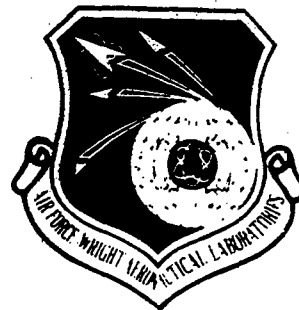


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CRITICAL PROCESSING CONDITIONS OF A
SPECIFIC TERNARY SYSTEM-MOLECULAR COMPOSITE

T. Helminiak
M. Wellman
W. F. Hwang
D. Wiff
V. Rodgers
C. Benner

Polymer Branch
Nonmetallic Materials Division

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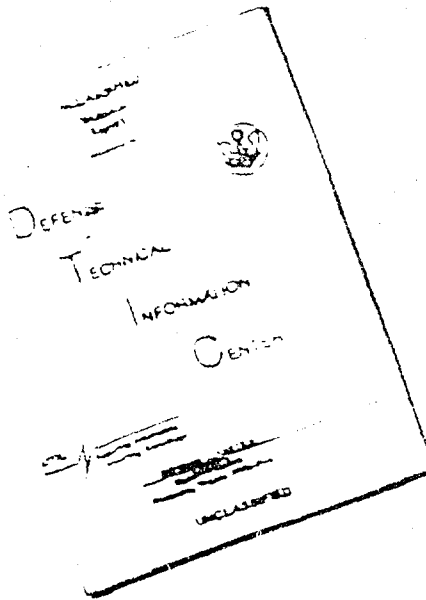
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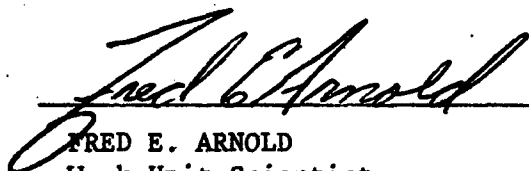
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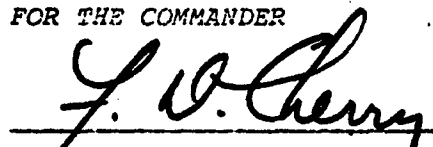
This report has been reviewed by the Office of Public Affairs (ASD/PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.


FRED E. ARNOLD
Work Unit Scientist


R. L. VAN DEUSEN, CHIEF
Polymer Branch
Nonmetallic Materials Division

FOR THE COMMANDER


F. D. CHERRY, Acting Chief
Nonmetallic Materials Division

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The phase relationships and thus the critical processing conditions, e.g., concentration and temp, (97 MSA/3 CSA), a rigid rod-like polymer (poly-para-phenylenebenzothiazole, PBT), and a flexible chain polymer (poly-2,5(6) benzimidazole, AB-PBI) was studied by means of cross-polarized light microscopy and small-angle light scattering (SALS) technique. Critical concentration points were observed and determined for all four ABPBI/PBT blends studies. When the polymer concentration was higher than the critical concentration, the ternary solution segregated into coexisting anisotropic and isotropic phases. The		

anistropic phase, containing practically only rigid rod-like PBT polymers, showed distinct nematic features both in the solution and in processed film, while the isotropic phase retained all the ABPBI molecules. Excellent agreement between the experimental and the theoretical binodial curve for the isotropic phase in the phase diagram lend strong support to Flory's recent theory concerning the behavior of mixtures of rigid rod-like ploymers with flexible coil polymers. The nematic isotropic transition temperature, IN-I, was also determined for various ABPBI/PBT blends at various concentrations. This study provides the insight of the important parameters such as concentration, temperature, composition, and rod-like polymer orientation of the ternary solution which are necessary for processing of PBPBI/PBT molecular composite films.

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2303, "Research to Define the Structure Property Relationships," Task No. 2303Q3 Work Unit Directive 2303Q307, "Structural Resins." It was administered under the direction of the Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. F. E. Arnold as the AFWAL/ML Work Unit Scientist. Co-authors were Dr. T. Helminiak, Capt. M. Wellman, Materials Laboratory (AFWAL/MLBP); and Dr. Wen-Fang Hwang, Dr. D. Wiff, Mr. Vincent Rodgers, and Mr. C. Benner, University of Dayton Research Institute.

This report covers research conducted from January 1980 to September 1980.

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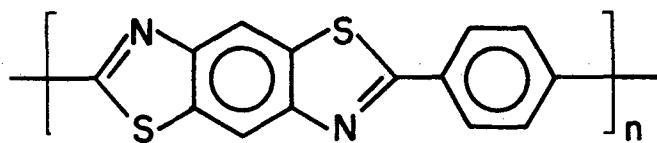
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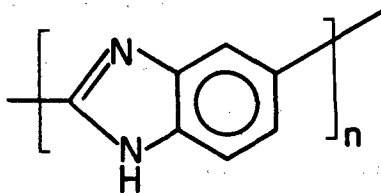
I. INTRODUCTION

The synthesis of rod-like aromatic heterocyclic polymers has created the opportunity to develop a new class of polymeric structural materials. Within this context a concerted effort is underway to investigate the concept of using a rod-like aromatic heterocyclic polymer blended with a coil-like aromatic heterocyclic polymer to form a molecular composite. These polymers are the subject of an extensive research and development program to explore their physical properties and mechanical behavior.^[3] The intent of this present program is to reinforce the coil-like or amorphous polymer with the rod-like polymer, thus forming a composite on the molecular level analogous to chopped fiber reinforced composites and possessing similar properties.^[1]

Various combinations of extended chain, rod-like polymers with chemically similar amorphous coil-like polymers have been investigated.^[2] A pair of polymers, rod-like poly-para-phenylene benzothiazole (PBT) - with its improved thermo-oxidative stability and solubility - and amorphous poly-2,5(6) benzimidazole (ABPBI) - chosen so as to be compatible with PBT - has been shown^[2,3] to be the most promising blend among those polymer pairs being studied.



PBT



AB-PBI

Previous attempts^[4,5] were made to obtain composite films via solutions which were ~2% by volume of various ABPBI/PBT compositions in methane sulfonic acid. Various processing techniques (e.g., vacuum casting, precipitation, and shear quenching) and various post-film treatments (e.g., mechanical stretching, "solvent stretching",^[2] and annealing) were explored. These variations showed that the mechanical properties as well as the morphology of the individual films could be significantly altered and that a pseudo-molecular composite had been prepared. This work identified an aggregate formation in the films which exhibited high degrees of composite type reinforcement, but unfortunately offered limited processing potential. The insight gained from this work led to the study of the morphological nature of the polymer solutions, both before and during processing. Without an understanding of the solution morphology it was difficult to predict or manipulate the morphology and properties of the composite films.

Consequently, the present investigation was initiated to determine morphologically the critical processing conditions of a ternary system as described above. The solvent used throughout this investigation was a mixed solvent containing 97% (by volume) methane sulfonic acid (MSA) and 3% chlorosulfonic acid (CSA).

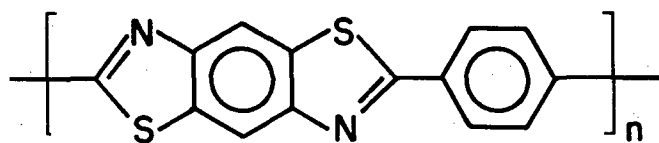
Two critical processing conditions were considered in the present case; i.e., concentration and temperature. Later, critical parameters such as molecular weight and molecular weight distributions of the rod-like polymer will be considered.

Thermodynamic considerations, especially phase relationships, of such a ternary system is of basic significance because any end-products (films, fibers, etc.) made from the ternary system are intrinsically influenced by the morphology present in the processing solutions. A statistical thermodynamic theory concerning the phase relationships of such a ternary system was recently put forward by Flory.^[6] This theory served as a guide

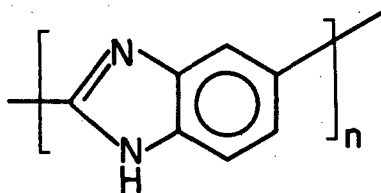
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for the present research and will be discussed first. Secondly, schemes for studying the morphology of such solutions will be presented. Finally, experimental results of the present ternary system and recommendations for further processing-morphology elucidation will be presented.

II. BEHAVIOR OF SOLUTIONS CONTAINING RIGID ROD-LIKE POLYMERS

A. Binary Systems

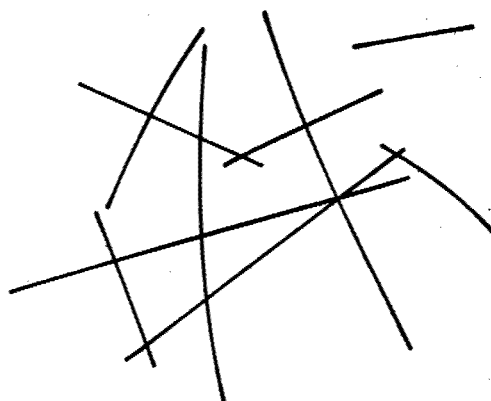
When linear flexible-chain polymers are dissolved in a solvent, they usually assume the configuration of a random coil, which may be represented schematically by Figure 1(a). If the chains are made of stiff units and are linked so as to extend the chain in one direction, then they must be rod-like and may be represented in Figure 1(b). Association with solvent may contribute to the rigidity and to the volume occupied by each polymer molecule.

As the concentration of the rod-like polymer solute is increased and the saturation point for the random array of rods is reached, the solution may simply become a saturated solution. With excess polymer or, if the condition of the solvent-polymer interactions are correct, additional polymer may be dissolved by forming regions in which the polymer chains and associated solvent approach a parallel arrangement as illustrated in Figure 1(c). These ordered regions are mesomorphic or liquid crystalline in nature and form an optically anisotropic phase incompatible with the isotropic phase.

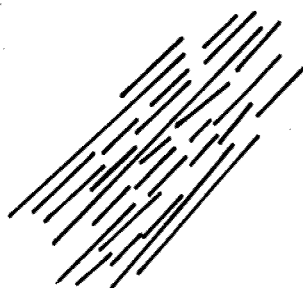
In his classic paper^[7] published in 1956, Flory theoretically examined the behavior of rigid rod-like polymers in solution and the conditions under which they would yield "tactodial" anisotropic phases. One of his phase diagrams is shown in Figure 2. The phase diagram relates temperature and the solvent-polymer interaction parameter, χ , to the volume fraction, v_2 , for polymer rods with an axial ratio of 100. The major predictions of the Flory's theory are:



(a) RANDOM COIL



(b) RANDOM RODS



(c) RODS IN LIQUID CRYSTALLINE NEMATIC STATE

Figure 1. Schematic Representation of Polymer States in Solution.

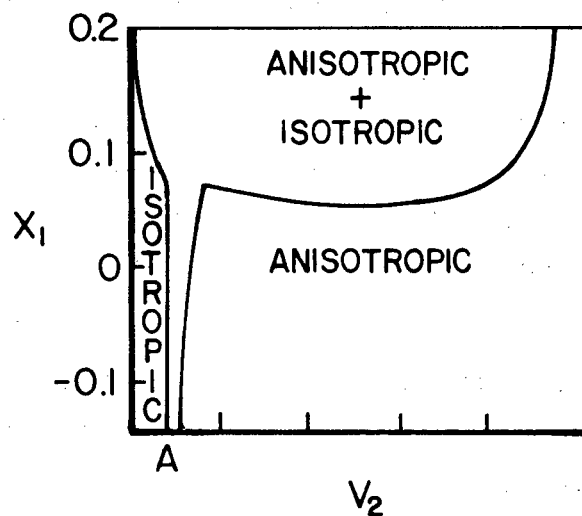


Figure 2. Diagram Relating the Solvent-Polymer Interaction Parameter (X_1) and the Volume Fraction (v_2) of Rod-Like Polymer Molecules With the Formation of a "Tactodial" Solution Phase (Ref. 7).

(i) At a constant low temperature (or constant χ_1 ; $\chi_1 > 0$), as the concentration of the rod-like polymers increases, the originally isotropic solution separates into an isotropic and anisotropic liquid crystalline phase as a consequence of the asymmetry of the particles. This is assumed to be an athermal process, i.e., without any attractive interaction energy being involved. This heterogeneous region exists for a very wide range of concentrations.

(ii) At a constant high temperature, as the concentration of rod-like polymers increases, the originally isotropic solution will pass through a very narrow heterogeneous (or biphasic) region, and finally the solution will become totally anisotropic.

(iii) If the concentration is greater than C_R as indicated in Figure 3, an isotropic solution cannot be obtained at any temperature.

The requirements for the formation of anisotropic liquid crystalline solutions in polymers with rigid chain backbone are^[8]

- (a) The polymer must have a rod-like conformation;
- (b) The molecular weight must exceed a minimum value, which may be expressed in terms of the aspect ratio;
- (c) A solvent must exist that is capable of dissolving the polymers beyond a critical concentration value.

In general, such rod-like polymers form liquid crystalline (LC) solutions as concentration increases due to their inherent rigid chain conformation. Such LC solutions are called lyotropic liquid crystals. Lyotropic systems also show a thermotropic behavior: on heating they become isotropic.

The formation of the liquid crystalline solution phase of rigid rod-like polymers can be recognized by the following characteristics.

