

# Viscosity Behavior of Microwave-Heated and Conventionally Heated Poly(ether sulfone)/Dimethylformamide/Lithium Bromide Polymer Solutions

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**ABSTRACT:** This article investigates the viscosity behavior of new membrane dope solutions of poly(ether sulfone) (PES) and dimethylformamide with low-molecular-weight halogenated lithium bromide (LiBr) additives prepared with two different techniques: (1) a microwave (MW) technique and (2) a conventional heating (CH) technique. In addition, the influence of different concentrations of anhydrous halogenated LiBr additives (0–5 wt %) on the viscosity behavior is analyzed. The viscosity of the dope solutions was assessed with a conical rheometer equipped with a high-viscosity adapter. The results revealed that the pure

PES solutions prepared by the MW and CH techniques exhibited pseudoplastic and Newtonian behavior, respectively. Both the MW and CH PES solutions containing the LiBr additives exhibited dilatant behavior, which obeyed the power law. The apparent viscosity of all the dope solutions prepared with the MW technique was lower than that of those prepared with the CH technique. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 302–307, 2008

**Key words:** additives; halogenated; membranes; poly(ether sulfones); viscosity

## INTRODUCTION

The introduction of a suitable additive to a casting solution is a convenient and efficient method of increasing the hydrophilic property of a membrane, and the compatibility of polymers with additives can often play a decisive role in the physical modification of fiber-forming polymers. The additives may be water, inorganic salts, low-molecular-weight organics, surfactants, polymers, mineral fillers, or blends of all of these. There are several mechanisms through which such additives can affect the final membrane properties,<sup>1–6</sup> and rheometry has been shown to be a very sensitive technique for detecting physical and chemical changes in these blends.<sup>7</sup>

The presence of the additives in the dope not only changes the thermodynamic state of the dope but also influences the conformation and dynamics of the polymer, which in turn affects the kinetics of phase separation.<sup>8</sup> However, the latter is seldom mentioned in the literature. Nevertheless, the rheological properties of multicomponent polymer systems are related closely to the interaction between

the components and the phase configuration; the rheological response can reflect a change in the conformation of macromolecules exactly.<sup>9</sup> In a membrane-forming system, rheological properties are significantly affected by the quality of the solvent mixture,<sup>10</sup> which is usually degraded by additives in dimethylformamide (DMF). Although DMF is a dipolar, nonaqueous compound representative of amidic solvents, because of their ability to modify the potential reactivity of reacting states in electron- and proton-transfer reactions, these amides are widely used in settings such as solvent–reactivity relationships. DMF as a pure solvent is certainly to some extent associated by means of a nonspecific dipole–dipole interaction, and it is of particular interest because significant structural effects are absent on account of the lack of hydrogen bonds. Therefore, it may work as an aprotic, protophilic solvent of a large dipole moment (3.24 D) and a high dielectric constant (36.70) at 298.15 K.<sup>11</sup> Besides that, poly(ether sulfone) (PES) is an important polymeric membrane material because of its chemical resistance, mechanical strength, thermal stability, and transport properties,<sup>12</sup> with a low dielectric loss or tangent loss (0.0022 at 1 Hz).

A change in the rheological properties of the dope, including a change in the viscosity, can influence the nonsolvent–solvent exchange, the velocity of phase separation, and the gelation dynamics.<sup>10</sup> To some extent, the competition between the three

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dynamic processes determines the structure and performance of the resultant membrane. Therefore, rheology is likely to be a powerful tool for an investigation into the mechanism of membrane formation.<sup>9</sup> The mechanisms through which these additives can affect the final membrane characteristics have been reported through the changing solvent capacity of additives,<sup>13</sup> phase inversion kinetics, and thermodynamic properties.<sup>10,14</sup> Torrestiana-Sanchez<sup>6</sup> reported the effect of the introduction of poly(vinyl pyrrolidone) and poly(ethylene glycol) on the thermodynamic and rheological properties in PES casting solutions. Idris et al.<sup>15</sup> and Gordeyev et al.<sup>16</sup> revealed that the morphology and performance of membranes are strongly influenced by the rheological properties and the shear history imposed on the dope solutions.

