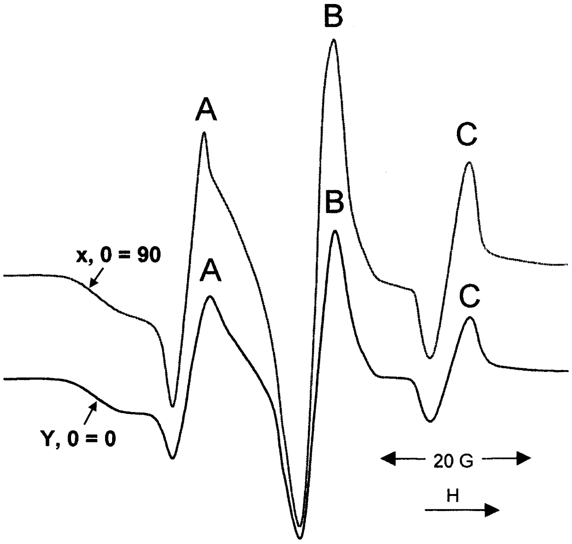

Fig. 5. ESR spectra of A-Asym-60-65 membrane. The membrane was immersed in TEMPO solution for 24 h and then rinsed with water to remove the residual solution.

Fig. 5 shows two overlapping spectra corresponding to weakly restricted and highly restricted spin probes. One, which is weakly restricted, is sitting inside the pores and the movement is restricted due to the space inside the pore. Thus, the intensity of three lines is varying. The intensity of two high field lines provides a measure of the amount of nitroxide tumbling [16]. The width of each line, peak to peak (4 G) and spacing between lines (‘A’ to ‘B’ and ‘B’ to ‘C’) (17 G) remain the same as shown in Fig. 4 where the motion of the radical is not restricted. The other one, which is highly restricted, is interacting with the polymer molecule. This radical will give a signal in which the width of each line (peak to peak) is more than 4 G and the spacing between two lines will be more than 17 G. Although the ESR signal in Fig. 5 is an overlap of signals from two different sources, the ratio of the height of the second peak to that of the first peak, called *b*/*a* ratio, can still be considered as a measure for the restriction of the motion of the radical probe in the pore because of the following two reasons.

1. The second signal due to the spin probe that is interacting with polymer will not depend on the pore size.
2. The width of the each peak measured from top to bottom (4 G) and the distance between two peaks from top to top (17 G) are the same as those obtained from the signal of the radical probe in free motion (Fig. 4). Thus, the peaks observed in Fig. 5 could primarily represent the signal originating from the radical probe in the pore.

The pattern of the ESR spectra was the same when the asymmetric membranes were subjected to ESR experiments after being used for reverse osmosis experiments with feed solutions including either TEMPO only or both sodium chloride and TEMPO. Spectra X and Y are recorded corresponding to the magnetic field perpendicular to ($\theta = 90°$) and parallel to ($\theta = 0°$) to the membrane. The *b*/*a* ratios in both spectra recorded at $\theta = 90$ and 0° are approximately the same, which suggest that the free radicals are randomly distributed in the membrane. The figure clearly shows three distinct peaks. However, unlike Fig. 4, the height of each peak is no longer equal. Using the ESR spectra obtained after reverse osmosis experiments, the ratio *b*/*a* was calculated for each of the asymmetric membranes ($\theta = 90°$). Fig. 6 shows the plot of *b*/*a* versus shrinkage temperature. The *b*/*a* ratio increases from 1.3 to 1.9 as the temperature increases. This indicates that TEMPO becomes less mobile as the pore size of the membrane decreases with an increase in shrinkage temperature.

A dense film (A-dense) was subjected to ESR study after wetting the membrane with few drops of water. The excess of water was removed from the surface. The *b*/*a* ratios were 1.9 and 1.9 for the spectra X and Y, respectively. It should

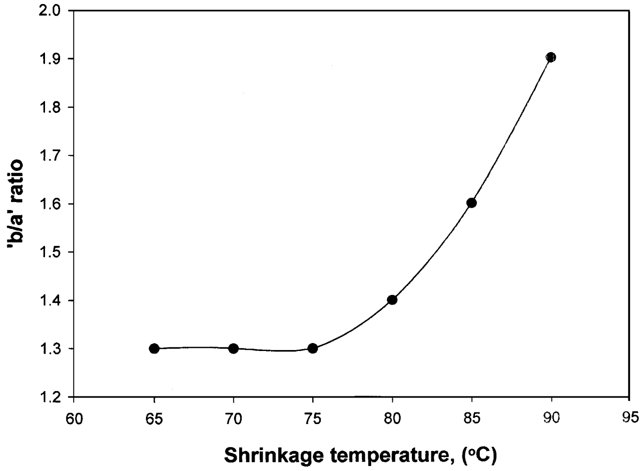

Fig. 6. *b*/*a* ratio versus shrinkage temperature for asymmetric cellulose acetate. Reverse osmosis experiments are conducted an aqueous feed solution of sodium chloride (0.1 wt%) and TEMPO (0.05 wt%).

