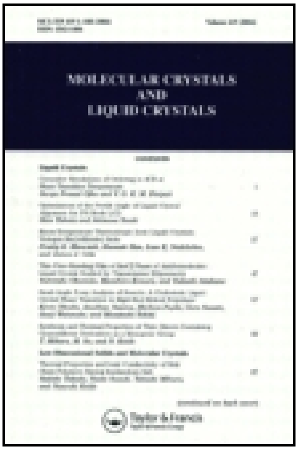

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Rheokinetic Study of Concentrated High Molecular Weight Emeraldine Base in N-Methyl-2-Pyrrolidinone Solutions Containing 2-Methyl-Aziridine

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Rheokinetic Study of Concentrated High Molecular Weight Emeraldine Base in N-Methyl-2-Pyrrolidinone Solutions Containing 2-Methyl-Aziridine

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Concentrated solutions of ultra-high molecular weight (HMW) emeraldine base (EB) are obtained when near stoichiometric quantities of 2-methyl-aziridine (2MA) per polymer repeat unit are co-dissolved in N-methyl-2-pyrrolidinone (NMP). Hydrogen bonds are formed between the secondary and tertiary EB nitrogen atoms found in the polymer repeat unit, and both the 2MA additive and the NMP solvent molecules. The rheological behavior of such solutions is quite different from that of EB/NMP solutions without 2MA. The principals of rheokinetic analysis are used to investigate the mechanism of the EB•2MA complex formation in the concentrated EB/NMP/2MA solution systems. The reaction rate, equilibrium constant and activation energy associated with the complexation are determined. Further, the stability of variable 2MA/EB molar composition and the kinetic effects due to variable temperature are reported for 20% (w/w) EB solutions.

Keywords: conducting polymer processing; polyaniline; rheology

INTRODUCTION

Richard Gregory and his colleagues at Clemson University have extensively studied the rheological and gelation properties of concentrated low molecular weight emeraldine base (EB) solutions by

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means of solution viscometry techniques.[1] We previously [2, 3, 4] reported approaches for preparing stable, highly concentrated, high molecular weight (HMW) EB/NMP solutions that involve co-mixing small amounts of secondary amines with the polymer and the solvent. Extruded articles, e.g., solid fibers, are easily obtained at a commercial scale from these solutions. However, in order to optimize the physical properties of the produced fiber, tight control over the complex set of parameters involved with the extrusion process itself must be exercised and understood. This note describes one very important aspect of the wet extrusion process itself, namely the rheological properties of the concentrated polymer solutions.

EXPERIMENTAL

2.1 Concentrated EB Solution Preparation

HMW EB was synthesized in our laboratory. Its MW (Mw > 250,000) was determined by GPC analysis.[5] Concentrated EB/NMP/2MA solutions were prepared by slowly adding a pre-determined weight of dried and sieved EB powder into a specified volume of NMP that contained variable amounts of 2MA in screw-top Teflon vials. After vigorously stirring the mixtures for a few minutes at room temperature, the tightly sealed Teflon vial was placed into an oven and heated to 60 °C for ~30 minutes. During this period, every few minutes, the EB/NMP/2MA mixture was taken out of the oven and then vigorously stirred. After following this mixing process, a homogeneous liquid solution free from gel particles was obtained. The concentrated EB/NMP/2MA solutions (20% w/w) prepared with varying 2MA/EB molar ratios (ranging from 1.5 to 3.5) were used for the rheology measurements.

2.2 Concentrated EB Solution Rheokinetic Study

These rheology studies employed a Brookfield RVDV - III cone and plate rheometer. A cone spindle, CP-52, with a semi-vertical cone angle of 3.0° was used for concentrated polymer solution viscosity measurements.

After cooling to room temperature, ~0.5ml of the polymer solution was transferred to the sample cup of the rheometer. The cup was controlled at a desired temperature by means of a VWR-1160 temperature controller. Gelation studies of the solutions were preformed by monitoring the viscosity change with time at a constant shear rate (0.8 sec^{-1}) and at three temperatures (25, 40, and 60 ± 0.1°C).

