

# Physical Stabilization or Chemical Degradation of Concentrated Solutions of Polyaniline Emeraldine Base Containing Secondary Amine Additives

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**ABSTRACT:** In this study, we systematically investigated 39 secondary amines as additives in concentrated EB/NMP solutions for gelation and degradation. We discovered that when both the width (defined as the longest distance between two hydrogens in the plane perpendicular to the NH bond of the amine) and depth (defined as the longest distance between two atoms in a plane perpendicular to the width) of the amines are  $<4.53$  Å and their  $pK_a$  is  $>7.7$ , the amines significantly extend the gelation times of 20 mass % EB/NMP solutions for more than 12 h. However, some of these amines also significantly degrade the polymer. Amines with small width and depth and strong basicity, such as azetidine and pyrrolidine, can significantly destroy the EB structures. This was evidenced by order-of-magnitude decreases in doped film conductivity, by significantly changed UV–vis spectra, and by significantly reduced molecular weights of the aged EB solutions as measured by gel permeation chromatography (GPC). However, when both the width and depth of amines are  $>4.53$  Å, these amines neither prolong gelation time nor appreciably degrade EB.

## Introduction

Conducting polymers are a unique class of materials that combine the electrical conductivity of metals with the material properties of plastics.<sup>1</sup> Among the conducting polymers, polyaniline (Pani) has received a significant amount of interest due to its environmental stability, ease of processing, and inexpensive polymerization. Pani possesses several oxidation states. Three commonly reported ones are the fully reduced leucoemeraldine base (LEB), the half-oxidized emeraldine base (EB), and the fully oxidized pernigraniline base (PNB).<sup>2–4</sup> Among these three forms, only the half-oxidized EB is electrically conductive when it is doped with protonic acids. Recent theory suggests the possibility of attaining very high conductivities ( $\sim 10^6$  S/cm) for Pani processed from defect-free, extremely high molecular weight samples.<sup>5</sup> Therefore, the EB form is the material of interest for Pani researchers.

The widespread use of EB has been limited due to its poor solubility.<sup>6–8</sup> Although *N*-methyl-2-pyrrolidinone (NMP) is one of the common solvents for dissolving Pani in the EB form,<sup>9</sup> when the concentration is above  $\sim 6$  mass %, rapid gelation takes place.<sup>6,7,10</sup> Recently we reported that adding a small amount of secondary amines to NMP could significantly enhance the solubility of EB.<sup>11–13</sup> Doing so also stabilizes the concentrated, high molecular weight EB/NMP/amine solutions for up to 30 h, making it practical to wet spin fiber from concentrated EB solutions.<sup>14</sup>

A drawback of the amines that we initially used is that some of the amines, such as pyrrolidine (PY), reduced EB into an LEB-like derivative through a ring substitution.<sup>13,15,16</sup> The films made from these EB/NMP/amine solutions lost the intrinsic properties of EB. Therefore, the degraded Pani possesses low conductivity and poor mechanical properties. To search for suitable

amines which can inhibit the gelation but do not degrade the EB structure, we investigated a large number of secondary amines for gelation inhibition and degradation and found that the effectiveness of the secondary amine at inhibiting gelation is correlated with the amine's geometric and electronic factors. In this paper, we proposed a general trend to determine whether a secondary amine can serve as a gel inhibitor (GI). On the basis of our studies, secondary amines can be divided into three categories:

- (1) Nondegrading GIs prolong gel time for at least 12 h, with no appreciable degradation of EB structure.
- (2) Degrading GIs prolong gel time for at least 12 h, but with appreciable degradation of EB structure.
- (3) Non-GIs do not prolong gel time for longer than 1 h.

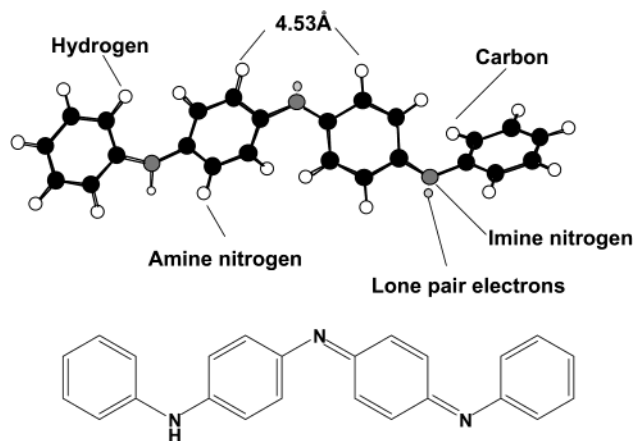
## Experimental Section

**Materials.** Thirty-nine secondary amines were purchased from commercial sources (Fluka and Aldrich) and were of the best available grade. The EB was purchased from NESTE Oy (Helsinki, Finland). The NMP was ACS reagent grade and stored over 3 Å molecular sieves to remove water.

**Polymer Solutions and Films.** A 20 mass % sample of dried EB powder was stirred into a solution of NMP containing GI until a particle-free homogeneous solution had formed for certain amines. The amine:EB tetrameric repeat unit ( $\{EB\}$ ) (see Figure 1) molar ratio was 2:1 in all cases unless specified. A typical solution was prepared as follows: in the case of 2-methylaziridine (2MA), 543 mg ( $1.5 \times 10^{-3}$  mole) of EB was added into 2 mL of NMP containing 170 mg ( $3.0 \times 10^{-3}$  mol) of 2MA. After these three compounds were well mixed, the mixture was kept in a tightly sealed Teflon vial at room temperature. For several days thereafter, the mixture was periodically monitored for gelation by tilting the vial to check the fluidity of the solution or the mixture.

The solution (or mixture), aged for  $\sim 1$  h, was then cast onto a glass slide ( $2 \times 3$  in.). The glass slide coated with the wet film was placed in a 60 °C oven for a few hours to prepare a thermally annealed film,  $\sim 50$   $\mu$ m thick. This was then protonated by immersion in 1 M aqueous HCl for 24 h. The doped films were air-dried under controlled ambient conditions

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**Figure 1.** Computer model of the EB tetramer showing the two ortho hydrogens around the imine (above), and the structure of the aniline EB (with the terminal amines removed) (below).

(relative humidity < 8% and temperature  $\sim 25$  °C) for 24 h and then were ready for further testing.

**Conductivity Measurements.** The electrical conductivity for the fully doped EB film specimens were measured with the four-point probe technique.<sup>17</sup> All conductivity values are reported at room temperature (298 K). The four Pt wires on the sample surface were in line, spaced 2.5 mm apart. An HP digital multimeter was used to supply a constant current in the range of 0.01–30 mA, and simultaneously measure the resistance. During the measurement, a constant current was maintained on the two outer wires after verification of ohmic behavior. The voltage across the two inner wires was measured to determine the conductivity of the tested film. If the film was too brittle, conductivity measurement was not always possible.

