

# Metal-Solvating and Self-Association of Amphiphilic Polyamides Containing Poly(oxyethylene) Blocks

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**ABSTRACT:** An amphiphilic poly(ether amide) consisting of hydrophilic poly(oxyethylene) amide blocks was prepared from the copolymerization of sebacic acid and two poly(oxyalkylene) diamines including a poly(oxyethylene) diamine (POE-amine at 2000  $M_w$ ) and a poly(oxypropylene) diamine (POP-amine at 230  $M_w$ ). The copolymer was estimated to have an average molecular weight of 15,000  $M_w$  (GPC) or approximately three hydrophilic POE segments per strain. The presence of POE segments rendered polymer hydrophilicity and complexing ability for  $\text{Li}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{Pd}^{+2}$ , and  $\text{Cu}^{+2}$  salts. In particular, lithium perchlorate affected the copolymer to the greatest extent in enhancing electrostatic dissipation or reducing surface resistivity as low as  $10^{5.0}$   $\Omega/\text{sq}$  (cross-sectional area) at 1/180  $\text{Li}^+/\text{EO}$  from  $10^{7.2}$   $\Omega/\text{sq}$  (without metal ion). In such a metal complexation, the copolymer showed a new POE segmental crystalline phase at a melting temperature between  $-10.4$  and  $-14^\circ\text{C}$ , accompanied with the metal-free original phase of  $-31^\circ\text{C}$ . In static toluene/water, the metal ions had no effect on the copolymer surfactancy in lowering the interfacial tension, reaching 4.4 dyn/cm at a critical micelle concentration (cmc) of 0.01 wt %. When mixing toluene and water, the lithium or nickel ions were found to be detrimental to the emulsifying process. Without the metal ion, fine droplets at average sizes of 4.5–5.0  $\mu\text{m}$  were observed in the copolymer/toluene/water emulsification. These amphiphilic behaviors of the POE-segmented polyamide with or without metal ions were explained by the competing noncovalent bonding interactions among POE/metal ion/water. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 612–621, 2002

**Key words:** polyamides; hydrophilic polymers; block copolymers; polyelectrolytes; surfactants

## INTRODUCTION

The presence of poly(oxyethylene) (POE) blocks may result in the characteristic hydrophilicity, crystallinity, and metal-binding ability of copolymers, primarily attributable to dipole–dipole interaction of the  $-(\text{CH}_2\text{CH}_2\text{O})_x-$  structure.<sup>1–3</sup> By

varying the length, weight fraction, and functionality of the POE-derived copolymers, one can tailor the polymer properties into a variety of industrial applications including surface-active agents,<sup>4,5</sup> drug-control release,<sup>3</sup> gels,<sup>6</sup> dispersants,<sup>7</sup> antistatics,<sup>8</sup> solid electrolytes,<sup>3,9</sup> and so forth. Among these applications, copolymers containing POE segments may be used as electrostatic-dissipating materials with a suitable range of surface resistivity from  $10^{10}$  to  $10^7$   $\Omega/\text{sq}$  (cross-sectional area). The POE segments in the structure provide the hydrophilicity for adsorbing moisture in the atmosphere and facilitate the lowering of surface resistivity.<sup>10–14</sup> For

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example, the copolymer structures composed of polyether-segmented poly- $\epsilon$ -caprolactam and polyether-ester-amide derived from polyethylene glycol and aminocarboxylic acid have been determined.<sup>11,12</sup> Furthermore, the factors including weight fraction and segmental crystallinity of the POE segments were found to be important in modifying the hydrophilicity of poly(styrene/butadiene/styrene),<sup>13</sup> polyamide,<sup>8,14</sup> polypropylene,<sup>15</sup> and epoxies.<sup>16</sup> The resultant copolymers had an enhanced hydrophilicity resulting from the existence of a possible hydrogen-bonding association between POE and water.

In the literature, it has been broadly established that metal salts can interact with different classes of polymers in altering their properties. For example, lithium salts can effectively promote the ionic conductivity of POE-derived polymers used as solid electrolytes.<sup>3,9</sup> The interaction of dendritic polymers with metal salts, followed by reduction, to form metal nanoclusters including gold, platinum, silver,<sup>17</sup> and copper<sup>18,19</sup> was found to be of academic and industrial interest. In biological processes, the metal-induced phase change in aqueous solution may occur in a very low concentration of metal ion. A specific example of Fe(III) coordination with a naturally occurring and amphiphilic polypeptide, resulting in the micelle transformation into different shapes, was reported.<sup>20</sup>

In this study, we report the preparation and characterization of a novel POE-segmented polyamide, as well as the metal ion effects on its self-association properties. The poly(ether amide) (PA), of 52 wt % POE composition, is hydrophilic but insoluble in water. The copolymer is considered to be amphiphilic with respect to its constituents, including distinct blocks of hydrophilic POE amides, less-hydrophilic POP amides, and hydrophobic C<sub>8</sub>H<sub>16</sub> amides. Various metal ions including Li<sup>+</sup> and Ni<sup>+2</sup> were used to complex with the amphiphilic copolymer through the POE segments. Upon the metal coordination, the changes in the amphiphilic nature and self-association properties of the copolymer were studied.