RESULTS AND DISCUSSION

The characteristic rheological behavior observed for the concentrated HMW EB/NMP/2MA solutions is shown in Figure 1. Three distinct rheological regions were found. *Region I* is characterized by a sharp decrease in viscosity with time. This behavior is most likely attributable to the formation of an EB•2MA H-bond complex that serves to block the interactions between the polymer chains. *Region II* represents the period of time during which there is no appreciable change in the viscosity of these solutions. We believe that in *Region II*, the solution has reached an equilibrium state in which approximately two 2MA molecules are H-bonded with the two available imine nitrogens of the polymer repeat units through hydrogen bonds. In other words, a thermodynamically meta-stable complex is formed through these H-bond interactions. After a prolonged period of solution stability, the solution phase separates due to the prolonged effects of continuous shearing, and *Region III* behavior is observed. In *Region III*, the intermolecular polymer H-bonding is re-established, leading to the cessation of fluidity as a three-dimensional physically cross-linked gel network forms.

Figure 2 presents the viscosity profiles for four 20% (w/w) EB solutions containing varying 2MA/EB molar ratios in NMP at 25 °C as a function of time. The three distinct rheological regions were found for each viscosity profile. The data for the various regions will be discussed separately in detail below.

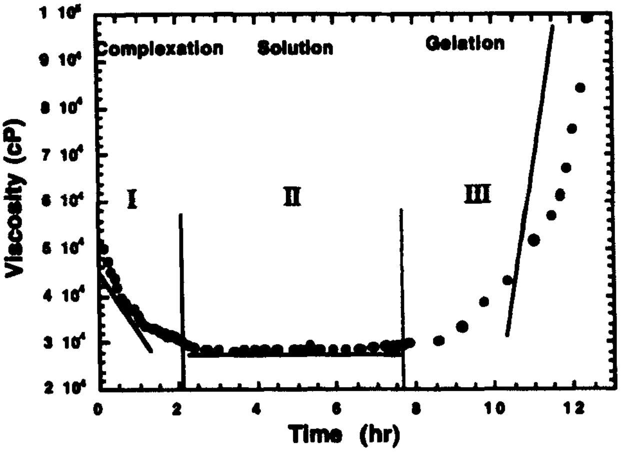

FIGURE 1 Representative viscosity curves versus time showing three distinct regions: (I) EB•2MA H-bond complexation region; (II) Equilibrium region; and (III) Gelation region.

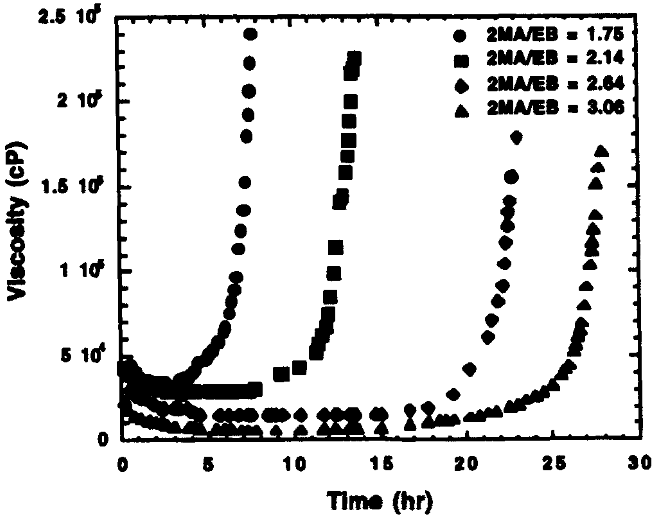

FIGURE 2 Viscosity as a function of time and 2MA/EB molar ratio at a constant temperature (25 °C), concentration (20% w/w), and shear rate (0.8 sec^{-1}).

3.1 Formation of HMW EB/NMP/2MA Solutions: Region I

Figure 3 shows a log-log plot of viscosity vs. time for *Region I* data presented in Figure 2. As the 2MA:{EB} molar ratio increases from 1.75 to 3.06, the time to formation of the solution phase (*Region II*) increases from a couple of hours to more than 5 hours, and the initial viscosity decreases from ~55,000 to ~25,000.