**Determination of the  $pK_a$ .** The  $pK_a$  of the secondary amine was determined by titrating  $\sim 1$  g of the amine in water (50 g) with 0.1 M HCl while monitoring the pH. The amount of acid added was plotted vs the pH. The pH at the inflection point in this curve was taken as the amine's  $pK_a$ .<sup>18</sup> Some amines were not fully soluble in water at the start of the titration, but in all cases the amine solubilized before the inflection point was reached. This solubility was checked in a few cases by increasing the amount of water used; the  $pK_a$  values agreed within  $\pm 0.2$  for three trials. The titration method of determining the  $pK_a$  assumes that the activity coefficients of the base and the acid forms are equal. Comparison to literature values,<sup>19</sup> where available, showed that our  $pK_a$  values were higher by 0.2–0.3 units. We used this value as our experimental uncertainty.

**Modeling of the Secondary Amines.** Molecular modeling was performed with the Chem3D program (version 6.0, CambridgeSoft) using the MM2 force field, and the structures were refined to a root-mean-square (RMS) gradient of  $< 0.01$ . The global minimum for each amine was found by an iterative process. For the structure calculations, all conformers within 2.0 kcal/mol of the global minimum were examined, and the values given are for the structure with the smallest width, depth, and size (these are defined in a later section). Although the absolute size values may vary from use of one software program to another, this study was performed by comparison among values. Thus, if one uses other software programs, these comparisons should provide the same results, independent of which software program is used.

**Molecular Weight Determination.** The molecular weight of the EB powder was determined using a gel permeation chromatography (GPC) system consisting of an HPLC pump (Waters 2960), an autosampler, an autoinjector, and two polystyrene columns (Waters styragel RH 4E and 5E,  $4.6 \times 300$  mm). The column temperature was controlled at 50 °C. A photodiode array (PDA) (Waters 996) detector was used to

determine the molecular weight and to collect the UV–vis spectrum for each solution.

NMP containing 0.1 mass % LiCl was used as an eluent. The flow rate of the eluent was 0.35 mL/min. The same solvent was used to dilute the 20 mass % EB/NMP/amine solutions with different aging times to 0.02 mass % EB solutions for the GPC and UV–vis studies. To ensure complete EB dissolution, the solutions sat at room temperature for at least 12 h before the samples were injected into the columns. Before injection, the solutions were filtered through a  $0.45 \mu\text{m}$  Teflon filter (Millipore). The injection volume was 50  $\mu\text{L}$ . The peak molecular weight ( $M_p$ ) was calculated by calibration with nine different polystyrene standards (purchased from Polymer laboratories, Inc.) with molecular weights between 2930 and 7 500 000. The average molecular weight of NESTE EB we calculated is 120 000, the same as the literature value.<sup>20</sup> The peak molecular weight ( $M_p$ ) for this EB is 86 100.

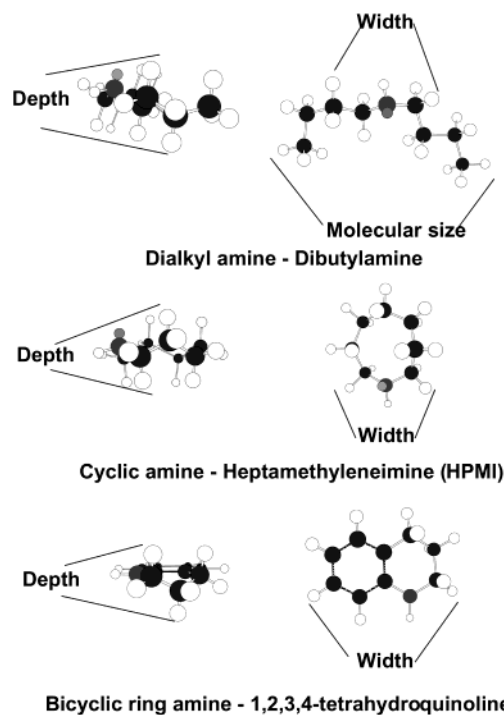
## Results and Discussion

We have proposed that secondary amines function as GIs by intercalating between chains and forming a hydrogen bond between the imine nitrogen of the EB and the hydrogen of the amine.<sup>13,14,21</sup> We postulated that an amine of sufficient steric bulk should not be able to form this hydrogen bond and would, therefore, not inhibit gelation.

To study the possible interactions, we modeled the conformation of a tetramer of aniline (with the terminal amine removed) in the EB form (Figure 1). The resulting minimized structure shows the expected twist of the aromatic rings along the chain. The distance between the two ortho hydrogens next to the imine nitrogen of the EB was calculated to be 4.53 Å (see Figure 1). An amine that approaches the imine lone pair electrons in order to form a hydrogen bond has to be small enough to avoid interacting with these two flanking hydrogens.

**1. Gelation Behavior of EB/NMP/Amine Solutions.** Molecular modeling was performed on 39 secondary amines. From the minimum energy conformation, three size parameters, which we hoped would be surrogates for the steric size, were derived: the width, defined as the longest distance between two atoms in the plane perpendicular to the NH bond of the amine; the depth, defined as the longest distance between two atoms in a plane perpendicular to the width; and the molecular size, defined as the longest distance between any two atoms in the entire molecule (see Figure 2). The calculated width, depth, and molecular size for the amines are summarized in Tables 1–5.

We reasoned that the  $pK_a$ s of the amines might be useful as an estimate of the strength of the hydrogen bond between the secondary amine hydrogen and the EB imine nitrogen if no steric hindrance was involved. We wanted to know if changes in the  $pK_a$  correlated with changes in the amount of degradation of the EB. Tables 1–5 show the measured  $pK_a$  (and the available literature values<sup>22</sup>), as well as the gelation result of the solutions and the conductivity of the HCl-doped films. From Tables 1–5, we find that both width and depth are more important than molecular size. When both width and depth of an amine are  $< 4.53$  Å, the amine can inhibit gelation of its 20 mass % EB/NMP solution for more than 12 h. However, the basicity of amines is as important as their geometric parameters. Some amines, such as thiazolidine, 1,2,3,4-tetrahydroquinoline, are small enough to interact with the imine nitrogen. However, due to their weak basicity ( $pK_a < 6.5$ ), they cannot effectively prevent gelation either. Dibenzylamine is an illustration of a typical non-GI. Its



**Figure 2.** Size parameters from molecular modeling illustrated for several amines: top view (right) and side view (left).