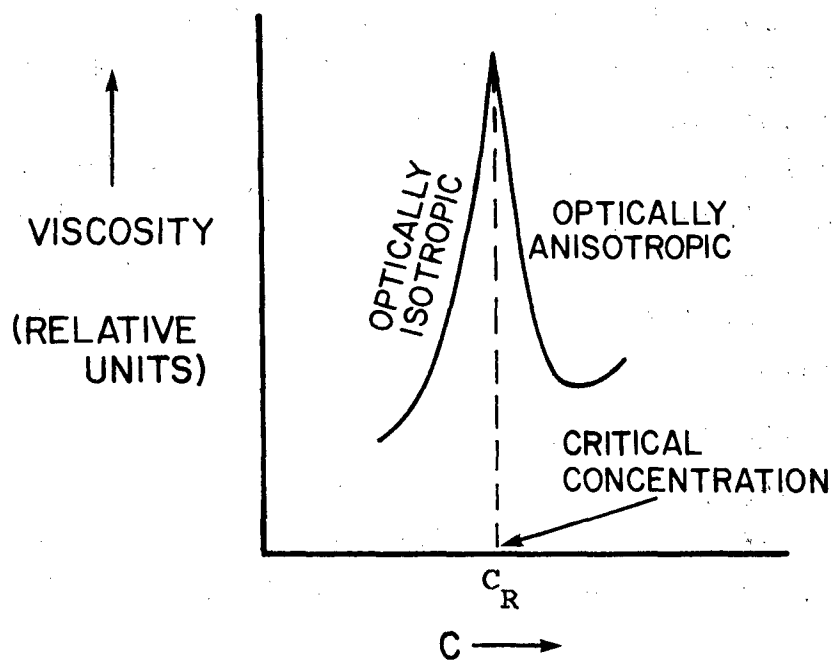


Figure 3. Viscosity Behavior of Rod-Like Polymers as a Function of Concentration.

- (i) Visual observations of turbidity and opalescence upon stirring;
- (ii) Depolarization of plane polarized light;
- (iii) Solution viscosity (see Figure 3) showing a critical concentration point; and
- (iv) Orientation in a magnetic field.

As shown in Figure 3, as the concentration of the rod-like polymer is increased the bulk viscosity also increases. The slope of the curve, however, abruptly changes when a critical concentration point is reached. The viscosity now begins to drop and the solution consists of two phases. As more polymer is added, the viscosity drops further and the amount of anisotropic phase increases. This continues until a saturation point is reached at which solid polymers will be excluded from the solution and the viscosity will rise again.

B. Ternary Systems

The above described characteristics (Figures 2 and 3) of the liquid crystalline solution of a binary system may also be applied to a ternary system containing at least one rod-like component.

High molecular weight, flexible polymers are in general incompatible with one another, and the solubility of these polymers in a solvent is rather limited. When two such polymers can be dissolved in a common solvent and attain a high or moderate concentration, the resultant solution may separate into two coexisting isotropic phases, each containing a high concentration of one polymer and a low concentration of the other polymer.

The behavior of the solutions containing rigid rod-like polymer molecules is drastically different. A theory recently put forward by Flory^[9-12] states that if a stable concentrated solution of two types of rod-like polymers can be prepared in a common solvent, then a single anisotropic phase, i.e., a lyotropic, nematic liquid crystalline phase may be obtained. When such a single phase solution is diluted, an isotropic phase will appear

and will be in thermodynamic equilibrium with the anisotropic phase. The concentration range in which the two phases co-exist is much wider than that of the binary system as described above. Upon further dilution, the anisotropic phase will vanish and only a single isotropic phase remains. The concentration of rod-like polymer in, and the molecular weight distribution between, the two co-existing phases were recently investigated by Kwolek, et al., [13] and by Aharoni and Walsh. [14,15] Their results were shown to be in general agreement with the theory. [16,17]

When one of the rod-like polymers is replaced by a flexible chain polymer, the solution behavior of such a ternary system is also different from the systems described so far.

In a theory recently developed by Flory, [6] the statistical thermodynamics of a ternary system consisting of an isodiametrical solvent (component number 1), a rod-like polymer solute (component number 2), and a random-coiled polymer (component number 3) is considered. The diameters of components 2 and 3 are assumed to be equal to that of the solvent. The axis ratio of component 2 is x_2 and the contour length of component 3 is x_3 ; i.e., the molecular volumes of the three components are in the ratio of $1:x_2:x_3$. The axis ratio x_2 may also be denoted as the aspect ratio of the rod-like molecule. The theoretical treatment is restricted to "athermal" mixtures; i.e., to systems in which the exchange of free energy is null.

C. Theory

The solutes of the ternary systems treated in Flory's paper represent extremes. The one consists of rigid particles of well-defined geometrical form and the other of molecules possessing a substantial degree of flexibility, which therefore may assume highly irregular spatial configurations. The profound differences in their mixing behavior are reflected in their limited compatibility with one another. Partitioning of the solute molecules between nematic and isotropic phases in

equilibrium, as considered here, is reminiscent of the "fractionation" of the pair rod-like solutes differing in axis ratio considered in Reference 10. Here, however, it is even more marked than for systems encountered in Reference 10.

When the total concentration of the blended polymers is increased beyond a critical concentration point (C_R), liquid crystalline domains, or phases will form, in which the rod-like solute molecules are preferentially aligned with the cylindrical axis of the domain. The degree of orientation of these molecules may be expressed in terms of a "disorientation factor" y , which is defined by a model as illustrated in Figure 4.

The mixing partition function (i.e., number of ways of inserting n_2 rod-like molecules and n_3 coil-like solute molecules into n_0 lattice sites) for the anisotropic phase in equilibrium with the isotropic phase is derived to be:

$$Z_m = \frac{[n_0 - n_2(x_2 - y)]! y^{2n_2}}{(n_0 - x_2 n_2)! n_2! n_0^{n_2(y-1)}} \quad (1)$$

$$Z_m = \frac{(n_0 - x_2 n_2)! Z_3^{n_3}}{(n_0 - x_2 n_2 - x_3 n_3)! n_3! n_0^{n_3(x_3 - 1)}} \quad (2)$$

$$Z_m = \frac{[n_0 - n_2(x_2 - y)]! y^{2n_2} Z_3^{n_3}}{n_1! n_2! n_3! n_0^{[n_2(y-1) + n_3(x_3 - 1)]}} \quad (2)$$

where

$$n_0 = n_1 + n_2 x_2 + n_3 x_3 \quad (3)$$

and Z_3 is the internal configuration partition function for the random coil. The first factor in Eq. 1 expresses the expected number of configurations the rod-like molecules may assume in the empty lattice. The second term in Eq. 1 takes into account the configurations accessible to the n_3 random coils subsequently added to the lattice. Introduction of the Stirling's approximations for the factorials in Eqs. 1 and 2 leads to

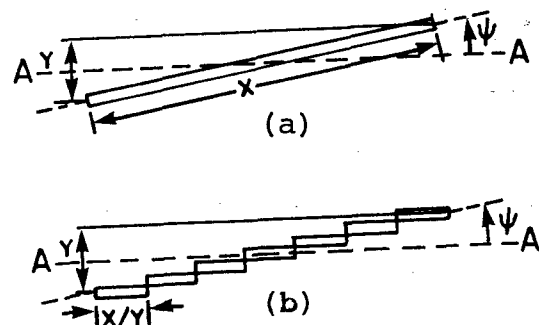


Figure 4. (a) A Rod-like Particle of Axis Ratio x Oriented at Angle ψ to the Domain Axis AA . (b) The Model Comprising $y = x \sin \psi$ Submolecules, Each Submolecule Being Parallel to the Domain Axis AA .

$$\begin{aligned}
-\ln Z_m = & n_1 \ln v_1' + n_2 \ln v_2' + n_3 \ln v_3' - n_0 [1 - v_2'(1 - y/x_2)] \\
& \times \ln [1 - v_2'(1 - y/x_2)] + n_2(y - 1) - n_2 \ln (x_2 y^2) + \quad (4) \\
& n_3(x_3 - 1) - n_3 \ln (x_3 Z_3)
\end{aligned}$$

where v_1' , v_2' , and v_3' are the volume fractions of the respective components.

Equating $2Z_m/2y$ to zero, one obtains

$$\exp(-2/y) = 1 - v_2'(1 - y/x_2) \quad (5)$$

Eq. 5 relates the disorientation factor to v_2' and x_2 in the anisotropic phase in which the system is most stable.

The chemical potentials that follow from Eq. 4 are given by

$$\begin{aligned}
(\mu_1 - \mu_1^\circ)/RT = & \ln v_1' + v_2'(y - 1)/x_2 + v_3'(1 - 1/x_3) - \\
& \ln[1 - v_2'(1 - y/x_2)] \quad (6)
\end{aligned}$$

$$\begin{aligned}
(\mu_2 - \mu_2^\circ)/RT = & \ln(v_2'/x_2) + v_2'(y - 1) + v_3'x_2(1 - 1/x_3) - \\
& y \ln[1 - v_2'(1 - y/x_2)] - 2 \ln y \quad (7)
\end{aligned}$$

$$\begin{aligned}
(\mu_3 - \mu_3^\circ)/RT = & \ln(v_3'/x_3) + v_2'(x_3/x_2)(y - 1) + v_3'(x_3 - 1) - \\
& x_3 \ln[1 - v_2'(1 - y/x_2)] - \ln Z_3 \quad (8)
\end{aligned}$$

where y is understood to assume its equilibrium value given by Eq. 5. Substitution from Eq. 5 in each of the above equations yields the chemical potentials of the three components in the anisotropic phase.

$$(\mu_1 - \mu_1^\circ)/RT = \ln v_1' + v_2'(y - 1)/x_2 + v_3'(1 - 1/x_3) + 2/y \quad (9)$$

$$\begin{aligned}
(\mu_2 - \mu_2^\circ)/RT = & \ln(v_2'/x_2) + v_2'(y - 1) + v_3'x_2(1 - 1/x_3) + \\
& 2(1 - \ln y) \quad (10)
\end{aligned}$$

While the chemical potentials for the isotropic phase has been derived in Ref. 7.

$$(\mu_1 - \mu_1^0)/RT = \ln v_1 + v_2(1 - 1/x_2) + v_3(1 - 1/x_3) \quad (12)$$

$$(\mu_2 - \mu_2^0)/RT = \ln(v_2/x_2) + v_2(x_2 - 1) + v_3x_2(1 - 1/x_3) - \ln x_2^2 \quad (13)$$

$$(\mu_3 - \mu_3^0)/RT = \ln(v_3/x_3) + v_2x_3(1 - 1/x_2) + v_3(x_3 - 1) - \ln x_3^2$$

At the equilibrium between the two phases, one obtains by equating the chemical potentials given by Eqs. 9, 10, and 11 in the anisotropic phase to the corresponding chemical potentials in the isotropic phase given by Eqs. 12, 13, and 14, respectively, the following relationships

$$\ln(v_1'/v_1) = A - B - 2/y \quad (15)$$

$$\ln(v_2'/v_2) = (A - B)x_2 - 2 \ln(x_2^\alpha/y) \quad (16)$$

where

$$A = v_2(1 - 1/x_2) + v_3(1 - 1/x_3) \quad (17)$$

and

$$B = v_2'(y - 1)/x_2 + v_3'(1 - 1/x_3) \quad (18)$$

Elimination of (A-B) by combination of Eq. 17 with 16 gives

$$\ln(v_2'/v_2) - (x_2/x_3)\ln(v_3'/v_3) - 2x_2/y - 2 \ln(x_2^\alpha/y) \quad (19)$$

For given x_2 , x_3 and v_2' , these equations may be solved for y , v_3' , v_2 and v_3 as follows. One first obtains y from Eq. 5 from x_2 and v_2' . Choice of trial values for v_3 and v_2 permits evaluation of A according to Eq. 18, and of v_3' by use of Eq. 19. Substitution of y , v_2' and v_3' in Eq. 19 gives B . Equation 16 may then be used to obtain a value for v_2 to replace the trial v_2 . The value of v_2 that is consistent with the chosen v_3 may then be determined by iteration. Substitution of $v_1' = 1 - v_2' - v_3'$ in Eq. 15 yields a value of v_1 which may then be chosen and the procedure repeated, and so forth until a satisfactory solution is obtained.

III. EXPERIMENTAL

A. Materials and Solution Preparation

The polymers used for the preparation of concentrated solutions were poly-2,5 (6) benimidazole (ABPBI---AF-R-56, outside cut B, $\rho = 1.4\text{--}1.6 \text{ g/cm}^3$, $[\eta]_{\text{imh}} = 11\text{--}17 \text{ dl/g}$, $M_w = 100,000\text{--}300,000 \text{ g/mole}$) and poly-para-phenylene benzobisthiazole (PBT-2122-57, $[\eta] = 18 \text{ dl/g}$, $\rho = 1.64 \text{ g/cm}^3$, $M_w = 30,000 \text{ g/mole}$). The former is assumed to have a random-coiled conformation, while the latter has been proven to be rigid rod-like.

The concentrated solutions were prepared by dissolving predetermined composition of ABPBI/PBT in a mixed solvent of 97% (by volume) methane sulvonic acid with 3% chlorosulfonic acid. All the polymers were used as received without further purification. The solvents were re-distilled at reduced pressures. The solutions were stirred at room temperature by using a magnetic stirrer for several days until a "stable" solution was obtained. A "stable" solution is defined as a solution in which its morphology, when observed under an optical microscope with crossed polars, does not change. The concentrations of the solutions were expressed in the unit of weight percentages.