Previously, for the production of polymeric membranes, homogeneous dope solutions were prepared with a media flame, oil bath, and electrothermal heating for a minimum of 6 h to a maximum of 24 h at 60–95°C.<sup>17–19</sup> Among these methods, electrothermal heating, also known as conventional heating (CH), is the most common currently used method. These initial processes are expensive and time-consuming. Unfortunately, the number of appropriate initial processes of polymeric membrane preparation, which can be used in such production, is limited.

The influence of halogenated low-molecular-weight lithium bromide (LiBr) additives on the viscosity behavior of PES dope solutions prepared with the microwave (MW) technique has so far not been reported. Thus, the objective of this article is to study the viscosity behavior of PES/DMF/LiBr polymer dope solutions prepared with MW and CH techniques.

## EXPERIMENTAL

### Materials

PES [Ultrasont E 6020P; weight-average molecular weight = 58,000, weight-average molecular weight/number-average molecular weight = 3.6] was used as the polymer and was procured from BASF. The solvent DMF [HCON(CH<sub>3</sub>)<sub>2</sub>; weight-average molecular weight = 80.14 g/mol] of 99.8% purity was purchased from Labscan Asia Co., Ltd., and was used without further purification. Analytical-grade, anhydrous LiBr (>99%, molecular weight = 86.84) was procured from Acros Organic (USA). LiBr was dried with MWs at a high pulse for 10 min before dissolving into the solution.

### Dope preparation

The prepared dope solutions consisted of 20% PES and various compositions of DMF and LiBr as tabu-

**TABLE I**  
**Formulations of Different Dope Solutions**

No.	PES (wt %)	LiBr (wt %)	DMF (wt %)
1	20	0	80
2	20	1	79
3	20	2	78
4	20	3	77
5	20	4	76
6	20	5	75

lated in Table I. These solutions were prepared with two different techniques, as described next.

### MW technique

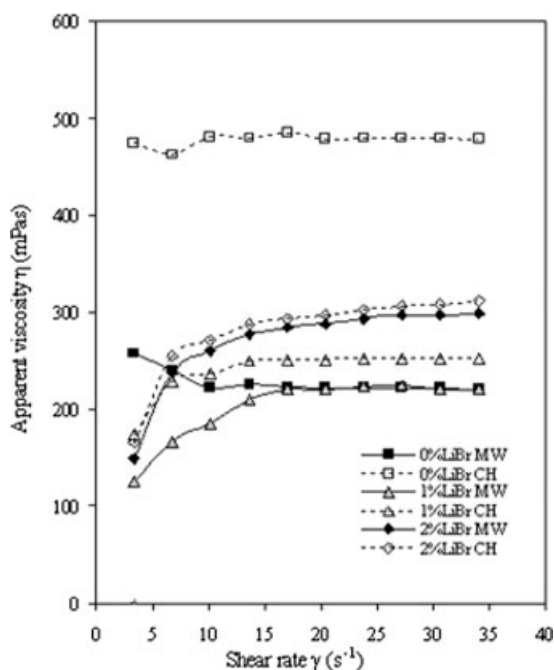
In this study, a National domestic MW oven (model NN-5626F) with the following specifications was used: rated power output of 900 W (240 V, 50 Hz) and operation frequency of 2450 MHz. The oven was modified in such a manner that the two-necked glass vessel was sealed and directly placed in the MW oven. Care was taken so that  $\lambda$  was less than 5 cm to ensure safety. PES and LiBr were initially dried in the MW oven for about 10 min at a medium pulse to remove the moisture content. The polymer was next dissolved in DMF. The dissolution process was performed in the two-necked glass vessel setup mentioned earlier, which had a glass connector attached to the reflux condenser, a thermocouple to control the temperature, and a stirrer inside the vessel to ensure homogeneity. The temperature of the dope solution was kept at 85–95°C and was measured by the thermocouple. The MW heating time was 15 min (set at low to high pulses), and the dissolution time was kept to a maximum of 1 h.

### CH technique

In CH, the polymer dissolution process was carried out in a 1-L, four-necked, round-bottom flask with a stirrer and condenser as described elsewhere.<sup>20</sup> A Barnstead/Electrothermal electrothermal heater (230 V, 50/60 Hz, 300 W) was used. The dope temperature was kept constant at 90–95°C with stirring, and the dissolution of the polymer took 7–24 h.