## EXPERIMENTAL

### Materials

Sebacic acid was purchased from Aldrich Chemical Co. (Milwaukee, WI). Poly(oxypropylene)-*b*-poly(oxyethylene)-*b*-poly(oxypropylene) diamines

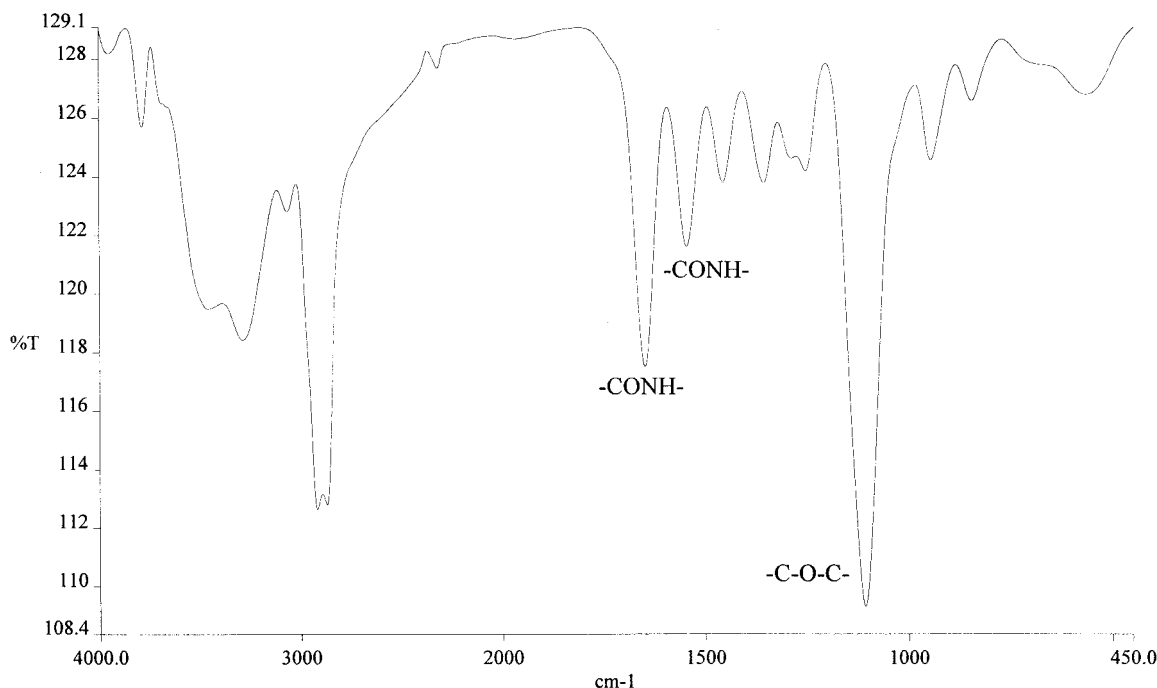
[MW 2000 (i.e., Jeffamine<sup>®</sup> ED2001)] and poly(propylene glycol) bis(2-aminopropyl ether) [MW 230 (i.e., Jeffamine<sup>®</sup> D230)] were purchased from Huntsman Chemical Co. (Austin, TX) or Aldrich. All metal salts including lithium chloride, potassium chloride, calcium chloride, palladium chloride, nickel chloride, and other metal salts were obtained from Aldrich and used as received.

### Preparation of POE-Segmented Polyamides

The preparation of the POE-segmented poly(ether amide) (PA) involved the use of sebacic acid and the combination of two amines at 1 : 1M ratio of acid/amine. Typical experimental procedures<sup>8</sup> are described below. A 250-mL, three-neck, round-bottom resin flask, equipped with heating device, temperature controller, mechanical stirrer, Dean–Stark trap, air condenser, and nitrogen inlet–outlet line, was charged with sebacic acid (77.8 g, 385 mmol) and poly(oxypropylene)-*b*-poly(oxyethylene)-*b*-poly(oxypropylene) diamines [MW 2000 (i.e., Jeffamine<sup>®</sup> ED2001), white waxy solid, m.p. 37–40°C, total amine 0.95 mequiv/g; 150 g, 75 mmol]. With stirring, the mixture was heated to 150°C for 4 h, followed by addition of the second amine, poly(propylene glycol) bis(2-aminopropyl ether) [MW 230 (i.e., Jeffamine<sup>®</sup> D230), liquid product with amine content of 8.45 mequiv/g; 71.3 g, 310 mmol]. The reaction was maintained at 220°C for an additional 4 h. During the process, water was generated and removed under nitrogen flow through a Dean–Stark trap. At 220°C, the product mixture, a viscous light-colored liquid, was poured into a flat stainless steel container and allowed to cool to room temperature. The solid sample was conditioned for 24 h at room temperature under an atmosphere of 50% relative humidity and measured to have a surface resistivity of 10<sup>7.4</sup> ohm/sq. The average molecular weight was estimated to be 15,000 with a polydispersity of 1.5 ( $M_w/M_n$ ) by using gel-permeation chromatography (GPC). A typical FTIR spectrum (Fig. 1) showed the characteristic absorption at 1645 and 1546 cm<sup>-1</sup> (carbonyl of amides), and 1100 cm<sup>-1</sup> (C—O—C ethers). This PA prepared from sebacic acid and two polyether amines at 1 : 1 stoichiometric molar ratio of acid/amine was calculated to contain 52 wt % of hydrophilic POE segments.