B. Determination of the Critical Concentration

The critical concentration is the minimum concentration of polymers in a solvent needed to yield an anisotropic phase. This concentration was determined for a given polymers-solvent combination by slowly "titrating" a liquid crystalline solution of known concentration with the given solvent while continuously stirring the concentrated solution on a magnetic stirrer. The total weight of the solution was measured, and the concentration calculated, until the point was reached at which light transmission under crossed polars or stir-opalescence disappeared. The weight fraction of polymers at the critical point was then calculated from the weight of solvent added. For each concentration, the stirring at room temperature usually lasted from three

days to more than a week, depending on the viscosity of the solution.

C. Determination of the Critical or Clearing Temperature

The critical or clearing temperature is the temperature at which the anisotropic phase in a solution of known concentration and known composition becomes isotropic. A drop of the dope solution pressed between a microscope slide and a thin square cover glass was heated on a hot stage at a heating rate of 2°C/min. The morphological changes of the solution as a function of temperature were observed with a polarizing light microscope under crossed polars. The critical temperature for each solution was determined to be that temperature at which the domain structures or features present in the liquid crystalline solution phase disappeared completely. At this temperature the viewed area of the microscope becomes as dark as that observed in an isotropic solution.

A Bausch & Lomb LI-2 polarizing light microscope was used throughout the experiments. The hot stage used was a Mettler FP 52 hot stage with -20°C to 300°C temperature range. The path length of the light through the solution was about 300µm as measured by a micrometer.

D. Small-Angle Light Scattering (SALS)

A Spectra-Physics 155 helium-neon gas laser with wavelength of 6328Å was used. Thin film specimen was prepared from the concentrated solution by smearing a drop of solution on a microscope slide and subsequently quenching it in distilled water. This quenched film was then placed between the crossed polarizer and analyzer of the SALS apparatus. The light scattering patterns were recorded on photographic films. The experimental arrangement is illustrated in Figure 5.

E. Small-Angle X-Ray Scattering (SAXS)

The small-angle x-ray scattering experiments were performed at the National Center for Small Angle Scattering

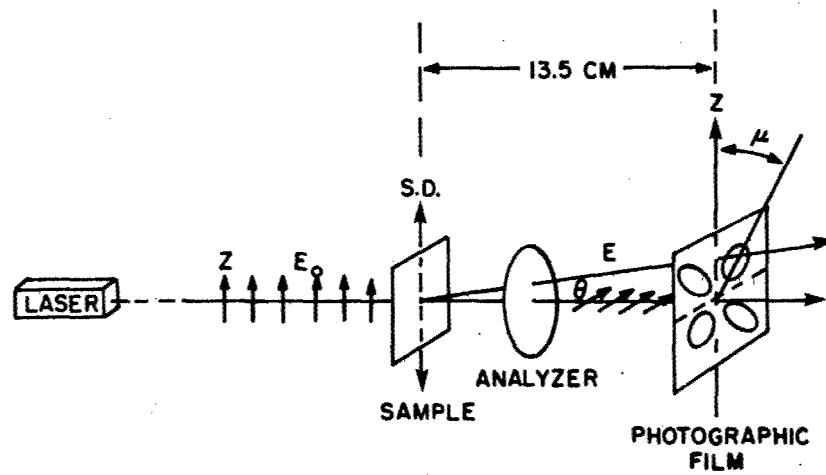


Figure 5. Experimental Set-Up for SALS Study.

Research (NCSASR), Oak Ridge National Laboratories (ORNL), Oak Ridge, Tennessee. A 5-m SAXS camera coupled with a two-dimensional position sensitive detector was used. The x-ray source was a CuK_α radiation with a wavelength of $1.5417\text{\AA}$, operated at 45 Kv, 50 mA. Glassy carbon was used as the standard for the determination of the transmission coefficients of the testing specimens. The samples examined were cast films, [18,19] heat treated cast films, [20,21] prepared from dilute solutions - and quenched films - prepared from anisotropic solutions of ABPBI/PBT blends. [21]

F. Numerical Analysis

A computer program was written by Mr. Vincent Rodgers, UDRI, for the numerical analysis of the phase relationships of a (solvent/rod-like polymer/random coiled polymer) ternary system. The computer program is listed in Appendix A. The program was used to calculate the values of v_1' , v_2' , v_3' , y from known values of x_2 , x_3 and trial values of v_2 and v_3 . These values were then used to compose the phase diagram.

Each phase diagram may be represented as an equilateral triangle phase diagram as illustrated in Figure 6. Each corner of the triangle represents one of the pure components, each edge of the triangle represents the mixtures of the two components shown on adjacent corners, and the interior of the triangle represents mixtures of all three components. As shown in Figure 6, any point along the binodal curve is defined by the values of v_2 , v_3 and v_2' as indicated in Figure 6. The dashed line represents the conjugated phases along which all the solutions of different composition will have the same value of v_2' .

IV. RESULTS AND DISCUSSION

A. Dilute Solutions

The dilute solutions (2% by volume of ABPBI/PBT blends) of various compositions were brown in color and transparent. When a drop of such solutions was observed under crossed polars, it appeared dark, i.e., no light was transmitted. The dilute

solutions were optically isotropic. In other words, the dimensions of the structural features (if present) in the solutions were much smaller than the wavelength of the visible light and they were randomly oriented.

Small angle light scattering studies also indicated that there were no superstructural units in the solution and in the film specimen prepared from vacuum casting.

To test if there were small structures (dimensions of the order of 100-1000Å) and if there existed long range orders between them, small-angle x-ray scattering techniques were used. The scattering patterns from the as-cast films of 80/20 and 70/30 ABPBI/PBT blends are in Figures 7 and 8, respectively. As can be seen, the scattering patterns from those systems are spherical in shape. This implies that the scattering particles (presumably PBT molecules) in the film specimen must be either isotropic or randomly oriented anisotropic regions.

For such systems, the Guinier law^[17] may be applied, under the further assumption that the scattering system is dilute, to determine the sizes of the structural units. The Guinier Law states that, for scattering at extremely small angles, $2\theta = 0^\circ - 0.5^\circ$, the scattering intensity as a function of the scattering angle, 2θ , can be expressed as

$$\log I(\epsilon) = \log N (\rho - \rho_0)^2 V^2 = \frac{4\pi}{3\lambda^2} (0.434 R_g^2 \epsilon^2) \quad (20)$$

where $\epsilon = 2\theta$, N is the number of the scattering particles, λ the wavelength of x-rays, $(\rho - \rho_0)$ the average electron density difference between the scattering particle and its surroundings, V the volume of the scattering particle, and R_g the radius of gyration of the scattering particle.

A plot of $\log I(\epsilon)$ vs ϵ^2 , i.e., the so-called Guinier plot should yield a straight line with the initial slope, α , and the mean radius of gyration of the scattering particles can be determined from

$$R_g = 0.416 \lambda \sqrt{|\alpha|}, \quad \lambda = 1.5417\text{\AA} \quad (21)$$

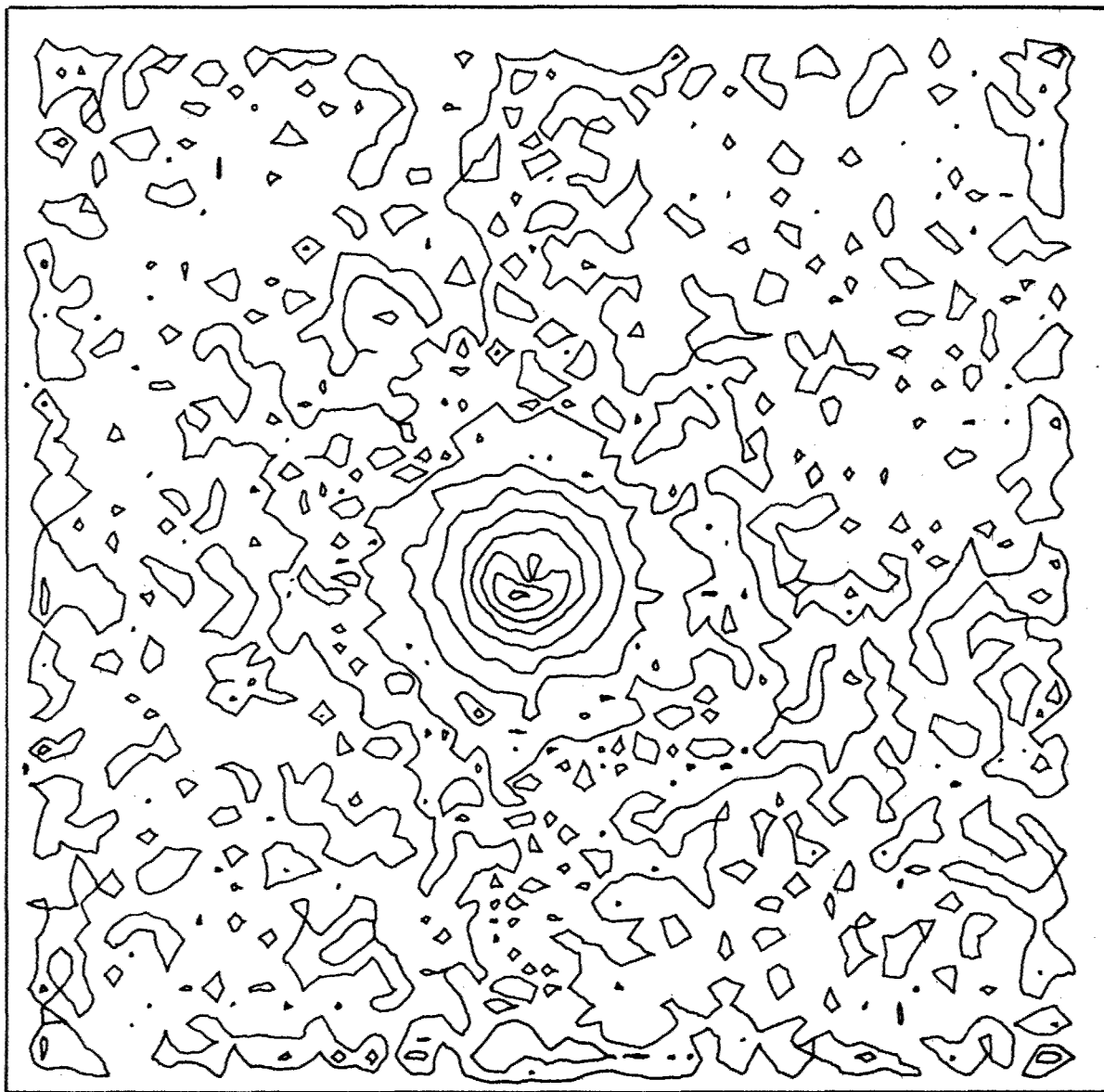


Figure 7. SAXS Pattern of 80/20 ABPBI/PBT Cast Film.

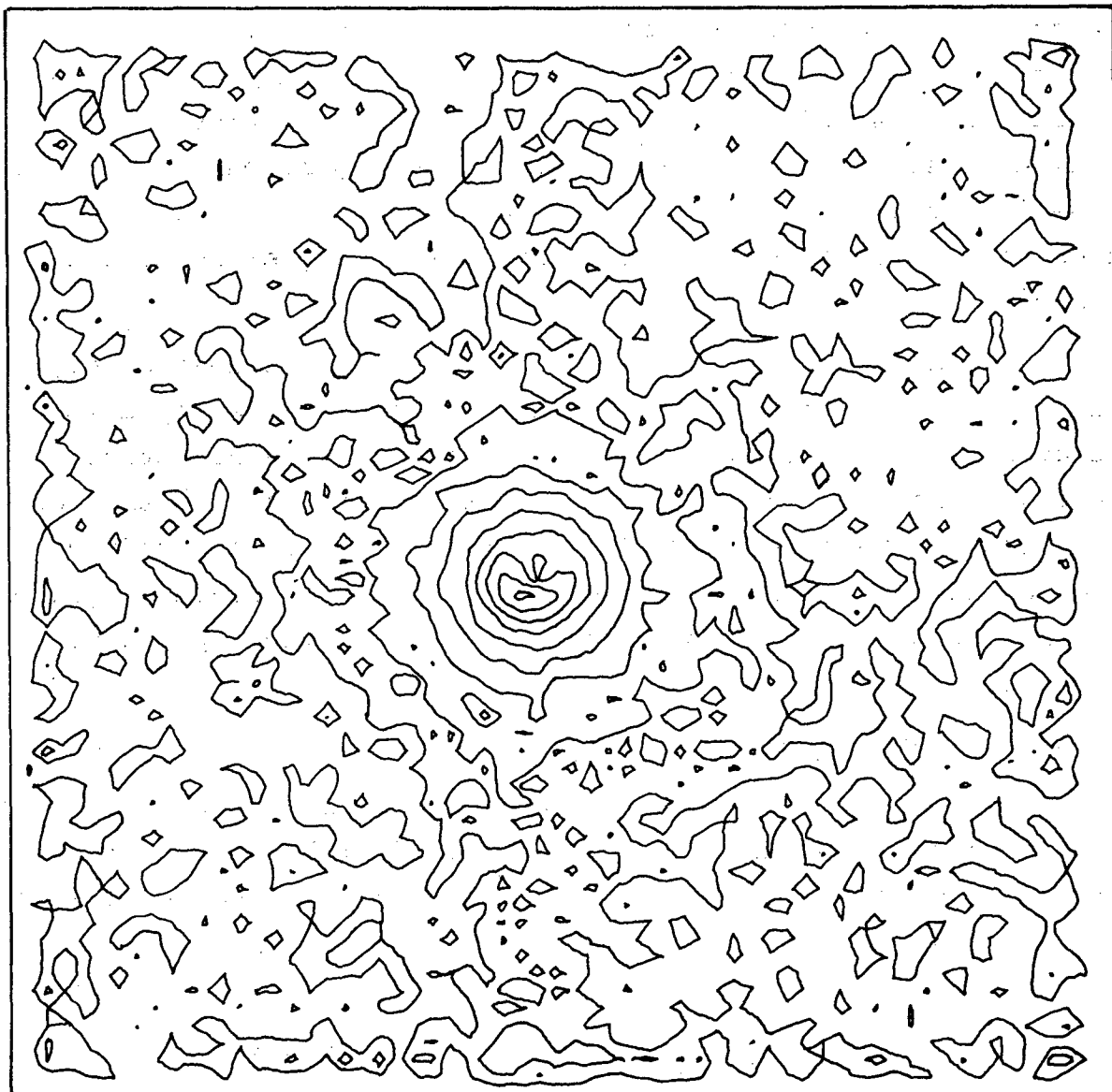


Figure 8. SAXS Pattern of 70/30 ABPBI/PBT Cast Film.

