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Specific Interaction이 있는 Rigid-rod/Coil/Slovent 삼성분계의 상거동

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Critical Phase Behavior of Ternary System; Rigid-rod/Coil/Solvent System with Specific Interaction

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요 약: 본 연구에서는 coil 성분으로서 nylon, NaAMPS (poly(sodium 2-acrylamido-2-methylpropane sulfonate)), HAMPS (2-acrylamido-2 methylpropane sulfonic acid) 및 sulfonated 케블라 (poly((*p*-phenyleneterephthalamido) propanesulfonate))를, rigid-rod성분으로서 PBZT (poly-1,4-phenylene benzobisthiazole)를, 그리고 용매로 MSA (methansulfonicacid)를 사용하여 용액 중에서의 이들의 상거동을 고찰하였다. PBZT/nylon/MSA 삼성분계의 상거동은 Flory의 상거동 이론과 잘 일치하였으나 그 외의 coil 성분이 포함된 삼성계에서는 Flory의 이론치와 상당히 차이를 보이는 것이 관찰되었다. 이와 같은 상거동에 영향을 주는 것은 PBZT와 coil 성분과의 사이에 존재하는 이온간의 specific interaction 차이로 해석할 수 있으며 이를 FTIR과 WAXD에 의해 고찰하였다. 실험결과를 Flory 이론에 의한 해석과 비교한 바 rigid-rod/coil/slovent 삼성분계에서는 rod와 coil 사이의 intermolecular ionic interaction이 상거동에 영향을 주는 인자로 판단되었다.

ABSTRACT: This paper reported the phase diagrams of PBZT (poly-1,4-phenylene benzobisthiazole)/nylon/MSA, PBZT/poly(sodium 2-acrylamido-2 methylpropane sulfonate) NaAMPS)/MSA, PBZT/2-acrylamido-2 methylpropane sulfonic acid (HAMPS)/MAS, and PBZT/poly (*p*-phenyleneterephthalamido) propanesulfonate) (PPTA-PS)/MSA. The ternary phase diagram of rigid rod polymer PBZT and amorphous nylon in methanesulfonic acid (MSA) solvent was found to follow Flory's prediction of a rod/coil/solvent ternary system very well. When sulfonated polymers, such as NaAMPS polymer and PPTA-PS, were used instead of nylon in a ternary solution, it was found that the phase behavior deviated from Flory's theory due to the possible coil/rod intermolecular interaction in the ternary solution. It was found that for the PBZT/nylon/MSA system, the X_3 value was consistent with the contour length of the coil molecules as predicted by Flory's theory. However, both PBZT/HAMPS-monomer/MSA and PBZT/NaAMPS polymer/MSA systems showed an X_3 value of unity. The ternary phase diagram of PPTA-PS system shows an X_3 value larger than 1, which indicates the ionic interaction is not perfect like PBZT/NaAMPS polymer/MSA and PBZT/HAMPS monomer/MSA system. This suggests that the degree of intermolecular interaction between rod and coil plays an important role in determining the phase behavior of rod/coil/solvent ternary system.

Keywords: ternary system, ionic interaction, NaAMPS, sulfonated kevlar, PBZT.

INTRODUCTION

For the processing of molecular composite consisting of rod and coil, it is desirable to have a molecular morphology in which the rigid-rod molecules are evenly dispersed in the coil-like polymer. With this morphology, rod molecules can reinforce the coil-like molecules with maximum reinforcement effect. This structure is obtained by using a common solvent in the isotropic state just below the critical concentration. However, the thermodynamic phase separation between rigid-rod and flexible molecules is inevitable during the coagulation and consolidation process.[1-4] One possible way to minimize the phase separation problem is to enhance the miscibility behavior by utilizing the chemical bonding between two components, such as covalent bonding,[5] donor-acceptor interaction,[6] ionic bonding,[7,8] hydrogen bonding,[9] or charge transfer interaction.[10] For the application of rod-coil system in strong acid solvent, the ionic interaction of acid-base nature has been found most strong among other interactions.

L. S. Tan et al.[11] have reported the use of poly(sodium 2-acrylamido-2 methyl propanesulfonate) (NaAMPS polymer), a high molecular weight alkyl polymer with sulfonated side chains, in forming a molecular composite film with poly[-1,4-phenylene benzobisthaizole] (PBZT). They prepared the transparent film of 50/50 PBZT/NaAMPS mixture which has the phase separaiton within less than 500 Å resolution. This system represents a new class of rigid-rod molecular composite that is different from other rigid-rod molecular composite. Most previous systems, such as PBZT/ABPBI/MSA,[12] PBZT/PEEK/MSA,[13] or PBZT/nylon/MSA[14] do not contain specific intermolecular interaction between the coil and the rigid-rod. Due to the presence of the sulfonated side groups of NaAMPS polymer, it serves as an ideal model compound to study the effect of coil-chain interaction on the ternary phase behavior. Specific ionic interaction between the rod and coil may give rise to unique properties for the processing of molecular composites.