### Preparation of Metal Complexes of PA

A 250-mL, three-neck, round-bottom resin flask, equipped with heating device, temperature con-



**Figure 1** FTIR absorption of poly(ether amide) (sebacic acid/ED2001/D230).

troller, mechanical stirrer, nitrogen inlet–outlet line, and Dean–Stark trap was charged with lithium perchlorate trihydrate (10.0 g, 94 mmol) in 100 mL ethanol and the PA (25 g, 1.6 mmol) prepared from the above procedures. The reaction mixture was heated to 120°C with stirring for 1 h. During the process, the solvent was removed through a Dean–Stark trap. The product was further subjected to a high vacuum at 80°C for 3 h and then poured into a flat container. At room temperature, the solid sample plaque was conditioned before measuring its surface resistivity. Various metal salts including  $K^+$ ,  $Ca^{+2}$ ,  $Pd^{+2}$ ,  $Cu^{+2}$ , and  $Ni^{+2}$  were introduced to the polyamide in the same manner. The results are summarized in Table I and Table II.

### Measurement

FTIR absorption was recorded by a Perkin–Elmer Paragon 500 FTIR spectrometer (Perkin Elmer Cetus Instruments, Norwalk, CT). Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were performed on a Seiko S II model SCC/5200 (Seiko Instruments, Tokyo, Japan). GPC analyses were performed in a Waters apparatus (515 HPLC pump, 717 autosampler, 2410 refractive index detector; Waters Associates, Milford, MA) with a calibration from the

polystyrene standard. Surface tension and interfacial tension were measured by using a K9 mobile tensiometer (Krüss, Germany). The emulsion solution was examined by optical microscope (Model BHT; Olympus, Lake Success, NY) at  $\times 1000$  magnification. The particle size was analyzed by a 90 Plus particle sizer (Brookhaven Instrument Co., Holtsville, NY). Surface resistivity was measured by using an ST-3 Model tester (Simco Co., Japan) according to ASTM D257-93. All samples were conditioned in a 50% relative humidity atmosphere at 30°C for 24 h before measurements were taken, except that samples for hydrophilicity measurements were conditioned in a 50% relative humidity atmosphere until equilibrium was reached.

## RESULTS AND DISCUSSION

### Synthesis and Characterization of PA

The poly(oxyalkylene) diamine–incorporated polyamides were prepared according to the method reported previously.<sup>8</sup> To prepare an amphiphilic PA, both the hydrophilic poly(oxyethylene) (POE) and the less-hydrophilic poly(oxypropylene) (POP) diamines were employed as comonomers. The POE-diamine (I) (MW 2000) and the POP-diamine (II)

**Table I Surface Resistivity of PA Complexed with Various Metal Salts**

Molar Ratio (Metal/EO) <sup>a</sup>	Weight Fraction <sup>b</sup> (wt %)	Surface Resistivity (10 <sup>x</sup> Ω/sq)
PA		
0	0	7.4
K <sup>+</sup> /EO		
1/3	30.0	5.2
1/9	10.0	5.3
1/15	6.0	5.5
1/45	2.0	5.4
1/180	0.5	5.7
Ca <sup>+2</sup> /EO		
1/9	10.0	6.6
1/18	5.0	6.5
1/63	1.4	6.6
1/117	0.8	7.0
1/350	0.3	7.2
Pd <sup>+2</sup> /EO		
1/18	13.2	5.6
1/63	3.7	6.4
1/117	2.0	6.2
1/270	0.9	6.3
Cu <sup>+2</sup> /EO		
1/18	10.2	5.5
1/63	2.9	6.1
1/270	0.7	6.2
1/350	0.5	6.6
Ni <sup>+2</sup> /EO		
1/18	3.7	5.4
1/63	1.0	6.1
1/117	0.6	6.4
1/270	0.5	6.6

<sup>a</sup> All metal salts are in chloride forms.<sup>b</sup> Weight fraction: metal salt/PA.

