

NOTE

Raman Scattering of PPO Membranes

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INTRODUCTION

The¹ nature of polymer– and polymer– interaction influences the structure of dense membranes that are cast from polymer solutions. Kesting¹ discussed in detail the formation of nodules, nodule aggregates, and super nodular aggregates on the surface of asymmetric membranes. Khulbe et al.² reported the change in the morphology of the surface with the thickness of the dense membrane. In our earlier study³ of the PPO membranes, prepared by using different solvents, it was observed that the Raman spectra (RS) of the top surfaces were different from each other. PPO is a semi-crystalline polymer.⁴ Various morphologies are possible between a completely crystalline and completely amorphous confirmation.

In the present communication we are presenting the observations by RS of the bottom surfaces of dense membranes. The results are further compared with the top surfaces of the membranes. These membranes were used for the gas separation.³

EXPERIMENTAL

Poly (2,6-dimethyl-1,4-phenylene oxide) (intrinsic viscosity = 1.79 dLg⁻¹ in chloroform at 25°C) was sup-

plied by General Electric Co., Selkirk, NY. The method for the preparation of membrane is described elsewhere.³ Table I shows the solvents used for the preparation of membranes, their boiling points, and the code name given to the membrane. Raman spectra (RS) were collected on a Dilor labram laser Raman microprobe system equipped with an Olympus BX40 microscope equipped with confocal instrument.³ Membranes were placed on a microscope slide, and He/Ne laser (615 nm) was used for excitation. Spectra of membranes were collected over the wave length range 900–1860 cm⁻¹ using a confocal hole 100 μm, which gives a depth resolution of 1 μm. The laser beam was focused right on the surface of the sample.

RESULTS AND DISCUSSION

The RS spectra of the PPO powder and the summary of the frequencies of RS as observed in PPO powder with respect to their possible groups are discussed elsewhere.³ In Figure 1, curves A and B show the RS of the top and bottom surfaces of the PPO–CS₂ membrane, respectively. Curve C indicates the differences between curve A and B.

As the solvent evaporates in the process of membrane formation, the surface of the casting solution starts to cool, and solution density increases, and both factors tend to set up vertical convection currents through the nascent membrane. Thus, there will be a temperature and density gradient between the bottom

Table I Solvent Used for the Preparation of Membranes and the Membrane Code

Solvent	Boiling Point °C	Name of the Membrane
Carbon disulfide	46.3	PPO—CS ₂
Benzene	80.1	PPO—TCE
Trichloro ethylene	89.6	PPO—C ₆ H ₆
Toluene	110.6	PPO—CH ₃ C ₆ H ₅
Chlorobenzene	132	PPO—ClC ₆ H ₅
Bromobenzene	156.2	PPO—BrC ₆ H ₅

surface (interface between casting solution and casting surface) and the top surface (interface between atmosphere and casting solution). Beside this, with any polymer solution there are a host of competing forces referred to as polymer-solvent interaction and polymer-polymer interaction.

Because polymeric films can be processed in a variety of ways (casting of solutions by doctor blade or spinning), it is fairly common that some orientation, either in plane or out of plane will be induced in functional groups. These reactions and change in properties could also be responsible for the change in RS between the top and the bottom surface of the membrane.

Similar results were obtained with PPO-TCE, PPO-C₆H₆, and PPO-CH₃C₆H₅ membranes. In the PPO-TCE membrane the frequency of the 1298 cm⁻¹ band, which is due to the R—O—R and C—C bridge bond, shifted toward higher frequency from powder. No significant differences between the top and bottom sur-

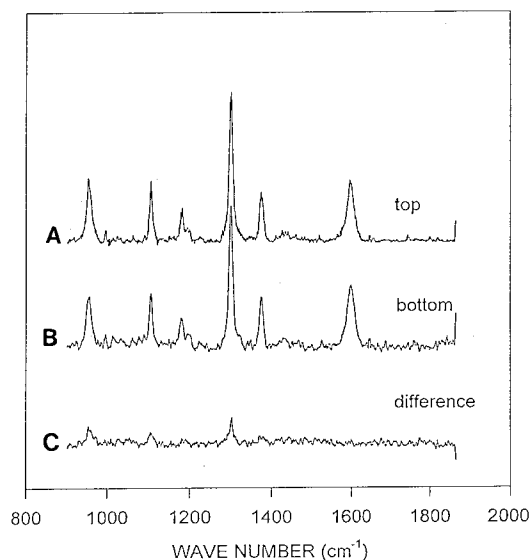


Figure 1 Raman spectra of PPO-CS₂ membrane. (A) top surface; (B) bottom surface; (C) differences between (A) and (B).

