

# NOTE

## Aging Effect of Casting Solution on Performance of Membrane by Electron Spin Resonance Technique

K. C. KHULBE, T. MATSUURA

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

Received 7 July 1999; accepted 24 July 1999

### INTRODUCTION

Membrane manufacturers have often noted the effect of aging of a casting solution on membrane performance. It depends to a large extent on structural arrangement and mobility of polymer molecules in a casting solution, because the solution property is an important factor affecting membrane morphology. The nature of the various polymer–polymer and polymer–solvent interactions exerts a great influence upon the structure of membranes as they are cast from polymer solutions. Polymer conformational structure is governed not only by the overall composition and temperature of the polymer solution, but also by other factors such as the method of mixing and storage time.

Ma et al.<sup>1</sup> drew attention to the aging effect of the casting solution on the characteristics of hollow fiber membranes. They observed that the viscosity of the casting solution and the performance of the membranes prepared from the aged cast solution were affected by the storage time. From their observation it seems that the solution structure changes during the storage time. The term solution structure refers to the state of aggregation and disposition of polymer segments within the casting solution. No single physicochemical parameter has been identified to completely characterize the solution structure. Understanding these affects is important for quality control in membrane manufacturing.

In the present communication we are reporting the change in the mobility of polymers in the casting solu-

tion as detected by electron spin resonance (ESR). ESR is sensitive to the local environment of the radical probe, able to measure very rapid motion, and usually featured by the absence of interfering signals from the environment. The NO\* spin labels (TEMPO) are used to monitor the motion of polymers in the casting solution.

The affect of the casting solution structure on the ultrafiltration (UF) performance of membranes prepared from aged casting solutions is also reported.

### EXPERIMENTAL

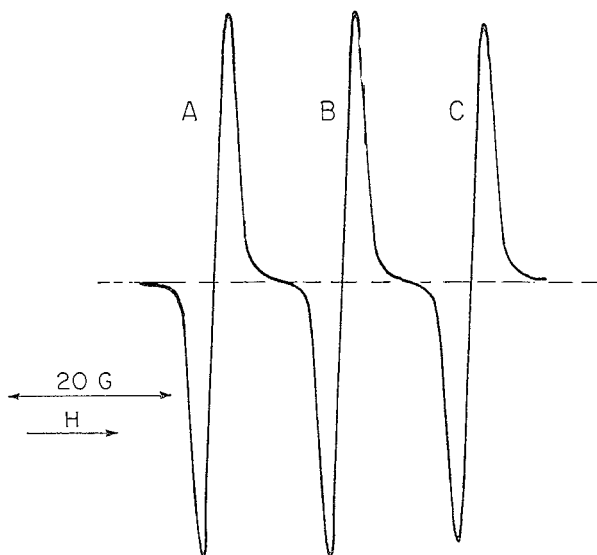
Poly(ethersulfone) (PES, Victrex 4100P) supplied by Imperial Chemical Industries was dried in an oven at 160°C for 24 h prior to use. A solution of PES (15 wt %) and polyvinyl pyrrolidone (PVP, 15 wt %) in 1-methyl-2-pyrrolidinone (NMP) was prepared as a stock solution and filtered through a 5- $\mu\text{m}$  filter. PVP was added as an additive. A radical probe (2,2,6,6-tetramethyl-1-piperidinyloxy, free radicals, abbreviated as TEMPO) was also added to a portion of the stock solution (0.03% of the solution) to study the mobility of the probe in the casting solution against storage time. The undoped solution membranes were cast on predetermined days. The details of the techniques for the preparation of the membrane and ESR study are described elsewhere.<sup>2–4</sup> The membrane was mounted immediately after the preparation (without storage) in an ultrafiltration cell and compressed under water at 60 psig for at least 20 h before UF experiments were carried out at 50 psig. The effective area of the membrane was 13.6 cm<sup>2</sup>. The conditions of the UF experiments are as follows:

1. feed; polyethylene oxide (PEO, mol wt = 100,000) solution (0.05 wt %);

Correspondence to: K. C. Khulbe.

Contract grant sponsors: Environmental Science and Technology Alliance Canada (ESTAC); Natural Science and Engineering of Canada.