**Table 1.** Summary of the Width, Depth, Molecular Size, and  $pK_a$  of Amines and Experimental Results for Dialkyl Amines<sup>a</sup>

Name Structure	Width (Å) Depth (Å) Molecular size (Å)	$pK_a$ <sup>1</sup> $pK_a$ <sup>2</sup>	Gelation time (hr)	$\sigma_{TA}$ (S $cm^{-1}$ )
Diethylamine 	4.67 3.12 6.22	11.3 11.0	~0.8	64.1
Dipropylamine 	4.63 3.19 8.55	11.4	~0.5	21.6
Diisopropylamine 	4.76 4.38 6.20	11.5 11.0	~0.8	10.2
Dibutylamine 	4.63 3.10 9.79	11.1 11.3	~0.5	74.4
2-Propylaminoethanol 	4.90 3.87 8.17	10.2	~0.5	41.7
Dicyclohexylamine 	4.75 5.02 9.98	10.8	~1.0	44.8
Dibenzylamine 	4.15 4.98 8.17	7.7	<0.2	12.5
N-Ethylbenzylamine 	4.70 4.99 7.57	10.1	~0.5	27.8

<sup>a</sup>  $\sigma_{TA}$ : Conductivity of a thermally annealed film. <sup>1</sup>This set of  $pK_a$  value was measured by the authors. <sup>2</sup>This set of  $pK_a$  values was found from the literature if it is available.<sup>22</sup>

width is less than 4.53 Å, but its depth is larger than 4.53 Å, and its  $pK_a$  is 7.7. The EB/NMP/dibenzylamine mixture gelled up within the shortest time (<10 min)

**Table 2.** Summary of the Width, Depth, Molecular Size, and  $pK_a$  of Amines and Experimental Results for Cyclic Amines of Varying Ring Sizes

Name Structure	Width (Å) Depth (Å) Molecular size (Å)	$pK_a$ <sup>1</sup> $pK_a$ <sup>2</sup>	Gelation time (hr)	$\sigma_{TA}$ (S $cm^{-1}$ )
2-Methylaziridine (2MA) 	2.62 2.30 4.37	8.5	> 300	11.7
Azetidine (AZ) 	2.77 1.87 3.80	11.3 11.3	>300	Film is too brittle to measure
Pyrrolidine (PY) 	4.08 1.82 4.22	11.5 11.3	>300	1.6
Piperidine (PP) 	4.19 3.10 4.90	11.3 11.1	>300	4.4
Hexamethyleneimine (HXMI) 	4.14 3.09 5.21	11.4	>300	3.6
Heptamethyleneimine (HPMI) 	4.05 3.11 5.89	11.2	>300	2.2
















**Table 3.** Summary of the Width, Depth, Molecular Size, and  $pK_a$  of Amines and Experimental Results for Pyrrolidine Derivatives

Name Structure	Width (Å) Depth (Å) Molecular size (Å)	$pK_a$ <sup>1</sup>	Gelation time (hr)	$\sigma_{TA}$ (S $cm^{-1}$ )
3-Pyrroline 	3.70 1.82 4.11	10.5	>300	0.1
2,5-Dimethylpyrroline 	4.01 4.40 6.35	10.4	>100	15.9
Thiazoline 	4.16 1.81 4.50	6.5	0.8	7.8
3-Hydroxypyrrolidine 	4.09 2.92 5.14	10.4	>300	$7.3 \times 10^{-2}$
2-Methylimidazoline 	4.57 4.61 5.13	11.3	~0.3	25.5
R-(-)-Pyrrolidine-2-methanol 	4.03 3.87 5.11	10.5	>300	Film is too brittle





of all of the studied amines. This fast gelation is possibly due to the large depth and weak basicity of dibenzylamine.

A plot of the max value of width and depth of amines vs their  $pK_a$  is shown in Figure 3. All of the secondary amines with a width and a depth <4.53 Å and a  $pK_a$

**Table 4. Summary of the Width, Depth, Molecular Size, and  $pK_a$  of Amines and Experimental Results for Piperidine Derivatives**

Name Structure	Width (Å) Depth (Å) Molecular size (Å)	$pK_a^1$ $pK_a^2$	Gelation time (hr)	$\sigma_{TA}$ ( $S\text{cm}^{-1}$ )
1,2,3,6-Tetrahydropyridine 	4.19 3.11 4.98	10.4	~16	$4.3 \times 10^{-3}$
Morpholine 	4.19 3.12 4.86	8.7 8.3	>300	$5.4 \times 10^{-3}$
Thiomorpholine 	4.17 3.12 5.07	9.0	>300	$5.7 \times 10^{-4}$
2-Methylpiperidine 	4.71 3.10 6.01	11.3	2	54.1
4-Methylpiperidine 	4.19 3.10 5.93	11.3	>100	1.5
4-Hydroxypiperidine 	4.19 3.10 5.65	10.4	>100	$6.4 \times 10^{-2}$
3,5-Dimethylpiperidine 	4.19 4.40 6.02	11.2	>200	1.2
2,6-Dimethylpiperidine 	4.85 3.10 6.78	11.3	1	31.4
2,6-Dimethyl-morpholine 	4.18 3.11 6.68	8.7	>200	$3.8 \times 10^{-4}$
2,2,6,6-Tetramethylpiperidine 	4.88 3.84 6.75	11.8	0.85	69.9
2,2,6,6-Tetramethyl-piperidi-4-one 	4.87 3.86 6.76	8.0	0.9	67.1
1,4-Dioxo-8-azaspiro[4.5]-decane 	4.19 3.25 7.00	9.5	>200	$1.5 \times 10^{-5}$
Ethyl isonipecotate 	4.19 3.10 9.55	10.2	>300	$3.6 \times 10^{-4}$
N,N-Diethyl nipecotamide 	4.19 5.18 9.20	10.0	>300	$3.6 \times 10^{-4}$
1-Acetyl piperazine 	4.19 3.11 6.73	8.4	~0.5	$5.5 \times 10^{-5}$

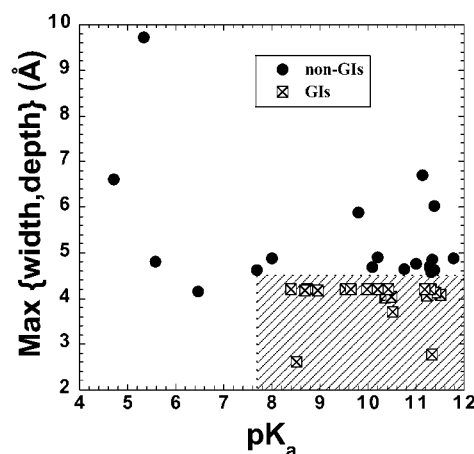
**Table 5. Summary of the Width, Depth, Molecular Size, and  $pK_a$  of Amines and Experimental Results for Bicyclic Ring Amines**