### Viscosity measurement of the PES/DMF/LiBr dope solutions

The apparent viscosity (mPa s) of the dope solutions was measured with Brookfield (USA) model DV-III digital rheometer equipped with a sample adaptor (SC4-31). The viscosity measurements as a function of the shear rate were performed at the ambient temperature (25°C). Each flow curve was obtained as an average of at least three measurements.



**Figure 1** Apparent viscosities of MW and CH PES/DMF solutions with 0–2 wt % LiBr additives at different shear rates.

### Rheological properties of the PES/LiBr solution

The rheological properties of the PES/DMF/LiBr solution were interpreted with the power law according to the following equation:<sup>21</sup>

$$\tau = k\gamma^n \quad (1)$$

where  $\tau$  is the shear stress (Pa),  $\gamma$  is the shear rate ( $\text{s}^{-1}$ ),  $n$  is the flow behavior index (dimensionless), and  $k$  is the consistency index ( $\text{Pa s}^n$ ).

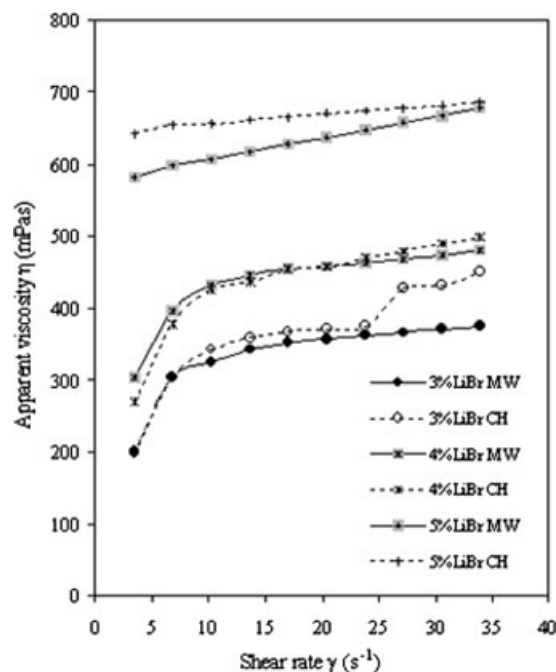
## RESULTS AND DISCUSSION

The apparent viscosities exerted by the MW and CH PES/DMF/LiBr solutions as a function of the shear rate measured at  $25^\circ\text{C}$  are depicted in Figures 1 and 2. At very low shear rates (region below  $10 \text{ s}^{-1}$ ), fluctuations and nonlinear data are observed for most of the solutions because of the limitations of the equipment precision. However, it can be observed that at shear rates above  $10 \text{ s}^{-1}$ , the viscosities of the dope solutions are almost constant. Similar observations have been reported for other membrane solutions.<sup>15</sup> In general, two main observations can be made for the PES/DMF solutions containing various concentrations of LiBr additives.

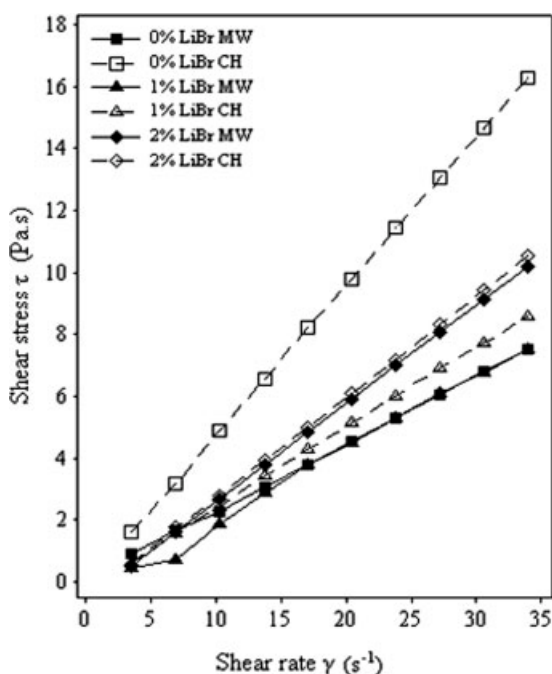
First, the apparent viscosities for all the MW solutions are lower than those of the solutions prepared with CH, and this can be clearly observed in Figures 1 and 2. However, the viscosity difference is not as significant as that of the pure PES solution. It is