For the ternary system consisting of rod/coil/solvent, classical Flory's theory[15] which assumes athermal condition was found to be in good agreement with experimental results simply by considering the aspect ratio of rod molecules and contour length of coil molecules.[16] When there exists a specific ionic interaction between rod and coil, the critical behavior should be different from that predicted by Flory's theory. The ternary phase diagram of the three component solution described by Flory, is based upon the topological difference (rigid-rod and flexible coil) of the two polymers and does not contain any description of specific interactions between them. However, specific interaction may be desirable in forming multi-functional materials without thermodynamic phase separation.

Therefore, this study is to investigate the effect of specific interaction between the rod and coil polymers on the ternary phase diagram and the coagulation behavior of the two-component molecular composite. The deviation of critical behavior resulting from Flory's theory can be interpreted as the effect of intermolecular interaction in the ternary system. By utilizing NaAMPS and poly(*p*-phenyleneterephthalamido propanesulfonate) (PPTA-PS) polymers which could offer the ionic interaction with PBZT molecules and studying the coagulation behavior of ternary systems with specific interaction, the effect of ionic interaction during the coagulation process was studied. The composition ratio of rod and coil components before and after coagulation process was analyzed using FTIR analysis. Since the NaAMPS polymer or

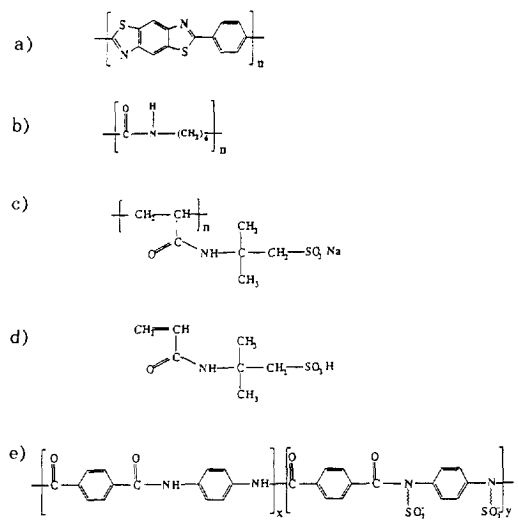

Figure 1. Chemical structures of components; a) PBZT, b) nylon, c) NaAMPS polymer, d) HAMPS monomer, and e) PPTA-PS.

PPTA-PS is soluble in water, the coagulated composition should be different depending upon the initial solution morphology and coagulation stage. Also, the effect of critical concentration on the coagulation composition was studied.

EXPERIMENTAL

Materials. PBZT was prepared by SRI International in the form of a dope in polyphosphoric acid and these dopes were coagulated and pulverized into PBZT flakes by neutralizing and drying. The details of preparation procedure are well explained in the Ph. D. thesis of C. A. Gabriel.[17] The rigid-rod component was PBZT which has a paracatenated backbone leading to a rodlike polymer;[18] its chemical structure is sketched in Fig. 1-a. The intrinsic viscosity of PBZT is 16 dl/g in methane sulfonic acid (MSA) solution, corresponding to an average molecular weight of 27000.

For the flexible molecules, four different compounds were used: Nylon, NaAMPS polymer, HAMPS monomer, and PPTA-PS. The nylon (Zytel^{TM} 330), obtained from DuPont, was an amorphous polymer with a molecular weight of 14000(Fig. 1-b). NaAMPS polymer (Lubrizol), the trade name of poly(sodium 2-acrylamido-2 methylpropanesulfonate) from Lubrizol Co. (Fig. 1-c), is a linear polymer (with molecular weight about $3\text{-}4\times10^6$) containing sulfonated side groups and is soluble in both MSA and H_2O. "Lubrizol 2420" as received was a milky white, viscous, aqueous liquid. It was precipitated into a mixture of toluene and methanol yielding a wax-like substance. After filtering, washing, and drying, NaAMPS polymer was a powder.[11] NaAMPS polymer was known to degrade after long-term exposure in acid. After two weeks in MSA, the inherent viscosity of NaAMPS polymer/MSA solution was found to decrease by 15 %.[11] The HAMPS monomer was also obtained from Lubrizol Co. and the chemical structure is shown in Fig. 1-d. Poly(*p*-phenylene terephthalamide propane sulfonate) (PPAT-PS), a sulfonated version of Kevlar, with an average molecular weight of 25,000 was provided by J. Reynolds.[19] PPTA-PS was prepared by reacting poly(p-phenylene terephthalamide) with 1-3 propane sultone. Its chemical structure is shown in Fig. 1-e. PPTA-PS is soluble in both water and MSA. Elemental analysis showed that 66% of the PPTA polymer backbone was sulfonated.[9]

Ternary Phase Diagram. The ternary phase diagram of the rod/coil/solvent system was studied by varying the rod/coil polymer composition from 100/0 to 10/90. For a given rod/coil composition, the critical concentration was determined by slowly titrating an anisotropic solution of known concentration until the solution became isotropic. For each concentration, the ternary solution was stirred at room temperature under dry nitrogen for one to two days to assure achieving a homogeneous solution. Most

isotropic solutions were optically transparent and dark green, while the anisotropic solutions were opaque and yellowish green. The isotropic phase was confirmed by using optical microscopy under crossed polarizer. The concentration at which the anisotropic phase disappeared was chosen to be the critical concentration for a given composition. The weight fraction of polymers at the critical point was then calculated from the weight of solvent added.