Name Structure	Width (Å) Depth (Å) Molecular size (Å)	$pK_a^1$	Gelation time (hr)	$\sigma_{TA}$ ( $S\text{cm}^{-1}$ )
Indoline 	4.80 1.82 6.44	5.6	4	$5.1 \times 10^{-7}$
1,2,3,4-Tetrahydroquinoline 	4.59 3.10 7.20	4.7	0.5	4.1
1,2,3,4-Tetrahydroisoquinoline 	4.19 4.40 7.22	9.6	12	0.3
Decahydroquinoline 	6.02 5.40 6.97	11.4	1	37.4

value >7.7, can serve as GIs (highlighted gray region). In most cases, EB solutions using these GI amines did not gel for more than 300 h.

**2. Chemical Degradation.** The purpose of adding the secondary amines to EB/NMP solution systems is to inhibit gelation. However, when amines are present in the EB/NMP solution, the prolonged gelation time might be due not only to the hydrogen bonding between secondary amine hydrogens and EB imine nitrogens but also to the chemical reduction of EB. The former interaction is what we expect and prefer, and the latter is what we try to avoid.

The conductivity of doped EB films is an indicator of the structural integrity of the Pani. The conductivity of an HCl-doped EB film made from an EB/NMP solution is in the range of 5–80  $S\text{cm}^{-1}$ .<sup>4,23</sup> If the conducting structure were degraded (e.g., the conjugated chains were distorted and broken), the conductivity of the film would be lower. From the conductivity data in Tables 1–5, one notes that all of the HCl-doped EB films made with non-GIs (mixture aged for 1 h) had conductivities in the range of 10–80  $S\text{cm}^{-1}$ . On the other hand, the HCl-doped films made with GIs (solution aged for 1 h) had conductivities <5  $S\text{cm}^{-1}$ . Besides decreasing in conductivity, some resulting materials lose their mechanical properties so much that we could not make any

**Figure 3.** Plot of GI efficiency based on the max of width and depth of amine vs  $pK_a$  (GI, solution gelation time > 12 h; non-GIs, solution gelation time < 1 h).



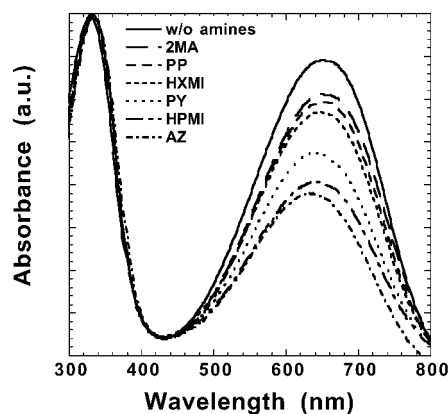
films from EB/NMP's containing these GIs. All experimental evidence suggests that all GIs at the amine:{EB} molar ratio of 2 may degrade EB to a certain degree, even within 1 h.

On the basis of the studies we have done so far, we find that dialkylamines and most bicyclic amines are too large to interact with the EB imine nitrogen and, therefore, do not effectively inhibit gelation. On the other hand, cyclic secondary amines, and most of the PY and piperidine derivatives, can serve as GIs due to their small width and depth. To further investigate how the  $pK_a$  and the width (and depth) of the amine determine its reactivity toward the EB structure, we selected several cyclic amines (listed in Table 2) to conduct further studies.

A number of factors can affect the ability of a secondary amine to degrade EB. Besides the width and depth (steric hindrance) and basicity (nucleophilicity) of amines, solution age and amine concentration are also important. Thus, we investigated the effects of solution aging time and amine concentration as well. A sample of the 20 mass % EB/NMP/cyclic amine solutions was removed at selected time intervals, and then was diluted to a 0.02 mass % EB solution by using NMP containing 0.1 mass % LiCl for GPC study. At the same time the UV-vis spectrum was collected. The reason for adding LiCl to the GPC solution was to eliminate the aggregation between EB molecules and accurately determine molecular weight. This method was reported by Angelopoulos et al.<sup>24</sup> These UV-vis and GPC results are discussed separately in the following sections.

**2.1. UV-Vis Characterization.** Optical properties play an important role in elucidating the basic electronic structure of conducting polymers. Appreciable changes in the optical absorption are associated with changes in chain conformation, oxidation states, and the extent of protonation of Pani EB. Therefore, UV-vis spectroscopy is commonly used to characterize the structure of Pani molecules.<sup>25–31</sup> There are two classic peaks<sup>25,32,33</sup> in the UV-vis spectrum of EB/NMP solutions: The peak at  $\sim 330$  nm (called the B peak) corresponds to a  $\pi \rightarrow \pi^*$  transition in the benzenoid ring;<sup>27,34</sup> the second peak, at 630–660 nm (called the Q peak), is usually assigned to the transition of an electron from the highest occupied molecular orbital (HOMO,  $\pi_b$ ) of the benzenoid part of the EB to the lowest unoccupied molecular orbital (LUMO,  $\pi_p$ ) of the quinoid ring.<sup>32,35,36</sup> Decreasing the EB concentration in NMP solution and/or adding LiCl to the EB/NMP solution will increase the intensity of the Q peak and cause a 15–20 nm red shift of the Q peak due to the changes in the EB chain conformation.<sup>24,37–39</sup>

The intensity ratio of the peak at  $\sim 635$  nm to the peak at  $\sim 330$  nm is called the Q/B ratio (quinoid:benzenoid). It is proportional to the composition of the quinoid units and benzenoid units along the EB backbone, as well as to other factors. A typical value of the Q/B ratio in a UV-vis spectrum of  $\sim 0.1$  mass % EB/NMP solution is 0.82–0.89.<sup>26–31,39</sup> However, as the EB is reduced toward LEB, the following three spectral changes occur: (1) the Q/B ratio approaches 0; (2) the Q peak shifts from  $\sim 635$  to 645 nm at the start of the reduction; (3) the B peak gradually shifts from  $\sim 330$  to 347 nm.<sup>27,31</sup> When the EB is oxidized toward PNB, the following three spectral changes are expected as well: (1) the Q/B ratio immediately decreases from  $\sim 0.88$  to 0.67 as EB oxidation starts, and then remains constant at  $\sim 0.67$  during the



**Figure 4.** UV spectra of EB solution with cyclic amines (solution samples were collected after the EB solution was aged for 1 h; amine:{EB} molar ratio = 2.0).