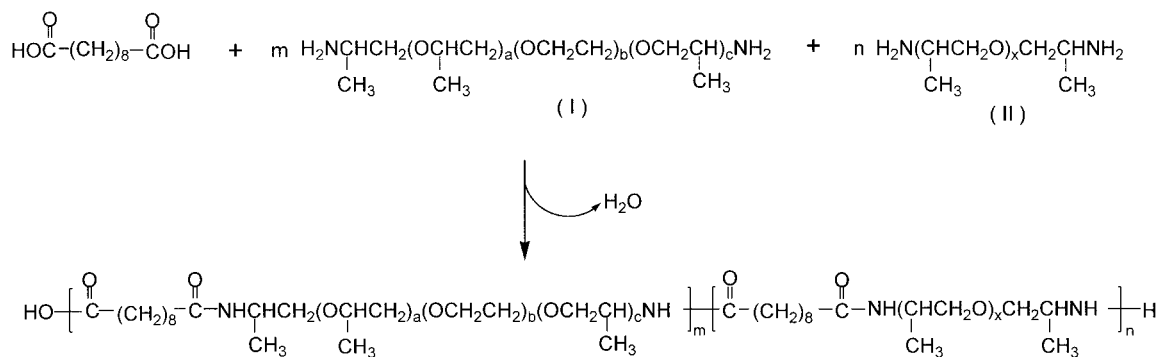
(MW 230) at a designated molar ratio, were combined and allowed to react with the stoichiometric equivalent of sebacic acid, that is, 1 : 1M ratio of total -NH<sub>2</sub> to -COOH, according to the reaction **Scheme 1**. The POE-diamine (I) monomer actually consists of a middle POE block and two capped POP blocks at both ends. With an oxyethylene-rich backbone (i.e., oxyethylene/oxypropylene molar ratio at 39.5/5.0), this starting monomer is water soluble and considered to be a POE amine. The second amine monomer, POP-diamine (II) of MW 230, is a low molecular weight poly(oxyalkylene) diamine with a less-hydrophilic POP backbone. These poly(oxyalkylene) amines are commercially available products prepared from catalytic reductive amination of the corresponding polyoxyalkylene glycol.<sup>21,22</sup>

By adjusting the molar ratio of two amines used, the amphiphilic PA containing approximately 50 wt % of POE composition is the optimized structure. The copolymers with a POE composition higher than 52 wt % have poor dimensional stability, whereas those below 50 wt % are either hydrophobic or of unacceptable hydrophilicity, according to the measurement of surface conductivity.<sup>8</sup> The PA can be prepared in two different reaction modes, including consecutive amine addition and one-pot addition using the mixture of two amines. Both products were not differentiable with respect to their GPC analyses and both physical and spectroscopic properties. The resultant copolymers are elastomeric solids with good structural integrity and melting points around 28 to 35°C. This 52 wt % POE-segmented PA is soluble in most organic solvents such as ethanol, chloroform, acetonitrile, THF, DMF, acetone, and toluene. However, the copolymer is insoluble in water, mainly because of the presence of hydrophobic C<sub>8</sub>H<sub>16</sub> sebacamides in the structure and high molecular weight. The metal salt-solvating PAs were made by introducing the metal salts in ethanol after the completion of the polymerization process. With and without metal salt addition, the copolymers showed a similar molecular weight distribution at a narrow range of 15,000–18,000 Da with a polydispersity of 1.5 (Table III).

**Table II Surface Resistivity of PA Complexed with Lithium Salts**

Lithium Salt	Molar Ratio (Li <sup>+</sup> /EO)	Weight Fraction <sup>a</sup> (wt %)	Surface Resistivity (10 <sup>x</sup> Ω/sq)
None	0	0	7.4
LiCl	1/45	1.0	6.2
LiCl	1/180	0.3	6.4
LiBr	1/180	1.1	5.4
LiBr	1/350	0.6	5.7
LiI	1/45	8.6	4.6
LiI	1/180	2.2	5.0
LiClO <sub>4</sub>	1/45	7.4	4.9
LiClO <sub>4</sub>	1/180	2.0	5.0
LiClO <sub>4</sub>	1/350	1.0	5.6
Li <sub>2</sub> CO <sub>3</sub>	1/180	0.9	5.7
Li <sub>2</sub> CO <sub>3</sub>	1/350	0.5	5.8
CF <sub>3</sub> SO <sub>3</sub> Li	1/180	1.9	5.1
CF <sub>3</sub> SO <sub>3</sub> Li	1/350	1.0	5.6

<sup>a</sup> Weight fraction: metal salt/PA.



(I) POE-diamine:  $a+c=5.0$ ,  $b=39.5$  (Approx.  $M_w = 2000$ , i.e., Jeffamine<sup>R</sup> ED2001)

(II) POP-diamine:  $x=2.6$  (Approx.  $M_w = 230$ , i.e., Jeffamine<sup>R</sup> D230)

**Scheme 1** Copolymerization of sebacic acid and two different poly(oxyalkylene) diamines.

### Thermal Stability

The relative thermal stability of the PA and the nickel salt-solvating PA was analyzed by TGA in both nitrogen and air to understand their relative thermal stabilities. It appeared that the addition of nickel (II) chloride with molar ratios from 1/350 to 1/117 and to 1/18 of  $\text{Ni}^{+2}/\text{EO}$  in PA had no significant effect on the copolymer thermal stability in nitrogen. All of these samples had an identical 50 wt % decomposition temperature at 399°C. However, under the oxidative conditions, the presence of nickel (II) chloride rendered the copolymer slightly more stable, as indicated in Figure 2 [curve (d)]. The 50% weight loss temperature shifted from 382 to 390°C for the  $\text{Ni}^{+2}/\text{EO} = 1/18$  copolymer. There is no literature report of the  $\text{Ni}^{+2}$  effect on polyoxyethylene block; however, the effects of NaCNS and other metals on the stability of polyoxyethylene block have been reported.<sup>23,24</sup> These studies provide evidence that

both anion and cation could play a role in the stabilization of PEO polymers.