The Guinier plots of the 90/10, 80/20, 70/30 ABPBI/PBT as cast films are shown in Figure 9. The radius of gyration was calculated according to Equation 21 to be 117, 124, and 133A, respectively. However, as can be seen in Figures 7 and 8, the resolution of the scattering intensity at extremely small angles was not good - which may be due to the impurities present in the specimens - so that interpretations of the experimental data will not be feasible at this stage. Improvements in the resolution can be achieved, however, by increasing the sample-to-detector distance.

From this morphological evidence two conclusions may be drawn. Firstly the rod-like polymer was sufficiently dispersed so that no detectable coherent scattering could be detected. That is, no long range order was detected. Secondly, even though aggregates may be present in as-cast films, there is insufficient common orientation present between aggregates to provide improved mechanical properties and thus make casting a viable processing technique.

B. Moderately Concentrated Solutions

A series of 40/60 ABPBI/PBT blends of different concentrations were prepared and were examined with a polarizing microscope and by SALS techniques. Quenched film specimens were also examined. The experimental results were summarized in Table 1.

As shown in Table 1, when the concentration of the blend was equal to or higher than 3.4%, the solutions were opaque and exhibited stir-opalescence. When such solutions were observed with an optical microscope under crossed polars, colored (mostly red, yellow and green colors) streaked textured anisotropic regions were observed mixed with isotropic dark regions. Optical micrographs for such solutions are shown in Figures 10 and 11. Similar results were obtained for the film specimen, as shown in Figure 12, which shows the distinct nematic features.

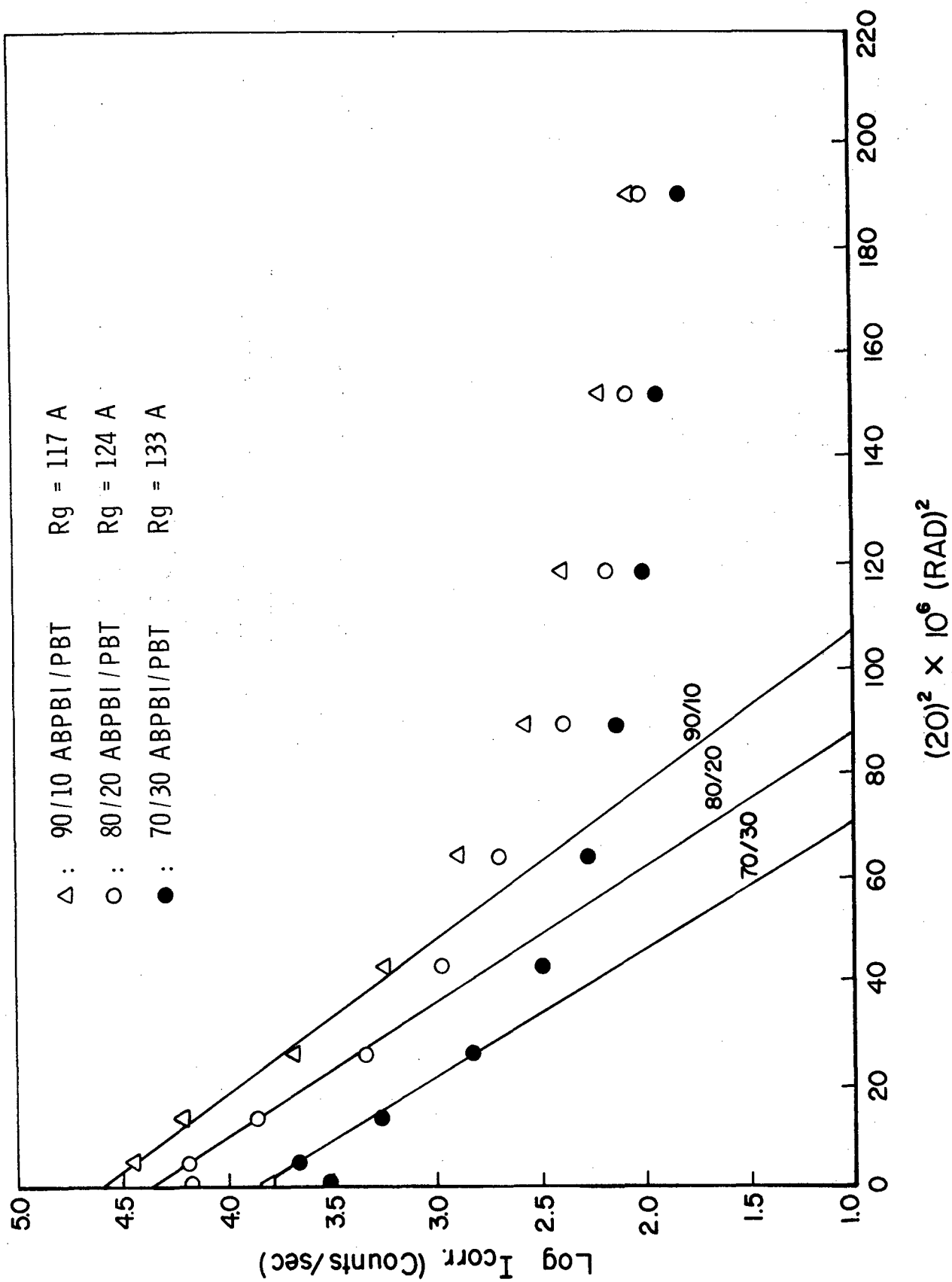


Figure 9. Guinier Plot of SAXS of ABPBI/PBT Polymer Blends.

TABLE 1
SALS AND OPTICAL MICROSCOPY OBSERVATIONS
OF 40/60 AB-PBI/PBT BLEND

Conc. wt %	Solution Appearance	Stirring (days)	OM		SALS (film)	Film Appearance
4.4	opaque, stir- opalescence	3	brilliant colored rod-like aggregates (Fig. 10)	brilliant colored rod-like aggregates (Fig. 12)	$\sim 45^\circ$ H _v pattern indicates rod- like aggregates, molecular axis // aggregate axis (Fig. 13)	shiny, whitish regions dispersed in isotropic transparent matrix
3.4	opaque, stir- opalescence	3	fine, greenish textured regions (Fig. 11)	yellow- greenish rod-like aggregates	same as above (Fig. 14)	same as above
2.7	translucent, no stir- opalescence	1		colored rod-like aggregates	same as above	same as above
2.7	translucent, no stir- opalescence	3	greenish colored, no texture observed	green colored, no texture observed	no H _v pattern observed	homogeneous, transparent
1.8	translucent, no stir- opalescence	3	dull green colored, no texture	very faint greenish colored, no texture, a lot of voids	same as above	same as above

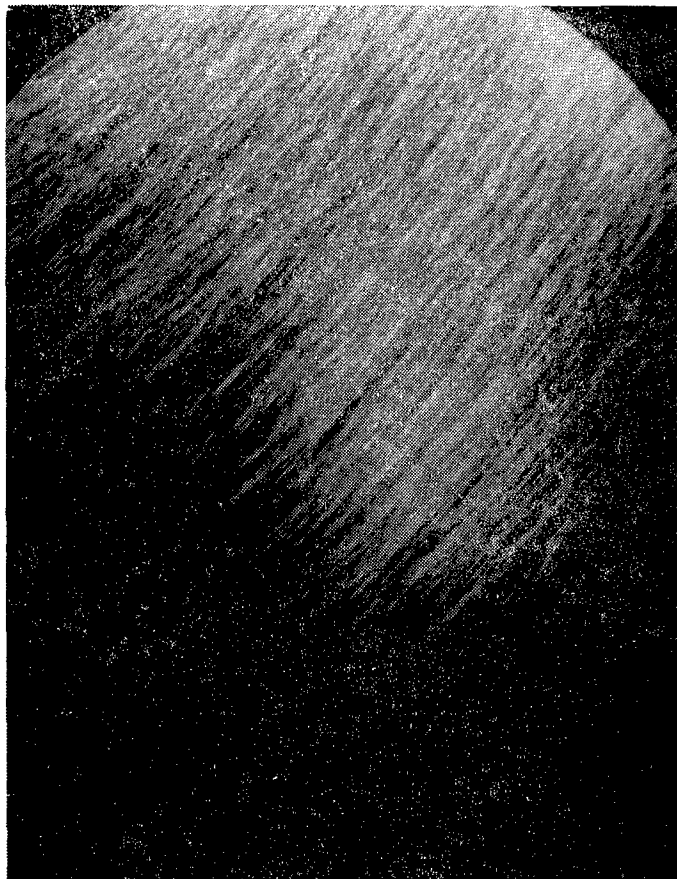


Figure 10. Optical Micrograph - 3.11%.

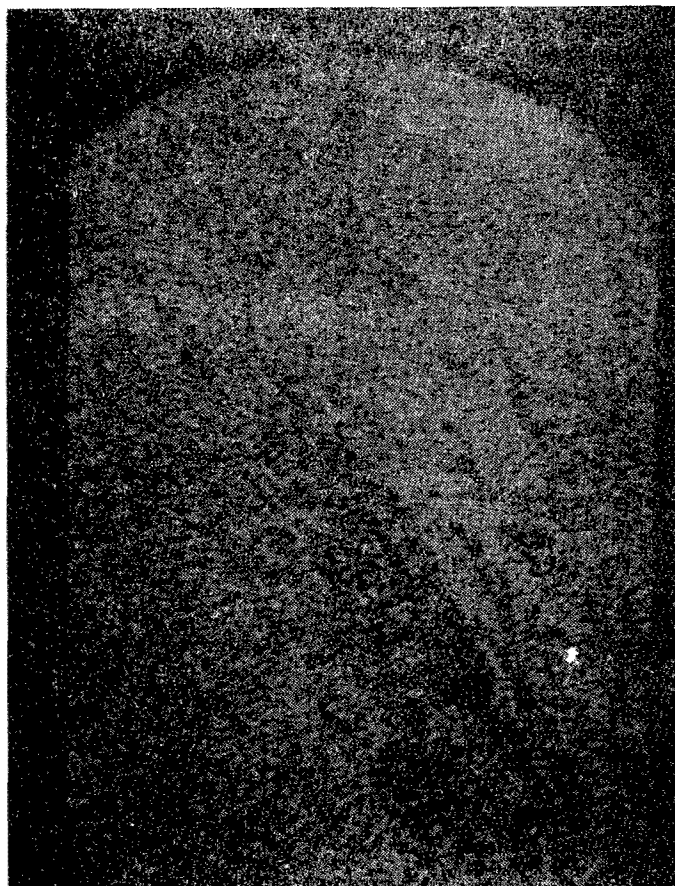


Figure 11. Optical Micrograph - 4.4%.

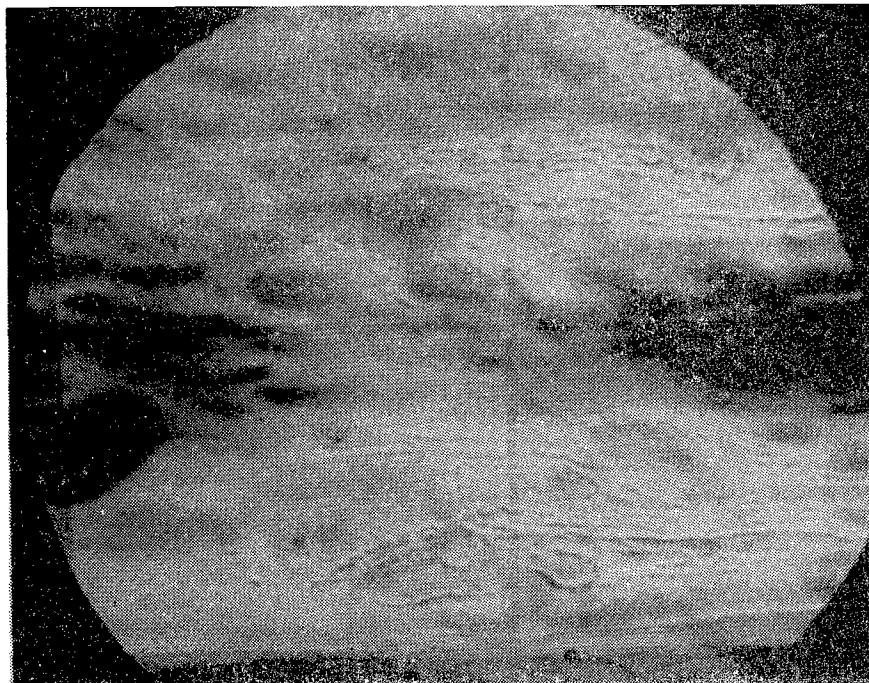


Figure 12. Optical Micrograph Showing Distinct Nematic Features.