Coagulation Behavior Analysis. For the Coagulation behavior analysis, the solutions of varying compositions and concentrations were prepared. The mixing of these solutions continued for 6-7 days until the completely homogeneous solutions were obtained. Thin films from these solutions were prepared on glass slides using a doctor blade. By placing 30-40 mL of solution on a glass slide and applying the shear force with doctor blade, the very thin smeared solution films were prepared on the glass slide. The prepared solution films were immediately coagulated in distilled water for 24 hours. The wet coagulated films were dried under air at room temperature or under vacuum between two teflon plates for 1-2 days at 100 ℃. Since NaAMPS polymer or PPAT-PS polymer is soluble in the water, the composition variation in the coagulated films was studied using a Beckman infrared spectrometer FT-1100.

WAXD was used to study the aggregation of PBZT molecules and phase separation of PBZT /NaAMPS polymer coagulated blends. WAXD patterns were recorded with a flat-film Statton (Warhus) camera using Cu Kα radiation, with a Ni filter, and a sample-to-filter distance of 5 cm.

RESULTS AND DISCUSSION

PBZT/Nylon/MSA System. The theory developed by Flory[15] describs the critical phase behavior of a ternary system consisting of an isodiametrical solvent, a rigid-rod polymer, and a flexible coil polymer. This theoretical analysis can be directly applied to the experimental results. For providing base data, pure PBZT in distilled methanesulfonic acid (MSA) solution was prepared and observed to be biphasic at 3. 65% weight fraction. Flory's classical theory on rigid-rod phase transition[15] is applicable here and gives a C_{Cr} of 3.6%. This result is remarkably close to the experimental C_{Cr} considering the *athermal* assumption involved in the theory.[15]

With the mixed solvent of 97/3 wt% ratio of MSA/CSA(chlorosulfonic acid), the critical behavior of PBZT/nylon/solvent system was studied and is shown in Fig. 2. The theoretical aspect ratio of PBZT molecules is estimated to be 256 from the model compound of repeat unit length of 12.2 Å, repeat unit width of 4.691 Å, and polymer molecular weight of 27000. The contour length of 300 for the Nylon flexible polymer was adopted for the theoretical calculation.[16] As seen in Fig. 2, the experimentally determined critical concentration shows increasing trend from 3.6% to 4.7% with increasing amount of coil molecules up to 70%. This means that the addition of coil molecules restricts the actual volume available for rod molecules relatively and the phase segregation phenomena is enhanced by more compact packing and alignment of rod molecules, resulting in higher critical concentration. The experimental results for PBZT/nylon/MSA-CSA system are in excellent agreement with the theoretically predicted values, as represented by the solid line in Fig. 2.

The sams phase diagram was constructed for PBZT/nylon/MSA system and shown in Fig. 3. The MSA used was 99% MSA "as is" from Aldrich Chemicals without distillation. By titrating the anisotropic solutions of 100/0, 70/30, 50/50,

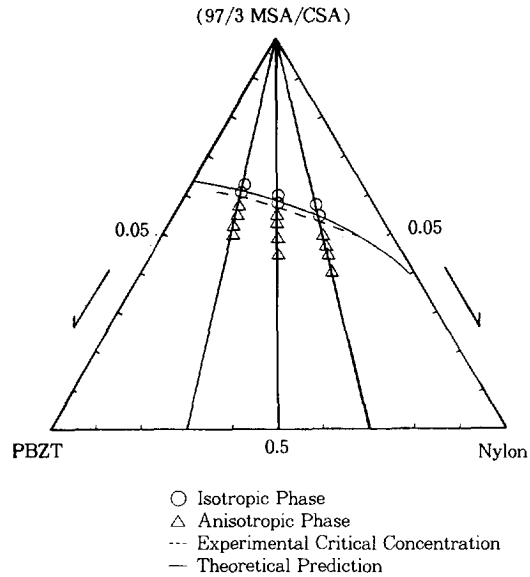

Figure 2. Critical phase diagram of PBZT/nylon/(97/3 MSA/CSA) system and theoretical calculation.

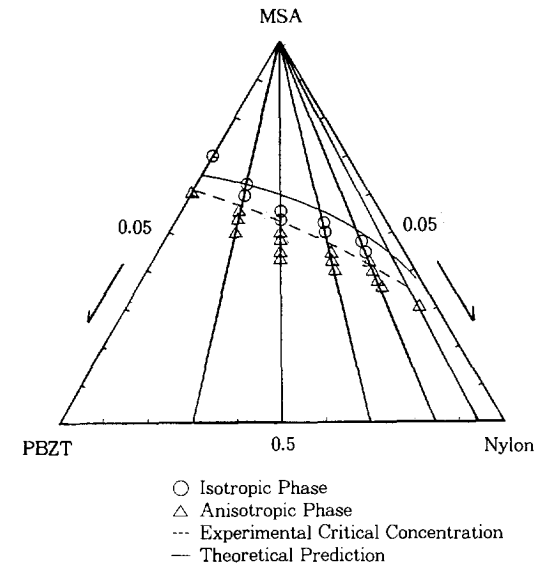

Figure 3. Critical phase diagram of PBZT/nylon/MSA system and theoretical calculation.