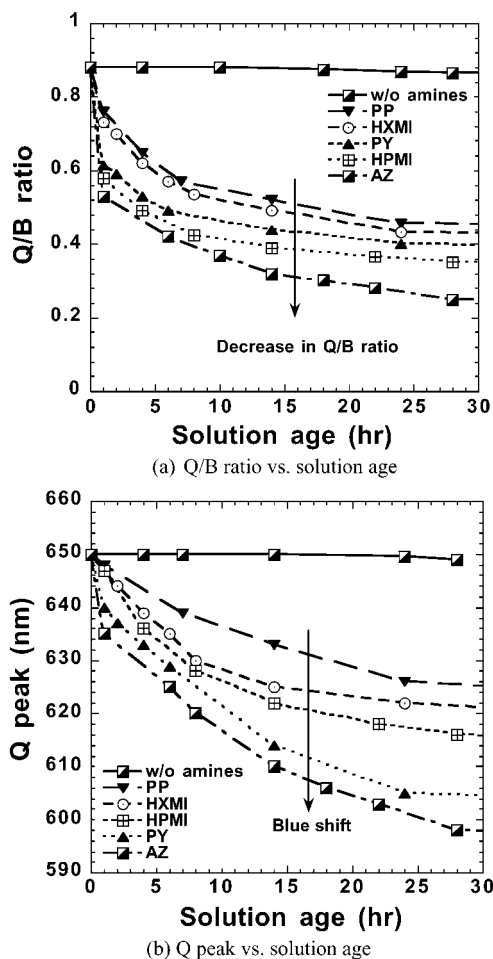
**Table 6. Summary of the Peak Positions and Q/B Ratio of the UV-Vis Spectra for 1-h Aged EB/NMP/Cyclic Amine Solutions (Amine:{EB} Molar Ratio = 2.0)**

cyclic amine	B peak (nm)	Q peak (nm)	Q/B ratio	decrease in Q/B ratio ( $\Delta$ )
without amine	329	651	0.88	
2MA	336	645	0.78	0.10
AZ	324	632	0.53	0.35
PY	333	640	0.61	0.27
PP	330	648	0.75	0.13
HXMI	330	647	0.72	0.16
HPMI	337	647	0.59	0.29

remaining part of the oxidation process; (2) the Q peak gradually shifts from  $\sim 635$  to 570 nm with increasing oxidation state; (3) the B peak remains at  $\sim 330$  nm.<sup>27,31</sup> Therefore, when the Q/B ratio in the UV-vis spectra of Pani/NMP or Pani derivative/NMP is substantially smaller than  $\sim 0.85$ , and the B and/or Q peak largely shift, these spectral changes suggest the amount of quinoid rings in the studied Pani or Pani derivatives is different from that in an intrinsic EB form.

The UV-vis spectra for the EB/NMP solutions (containing LiCl) aged 1 h, with or without amines, are shown in Figure 4. The peak positions and Q/B ratios for these spectra are summarized in Table 6. For the EB/NMP solution, the B peak and Q peak are located at 330 and 650 nm, respectively, and the Q/B ratio is  $\sim 0.88$ . This spectrum of EB is comparable to the ones reported in the literature.<sup>24,30,31,38,40</sup> Among these cyclic amines, 2-methylaziridine (2MA) has the second smallest sum of width and depth (4.92 Å), the smallest blue shift ( $\sim 6$  nm) in the Q peak, and the smallest decrease in the Q/B ratio ( $\Delta = 0.10$ ) that can be observed in the UV-vis spectrum of the EB/NMP/2MA solution. This result suggests that 2MA has the least reduction impact among these cyclic amines. On the other hand, the sum of width and depth (4.66 Å) of azetidine (AZ) is comparable to that of 2MA (4.92 Å), but in the spectrum of the EB/NMP/AZ solution, the blue shift (19 nm) of the Q peak and the decrease in the Q/B ratio ( $\Delta = 0.35$ ) are appreciably larger than those for 2MA. The fact that 2MA has the weakest basicity (the lowest  $pK_a$ ) of the cyclic amines is probably responsible for this result. Therefore, for amines with a similar degree of steric hindrance, such as AZ and 2MA, their basicity determines their strength of interaction with the EB imine nitrogen. The amine with a weaker basicity has less of a tendency to reduce the EB.

Besides 2MA, the other five in the cyclic amine family have similar basicities. As the sum of the width and the



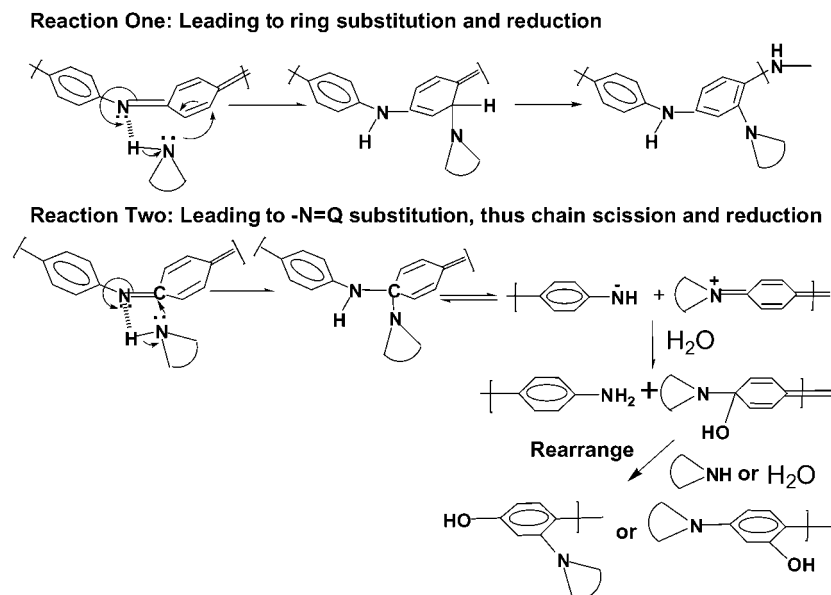
**Figure 5.** Effects of solution age on the Q/B ratio (a) and the Q peak (b) of the UV-vis spectra of the EB/NMP/amine solutions (amine:{EB} = 2.0).

depth of the amines increases, the decrease in the Q/B ratio and the blue shifts on both peaks becomes less appreciable. As the sum of the width and depth among AZ (4.66 Å), pyrrolidine (PY) (5.90 Å), heptamethylenimine (HPMI) (7.23 Å), hexamethylenimine (HXMI) (7.29 Å), and piperidine (PP) (7.29 Å) increases, the change in the Q/B ratio decreases from  $\Delta = 0.35$  to  $\Delta = 0.13$ , and the blue shifts on the Q peak decrease from 19 to 3 nm. Therefore, for amines with a similar basicity, the steric hindrance determines how easily the amines can access and interact with the EB imine nitrogen. The amine with the smallest hindrance degrades the EB structure the most.