Small-angle light scattering patterns of the quenched film specimens prepared from these moderately concentrated solutions are shown in Figures 13 and 14. A so-called $45^\circ H_V$ light scattering pattern (i.e., a "cross" pattern oriented 45° with respect to the sample axis and where the scattering intensity decreases monotonically from zero scattering angle to larger angles) was observed for each of the film specimens studied. The V_V LS patterns had elongated sausage-like shapes (not shown). These results imply that the optical axis of each individual rod-like polymer molecule (PBT) is aligned parallel to the aggregate axis of the anisotropic domains, according to the light scattering theory developed by R.S. Stein.^[16] This seems to correlate well with the observations from the above discussed microscope study. For the film specimen processed from a 4.4% solution, the angle of the cross is less than 45° (see Figure 14) which may indicate some degree of common orientation between the rod-like aggregates, as also observed with the optical microscope (see Figure 11). Detailed analysis and quantitative comparisons with the theoretical LS patterns, at this stage, are not feasible due to the difficulty of solving the correlation function in the development of small-angle light scattering theory.^[17]

For specimens prepared from more dilute solutions (concentrations $\leq 2.7\%$) no morphological features can be observed by using optical microscope or small angle light scattering techniques.

Manually smoothed small-angle x-ray scattering intensity curves along the sample axis (0° , dashed line) and perpendicular to the sample axis (90° , solid line) are shown in Figure 15 (for cast film of 40/60 blend from dilute solution), Figure 16 (for cast film of 40/60 blend from dilute solution and annealed), and Figure 17 (for quenched film of 40/60 quenched from 4.4 weight percent anisotropic solution). Comparing Figures 15, 16, and 17 indicates that specimens processed from dilute solution are microscopically isotropic (annealed or otherwise) while the specimens processed from moderately

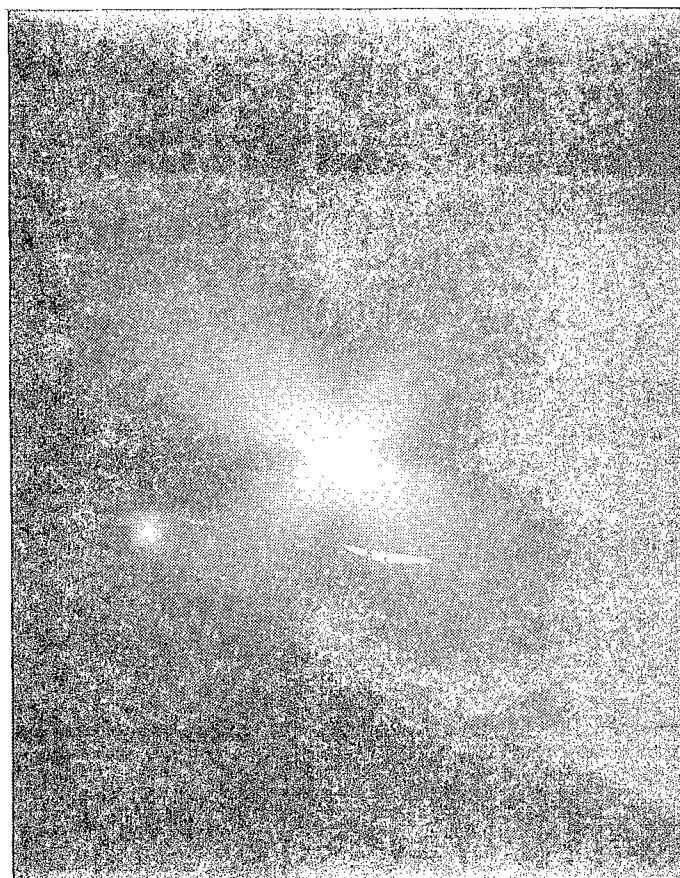


Figure 13. H_V SALS 45° Pattern From a 3.4% Solution.

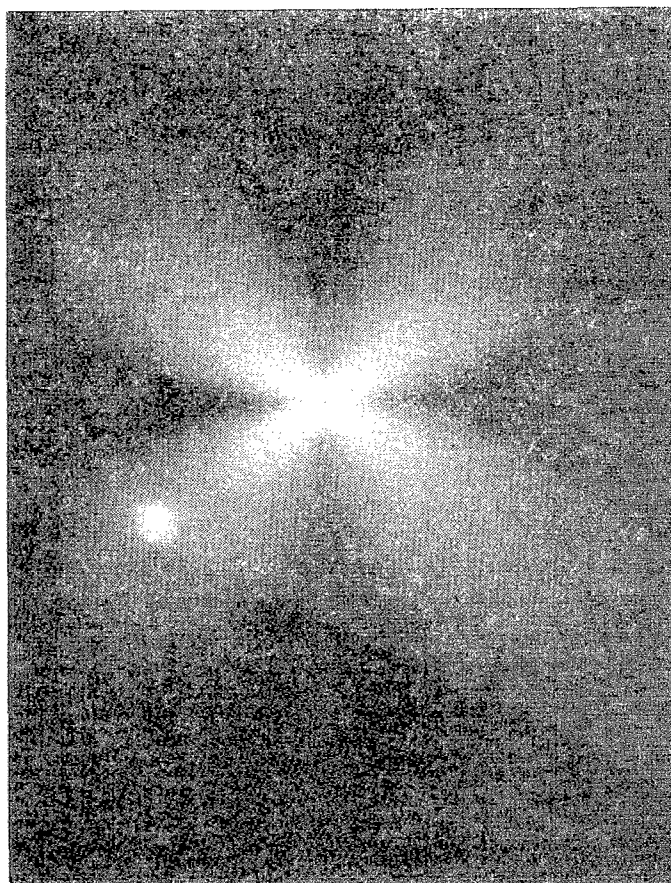


Figure 14. H_V SALS Pattern for Film Processed from a 4.4% Solution, the Angle is Less than 45° , Some Degree of Common Orientation.

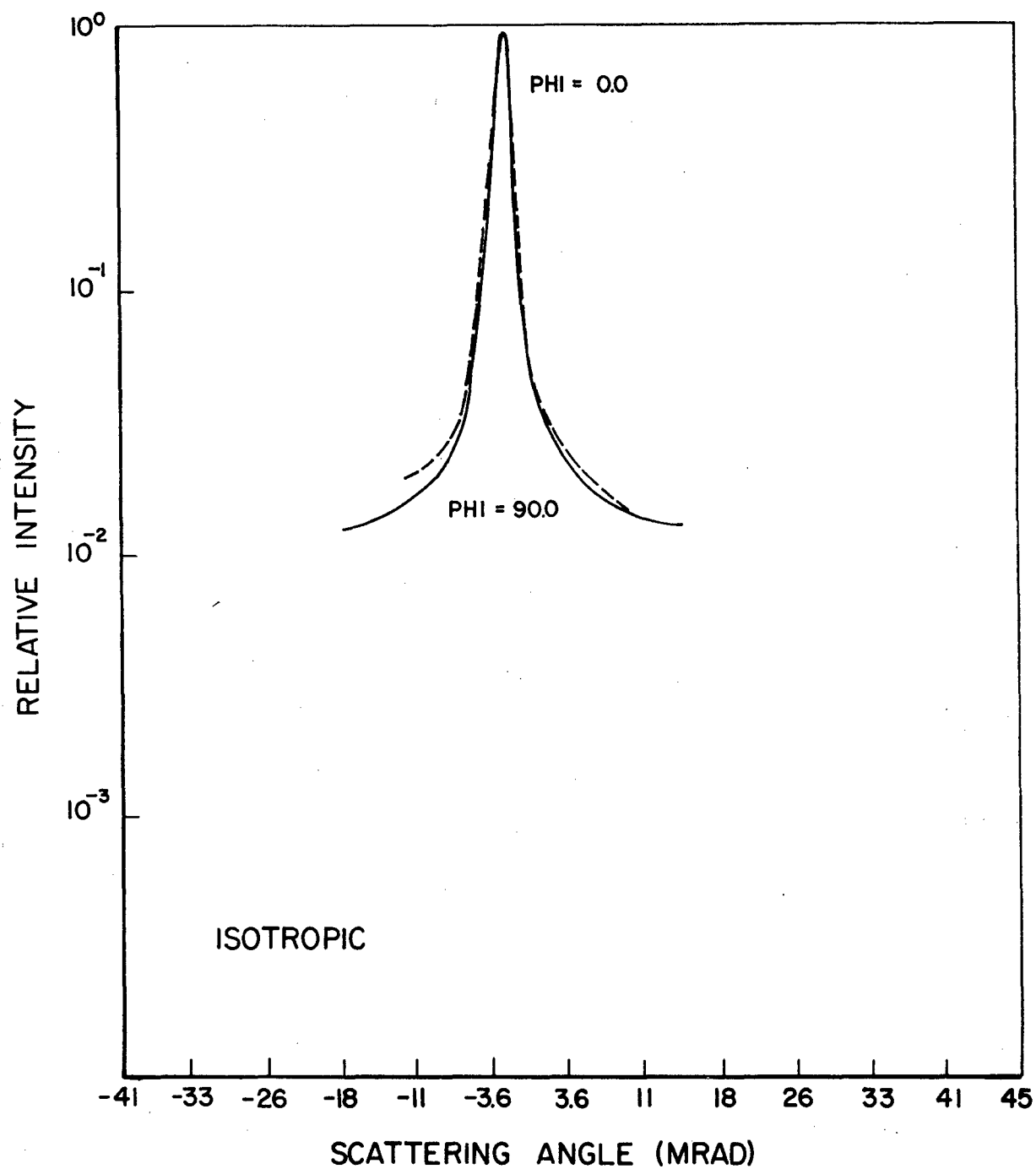


Figure 15. SAXS Intensity Distribution Curve of the Cast Film Prepared from Dilute 40/60 ABPBI/PBT Solution in MSA.

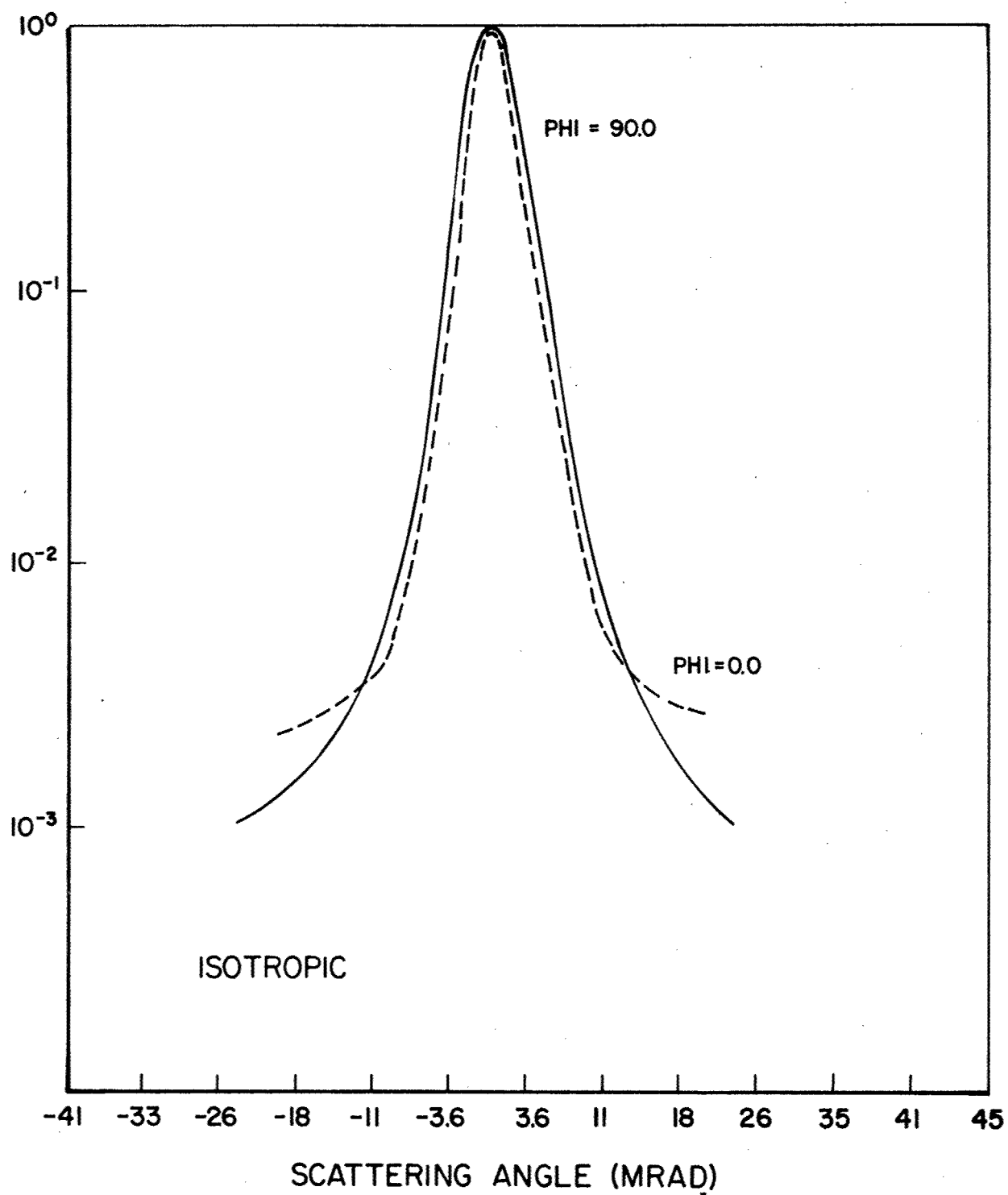


Figure 16. SAXS Intensity Distribution Curve of the Heat Treated Cast Film Prepared From Dilute Solution of 40/60 ABPBI/PBT Solution in MSA.