30/70, 15/85, 5/95 PBZT/nylon blends, all the critical concentrations were determined. They are 4.0%, 4.4%, 4.8%, 5.3%, 5.8%, 6.6% respectively. These experiment critical concentrations are a little bit higher than those predicted by the Flory's theory.

When compared with the PBZT/nylon/MSA-CSA critical phase boundary as shown in Fig. 2, some discrepancy of critical behavior can be found. It is due to the presence of small amounts of moisture in MSA solvent, which results in the aggregation of PBZT molecules.[12] The effect of the aggregation is a decrease of actual aspect ratio of rigid molecules in the solution. When the "as is" MSA phase diagram is used to backcalculate the aspect ratio of the rigid molecules, the calculated aspect ratio of PBZT molecules showed a value of 220, a decrease by 14%. According to the Halpin-Tsai Equation,[22] this will only have a minimum effect on the reinforcing efficiency. So the "as is" MSA would be acceptable for the practical applications. But using "as is" MSA also means that a certain degree of PBZT aggregation exists in the solution before coagulation.[5] Therefore, it is not surprising that WAXD result of consolidated block showed the evidence of aggregation of rigid-rod molecules. It is not clear whether additional aggregation is generated during the coagulation process, and further decreases the aspect ratio of the reinforcement entities, compromising the reinforcement efficiency of the rigid-rod molecules.

PBZT/NaAMPS Polymer/MSA and PBZT/HAMPS-monomer/MSA System. Various compositions of PBZT/NaAMPS polymer were codissolved in distilled MSA for forming homogeneous solutions for the critical behavior analysis. The compositions were 100/0, 70/30, 50/50, 40/60, 20/80 and 0/100 for PBZT/NaAMPS polymer weight ratio. The solutions could be either isotropic or anisotropic (nematic) depending on the polymer concentration. In having a sulfonate moiety on each side chain, NaAMPS polymer is deemed to have certain protonation inter-

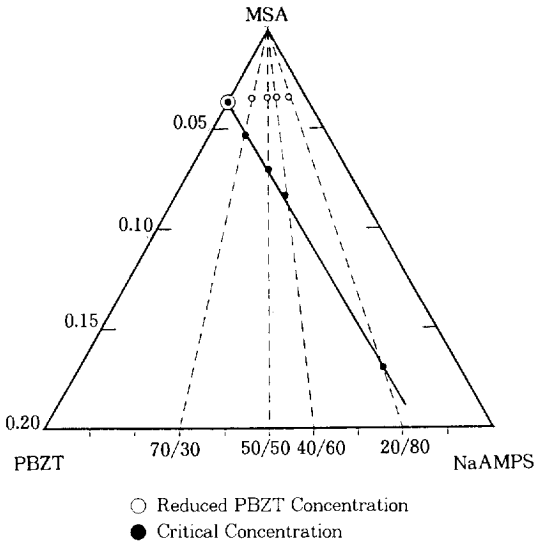

Figure 4. Critical phase diagram of PBZT/NaAMPS polymer/MSA system.

action with PBZT. Therefore, the effect of this interaction in the ternary solution of PBZT/NaAMPS polymer/MSA was examined by C_{Cr} determination. As shown in Fig. 4, the critical concentration increases drastically from 3.6% to over 16% with increasing the amount of NaAMPS polymer. When compared with critical concentrations of PBZT/nylon/MSA system in Fig. 2, the biphasic behavior occurs at much higher concentration. Considering the ternary phase equilibrium theory proposed by Flory,[15] the effective molar volume ratio X_3 for the NaAMPS polymer in the ternary solution would be unity just like that of the MSA solution. This is a surprising result in view of that NaAMPS polymer is a linear polymer with very high molecular weight; its X_3 should have been in the order of 10^3-10^4 leading to a much lower C_{Cr} for the ternary solution. However, the effect of ionic interaction between the protonated PBZT and NaAMPS polymer might have played a role here.

There are possibly two kinds of protonation interaction involving PBZT in the ternary system; PBZT with MSA and PBZT with NaAMPS polymer. Over a wide composition range the ternary phase diagram does not show any distinction between these two. The reduced PBZT content can be calculated from the experimental concentration. The reduced PBZT concentration at C_{Cr} is relatively constant regardless of NaAMPS polymer content and agrees with that of pure PBZT in MSA. The effect from a long coil-like NaAMPS polymer molecules is not evidenced. The linear relationship shown in the phase diagram seems to suggest that the protonated PBZT is unable to distinguish NaAMPS polymer from MSA in the ternary solution.

Finally, the Flory's modified lattice theory does take into account the excluded volume effect but not, by assuming *athermal*, the mixng free energy or intermolecular interaction. The excess protonation interaction between PBZT and NaAMPS polymer seems to balance the excluded volume effect from chain configuration and the gelation behavior of the large molecule NaAMPS polymer giving a X_3 value of unity.