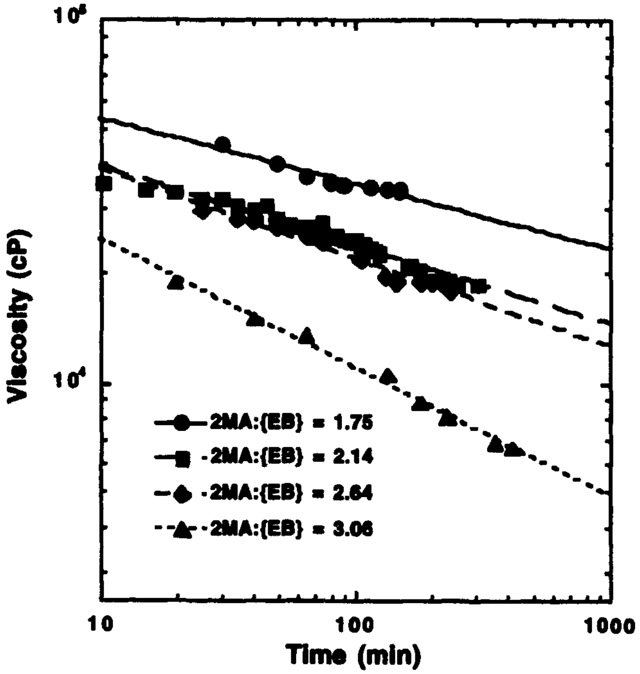

FIGURE 3 Viscosity as a function of time and 2MA/EB molar ratio in *Region I* at constant temperature (25 °C), concentration (20% w/w), and shear rate (0.8 sec^{-1}).

The process of a concentrated HMW EB/NMP/2MA solution formation in *Region I*, involves the EB•2MA complexation process itself. At this point in time, the polymers' intra-/inter-chain H-bonds are broken, and concurrently, 2MA molecules insert themselves at the imine sites along the polymer chains. This event enables the polymer to adopt an expanded chain conformation while in solution, and the viscosity typically decreases from its initial value by a factor of two. Rheokinetic analysis is a useful approach for understanding the kinetic mechanism associated with EB•2MA complex formation in the liquid phase. Such large viscosity "drops" are always associated with changes in either the polymer's concentration, and/or a polymer's molecular weight, and/or the interaction among polymer chains.[6]

3.1.1 Rate constant determination

In the formation of H-bonds between 2MA molecules and EB, the protons in 2MA molecules interact with the lone pair electrons in imine nitrogens of EB. Since there are two imine nitrogen sites in one EB tetrameric repeat unit ({EB}) (see Figure 4), it is reasonable for us to assume that a pair of 2MA molecules interact with one {EB} repeat, and also assume it is a third order reaction: first order in [EB] and second order in [2MA]. The formula of this complexation can be described as:

$$\{EB\} + 2\{2MA\} \Rightarrow \{EB \bullet 2 * 2MA\} \qquad (1)$$

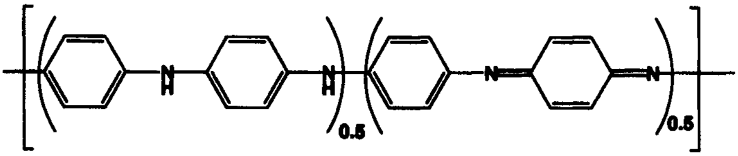

FIGURE 4 Chemical structure of EB tetrameric repeat unit ({EB}).

The viscosity of a polymer solution can be thought of as a measurement of the interaction between polymer chains. The viscosity of a pure EB solution is dominated by the interaction between amine hydrogen and imine nitrogen between the polymer chains. The formation of a EB•2MA complex blocks such polymer self-interaction, and results in the large viscosity decrease compared to a pure EB/NMP solution. Therefore, presumably, the viscosity of EB/NMP/2MA solution is solely dependent on the concentration of EB and independent of the concentration of the EB•2MA complex ([EB•2MA]). The empirical equation which is commonly used to correlate concentrated polymer solution viscosity (η) and concentration (c) is used here: [7, 8]

$$\eta = Kc^{5.4}M^{3.4} \qquad (2)$$

where K is an empirical constant which depends upon the polymer's nature, the temperature, and where M is the average molecular weight. After rearranging this equation to equation (3), we are able to use the *viscosity change* with time to monitor the EB•2MA complexation process:

$$c = [EB] = [EB]_0 - X = \sqrt[5.4]{\eta / KM^{3.4}} \quad (3)$$

where EB_0 is the initial concentration of {EB} and X is the concentration of the EB•2MA complex, both quantities in units of mole/l. At 25 °C, the value of $(KM^{3.4})^{1/5.4}$ is 10.33 ($cp^{1/5.4}$/mole/l) (which is determined as described later in Section 3.2).

The rate law for the reaction given in Equation 1 can be described as:

$$R_r = \frac{d[X]}{dt} = k[EB][2MA]^2 = k[EB_0 - X][2MA_0 - 2X]^2 \quad (4)$$

where R_r is reaction rate (mole/l/min), t is reaction time (min), *k* is the reaction rate constant ($(\text{mole/l})^{-2}$/min), and $2MA_0$ is the initial concentration of 2MA(mole/l).