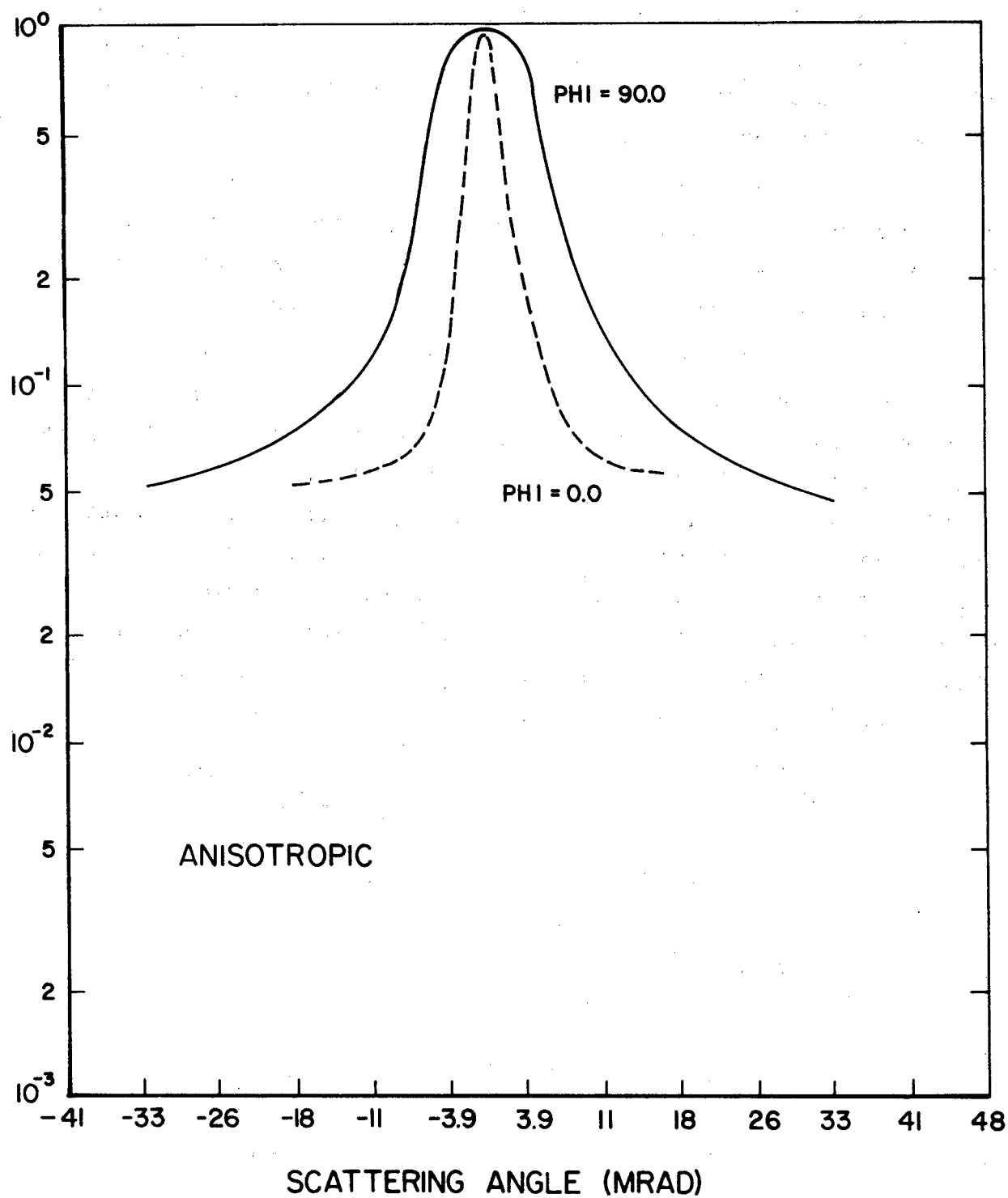


Figure 17. SAXS Intensity Distribution Curve of the Quenched Film Prepared from Anisotropic Solution (4.4 wt %) of 40/60 ABPBI/PBT in 97 MSA/3 CSA.

concentrated solution are microscopically anisotropic (see Figure 17) with rod-like scattering aggregates present. A detailed analysis of the SAXS data obtained was not feasible in support of the optical microscope findings due to the poor resolution of the scattering intensity at small angles.

As shown in Table 1 (comparing the two observations made for the 2.7 weight percent blend) a true blend was achieved only after the solution was stirred for a certain duration of time, i.e., until the morphology in the solution did not change.

As evidenced from these morphological examinations, there indeed exists a critical concentration, C_R , somewhere between 2.7% and 3.4 weight percent for the (solvent/ABPBI/PBT) ternary system. When the concentration of the polymers is greater than C_R the solution will segregate into an isotropic and an anisotropic phase. The anisotropic phase is nematic in character and may contain most of the rigid rod-like PBT molecules. There was no evidence for the formation of liquid crystalline states from the ABPBI polymers, while PBT solutions form liquid crystalline solutions (e.g., see Figure 18).

C. Solution Behaviors and Phase Relationships of (Solvent/ABPBI/PBT) Ternary Systems

As shown in the previous section, there indeed exists a critical concentration, C_R for the ABPBI/PBT polymer blend in the mixed solvent of 97 MSA/3 CSA; beyond which ($C > C_R$) the solutions segregate into two phases; i.e., there are anisotropic nematic domains dispersed in the isotropic solution. Before looking into the details of analysis and discussions of the phase relationships (phase transitions of these ternary systems) it is imperative to examine more closely the assumption that the ABPBI molecules exhibit flexible-coiled conformations while the PBT molecules exhibit rigid rod-like conformations. This is a necessary step to elucidate the origin for the formations of optically anisotropic liquid crystalline phases in these systems.

The PBT molecules, dissolved in MSA, CSA, or a mixture of MSA/CSA have been shown to exhibit a rigid rod-like conformation. [18]

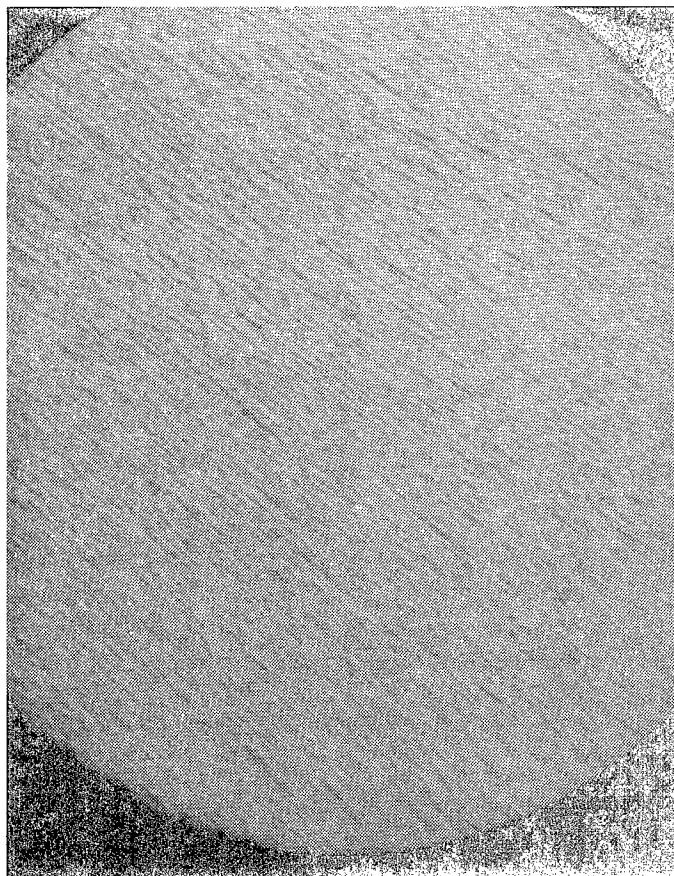
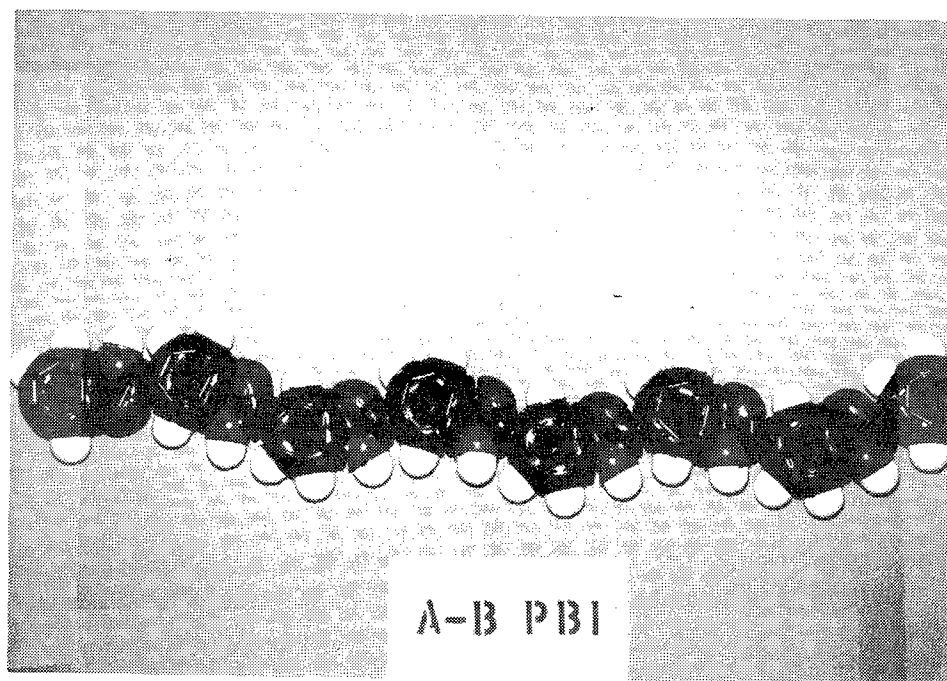


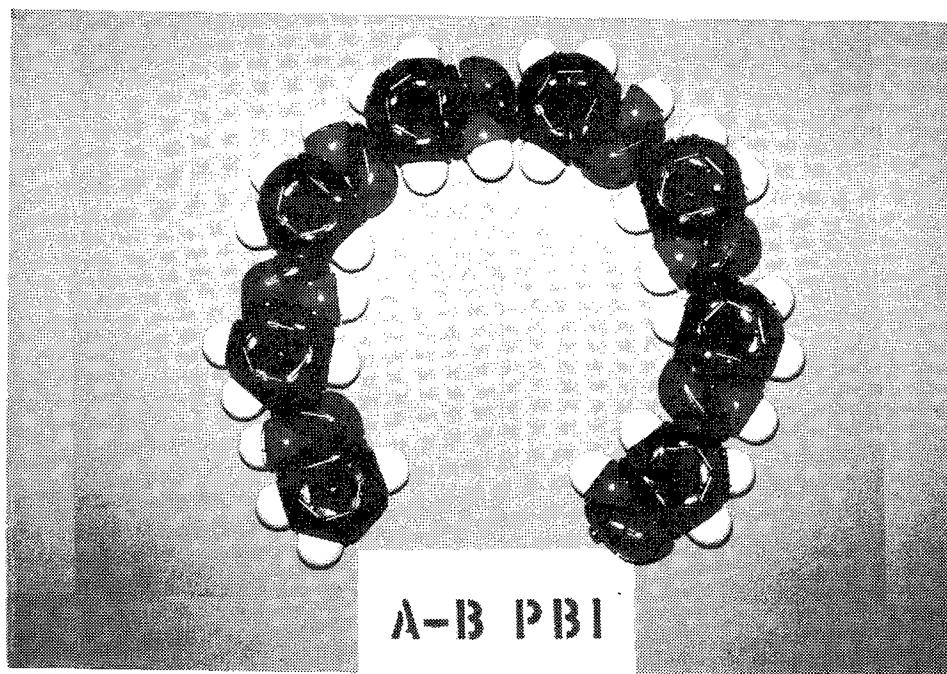
Figure 18. Pure PBT Solution.