The sole effect of ionic interaction on the critical concentration can be observed by studying the phase diagram of PBZT/HAMPS-monomer/MSA system, instead of using high molecular weight NaAMPS polymer. By constructing this phase diagram, the entanglement effect from ultra high molecular weight NaAMPS polymer can be removed completely. The phase diagram of PBZT/HAMPS-monomer/MSA system is shown in Fig. 5. The critical concentrations containing HAMPS-monomer are almost consistent with those of PBZT/NaAMPS polymer/MSA system. This suggests that HAMPS-monomer also acts like MSA solvent, corresponding to the contour length of coil molecule, X_3, equal to 1. There is no molecular weight effect observed on

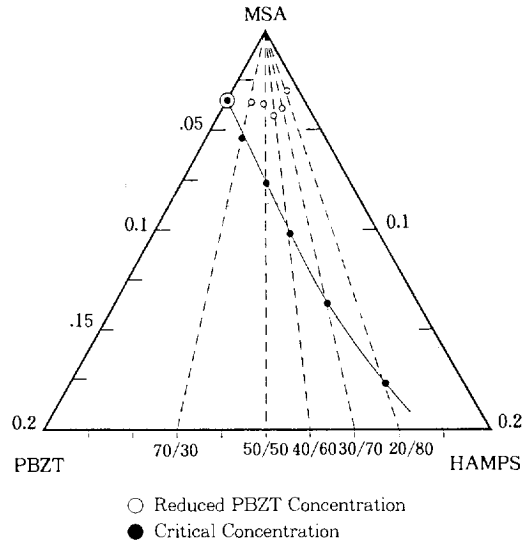

Figure 5. Critical phase diagram of PBZT/HAMPS monomer/MSA system.

the critical behavior of phase diagram. It can be concluded that the ionic interaction between PBZT and NaAMPS polymer molecules is the major factor to shift the C_{Cr} to higher concentration and result in the constant reduced PBZT content in the ternary system.

The coagulated films from six different solutions, 5.5% 50/50 PBZT/NaAMPS polymer, 7.6 % 50/50 PBZT/NaAMPS polymer, 4.0% 70/30 PBZT/NaAMPS polymer, 5.44% 70/30 PBZT/NaAMPS polymer, 5.6% 30/70 PBZT/NaAMPS polymer, and 9.9% 30/70 PBZT/NaAMPS polymer mixtures in MSA solvent, were prepared for the composition analysis. The characteristic spectra of NaAMPS polymer component can be observed at 1673.5 cm^{-1} which is believed to be the carbonyl stretching. For PBZT, the C=N stretching can be found at 1483.6 cm^{-1} and also shows a very strong absorption band at 959.1 cm^{-1} which is assigned to the C-S bond in PBZT component by using the IR table in reference.[20] Therefore, the unique chemical structures of PBZT and NaAMPS polymer component to be useful for the analysis of coagulation composition in FTIR spectrum are carbon-sulfur group at 959.1 cm^{-1} and C=O group at 1673.5 cm^{-1} respectively. By using these two IR spectra and measuring the areas of two peaks, the composition analysis of the two components in the coagulated blends was made.

When each area of the two absorption bands at 1673.5 cm^{-1} and 959.1 cm^{-1} were measured from the base line, the absorbance of each spectra can be expressed using Beer-Lambert law. The ratio of two absorbances in the blend is directly proportional to the ratio of product of absorptivity and concentration of each component, since the segmental length is the same. For this study, three reference samples were prepared by mixing the powder of 30/70, 50/50, and 70/30 PBZT/NaAMPS polymer composition.[21] Using Beer-Lambert law, the characteristic calibration curve of PBZT/NaAMPS polymer system can be made and the actual coagulated composition of PBZT/NaAMPS polymer system can be calculated.[22] Coagulated films of 7.6% 50/50 PBZT/NaAMPS polymer, 5.5% 50/50 PBZT/NaAMPS polymer, 4.0% 70/30 PBZT/NaAMPS polymer, 5.44% 70/30 PBZT/NaAMPS polymer, 5.6% 30/70 PBZT/NaAMPS polymer, and 9.9% 30/70 PBZT/NaAMPS polymer compositions were investigated using FTIR analysis. In Fig. 6, the IR spectra of different PBZT/NaAMPS polymer composition at 1673.5 cm^{-1} and 959.1 cm^{-1} are shown. With increasing PBZT content from 30% to 70% in PBZT/NaAMPS polymer mixture, the carbonyl stretching band around 1673.5 cm^{-1} becomes smaller and the PBZT characteristic absorption around 959.1 cm^{-1} becomes stronger.

By measuring the area of above two characteristic spectrums of coagulated PBZT/NaAMPS polymer blends, the composition variations after coagulation were calculated and are shown in

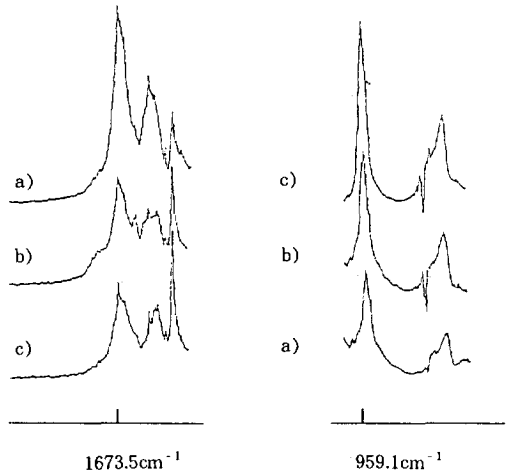

Figure 6. FTIR spectra of PBZT/NaAMPS polymer coagulated film with varying composition; a) 30/70, b) 50/50, and c) 70/30.