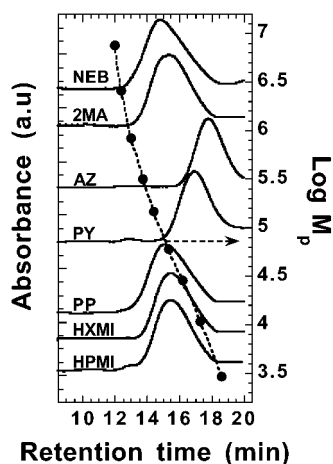
Figure 5 presents the aging effect on the Q/B ratio (a) and on the blue shift of the Q peak (b) for the five cyclic amines. The largest Q/B ratio drop and the largest blue shift are observed in the UV-vis spectra of the aged EB/NMP/AZ solutions. This again indicates that, among these five amines, AZ has the largest effects on the EB structure. The large Q/B ratio decreases in the UV-vis spectra suggest that amines reduce the original EB to an LEB-like material. However, the large blue shift on the Q peak indicates that the reduction of EB in the EB/NMP/amine solutions is not a simple oxidation state change but is instead due to more complicated structural changes. It has been reported that a blue shift of the Q peak together with the decrease in the Q/B ratio is caused by an increased energy gap between the HOMO ( $\pi_b$ ) of the benzenoid rings and the LUMO ( $\pi_q$ ) of the localized quinoid rings. This can result from twists

in the EB chains, which in turn can be brought about by quinoid ring substitutions.<sup>8,15,38,41</sup> Among the five cyclic ring amines (in Table 2), AZ has the least steric hindrance, if AZ would only attack the quinoid ring to produce a ring substituted LEB-like derivatives. Because of its small degree of steric hindrance, AZ should cause the smallest twists in the EB chains. Thus, we would observe the smallest blue shift on the Q peak for the EB/NMP/AZ solution, which is opposite to what we observed in Figure 5. This again suggests that the interaction between amines and EB is a more complicated reduction than a simple ring substitution. Furthermore, although all of the doped films made from aged EB/NMP/amine solutions lose their conductivity to a certain degree, the mechanical properties of these films are quite different. We could not make a film from the EB/NMP/AZ solution aged for 1 h. On the other hand, a flexible film was easily prepared from a 24 h old EB/NMP/PP solution. For the films made from solutions aged for the same length of time, the mechanical properties decrease in the order as following: PP > HXMI > HPMI > PP > AZ.

On the basis of our experimental observations, we hypothesize that, besides serving as proton donors to form hydrogen bonds, the amines can also serve as nucleophilic agents to attack the quinoid ring at different sites, resulting in different products.<sup>15,16,42</sup> In Figure 6, we illustrate two possible reactions occurring between an amine and EB. First reaction: GIs with a large degree of steric hindrance, such as PP, may mainly tend to attack the quinoid ring and lead to a ring substitution. This was also proposed by Han,<sup>15</sup> who hypothesized that protonation of the imine nitrogen could possibly promote nucleophilic attack at the meta position of the protonated quinoid ring. Therefore, the less stable quinoid ring would be reduced to the more stable benzenoid by ring substitution. This structural change causes a decrease only in the conductivity of the HCl-doped film, essentially leaving its mechanical properties intact.<sup>16,42</sup> The other possible chemical reaction for a secondary amine with a small degree of steric hindrance, such as AZ, involves direct attack at the  $-N=C<$  site. Under certain conditions, such as the presence of moisture or another impurity, chain scission together with polymer reduction may take place, to produce substantially lower molecular weight polymer. Matveeva<sup>43</sup> et al. proposed a similar reaction between water and EB molecules leading to chain scission. Chain scission helps explain the poor mechanical properties observed for the films made from the EB/NMP/AZ and EB/NMP/PY solutions, and also correlates with reductions in molecular weights of the polymer as discussed in the GPC section below. Furthermore, it has been reported that the Q/B ratio is much lower than 0.88 and that the Q peak shows a large blue shift when EB changes from polymer to oligomers.<sup>30,44</sup> Therefore, it appears likely that both chain scission and ring substitution occur in aged EB/NMP/AZ solutions and that it is this chemical reaction which is responsible for the large decrease in the Q/B ratio, as well as the large blue shift of the Q peak in the UV-vis spectra. On the other hand, it appears that PP mainly reduces the EB structure by ring substitution. The Q/B ratio drop and the blue shift on the Q peak resulting from PP are the smallest among these five amines. Regarding the amines between AZ and PP, in particular PY and HPMI, they each may interact with EB through two reactions, which



**Figure 6.** Schematic diagram of an amine attacking an imine center in an EB tetrameric repeat unit and leading to different reactions.

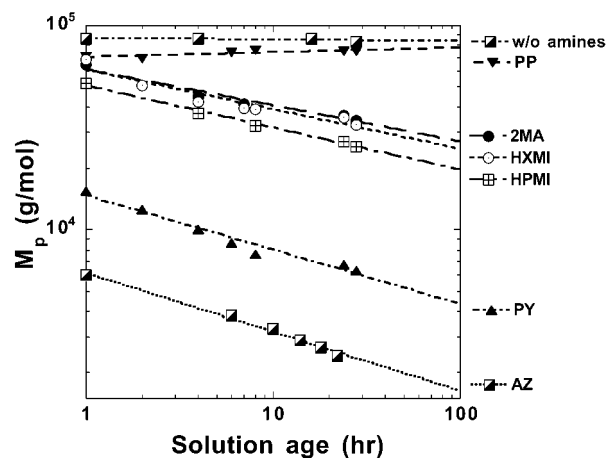


**Figure 7.** GPC chromatograms of the EB samples obtained at various EB/NMP/cyclic amine solutions after the solution sits for 1 h: from the top, without amine, 2MA, AZ, PY, PP, HXMI, and HPMI. Calibrated curve made by nine PS standards is shown (amine:{EB} = 2.0).

are reflected in the spectral changes. On the basis of the mechanical properties, we deduce that PY, due to its smaller degree of steric hindrance, still tends to react with EB through the second reaction pathway, while HPMI tends to preferentially react with EB through the first reaction pathway.