The AF-R-56 ABPBI polymers, was shown by Delano, et al.,^[19] not to form optically anisotropic solutions. They showed that with the sole exception of formic acid or formic acid/m-cresol solutions, results were not forthcoming from any solvent investigated. Even for formic acid/m-cresol concentrated solutions, their results were contradictory. On the one hand they claimed that "stir opalescence" was observed when the polymer concentration was higher than 2% by weight, while on the other hand the solution viscosity was still on the increase. Even higher concentrations yielded either gels or undissolved particles. This is contradictory to the usual solution viscosity behavior of rod-like polymers as illustrated in Figure 3. Upon examination of molecular models of the polymer, the molecule is found to be bent. The connecting bonds between each monomer unit in the polymer subtend an angle of 150° (Figure 19) instead of being "parallel and opposite directing" as postulated^[20] as a criterion for the formation of an ordered polymer solution. Two extreme conformations may be assumed for ABPBI molecules, the one being rigid rod-like (Figure 19a) while the other is flexible coil-like (Figure 19b). However, Delano, et al.,^[19] indicated that the energy required to sustain a rod-like conformation is thought to be beyond the capabilities of the ABPBI polymer. Experimentally, we have found that up to the concentration of 4.5 weight percent ABPBI in 97 MSA/3 CSA no LC solution was formed. Thus, it may be safely concluded that the present ternary system is indeed a solvent/rigid rod/flexible coil ternary system.

Following the procedure as described above, the critical concentrations for the 80/20 (by weight), 70/30, 60/40, and 40/60 ABPBI/PBT blends were determined. They were 4.24% (by weight), 4.05%, 3.58%, and 3.00% for the three blends, respectively, at room temperature. The generally decreasing trend of critical concentrations as the amount of rod-like PBT polymer is increased is in agreement with the predictions from Flory's theory^[4] as shall be discussed below.



(a) ABPBI -- Straight Rod-Like



(b) ABPBI -- Bent

Figure 19. Molecular Model Showing Conformations of ABPBI.

Theoretical calculations of the phase equilibria were carried out, according to the numerical analysis procedure as outlined in Section III (computer program is listed in Appendix A). Systems specified by $(x_2/x_3) = (10/10), (50/50), (100/100), (100/200), (100/300), (300/200), (300/300), (300/1000)$, and $(350/300)$, where x_2 and x_3 are axis ratios of the rod-like solute and the coil-like solute relative to the solvent were analyzed. Calculated phase diagrams are represented in Figures 20 through 28 for the ternary systems as specified above. In these diagrams, binodials for the isotropic and anisotropic phases are heavy lined and tie lines joining conjugate phases are light dashed. Full ranges of the volume fractions are shown in Figures 20 and 21. Only the upper portions of the phase diagrams for $x_2 = 100$ are shown (with $1 - v_1 < 0.2$). As for $x_2 = 300$, only the portions with $(1 - v_1 < 0.1)$ of the phase diagrams are shown. Some of the calculated values of $y, v_1, v_2, v_3, v_1', v_2',$ and v_3' , which were used for the constructions of those phase diagrams, are tabulated in Appendix B for references.

The above theoretical calculations of the phase relationships of the (solvent/flexible coil/rod-like) ternary systems have shown the following results (see Figures 20 through 28, and data tabulated in Appendix B):

(i) There is a marked discrimination between the disparate rod-like and coil-like solute species in the respective coexisting isotropic and anisotropic phases; i.e., phase segregation occurs when the concentration of solutes is beyond a critical point (the critical concentration points exist along the binodial curves as shown in the phase diagrams for any composition of the two polymers) in which the anisotropic phase contains only the rigid rod-like polymers and practically none of the flexible coiled polymers ($v_3' < 10^{-4}$) for all the calculations performed), while the flexible coiled polymers are retained in the isotropic phase.

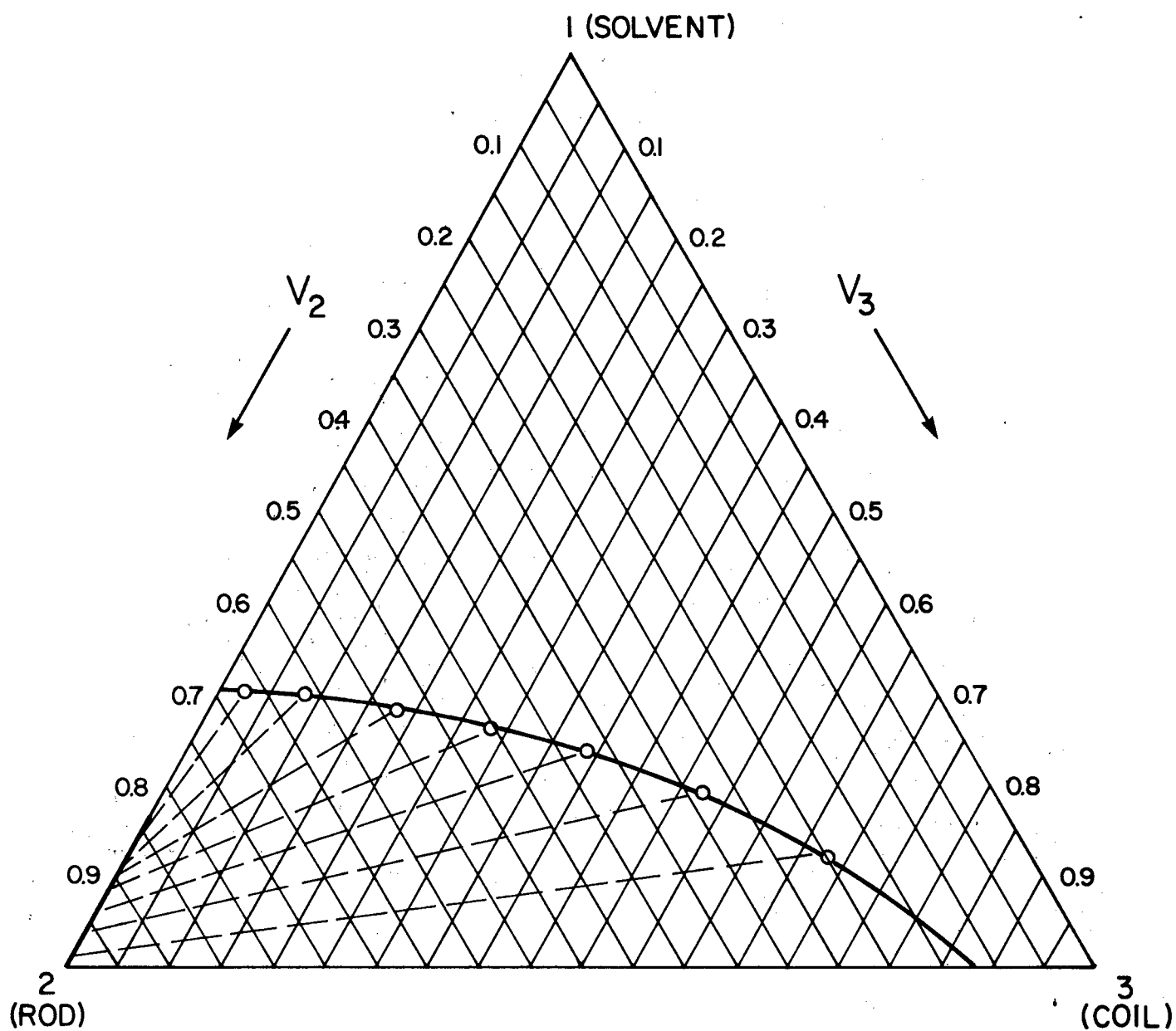


Figure 20. Theoretically Predicted Ternary Phase Diagram
With $x_2=x_3=10$.

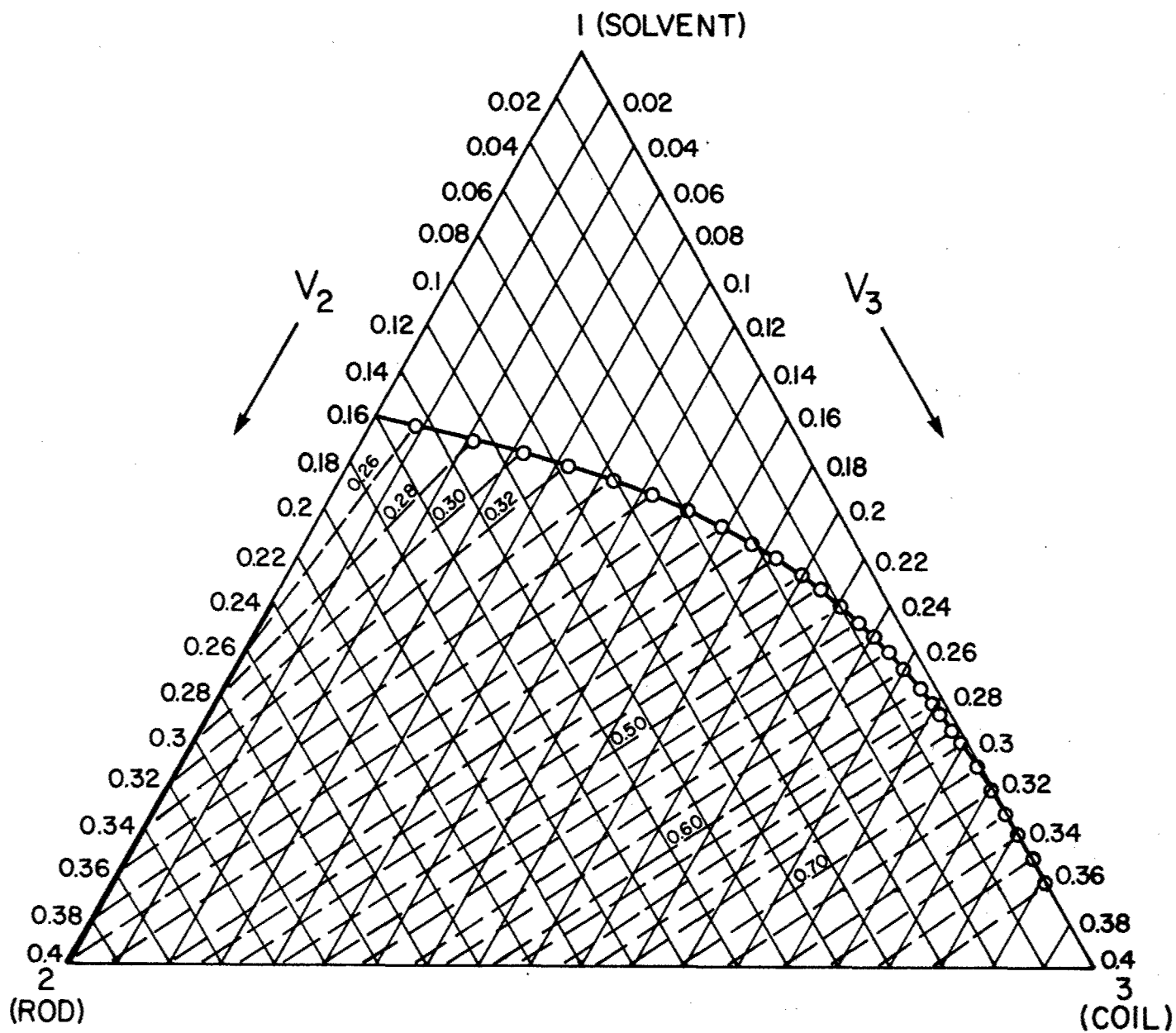


Figure 21. Theoretically Predicted Ternary Phase Diagram
With $x_2=x_3=50$.

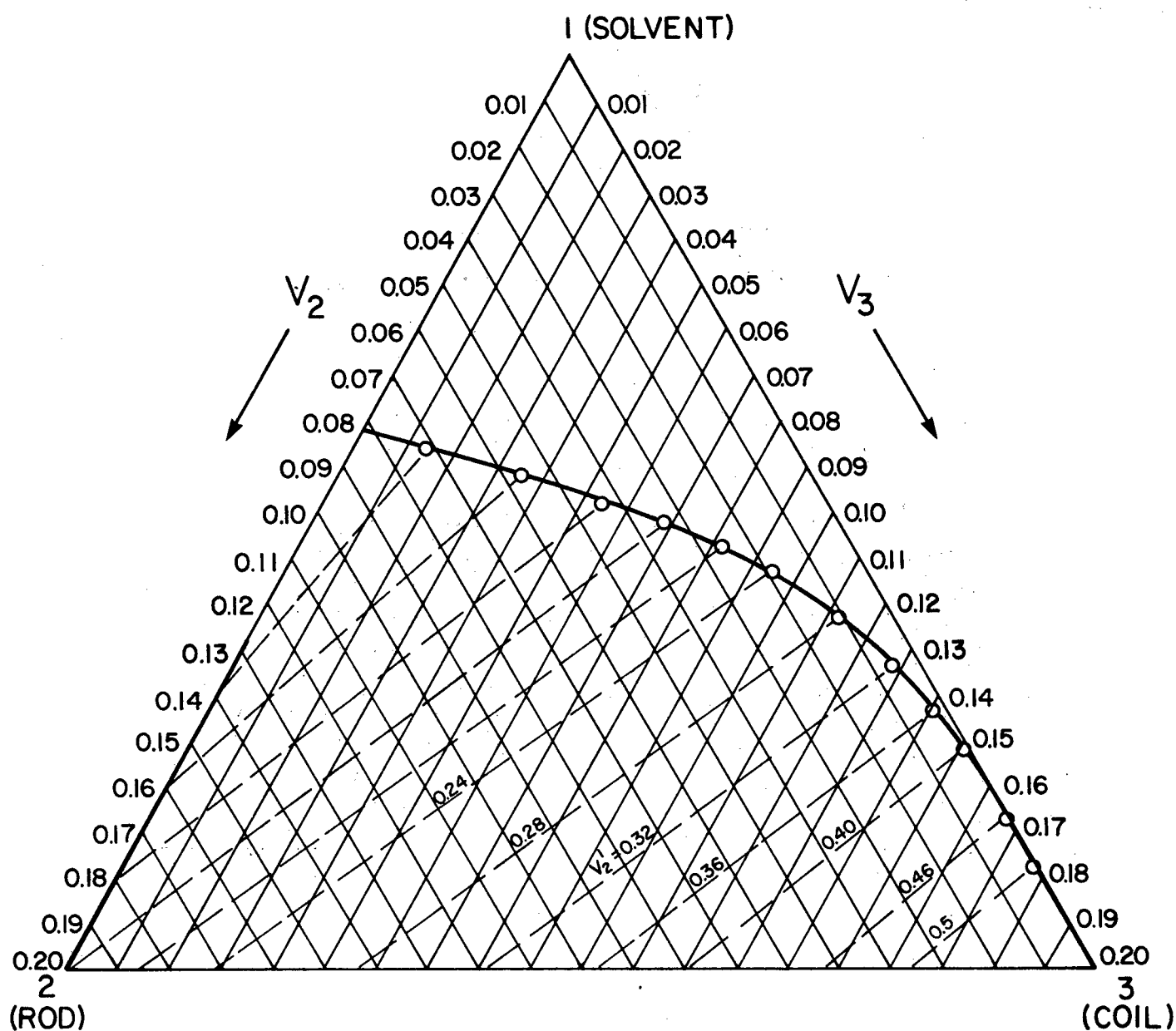


Figure 22. Theoretically Predicted Ternary Phase Diagram
With $x_2=x_3=100$.