Table 1. PBZT/NaAMPS Polymer Blends Composition Change before and after Coagulation Calculated from FTIR Analysis Data

sample composition identification	b_2C_2/b_1C_1	PBZT/NaAMPS polymer before coagulation	PBZT/NaAMPS polymer after coagulation
5.50 wt% ($\leq C_{Cr}$) PBZT/NaAMPS	0.37	50/50	51/49
7.61 wt% ($>C_{Cr}$) PBZT/NaAMPS	0.42	50/50	58/42
4.00 wt% ($\leq C_{Cr}$) PBZT/NaAMPS	0.58	70/30	70/30
5.44 wt% ($>C_{Cr}$) PBZT/NaAMPS	0.76	70/30	80/20
5.60 wt% ($<C_{Cr}$) PBZT/NaAMPS	0.27	30/70	39/61
9.98 wt% ($\leq C_{Cr}$) PBZT/NaAMPS	0.23	30/70	32/68

b_1: Absorptivity of NaAMPS polymer componenet.
C_1: Concentration of NaAMPS polymer componenet.
b_2: Absorptivity of PBZT componenet.
C_2: Concentration of PBZT componenet.

Table 1. All the composition ratio of PBZT/NaAMPS polymer is expressed as wt%. The PBZT/NaAMPS polymer coagulated compositions from solutions just below the critical concentration, such as 5.5% 50/50, 4.0% 70/30, and 9.8% 30/70 PBZT/NaAMPS polymer blends, are the same as the initial composition. This could be due to the molecular entanglement between PBZT and NaAMPS polymer or the ionic intermolecular interaction between two components. The isotropic solution morphology just below the critical concentration is directly transformed to the solid state during through the molecular interaction. However, when the concentration is far below or above the critical concentration, the coagulated compositions show different composition from the initial composition. This is due to either the heterogeneity of solution morphology which has the PBZT molecular domains in the NaAMPS polymer components or the free NaAMPS polymer which is soluble in the water.

When the PBZT and NaAMPS polymer are dissolved in MSA solvent, the ionic interaction is formed between the protonated PBZT molecules and the anionic sulfonic groups from both MSA and NaAMPS polymer. If the interaction is exclusively between the PBZT and the NaAMPS polymer, the stochiometric molar ratio of ionic species of PBZT and NaAMPS polymer should be 33/67 PBZT/NaAMPS polymer mol%. During the coagulation, the ionic network structure is preserved in the solid state and excess amount of NaAMPS polymer without molecular interactions should be dissolved out. The coagulation composition data needs further verification, but it is clear that the rod molecule is affecting the solubility of NaAMPS polymer and the critical concentration plays an important role during the coagulation process.

The effect of coagulation time of PBZT/NaAMPS polymer film was studied by immersing the coagulated films in the distilled water for 168 hours. The coagulated composition of PBZT and NaAMPS polymer component was calculated from FTIR analysis and was compared with the results of 24 hours coagulation. There is no difference of PBZT/NaAMPS polymer composition ratio between 24 hours and 168 hours coagulation. This suggests that within the first 24 hours, most coagulation occurs and the

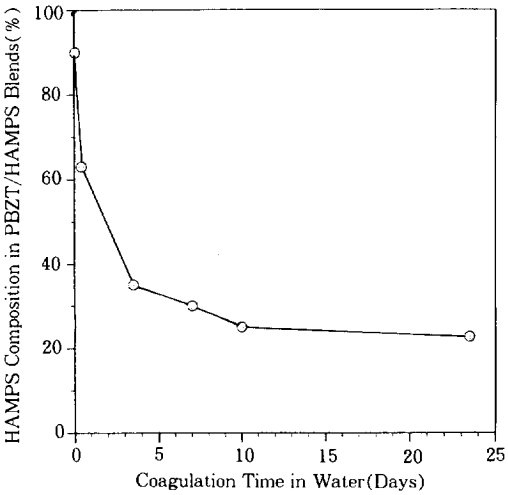

Figure 7. Coagulated composition change of PBZT/HAMPS-monomer blends with time.

excess NaAMPS polymer component without any intermolecular interaction is dissolved out. Longer coagulation time does not have any effect on the composition ratio of PBZT and NaAMPS polymer in the coagulated blends.

The coagulation behavior of PBZT/HAMPS-monomer/MSA system was also analyzed for 10/90, 30/70, 50/50, 70/30 PBZT/HAMPS-monomer blends. By studying the coagulation behavior containing HAMPS-monomer, instead high molecular weight NaAMPS polymer, the entanglement effect from NaAMPS polymer can be excluded during the coagulation process. It is interesting to notice that the coagulated HAMPS-monomer composition for 10/90 PBZT/HAMPS-monomer soultion decreased drastically as the coagulation time increases. As seen in Fig. 7, more than 90% of HAMPS-monomer is dissolved out at the initial stage of coagulation and after 24 hours and up to 12 days coagulation, almost same coagulated composition of 79/21 PBZT/HAMPS-monomer is sustained. This result suggests that for PBZT/HAMPS-monomer/MSA system coagulation, the ionic interaction might not be sufficient enough to hold the