In summary, from the above study, the chemical reactivity of these six amines is determined by their steric hindrance and basicity. The reactivity strength among the cyclic amines toward EB decreases in the following order: AZ  $\gg$  PY > HPMI > HXMI > PP > 2MA.

**2.2. GPC Characterization.** Figure 7 displays the GPC chromatograms for the EB/NMP/amine solutions aged for 1 h. The peak molecular weight ( $M_p$ ) of NESTE EB is 86 100. However, when cyclic amines were added to the EB/NMP solutions, the retention time of the EB increases, indicating a progressive decrease in the molecular weight. The calculated  $M_p$  values are summarized in Table 7. The EB in the NMP/AZ solution has the lowest molecular weight ( $M_p$  = 6000), which is a



**Figure 8.** Effect of solution age on the  $M_p$  of EB in NMP/cyclic amine solutions.

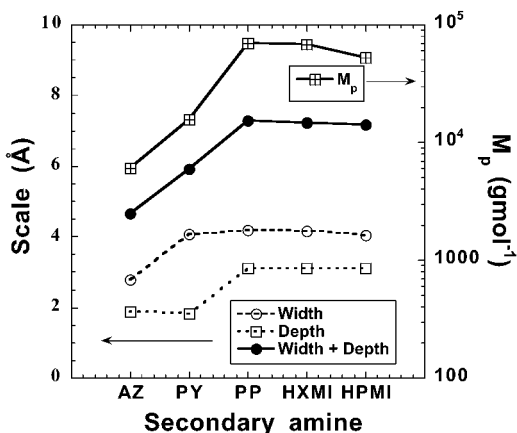
**Table 7. Summary of the GPC Results for the EB in NMP/Cyclic Amines for 1-h (Amine:{EB} Molar Ratio = 2.0)**

cyclic amine	$M_p$	exponent ( $n$ )	$A \times 10^4$ (mol g $^{-1}$ h $^{-n}$ )
without amine	86 100	-0.01	8.65
2MA	64 035	-0.18	6.98
AZ	6000	-0.29	6.08
PY	15 500	-0.27	6.06
PP	70 300	0.02	5.08
HXMI	68 400	-0.19	1.47
HPMI	52 080	-0.21	0.62

15-fold decrease in  $M_p$  compared to EB in NMP without any amines. This provides more supporting evidence that AZ aggressively destroys the EB structure within a short period of time. On the hand, the  $M_p$  of EB in the EB/NMP/PP solution shows the highest molecular weight value after any of the cyclic amines have been added to the solutions.

Figure 8 illustrates the effect of a solution's age ( $t$ ) on the peak molecular weight ( $M_p$ ) of EB dissolved in NMP with cyclic amine additives. The measured  $M_p$  values for the polymers decrease following a power law (see eq 1). The pre-exponent ( $A$ ) and exponent ( $n$ )





**Figure 9.** Correlation between geometric parameter and  $M_p$  of EB in 1-h aged NMP/cyclic amine solutions (amine:{EB} molar ratio = 2.0).

parameters are summarized in Table 7. The  $n$  value indicates the decay rate of EB based on the measured  $M_p$  for each sample in the different NMP/amine solution systems. It is clear that the molecular weight of EB in the AZ/NMP solution decays with the fastest rate.

$$M_p = At^n \quad (1)$$

Among the cyclic amines, even though 2MA has the smallest width, and its size is comparable to that of AZ, the molecular weight of the polymer in the NMP/2MA decreases at a much slower rate than that observed for the AZ/NMP solution. This suggests that 2MA does not chemically interact with EB to the same extent as AZ does. We attribute this result to the fact that the weakly basic 2MA molecule is a poor nucleophile and thus cannot engage in the chemical degradation of the polymer.

Figure 9 shows the correlation between the geometric parameters and the molecular weight of EB based on  $M_p$  measured for the EB/NMP/amine solutions aged for 1 h. AZ is the amine with the least steric hindrance, and thus has the greatest potential among the amines studied to chemically react with the imine sites ( $-N=C<$ ) of the polymer repeat unit and thus result in a chain scission that significantly degrades the EB. Among the solutions aged for 1 h, the molecular weight of the EB in an NMP/AZ solution decreases by  $\sim 90\%$ , i.e., from 86 100 to 6000. Although PY has a width similar to PP, HXMI, and HPMI, PY appears to degrade EB more severely than the other three amines. However, if we consider width together with depth, the total value of these two dimensions for PY is smaller than that of the other three amines. This again suggests that both the width and depth of amines contribute to the steric hindrance of amines, which in turn is important in determining the strength of amine interactions with the EB molecules. Among these five cyclic amines, the PP molecule has the largest steric hindrance. Therefore, as represented in Figure 6, PP reacts primarily with EB through the first reaction pathway, i.e., ring substitution *without chain scission*. This observation again supports the conclusion that there are different chemical reaction mechanisms for the degradation of Pani in the emeraldine oxidation state. Chemical reaction of a secondary amine such as PP with EB leads to ring substitution on the polymer backbone, which leads to an increase in the observed molecular weight as the

solution was aged, thus more ring substitution occurred (see Figure 8).

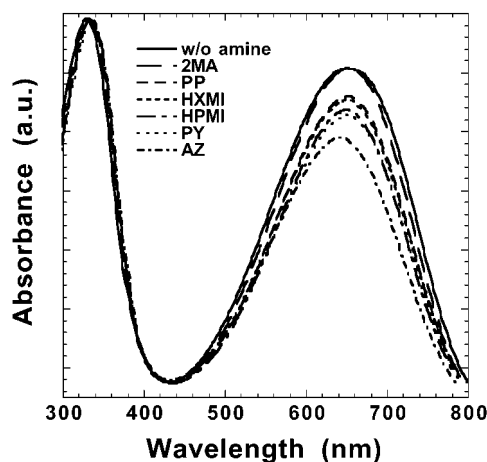
From our GPC study (Figure 8), we find that as we increased the solution aging time, the decay rate of the molecular weight of EB in the NMP/amine solutions decreased (based on the measured  $M_p$  values) in the following order: AZ > PY > HPMI > HXMI > PP. This suggests that the chemical strength (nucleophilicity) of these amines toward EB decreases in the same order. This order is also the same as we observed from the UV-vis characterization. We conclude that in the case of secondary amines possessing similar steric hindrance values, e.g., AZ vs 2MA, it is the basicity of the additive that governs the strength and nature of the chemical interaction/reaction with the Pani. This conclusion is supported by data acquired from *both* the UV-vis spectral characterization of the elution peaks (Q/B ratio and peak shifts) and the size-exclusion chromatography analysis ( $\Delta M_p$  based on retention times). The amine having weaker basicity has a reduced tendency to chemically react with the polymer which is a desired outcome for producing thermodynamically stable solutions at high concentration. On the other hand, for the case of secondary amines possessing comparable  $pK_a$  values, it is the steric hindrance factor, which determines the extent and nature of the interaction with the EB imine nitrogen. The amine with the smallest steric hindrance has the greatest tendency to chemically degrade the polymer structure. In summary, the reactivity strength among the cyclic amines toward EB decreases in the following order: AZ  $\gg$  PY > HPMI > HXMI > PP > 2MA.