observed that the difference in the apparent viscosity for the pure PES solution (without LiBr) prepared with the MW and CH techniques is very significant. The pure PES solution prepared with the MW technique has an approximately 50% lower apparent viscosity than the one prepared with CH (see Fig. 1). The low viscosity might be attributed to the fact that DMF and PES are materials with a high dielectric constant and a low dielectric loss. When these molecules are irradiated with MWs, they will attempt to align themselves with the electric field by rotation, and if the frequency of the molecular rotation is the frequency of MW irradiation (2.45 GHz), the molecules will continually align and realign themselves with the oscillating field, thus absorbing the electric energy by a mechanism called dipolar rotation.<sup>22</sup> The ability of these compounds to absorb energy readily under MW irradiation and convert the absorbed energy into heat results in a very short dissolution time and thus produces solutions of low viscosity. There is a possibility that MW radiation could cause polymer scission to occur, and this is reflected in the reduced viscosity.<sup>23</sup>

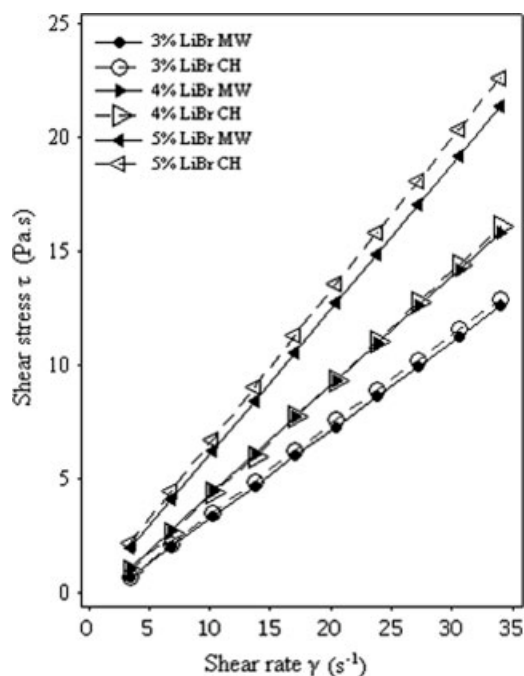
Second, the concentration of LiBr affects the viscosity of the solution, and this can be observed from Figures 1 and 2. With low concentrations of LiBr (1–2 wt %), a small increment in the viscosity is observed. A further increase in the LiBr concentration ( $>3 \text{ wt } \%$ ) results in much higher increments in the viscosity. The addition of anhydrous LiBr ( $>3 \text{ wt } \%$ ) to the casting solution in DMF results in com-



**Figure 2** Apparent viscosities of MW and CH PES/DMF solutions with 3–5 wt % LiBr additives at different shear rates.



**Figure 3** Shear stress versus the shear rate of MW and CH PES/DMF solutions with 0–2 wt % LiBr additives.



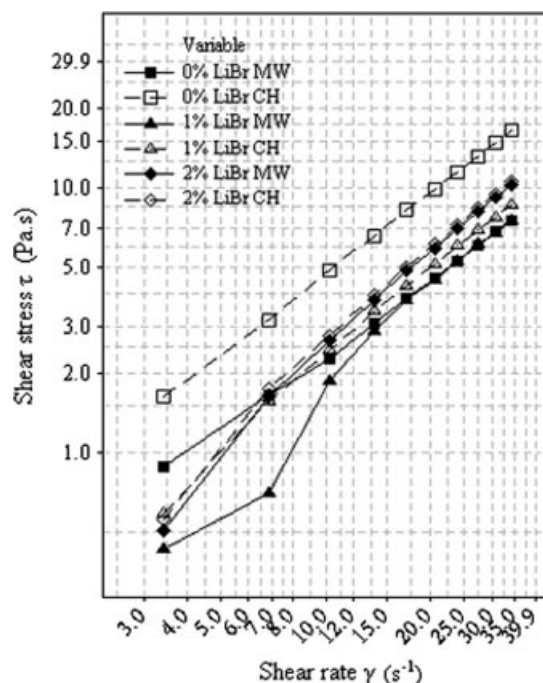
**Figure 4** Shear stress versus the shear rate of MW and CH PES/DMF solutions with 3–5 wt % LiBr additives.