Table 2. Coagulated Composition Change of PBZT/HAMPS-monomer Blends with Time

sample	1 hr	18 hrs	12 days
4.59% 70/30 PBZT/HAMPS-m	85/15	92/8	93/7
6.14% 70/30 PBZT/HAMPS-m	89/11	90/10	91/9
11.57% 70/30 PBZT/HAMPS-m	91/9	89/11	90/10

HAMPS-monomer with PBZT molecules. However, certain amount of PBZT/HAMPS-monomer remains in the coagulated structure due to the relatively weak ionic association between PBZT and HAMPS-monomer, when it is processed from just below the critical concentration. Similar results can be found for 30/70, 50/50, 70/30 PBZT/HAMPS-monomer coaulated blends and is shown in Table 2. Less than 9% of HAMPS-monomer still remains in the coagulated blends, after 6 days coagulation in the water.

WAXD analysis was made for the coagulated blends of PBZT and NaAMPS polymer at room temperature. Since these samples were prepared through the hand sheared quenching process, the small orientation effect of PBZT chain crystalline structure along the shear direction could be observed by the 4.0 Å d-spacing of moderate arc formation. Most diffraction patterns of the coaugulated blends exhibit the certain extent of micro-phase separation during the coagulation process as evidenced by strong reflection pattern corresponding to 3.5 Å and 6.1 Å d-spacing. Depending upon the concentration of polymers and composition ratio of two components, the coagulated microstructure should be different. Usually, the PBZT/NaAMPS polymer blends coagulated from solutions just below the critical concentration shows less phass separated and less disordered X-ray scattering pattern, compared with those prepared above the critical concentration. However, it is not clear from WAXD results whether the actual molecular level composite without appreciable phase separation was obtained or not.

PBZT/PPTA-PS/MSA System. The ternary phase diagram of PBZT/PPTA-PS/MSA system was constructed by varying polymer concentration and composition. When PBZT and PPTA-PS polymer are codissolved in MSA, the ionic association between protonated PBZT and sulfonate group in PPTA-PS polymer is formed and this intermolecular interaction should affect the critical behavior of ternary system, just like PBZT/NaAMPS polymer/MSA system.

In Fig. 8, the critical concentration of this ternary system occurs at higher concentration, compared with those of PBZT/nylon/MSA. The critical concentrations for this system are 3.6%, 5.3%, 6.9%, 8.6%, 10.9%, 13.6% with increasing sulfonated Kevlar composition. When the reduced PBZT concentration was calculated as shown in Fig. 9, it exhibits the constant value up to 50/50 PBZT/NaAMPS polymer composition and starts showing deviation from 50% sulfonated composition PBZT/PPTA-PS polymer blends. According to Flory's theory of ternary system, the experimental critical concentration of this system was analyzed. By varying the X_3 value from 300 to 5, the theoretical critical concentration was calculated with given value of X_2, 256, in order to match the experimental data. It turns out that X_3 value of this system corresponds to less than 5. This suggests that the ionic interaction of sulfonated Kevlar and PBZT may not be perfect, not like the PBZT/NaAMPS polymer/MSA system. However, it is evident that the ionic interaction beween PBZT and sulfonated Kevlar has a significant effect on the critical behavior of ternary system and the effect from the contour length of flexible molecules was not observed. Depending upon the extent of ionic interaction between rod and coil, the biphasic region occurs at different level, as compared with PBZT/nylon/MSA and PBZT/NaAMPS polymer/MSA system.

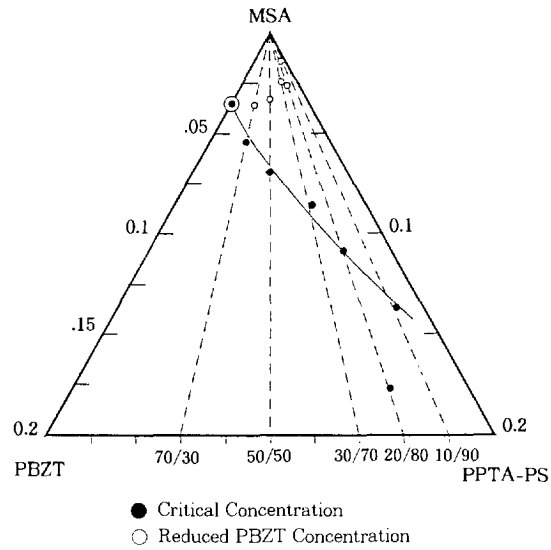

Figure 8. Critical phase diagram of PBZT/PPTA-PS/MSA system.

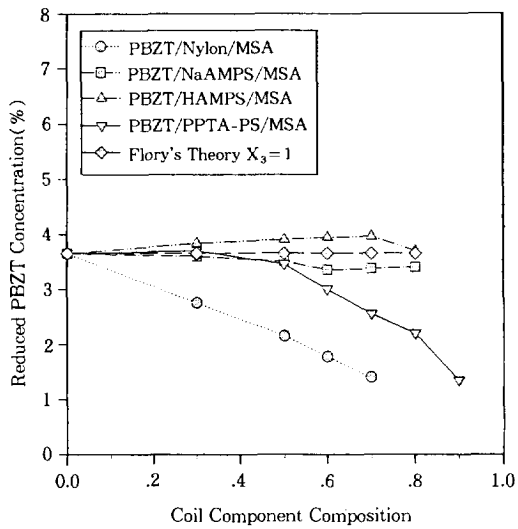

Figure 9. Reduced PBZT concentration of rod/coil/solvent ternary system with varying composition.