### Hydrophilicity of PA With and Without Metal Ions

The amphiphilic PA has both hydrophilic and hydrophobic functionalities in the same polymer chain. The apparent hydrophilicity of the PA with multiple hydrophilic POE-amide segments of MW 2000 can be measured directly from the moisture adsorption from the atmosphere. Because of the presence of the POE or  $-(\text{OCH}_2\text{CH}_2)_x-$  segments, the copolymer has a tendency of adsorbing water through hydrogen bonding. When the polymer was exposed to moist air, it was found that the samples gained weight at a rapid rate initially and reached equilibrium after 2–3 days. Under the atmosphere of 50% of relative humidity, the copolymers could adsorb up to 13 wt % of moisture as measured by TGA. However, the rate of saturation of moisture adsorption was

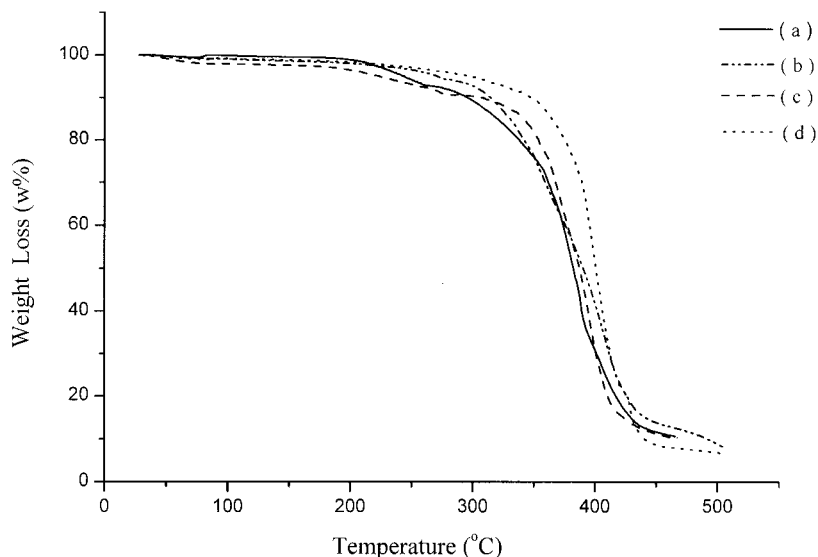
**Table III** Characteristics of Poly(oxyethylene-oxypropylene)-Segmented PA

Composition	$M_w$ (GPC)	Polydispersity ( $M_w/M_n$ )	(POE + POP) <sup>a</sup> (wt %)	H <sub>2</sub> O Adsorption <sup>b</sup> (wt %)
ED2001	2700	1.3	96.4	22
PA <sup>c</sup>	14800	1.5	67.1	13
PA/ $\text{Ni}^{+2}$	15700	1.6	67.1	15
PA/ $\text{Li}^+$	17700	1.5	67.1	11

<sup>a</sup> Calculated weight fraction based on the theoretical stoichiometry.

<sup>b</sup> Analyzed by TGA.

<sup>c</sup> PA, poly(ether amide) prepared from sebacic acid/ED2001/D230.



**Figure 2** Thermal degradation of PA/Ni<sup>2+</sup> at different Ni<sup>2+</sup>/EO ratios of (a) 0, (b) 1/350, (c) 1/117, and (d) 1/18 in air.

not affected by the Li<sup>+</sup> and Ni<sup>2+</sup> solvating on the copolymers, which gained 11 and 15 wt %, respectively, (Table III). It was roughly estimated to have 1.5 units of EO in binding with 1 mol of water molecules or H<sub>2</sub>O/EO = 1/1.5, regardless of the presence of metal ions.

#### Electrostatic and Ionic-Conducting Properties of POE/H<sub>2</sub>O Versus POE/Metal Ion

The POE segments in PA have characteristically expressed an affinity to both water and metal ions in affecting the electric conducting property, which can be probed by measuring their surface resistivities. In general, materials with a surface resistivity in the range of 10<sup>10</sup> to 10<sup>7</sup> Ω/sq are considered to be electrostatic dissipating and antistatics. For such a material, the accumulated electrostatics can be dissipated at a proper rate. As a controlled result, the polyamide in the absence of hydrophilic POE constituents, prepared from sebacic acid and the sole POP-diamine of MW 230 (Jeffamine<sup>®</sup> D230), exhibited a considerably high surface resistivity at a marginal 10<sup>9.5</sup> Ω/sq. In the presence of MW 2000 POE-diamide, the PA demonstrated a lower surface resistivity of 10<sup>7.4</sup> Ω/sq. The difference of two orders of magnitude is attributable to the POE hydrophilicity for adsorbing moisture. The water adsorption through hydrogen bonding with the POE segments and the consequent partial ionization of water molecules rendered the copolymer electrostatic dissipating

and, thus, of high surface conductivity.<sup>15</sup> Moreover, the mechanism for electrostatic dissipating was altered by adding metal salts to the copolymer. With respect to the examples shown in Table I, the copolymer was actually generated by the formation of  $-(\text{OCH}_2\text{CH}_2)_x-\text{M}^+$  complexes. Although the rates of moisture adsorption appeared to be of no significant difference ( $\sim 11$ – $15$  wt % for Li<sup>+</sup> or Ni<sup>2+</sup> versus 13 wt % without metal ion), their surface resistivities decreased significantly in the range of 10<sup>5</sup> to 10<sup>6</sup> Ω/sq. The presence of moisture is no longer the most important parameter; instead, the metal ion-induced second crystalline phase is the main mechanism for electron transfer.