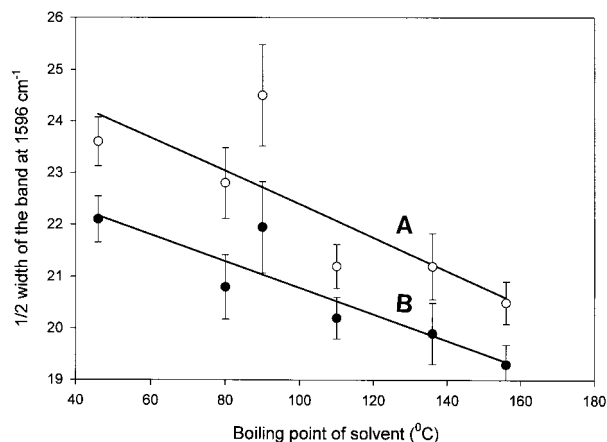


Figure 2 Half width of the band at 1596 cm⁻¹ vs. BP of the solvent used. (A) Top surface, (B) bottom surface.

faces were observed in PPO-ClC₆H₅ and PPO-BrC₆H₅ membranes. Both have high boiling point in comparison with other used solvents. From their RS spectra it was observed that the band at 1298 cm⁻¹ increased with the increase in the boiling point (BP) of the solvent used for the membrane preparation. The used solvents do not show any RS at 1298 cm⁻¹.⁵

Generally, with increasing crystallinity or state of order, absorption bands originating from interaction between conformationally regular units show decreasing bandwidths, while bands due to vibrations of amorphous regions with random conformation decrease in intensity. In other words, broader bands are observed from macromolecules in more amorphous regions, while sharper bands are associated with more crystalline regions. The effect is, however, qualitative, and it is not a straight forward matter to determine crystallinity from the bandwidth. Upon comparing the RS of PPO powder³ with those of the membranes, it was noticed that the band at 1596 cm⁻¹, which is assigned to the C—C stretch³ of the benzene ring, becomes sharper from powder to membranes. A similar effect is observed for the band at 1298 cm⁻¹. It suggests that the membranes have more crystalline phase than in the mother PPO powder.

On comparing RS of the top layer with the bottom layer of each membrane, it was noticed that the bands at 1596 cm⁻¹ and at 1298 cm⁻¹ of the bottom layer were sharper and narrower than the top layers. This again suggests that the bottom layer contains more crystalline phase than in the top layer.

Figure 2 shows the half width of the band at 1596 cm⁻¹, which is assigned to the benzene ring of the polymer,³ vs. boiling point (BP) of the solvent used for the preparation of the membranes. In Figure 2, curve A represents the top surface and B the bottom surface. From Figure 2 it seems that in both cases, i.e., the top and bottom, the half width decreases with an increase in the boiling point of the solvent with an exception of

Table II Ratio of the Height of the RS Bands at 1298 cm^{-1} to That of 1596 cm^{-1}

Membrane	Ratio for Top Surface	Ratio for Bottom Surface
PPO—CS ₂	2.7	2.2
PPO—C ₆ H ₆	2.4	2.2
PPO—TCE	2.7	2.4
PPO—CH ₃ C ₆ H ₅	2.6	2.3
PPO—ClC ₆ H ₅	2.3	2.2
PPO—BrC ₆ H ₅	2.3	2.2

the PPO—TCE membrane. In other words, crystallinity in the membrane depends on the BP of the solvent used. Figure 2 also reveals that the top surface is more amorphous than the bottom surface as the half width of the 1596 cm^{-1} band of the top surface is larger than the bottom surface.

Table II shows the ratio of the height of band at 1298 cm^{-1} to that of band at 1596 cm^{-1} of the top surfaces (column 1) and the bottom surfaces (column 2) of the membranes. In general, the ratio decreases with the increase of BP of the solvents, with the exception of the PPO—C₆H₆ and PPO—TCE membranes. It is reported that the mean roughness of the top layer (skin layer) depends on the BP of the solvent used (varied between 1.009 to 3.463 nm)³ with the exception of the PPO—TCE membrane (0.172 nm). The PPO—CS₂ membrane's surface layer contained supernodular aggregates. These supernodular aggregates consisted of nodules, while the other studied membranes did not have supernodular aggregates. The roughness parameter of the bottom surface varied from 0.13 (PPO—C₆H₆) to 0.255 nm

(PPO—BrC₆H₅). No general conclusion could be drawn between the boiling point of the solvents used and the roughness parameter of the bottom surfaces. It was observed that AFM images of all the bottom surfaces of the cast membranes were similar, as membranes were cast over glass plates, the surface of which was approximately of the same nature.³ Moreover, the ratio of the two bands is higher at the top in PPO—TCE and PPO—CS₂ membranes in comparison with other membranes. In an earlier study, PPO—TCE and PPO—CS₂ membranes showed better selectivity and lower permeability for O₂ and N₂ and CO₂ and CH₄ separation.³ It is possible that the orientation of the C—O—C group has some effect on the performance of the membranes.

CONCLUSIONS

From the present study following conclusions can be drawn: (a) top layer is more amorphous than the bottom layer of the dense membrane. (b) Crystalline phase in the dense membrane depends on the BP of solvent used for the preparation of the membrane.

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