be noted that the *b*/*a* ratio of the A-Asym-60-90 film was also 1.9. This means that the mobility of TEMPO in the A-dense film was restricted as strongly as in the A-Asym-60-90 membrane. Assuming that the mobility of TEMPO will be equally restricted in two membranes (or films) of different origins, when the pore sizes are equal, the above data indicate that the pore sizes of A-dense film is equal to that of A-Asym-60-90 membrane. It should also be noted that TEMPO was incorporated in the polymer solution when the A-dense film was prepared, while TEMPO was transferred from an aqueous feed solution to the A-Asym-60-90 membrane during the RO experiment. This indicates that the channel through which the feed solution is forced to flow during the RO experiment (with A-Asym-60-90 membrane) was of the same nature as the space in the polymer network into which TEMPO was retained during the process of preparing A-dense film. Such a space may as will be called segmental level packing defects trapped in a polymer matrix. These water flow channels should therefore be called network pores as suggested in earlier work [10].

The pore sizes of the asymmetric membranes were larger than that of A-Asym-60-90 membrane (and A-dense film as well) when they were shrunk at temperatures lower than 90°C. The pore size was the largest when the shrinkage temperature was 60°C and decreased monotonically with an increase in shrinkage temperature (Fig. 6). It should be reminded that the presence of aggregate pores was suggested in the asymmetric cellulose acetate membranes shrunk at temperatures lower than 90°C [10].

The aggregate pores are those which have been originated from spaces formed between polymer aggregates, and the sizes of the aggregate pores are larger than those of the network pores. Shrinkage is a process in which aggregate pores are either removed or transformed into network pores. More aggregate pores will be transformed into network pores at a higher shrinkage temperature, thus resulting in a smaller average pore size.

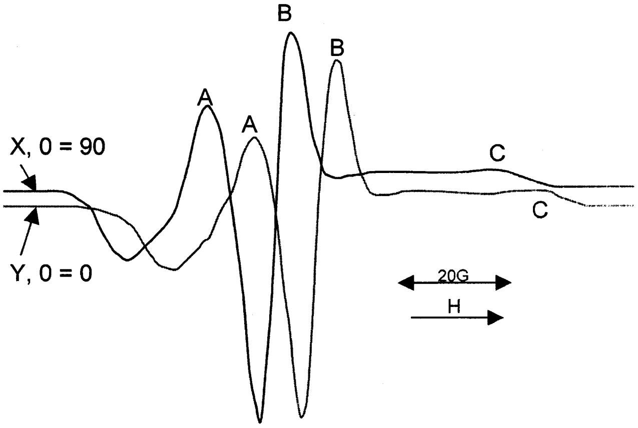

Fig. 7. Typical ESR spectra of a dry dense homogeneous cellulose acetate membrane containing TEMPO (0.05 wt%) in the casting solution.

When a dense film (B-dense) was subjected to ESR study after wetting, *b*/*a* ratios of 2.5 and 2.6, respectively, were obtained for spectra X and Y. This means that the space in the network of the B-dense film was smaller than that of A-dense film. It should be noted that no swelling agent, such as magnesium chloride and water, was added to the polymer solution from which B-dense film was prepared, while swelling agent was added to the polymer solution A. From these results, it can be concluded that the presence of swelling agent is necessary for water molecules to be imbibed into the polymer network to produce network pores that are sufficiently large for practical reverse osmosis applications. The above results also suggest that there are a number of dense films the structures of, which are different.

When these dense homogeneous films were kept immersed in water for more than 24 h, the ESR spectra for the A-dense film disappeared completely, indicating that TEMPO was leached out from the membrane. On the other hand, ESR spectra of the B-dense film could still be obtained with decreased intensities but very little changes in *b*/*a* ratio.

The above homogeneous films were also subjected to ESR studies in their dry state. The shape of typical ESR spectra is shown in Fig. 7. The spectra depicted in Fig. 7 are obviously very different from those in Fig. 5. The peaks are much broader and look less symmetric. In particular, the third peaks are hardly recognisable. The shapes of the spectra remind us of those obtained for polyethersulfone (PES) dry membranes. These results indicate that TEMPO in dry films is even less mobile than in wet dense films.

4. Conclusions

1. ESR technique is a useful tool to elucidate the structure of reverse osmosis membranes.
2. The pore size on the skin layer of the asymmetric cellulose acetate membrane shrunk at 90°C is the same as that of the dense film, when they are prepared from the same casting solution.

3. The pore sizes of the asymmetric membranes are larger when they are shrunk at lower temperatures.
4. The space in the polymer network (the origin of the network pore) in the dense film is smaller when no swelling agent is added to the casting solution.
5. The space in the polymer network in the dense film is smaller when the membrane is dry.

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