DSC analyses (Fig. 3) revealed the appearance of a new phase attributed to the M<sup>+</sup>–( $\text{OCH}_2\text{CH}_2$ )<sub>x</sub>–complexation. During the cooling process, the PA with Ni<sup>2+</sup>/EO = 1/270 to 1/63 exhibited a second crystalline phase with a crystalline temperature at  $T_c = -10.4$  to  $-14^\circ\text{C}$ , which was higher than that of the original POE segment phase. Without the metal ion, the PA exhibited a  $T_c$  peak at  $-31^\circ\text{C}$ . The new phase was attributed to metal ion-induced POE crystallization. Furthermore, the solvating effect was dependent on both the species and the quantity of the metal ions in the polymer matrix. As shown in Table I, the addition of potassium chloride significantly lowered the surface resistivity to the value 10<sup>5.2</sup> Ω/sq. With the increasing stoichiometric ratios of potassium ion to oxyethylene unit or K<sup>+</sup>/EO from

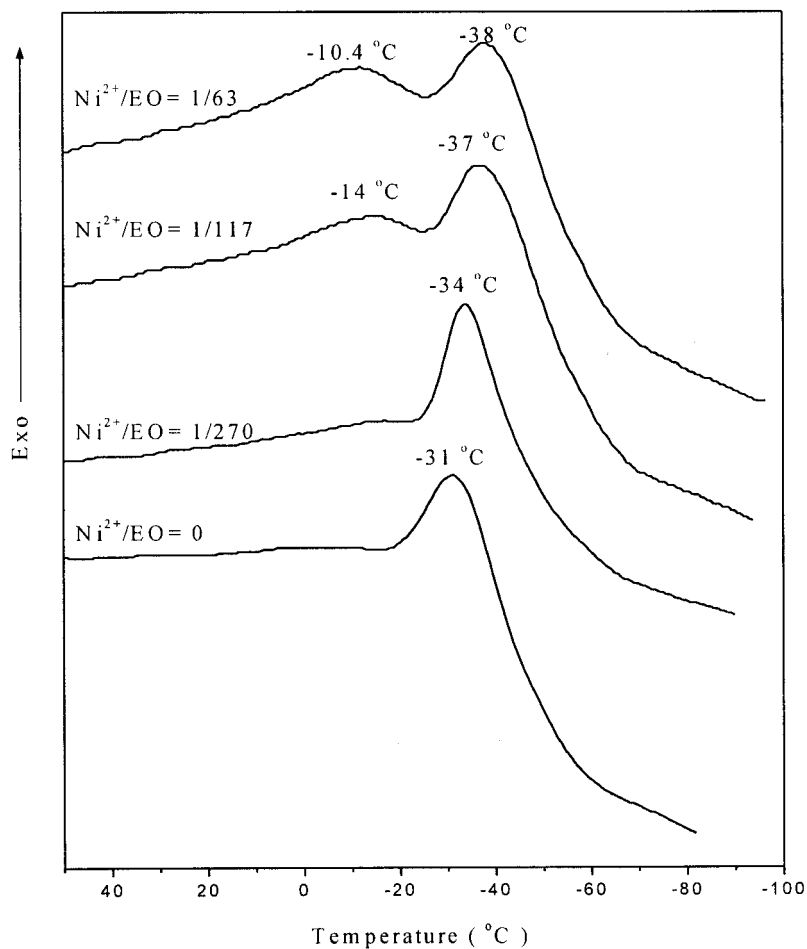


Figure 3 DSC peaks ( $T_c$ ) of PA and PA/Ni<sup>2+</sup> under cooling conditions.

1/180 to 1/3, the surface resistivity decreased from  $10^{5.7}$  to  $10^{5.2}$   $\Omega/\text{sq}$ . At a low metal ion ratio of  $\text{K}^+/\text{EO} = 1/180$  [i.e., 180 units of  $-(\text{OCH}_2\text{CH}_2)-$  sharing one  $\text{K}^+$ ], the conductivity was  $10^{5.7}$   $\Omega/\text{sq}$  compared to that of the metal-free copolymer at  $10^{7.4}$   $\Omega/\text{sq}$ . Adding more potassium salts up to 1/9 and 1/3 of  $\text{K}^+/\text{EO}$  only slightly increased the conductivity. The critical dose of the metal ions, extrapolated to be around the value between 1/9 and 1/3, indicated the saturation of metal ions solvating to the POE portions. Moreover, it also implied that the solvated  $\text{M}^+ / -(\text{OCH}_2\text{CH}_2)_x-$  species, rather than the bulk  $\text{M}^+$  species, affected the electrostatic dissipation. Other divalent metal salts including  $\text{CaCl}_2$ ,  $\text{PdCl}_2$ ,  $\text{CuCl}_2$ , and  $\text{NiCl}_2$  were also allowed to complex with the PA copolymer. Their relative efficacies, shown in Figure 4, were obtained by plotting surface resistivity versus various metal chloride additions.