By rearranging Equation 3 to solve for X, which is directly proportional to viscosity change (F(η)) with time, and using the integrated form of Equation 4, the reaction rate of the complex formation was determined with Region I (Figure 1) experimental data.[9] The relationship between F(η) and time are illustrated in Figure 5. Since these four sets of experiments had been done at the same temperature, the reaction rate constants for these reaction systems should be the same. Indeed, these four sets of experimental data superimpose one on another very well. This supports the argument that only reaction temperature governs the rate of the reaction.[10] It also proves that the EB•2MA complexation is a third order reaction. The average rate constant (~3.4×10^{-4} ($(\text{mole/l})^{-2}$/min)) was determined by linearly fitting the experimental data in Figure 5. This small value of *k* indicates the EB•2MA complexation is a slow process. These concentrated EB/NMP/2MA solutions need to take time to reach an equilibrium state.

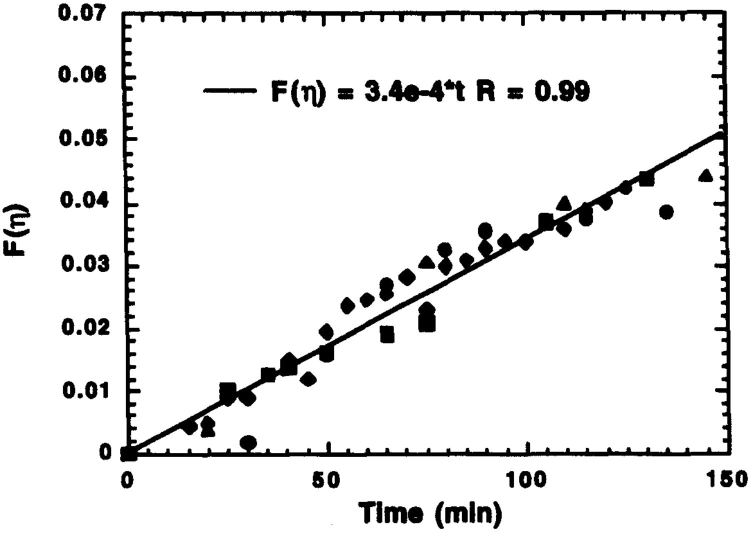

FIGURE 5 F(η) as a function of time for the four EB/NMP/2MA concentrated solution systems with a constant EB concentration (~20% w/w) and temperature (25 °C). (Corresponding to the experimental data in Figure 3).

3.1.2. Activation energy determination

In the solution preparation, thermal energy is very important to obtain a stable EB/NMP/2MA solution. Without providing enough energy to the system, the EB•2MA complex could be neither formed nor formed completely, and the gelation occurs rapidly. In order to determine the activation energy associated with the EB dissolution process, the effects of temperature on the stability of concentrated EB/NMP/2MA solutions were studied. The results are shown in Figure 6. By using equation (2) and the *Region I* experimental data from Figure 6, the F(η) as a function of time at three different temperatures were obtained. These are presented in Figure 7. *The rate constants at different temperatures are the slopes of these three curves.* When the temperature increases from 25 to 60 °C, the rate constant of the EB•2MA complexation increases ~22 times.

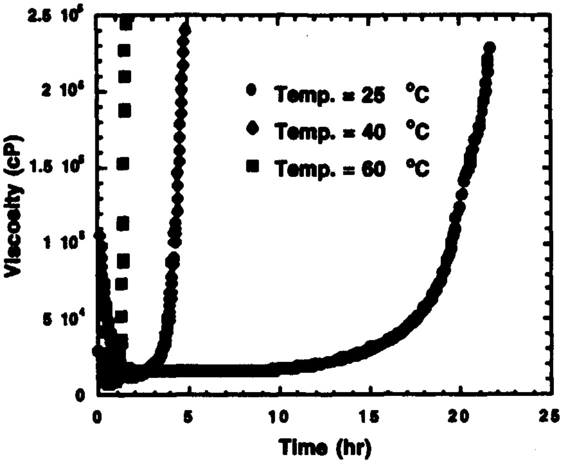

FIGURE 6 Viscosity as a function of time and temperature at constant concentration (20% w/w), 2MA/EB molar ratio (2.58), and shear rate (0.8 sec^{-1}).