plexes between anhydrous LiBr and DMF, resulting in reduced solvent power and transient crosslinks, and this is exhibited by the increased viscosity. LiBr interacts more strongly with DMF because of favorable interactions between LiBr and DMF. Besides the LiBr–solvent interactions, the association between  $\text{Li}^+$  cations and the polymer network could also be a contributing factor to the increase in viscosity. Bottino et al.<sup>24</sup> revealed similar findings and explained that the higher viscosity of a poly(vinylidene fluoride)–*N*-methylpyrrolidone solution containing LiCl compared to a salt-free solution resulted not only from LiCl–solvent interactions but also probably from interactions between  $\text{Li}^+$  cations and the strong electron-donating groups in poly(vinylidene fluoride).

Figures 3 and 4 depict the results of flow curves of the various dope solutions as the shear rate increases. The shear stress increases linearly as the shear rate increases at each concentration. A similar trend is observed for the logarithm of the shear stress versus the shear rate at each concentration, as shown in Figures 5 and 6. The flow curves and behavior for the CH PES dope solution and the MW solution show an almost similar trend. The results show that the power-law model adequately describes the experimental data for MW and CH pure PES/DMF and PES/DMF/LiBr dope solutions. From these plots, the values of the rheological parameters  $n$  and  $k$  have been evaluated, and they are tabulated in Table II. The results seem to suggest that a pure PES solution prepared by the MW technique exhibits pseudoplastic behavior with a flow

index value of  $n < 1$ , whereas that prepared with CH displays a Newtonian fluid with  $n = 1$ .

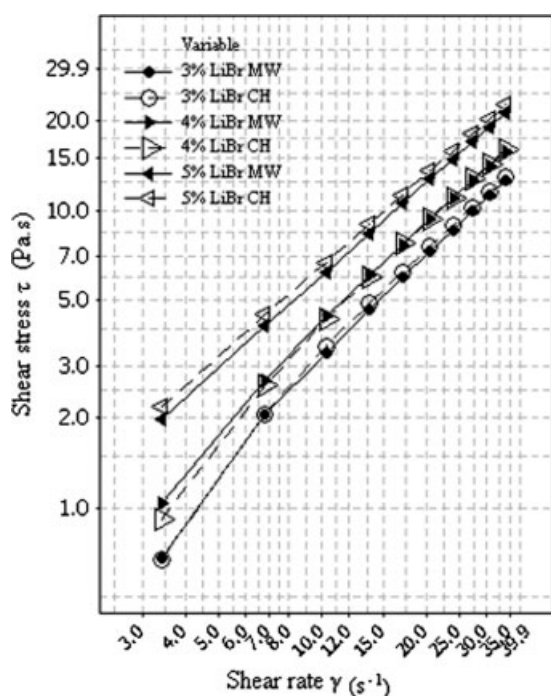
The addition of LiBr additives results in a change in the rheological behavior from pseudoplastic to dilatant. The flow index values of the PES dope solu-



**Figure 5** Logarithm of the shear stress versus the logarithm of the shear rate of MW and CH PES/DMF solutions with 0–2 wt % LiBr additives.

tions containing LiBr prepared with both methods are close to one another, with  $n > 1$  indicating dilatant fluids. The dilatant behavior may be explained by increased flexibility of the chains in the presence of LiBr in both techniques. The difference in viscosity between MW and CH could be related to the flexibility of the polymeric chains, which may be associated with the torsion angles of the polyether linkages, and maybe this flexibility of the polymeric chain is more aggressive in MW dope solutions. In addition, small amounts of chain scission could have occurred under MW radiation, producing solutions with slightly lower viscosity.<sup>23</sup> Low concentrations of LiBr (<3 wt %) do not have the tendency to increase the solvation power of PES, thus explaining the unchanged low apparent viscosities.