Journal of Applied Polymer Science, Vol. 75, 1788–1791 (2000)  
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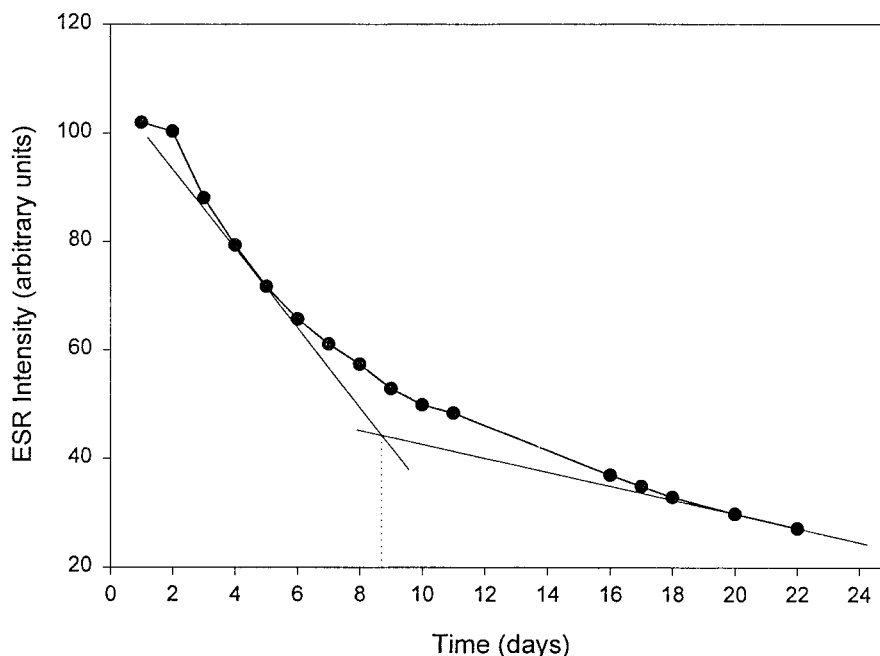
**Figure 1** The ESR spectra of  $\text{NO}^*$  radical in the casting solution.

2. operating pressure, 50 psig; and
3. temperature, room temperature.