Among the metal chloride species studied,  $\text{Pd}^{+2}$ ,  $\text{Cu}^{+2}$ , and  $\text{Ni}^{+2}$  were all quite effective for

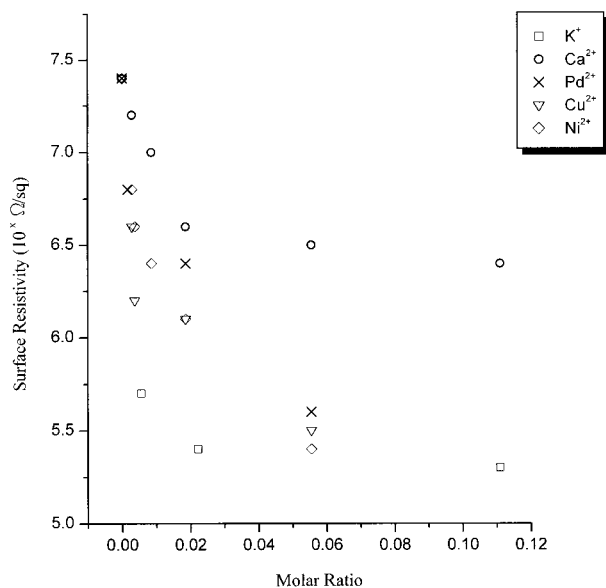


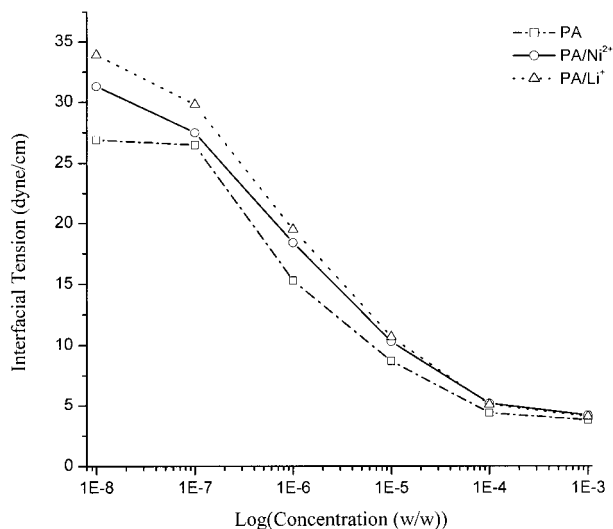
Figure 4 Surface resistivity of different metal chlorides added to the PA.

enhancing the surface conductivity, whereas  $\text{CaCl}_2$  was less effective. It appears that these metal salts render the copolymer in different degrees of ionic conducting effectiveness depending on the metal ionic species. In Table II, the results of various lithium salts including lithium chloride, lithium bromide, lithium iodide, lithium perchlorate, lithium trifluoromethylsulfonate, and lithium carbonate show the effect of the counter anions. The anion species actually play a significant role in controlling the surface resistivities. The lithium salt with a larger size of anions enhanced the electrostatic dissipation more effectively by the following trend:  $\text{CF}_3\text{SO}_3^- = \text{ClO}_4^- = \text{I}^- > \text{Br}^- = \text{CO}_3^{2-} > \text{Cl}^-$ . Overall, the hydrogen-bonding mechanism with moisture occurring in the metal-free copolymer was overwhelmed by the metal ion-conducting mechanism through the  $\text{M}^+ / -(\text{OCH}_2\text{CH}_2)_x -$  species, which were more effective for transferring electrostatics.

#### Self-Association in Toluene: Surface Tension, Interfacial Tension, and Emulsion

The POE segments rendered the copolymer amphiphilic, as evidenced by the self-associating property in solutions. In the literature, copolymers with different solvophilicity of blocks arranged in linear triblock<sup>5</sup> or comb-branch<sup>25,26</sup> structures were reported to be capable of forming micelles in xylene and aqueous solutions. The PA in our study exhibited a self-associating property in toluene because of the presence of the hydrophilic POE structure. The POP-amides and sebacamides blocks can contribute to the hydrophobic property. The estimated three POE hydrophilic segments randomly distributed in the linear block structure could result in a balance of hydrophilic and hydrophobic nature. The PA, dissolved in up to 1.0 wt % toluene, showed no significant change in surface tension or self-aggregating in this environment. However, the copolymer was capable of reducing the interfacial tension in toluene/water. The interfacial tension can be plotted against the concentration of the copolymer in toluene to show the critical concentration with respect to the interaction with water.