The results also suggest that the dilatant behavior is caused not only by the orientation but also by the molecular interaction of  $\text{Li}^+$  ions. In media of high-dielectric-constant DMF, the dissociable group is ionized, and macromolecules are assumed to have extended colorations because of repulsive electrostatic interactions between charged groups. Thus, the polymer–solvent interaction appears to be an important or dominant factor influencing the coloration, size, and shape of macromolecules.<sup>25</sup> Furthermore, the viscosity of the macromolecular solution is a function of the binding force between the solvent and dissociable groups of the macromolecule. Therefore, it is expected that an MW PES dope solution



**Figure 6** Logarithm of the shear stress versus the logarithm of the shear rate of MW and CH PES/DMF solutions with 3–5 wt % LiBr additives.

**TABLE II**  
Consistency Indices ( $k_{\text{MW}}$  and  $k_{\text{CH}}$ ) and Flow Behavior Indices ( $n_{\text{MW}}$  and  $n_{\text{CH}}$ ) of Various Dope Solutions for Both MW and CH

LiBr (w/w %)	MW			CH		
	$n_{\text{MW}}$	$k_{\text{MW}}$ (mPa/s)	$R^2_{\text{MW}}$	$n_{\text{CH}}$	$k_{\text{CH}}$ (mPa/s)	$R^2_{\text{CH}}$
0	0.938	2.691	0.999	1.009	4.660	0.999
1	1.322	0.782	0.984	1.138	1.639	0.995
2	1.262	0.289	0.991	1.235	1.446	0.992
3	1.231	1.753	0.993	1.245	1.733	0.991
4	1.163	2.762	0.996	1.218	2.337	0.995
5	1.033	5.628	1.000	1.014	6.360	1.000

with LiBr will contain more ionic groups than CH PES/LiBr dope solutions.

As the LiBr concentration increases from 1 to 5 wt %,  $k$  of the solution increases.  $k$  is related to the thickness of the dope: the higher the  $k$  value is, the higher the apparent viscosity is. However,  $n$ , which is the non-Newtonian degree, is related to the shear-thinning behavior: the lower the  $n$  value is, the greater the shear thinning and molecular alignment are. Hence, increasing the concentration to 5 wt % LiBr increases the viscosity drastically but without much change in the shear thinning and molecular alignment.

LiBr is an ionic substance that possesses large dielectric constants and is therefore very MW-reactive. Adding a small quantity to the polar solvent drastically increases the solvent heating temperature, and the dissolution of PES in solution takes only 15 min for the 1 wt % LiBr composition. Differences in solvation of the cations are also factors that can influence the Gibbs free energies of the ion–molecule interaction. This shows a tendency to form stable complexes with alkali-metal cations.<sup>26</sup> Although there is only a small difference in the viscosity behavior or flow curves for the PES/LiBr dope solutions with the two different techniques, the MW technique is able to prepare the dope solution in a very short time, as quick as 15 min for 1 wt % LiBr. In fact, 3 wt % LiBr takes almost 24 h to dissolve with CH versus less than 1 h for the MW technique. In addition, the dope solutions prepared with the MW technique produce generally lower viscosity solutions, which are easier to cast and spin, thus easing the processing of membranes. In fact, in a recent study,<sup>27</sup> membranes produced with the MW technique were far superior in terms of the flux rate to those prepared with the CH method.

## CONCLUSIONS

The Ostwald–deWaele model can satisfactorily describe the viscosity behavior of PES dope solutions

prepared by the MW and CH techniques. Pseudoplastic behavior has been observed in pure PES solutions prepared with MW, whereas Newtonian behavior has been observed for the CH PES solutions. The addition of LiBr has a marked influence on the viscosity of PES dope solutions, as shown by the flow curves. The rheological parameters also indicate that a PES solution with LiBr can be adequately classified as a dilatant fluid. The results also reveal that the MW PES dope solutions with and without LiBr are very stable, can be prepared in a very short time (the preparation time is reduced by as much as  $\approx 85\text{--}96\%$ ), and generally have a slightly lower viscosity. These characteristics minimize electric energy consumption and ease the process of spinning and casting of membranes, thus making the MW technique attractive.

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