### 2.3. Effect of Secondary Amine Concentration.

It is important to point out that the effect of the secondary amine's concentration, relative to the polymer mass in these binary solution systems, is also an important variable that impacts the rate of degradation or solution stabilization with respect to gelation phenomena. In the preceding studies, we purposefully adjusted the mole ratio of the secondary amine additive to the EB repeat unit to an exact value of 2 when preparing the 20 mass % EB/NMP/amine solutions. At this concentration there is exactly one molecule of amine for each imine nitrogen of the polymer on a molar basis, but 6.28 to 20% of amine on a mass basis, depending on the molecular weight of the amine, was in the EB/NMP/amine solution. Since these concentrations are relatively high for potentially reactive nucleophiles, the deleterious (or stabilizing) effects of these amine additives were easily observed. To investigate the potential effects of reduced additive concentrations of the secondary amines, we lowered the amine:{EB} molar ratio from 2.0 to 0.5 for the EB/NMP/cyclic amine solution systems to conduct GPC and UV-vis studies.

The UV-vis spectra collected for 24 h aged EB/NMP/amine solutions with amine:{EB} molar ratios of 0.5 are shown in Figure 10. Their measured  $M_p$  values, B and Q peak positions, and Q/B ratios are listed in Table 8. The observed changes in the UV-vis spectra and the change in the measured molecular weight, are *much less* pronounced than those observed for 1-h aged EB/NMP/amine solutions with a factor of 4 higher amine:{EB} molar ratio concentrations reported in the previous sections of this paper, even though these solutions were aged 24 times longer. We observed only minor decreases in the polymer molecular weights for solutions containing cyclic amines, except for the case of EB dissolved in





**Figure 10.** UV spectra of EB solution with cyclic amines (solution samples were collected after the EB solution was aged for 24 h; amine:{EB} molar ratio = 0.5).

**Table 8. Summary of GPC and UV-Vis Studies for the 24 h Aged EB/NMP/Cyclic Solution (Amine:{EB} Molar Ratio = 0.5)**

cyclic amine	$M_p$	B peak (nm)	Q peak (nm)	Q/B ratio
without amine	86 100	331	651	0.88
2MA	84 830	332	651	0.88
AZ	15 530	332	642	0.75
PY	63 570	335	646	0.78
PP	84 570	333	650	0.82
HXMI	83 430	333	650	0.80
HPMI	78 430	335	648	0.79

an AZ/NMP solution. Increased concentrations clearly accelerate the rates of chemical reactions. Additionally, as the concentration of the sterically hindered amines decreases, the Q/B ratio of EB in these solutions decreases slightly, and the Q peak slightly shifts toward the more high energy blue region of the spectrum. This suggests that, at lower amine concentrations, the chemically reactive nature of the amine toward the polymer is greatly reduced. Highly concentrated, thermodynamically stable fiber spinning solutions are achieved without significant polymer degradation if the amine additive concentration is minimized. Nevertheless, the trend in chemical reactivity among these cyclic secondary amines is identical to what we found in the work described in the previous sections.

## Conclusions

We have produced a predictive correlation for the selection of secondary amines that will inhibit the gelation of concentrated Pani EB solutions in NMP. This model states that, to be an effective GI, a secondary amine must have both width and depth of  $<4.53 \text{ \AA}$  and a  $pK_a$  of  $>7.7$ . These parameters can be implemented to search for other solvents and chemicals for EB polymer dissolution. Besides determining the amine's usefulness as a GI, we find that the geometric and electronic factors of an amine affect the degree of Pani EB degradation that occurs when the amine is added to the EB/NMP solution. A non-GI does not markedly degrade the EB within 1 h, regardless of its basicity. This is because non-GIs have width and/or depth  $>4.53 \text{ \AA}$ , and their sterically bulky structure limits their ability to interact with the imine nitrogen of the EB. On the other hand, all GIs degrade EB to a certain degree. Therefore, the conductivity of the resulting film made from these amine EB/NMP solutions is less than 10 S

$\text{cm}^{-1}$ . For amines with similar basicity, an amine with small width and depth tends to degrade the polymer more appreciably than one with large width and depth. For amines with similar width and depth, amines with strong basicity will degrade EB more aggressively than amines with weak basicity. In summary, amines with a small width and a strong basicity cause the most degradation. In addition, EB degradation depends on the interaction time between amine and EB, and on the amine concentration. The longer the contact time, and the higher the concentration of amines, the more severely the EB is degraded. To preserve the intrinsic properties of the EB polymer, one should minimize the concentration of the GI in preparing the concentrated EB solutions.

It is also important to note that the EB powder differs from one commercial source to another. Different methods of synthesizing EB give it different properties (such as chain branching). Therefore, although we have formulated a trend to find gel-inhibiting secondary amines for concentrated EB solutions, the amines that are near the borderline of the GI region can behave differently when used with different EB samples, EB concentrations, and amine:{EB} molar ratios. Nevertheless, we believe that the general trend for these amines to serve, as gel inhibition additives, will be the same as those reported here.

Although we did not study the reactivity of non-GIs toward EB, experimental observation suggests that some non-GIs, especially strong bases, do degrade EB as the solution ages. Furthermore, the GIs with atoms such as sulfur and oxygen on the ring seem to interact with EB molecules differently. Also, the UV-vis spectrum of EB in NMP/PP solutions shows evidence that PP degrades EB molecules. However, the molecular weight of EB, instead of decreasing, increased with solution aging time. The HCl-doped films made from EB/NMP solutions with some GIs, such as PP, have poor conductivity but good mechanical properties. On the other hand, the doped films made from other EB/NMP/AZ solutions have not only poor conductivity but also poor mechanical properties. All of these experimental observations suggest that the secondary amines attack EB molecules using different mechanisms. We conducted thorough investigations on these mechanisms and discussed them in a separate paper.<sup>42</sup>

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