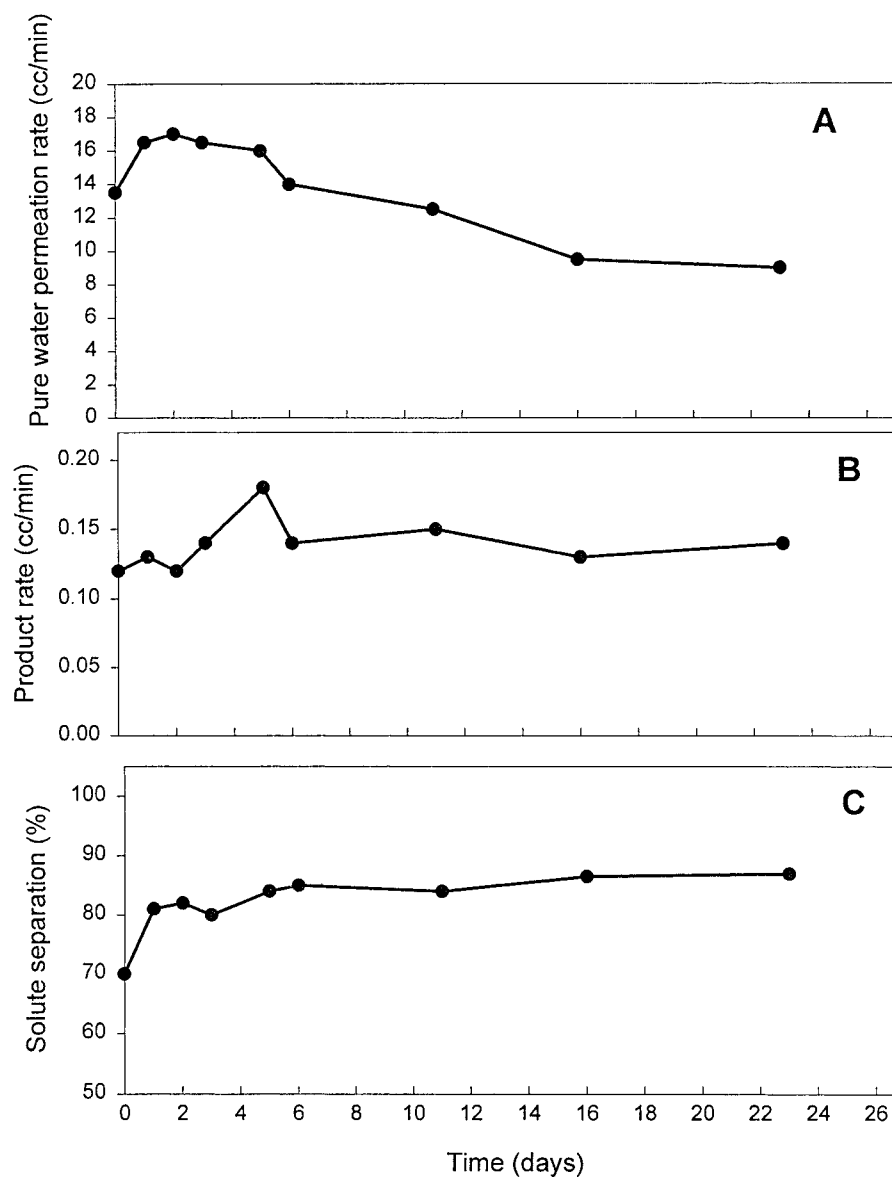
## RESULTS AND DISCUSSION

The nitroxide spin label is a monitor of motion from the internal rotation in a dilute solution to motion in crystalline and amorphous bulk material.

Figure 1 shows the ESR spectra of the  $\text{NO}^*$  radical in the casting solution where the radicals are tumbling rapidly.<sup>5,6</sup> It contains three hyperfine lines of equal height and two outer lines (lower and higher field) are at equal distance from the middle line B. Figure 2 shows the intensity of the first peak, A (height of A, peak to peak), of the  $\text{NO}^*$  radical (A) versus the storage time of the casting solution (days). The intensity continued to decrease. During the first 9 days the intensity decreased fast; after that the intensity decrease slowed down. The decrease in the intensity or increase in the half-width of the peak with an increase in storage time means that the mobility of the radical decreased as the storage time increased. It was noted that the spacing between the two outer hyperfine lines (A, C) increased from 29 to 36.5 Gauss after 29 days of storage time. Similarly, the peak width of A (peak to peak) increased from 9 to 10.5 Gauss. Similar results were observed with the other peaks (B, C). These characteristics indicate a decrease in the mobility of the radical. However, the decrease was minimal on a day basis; therefore, in the present study we measured the decrease in the intensity (arbitrary units) of the first peak as a parameter against the storage time. In the fresh casting solution polymer molecules are not arranged in a regular way and may be entangled with each other, because polymer-polymer interaction dominates in the early stage of solution preparation. As the time passes the polymer molecules in the solvent arrange themselves in a more regular way because solvent-polymer interaction becomes more pronounced. As



**Figure 2** The height of the first peak (A in Fig. 1) of the  $\text{NO}^*$  radical in the casting solution versus storage time (days).



**Figure 3** The effect of age of the casting solution on (A) pure water permeation rate, (B) product rate, and (C) solute separation.

the rearrangement of the polymer molecules in the casting solution is in progress the mobility of the NO\* radical decreases.

Figure 3(A–C) shows pure water permeation rate, product permeation rate when the feed contains PEO solute, and solute separation, respectively, versus storage time. The storage time is set to equal to zero after 4 h from the start of the first UF experiment. It seems that during the early days of storage the membrane performance is not stabilized. The pure water permeation rate increased from day 1 to day 2, remained constant from day 2 to day 6, and thereafter kept decreasing. It stabilized after day 17.

The product rate kept increasing from day 1 to day 6, decreased from day 6 to day 7, and remained constant thereafter.

The solute separation increased from 70% to more than 80% during the first 6 or 7 days and then it stabilized.

All the above data kept changing in the first 6 or 7 days before they stabilized. It should be noted that the change in polymer mobility was fast in the earlier stage of solution storage before the mobility stabilized. Therefore, the change in the mobility of the polymer in the casting solution is clearly reflected in the UF performance of the membrane.

## CONCLUSIONS

From the present study the following conclusions can be drawn:

1. The ESR technique can be used to study the effect of casting solution storage on the membrane performance.
2. The polymer in the casting solution tends to become less mobile in the early days of storage.
3. The UF performance data are erratic when membranes are prepared from casting solutions in their early stage of storage.
4. The ESR technique seems to contribute to the quality control of membrane manufacturing.

We are indebted to Ms. A. M. Lamarche (Physics De-

partment, Univ. of Ottawa) for running the ESR and providing useful discussions.

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