As shown in Figure 5, the PAs with and without metal ions exhibited a similar curve. It indicated that those solvated nickel or lithium salts in copolymer POE segments had no effect on the interaction with water at the toluene/water interface. Three examples showed the decrease of interfacial tension from about 35 to as low as 4.4



**Figure 5** Interfacial tension of PA, PA/Ni<sup>2+</sup>, and PA/Li<sup>+</sup> between toluene and water.

dyn/cm. Moreover, their critical micelle concentration (cmc) at the interface was estimated to be at  $1 \times 10^{-4}$  w/w in toluene or  $6.3 \times 10^{-6}$  M (on the basis of MW 15,800). Above the critical concentration, the PA tended to self-aggregate at the interface. The unusually low cmc value implies the high efficacy of polymer self-aggregation in occupying the interfacial surface area between the toluene and water phases. Such a low cmc value and self-aggregating phenomenon has been observed in the system of naturally occurring peptides in aqueous solution.<sup>20</sup> However, the PA that was dissolved in dry toluene did not self-aggregate into particles large enough to be observable to the light-scattering particle analyzer. Actually, the aggregation occurred only upon the addition of water. With agitation, the PA copolymer was capable of emulsifying toluene/water.

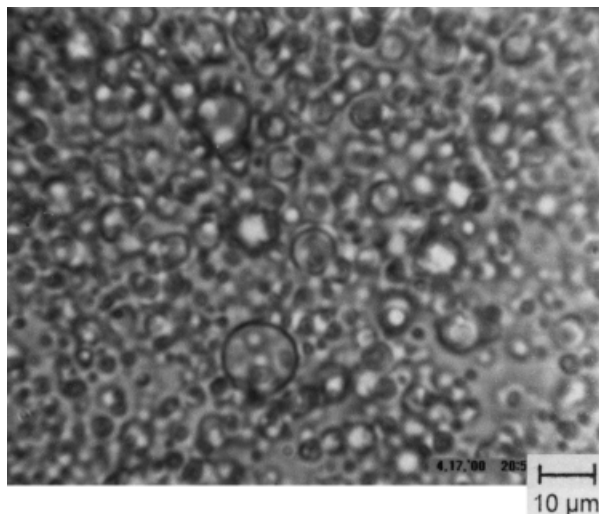
Emulsification into one phase was easily obtained by using the PA at only 0.1 wt % (above the cmc) in toluene. As shown in Table IV, with an increasing amount of water added to this 0.1 wt % of PA/toluene solution, a stable emulsification was observed, but only in the range of 20–50 wt % water content in toluene. The emulsifying droplets at sizes of 4.5–5.0  $\mu\text{m}$  were observed by the light scattering. Either below or beyond this water/toluene range (20–50 wt %), phase separation into layers was observed generally within 10 min after sample shaking. It was noted that the Ni<sup>2+</sup> or Li<sup>+</sup> solvated PA at 1/63 metal/EO had an inferior emulsifying effect on the metal-free PA. The results showed that, over a wide range of water/



toluene ratios, unstable phase separations were observed when metal ions were involved. This may be attributed to the competing noncovalent bonding interaction between POE/M<sup>+</sup> and POE/H<sub>2</sub>O. In POE/M<sup>+</sup>, the bonding sites of  $-(\text{OCH}_2\text{CH}_2)_x-$  could be occupied through the tight complexation with M<sup>+</sup> and the further noncovalent interaction with the surrounding water molecules was reduced. The emulsification was also independently observed by optical microscopy (Fig. 6), in showing a similar range of aggregating sizes.

## CONCLUSIONS

The copolymerization of sebacic acid and two hydrophilic/hydrophobic diamines afforded an amphiphilic poly(ether amide) at MW 15,800. The POE segments in the structure have the ability of complexing with moisture and metal ions such as Li<sup>+</sup>, K<sup>+</sup>, Ca<sup>+2</sup>, Ni<sup>+2</sup>, Pd<sup>+2</sup>, and Cu<sup>+2</sup>, resulting in low surface resistivity of 10<sup>5.0</sup> Ω/sq. The metal ion solvating also altered the crystalline phase of the copolymers. When dissolved in toluene, the copolymer behaved as a surfactant in reducing the interfacial tension (toluene/water) from 35 to 4.4 dyn/cm at an unusually low critical concentration of 1 × 10<sup>-4</sup> w/w or 6.7 × 10<sup>-6</sup> M. With agitation, the copolymer can easily emulsify toluene/water into droplets of 4.5–5.0 μm in diameter. However, the emulsification may be intervened by the presence of metal ions. These aggregating properties in solid form and in toluene solution are envisioned as the noncovalent interactions of the POE



**Figure 6** Emulsion of water/toluene/PA (20/80/0.08 by weight) at ×1000 magnification.

segments with water or metal ions. The hydrophilic/hydrophobic balance of the multiple POE, POP, and C<sub>8</sub>H<sub>17</sub> blocks in the poly(ether amide) structure may be altered through the metal-ion interaction with the POE segments.

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**Table IV** Phase Separation and Particle Sizes of PA and PA/Metal in Toluene/Water

Weight Percentage <sup>a</sup> (wt %)	Particle Size (μm)		
	PA <sup>b</sup>	PA/Ni <sup>2+</sup>	PA/Li <sup>+</sup>
2.5	+	+	+
7.5	+	+	+
12.5	++	+	+
20	5.0	+	+
30	4.8	+	++
50	4.5	+	++
62.5	++	++	++

<sup>a</sup> Weight percentage (wt %), water/toluene.

<sup>b</sup> PA, sebacic acid/ED2001/D230 (PA; 0.1 wt % in toluene).

+, Phase separation occurred immediately after mixing.

++, Phase separation occurred within 10 min after mixing.

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