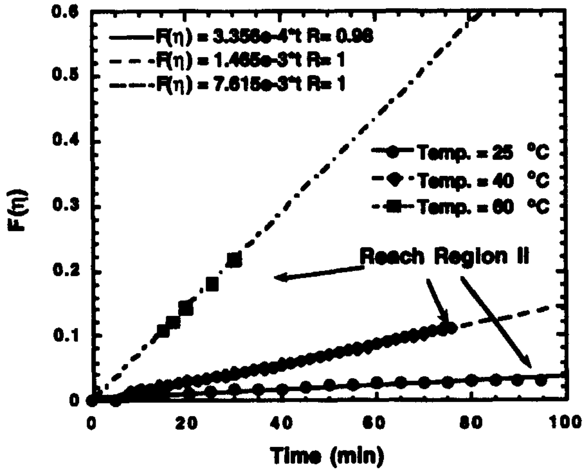

FIGURE 7 F(η)s as functions of time for 20% w/w concentrated EB/NMP/2MA solution systems at 25, 45 and 60 °C. (EB conc. 20% w/w, 2MA/EB = 2.59).

The *Arrhenius equation* relates the rate constant (*k*) for a reaction to the frequency factor (A), the activation energy (E_a (kJ/mole)) and temperature (T (K)): [11]

$$k = Ae^{-E_a / RT} \tag{5}$$

The activation energy and frequency factor can be determined from the temperature dependence of the rate constant. With the rate constants at different temperatures shown in Figure 7, the activation energy of EB•2MA complexation ~ 73.6 kJ/mole is obtained. Although this energy is much less than the normal covalent bond energy (>150 kJ/mole), it is about 3 times of a normal H-bonding energy (<25kJ/mole).[12] This indicates that EB•2MA complexes are formed through a physical interaction. This also suggests that on average, there are at least 3 H-bonds between two EB tetrameric repeat units. This energy, which is used to break polymer inter-/intra-chain H-bonding, and concurrently form the NMP/EB/2MA H-bond complex, explains the fact that external energy is required to activate the EB, NMP and 2MA molecules during EB•2MA complexation.

3.2 The Equilibrium State of HMW EB/NMP/2MA Solution: Region II

In this region, the rheological behavior and the viscosity of the concentrated EB/NMP/2MA solutions remain stable, and EB•2MA complexation reaches an equilibrium state. The viscosity values of these solutions depend on the 2MA and EB concentration and temperature. For a 20% w/w HMW EB/NMP/2MA solution system at 25 °C, as the 2MA/EB molar ratio increases, the solution viscosity in the equilibrium state greatly decreases from its initial value, and the duration of *Region II* behavior increases (see Figure 2). This is because the amount of the EB•2MA complex in Region II increases with the 2MA/EB molar ratio.

For the EB and 2MA complex formation (1), the equilibrium constant can be written as:

$$K_{eq} = \frac{X}{(EB_0 - X) * (2MA_0 - 2X)^2} \tag{6}$$

where K_{eq} is the equilibrium constant, X is the concentration of EB•2MA complex at an equilibrium state. Equation 3 is used to correlate solution viscosity and EB concentration, and using the four sets of experimental data in Figure 2, the values of K_{eq} and $KM^{3.4}$ can be determined. The EB and 2MA concentrations, solution viscosities in *Region II*, and the calculated results are summarized in Table 1.

TABLE 1 EB and 2MA concentration, solution viscosity and calculated results for $KM^{3.4}$.

$2MA_0/EB_0$ molar ratio	EB_0 (mole/l)	$2MA_0$ (mole/l)	η_{II} (cP)	$(KM^{3.4})^{1/5.4}$ ($cP^{1/5.4}$/mole/l)
1.75	0.77	1.34	33670	10.40
2.14	0.78	1.67	28310	10.51
2.66	0.80	2.12	14990	10.06
3.06	0.81	2.48	6810	10.36
	Average:			10.33

The average value of $(KM^{3.4})^{1/5.4}$ at 25 °C is 10.33 ($cp^{1/5.4}$/mole/l). The equilibrium constant K_{eq} is equal to 0.12 $(mole/l)^{-2}$. This small equilibrium constant indicates that only a small amount of the EB and 2MA (<10%) in solution participates in the formation of the EB•2MA complexes. However, even the small amount of the EB•2MA complexes plays an important role in concentrated EB/NMP/2MA solution system, it reduces the interactions between polymer chains, enhances the solution solubility and prolongs the solution gelation significantly.