The coagulated composition of PBZT/PPTA-PS was analyzed using FTIR analysis, after drying the film under air. When 50/50 PBZT/PPTA-PS solution of 6.8% was coagulated in the water for 24 hours, the coagulated composi-

tion shows 52/48 PBZT/PPTA-PS, which is almost same as the initial composition. The other coagulated compositions of 30/70 and 70/30 PBZT/PPTA-PS blends do not indicate any composition change, when compared with initial solution compositions. Therefore, if the initial solution composition is just below the critical composition, it seems that the coagulated composition is directly preserved in the solid state through the molecular entanglement or ionic interaction between rod and coil.

CONCLUSION

The phase diagrams of PBZT/nylon/MSA and PBZT/nylon/MSA-CSA were compared and interpreted using Flory's theory. The PBZT/nylon/MSA-CSA system showed phase behavior that agrees with Flory's theory, while PBZT/nylon/MSA system does not.This is due to the aggregation of PBZT molecules in as-is MSA solvents, resulting in the decreased aspect ratio from 256 to 220. The effect from reduced aspect ratio of rigid-rod molecules induced the higher critical concentration, which shows the deviation from Flory's theory.

The effect from strong ionic interaction between rod and coil molecules can be clearly observed from the ternary phase diagrams of PBZT/NaAMPS polymer/MSA, PBZT/HAMPS-monomer/MSA, and PBZT/PPTA-PS/MSA system, as compared with PBZT/nylon/MSA. The ternary phase diagram results showed that the biphasic behavior with specific interaction occurs at much higher concentration region and the reduced concentration of PBZT appears to be constant. Also it is different from that predicted by Flory's theory. This means that the PBZT is interacting with NaAMPS polymer or PPTA-PS as much the same way as the solvent molecule MSA. For PBZT/NaAMPS polymer/MSA and PBZT/HAMPS-monomer/MSA systems, it corresponds to X_3 equal to 1. This interpretation is reasonable in considering that both MSA and NaAMPS polymer have sulfonated groups in their structures and can connect the ionic association with the protonated PBZT molecules.

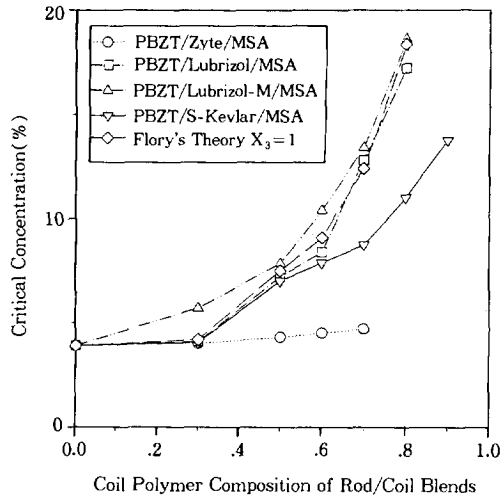

Figure 10. Experimental critical concentration of rod/coil/solvent ternary system with varying composition.

The effect of ionic intermolecular interactions on the critical concentrations can be easily observed by plotting the critical concentrations as a function of coil polymer composition. As shown in Fig. 10, the Flory's theoretical prediction with X_3 equal to 1 exactly follows the experimental data of PBZT/NaAMPS polymer/MSA and PBZT/HAMPS-monomer/MSA system. When the ionic interaction is not perfect like PBZT/PPTA-PS/MSA system, the critical concentration occurs at a little bit lower value, compared with PBZT/NaAMPS polymer/MSA system. For PBZT/nylon/MSA system, the critical concentration is much lower than other systems discussed above. Therefore, the extent of intermolecular interaction between rod and coil plays important role to determine the critical concentration of ternary system.

The composition of the coagulated system appeared to be determined not only by the initial rod/coil composition, but also by the solution concentration as well. From the coagulation results, it can be said that the critical concentration should play a very important role during the coagulation process for PBZT/NaAMPS polymer/MSA and PBZT/PPTA-PS/MSA system. The coagulated composition from just below the critical concentration is almost same as the initial composition through the ionic interaction as well as the entanglement effect. When the solution concentration is either much higher or lower than the critical concentration, the coagulated composition shows different value due to the heterogeneity of solution morphology or the water solubility of free NaAMPS polymer or PPTA-PS molecules. Even though the solution concentration is just below the critical concentration for PBZT/MAMPSPBZT-monomer/MSA system, the coagulation composition is not the same as the initial composition. It is because the entanglement effect from large molecules do not exist and the ionic association between rod and coil might not be sufficient enough to hold the flexible molecules together during the coagulation process in the water.

It is not clear at this point whether the ionic interactions between the two polymers are responsible for the co-coagulation, or they co-coagulate because of chain entanglement between the rod and the coil. It seems that the combined force of entanglement effect and ionic interaction contributes the preserved coagulation composition of the blends, when the solution is processed just below the critical concentration.

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