3.3 Concentrated HMW EB Solution Gelation: Region III

The gelation in concentrated EB/NMP/2MA solution is due to the H-bonding between polymer chains, therefore, it is a physical gelation. In the gelation process, due to EB•2MA complex dissociation and EB-EB H-bonding re-establishment, the solution losses its fluidity. The time of gel formation is one of the most important kinetic characteristics of curing since it is characteristic of some critical degree of conversion corresponding to the transition from viscous flow to the rubber like stage. More precise measurement of the time to gelation can be obtained by plotting the reciprocal of viscosity vs. time for data taken from *Region III* [13]. The longer gelation time a polymer solution has, the longer is the time during which the polymer solution can be processed. The effects of 2MA/EB molar ratio and temperature on the gelation time of the EB/NMP/2MA solution are presented in Figure 8.

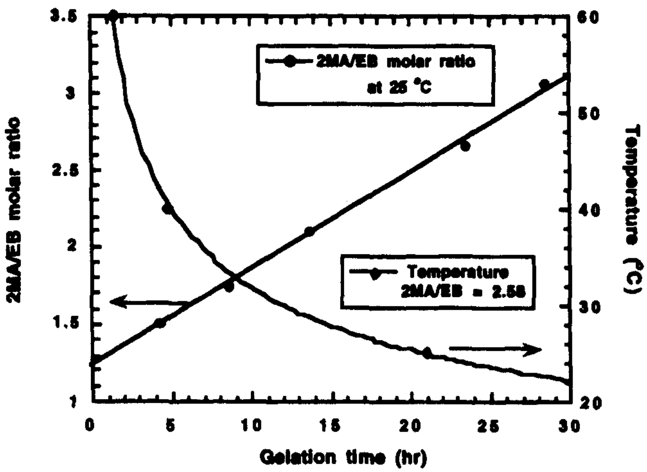

FIGURE 8 Concentrated EB/NMP/2MA solution gelation time as functions of 2MA/EB molar ratio and temperature. (EB conc. 20% w/w).

At a given EB concentration (20% w/w) and temperature (25 °C), the extent of formed EB•2MA complexes increases with the 2MA/EB molar ratio. With more EB•2MA complex formation, the concentrated EB/NMP/2MA solution possesses a larger stability associated with a lower solution viscosity and a longer duration of *Region II*. The solution gelation increase linearly with 2MA/EB molar ratio.

On the other hand, as the temperature increases from 25 to 60 °C, the solution gelation time decreases following a power-law. Increasing temperature accelerates the concentrated EB/NMP/2MA solutions gelation. Two possibilities exist that may account for this behavior. First, at elevated temperatures, the relatively volatile 2MA is more rapidly driven from the solution in the viscometer, and thereby decreasing the actual 2MA/EB complex concentration. Secondly, the concentrated solution simply phase separates. Experiments are under way to determine the cause of this phenomenon.

CONCLUSIONS

Dissolving large quantities of Emeraldine Base in the NMP/2MA solvent system involves the process of intermolecular H-bond breaking between EB chains, and the subsequent H-bond complexation between EB and

2MA molecules. An EB•2MA complex formation is a third order reaction that is first order in [EB] and second order in [2MA]. The small rate constant (~ 3.4 x 10^{-4} $(\text{mole/l})^{-2}$/min at 25 °C) indicates that the EB•2MA complexation process is slow at room temperature. The reaction needs time to reach an equilibrium state. Only when the solution reaches an equilibrium state will EB molecules take on an "expanded" conformation and possess the lowest self-interaction (viscosity). It has been proved that the electrical and mechanical properties of EB products (e.g. EB film and fibers) can be enhanced greatly by using *Region II* EB solution.[2]

Increasing the temperature effects the rheological behavior of concentrated EB/NMP/2MA solutions in different regions. In *Region I*, temperature will speed up EB•2MA complexation process (shorter time length of *Region I*). The activation energy (~73 kJ/mole) of this complexation suggests that sufficient energy must be provided during EB/NMP/2MA solution mixing to ensure complete EB•2MA complex formation. On the other hand, increasing temperature accelerates EB gelation process in *Region III*. By intelligently controlling temperature at the different regions, an optimized EB/NMP/2MA solution, with the highest EB solubility, the longest stability and the lowest viscosity, can be obtained.

The EB solution gelation linearly increases with 2MA/EB molar ratio. Higher 2MA/EB molar ratios give an EB/NMP/2MA solution with longer stability and lower *Region II* viscosity. Greater quantities of 2MA, as might be used if one were using co-solvents, are found to deteriorate the resulting polymer articles by embrittlement. Environmental safety is the other important factor driving to use small amounts of 2MA.

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