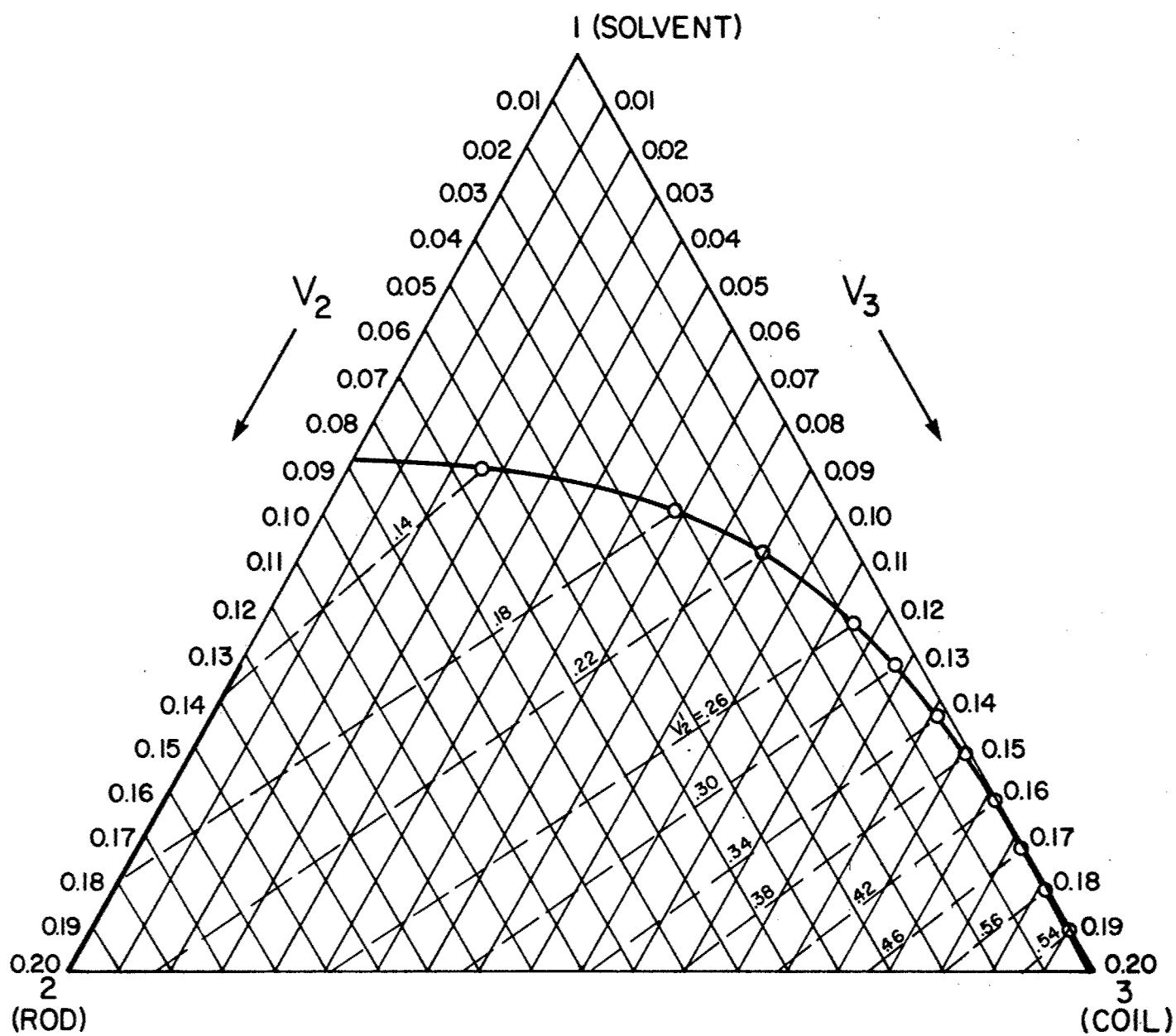


Figure 23. Theoretically Predicted Ternary Phase Diagram
With $x_2=100$, $x_3=200$.

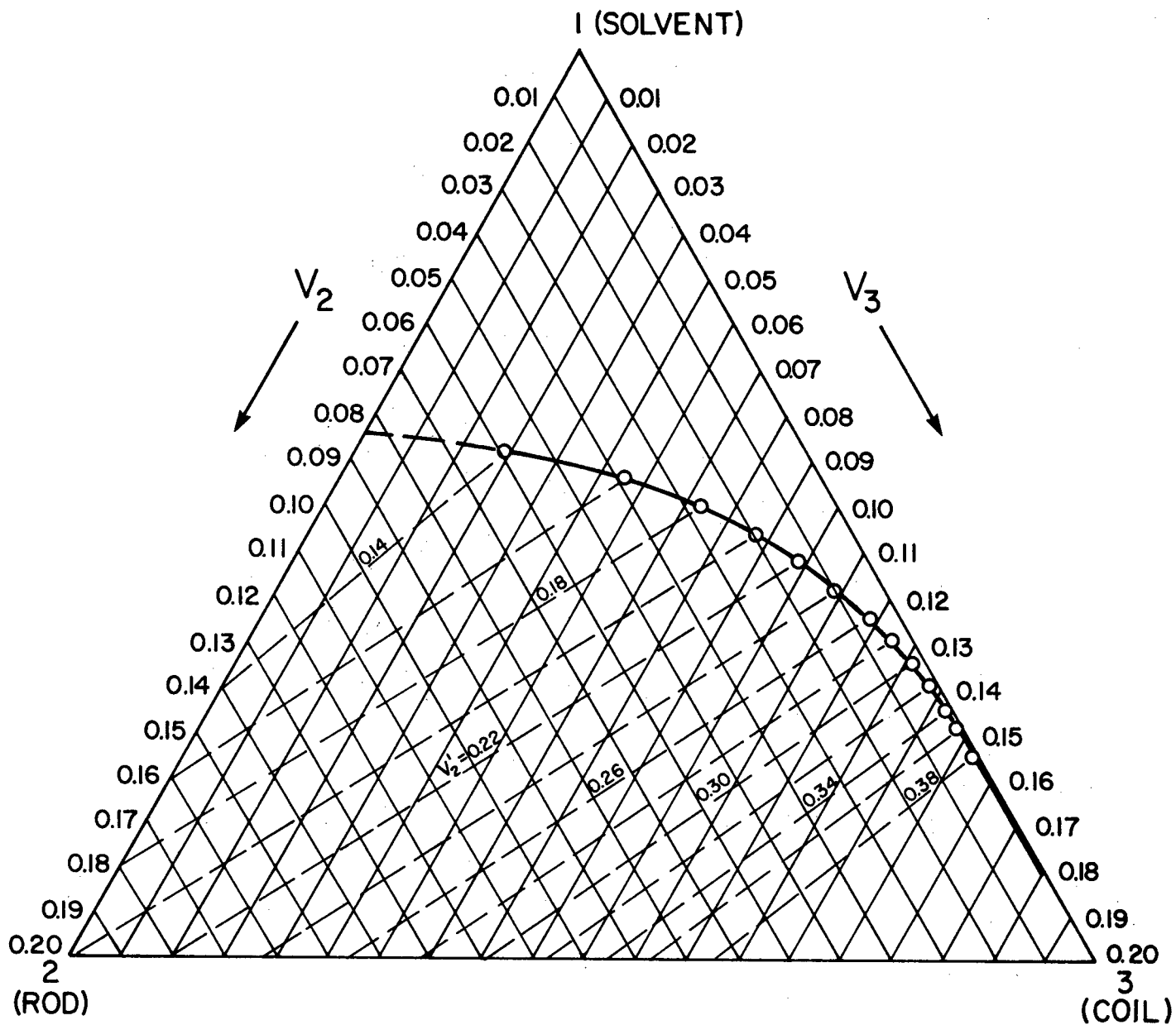


Figure 24. Theoretically Predicted Ternary Phase Diagram
With $x_2=100$, $x_3=300$.

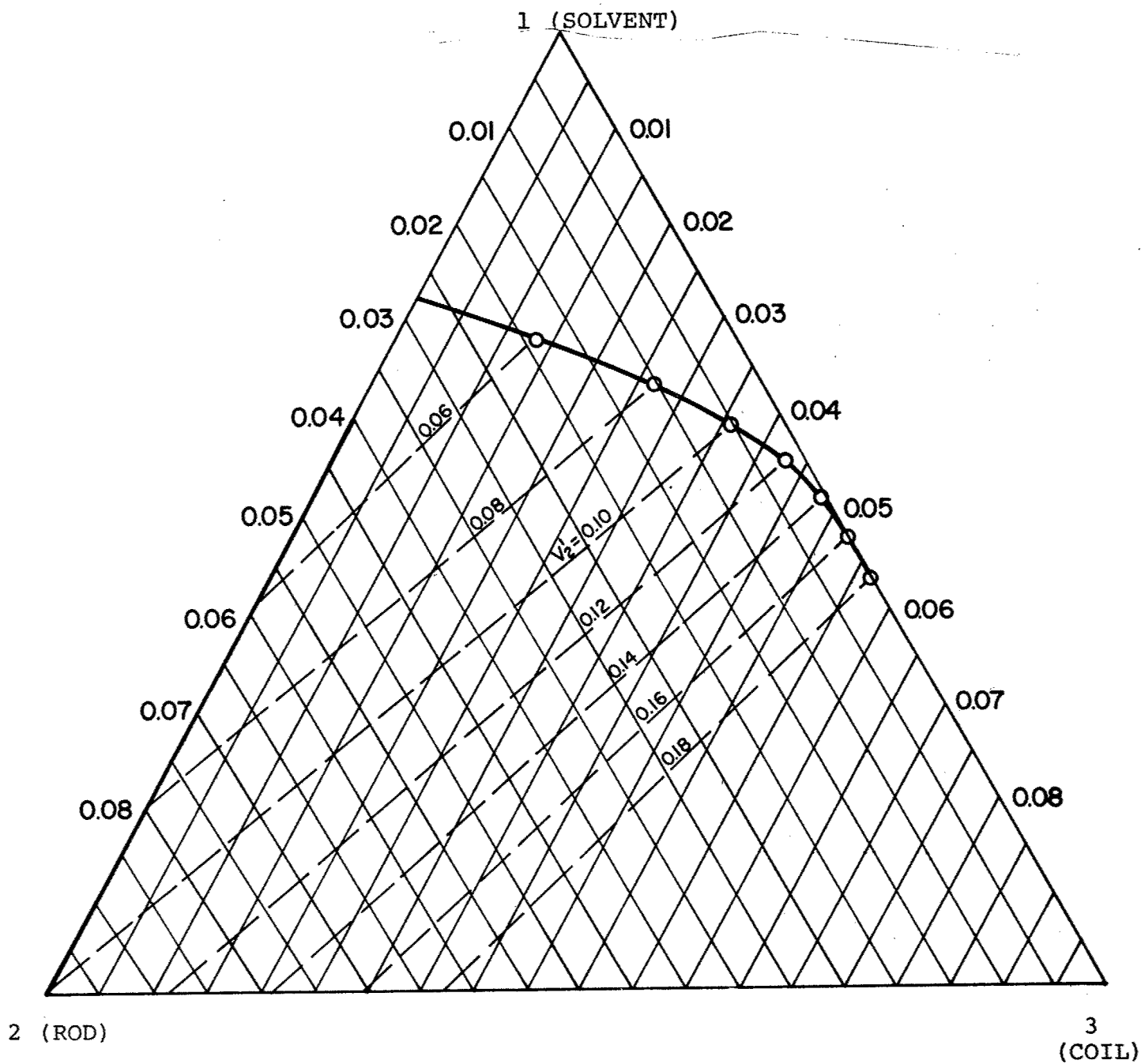


Figure 25. Theoretically Predicted Ternary Phase Diagram With $x_2=300$, $x_3=200$.

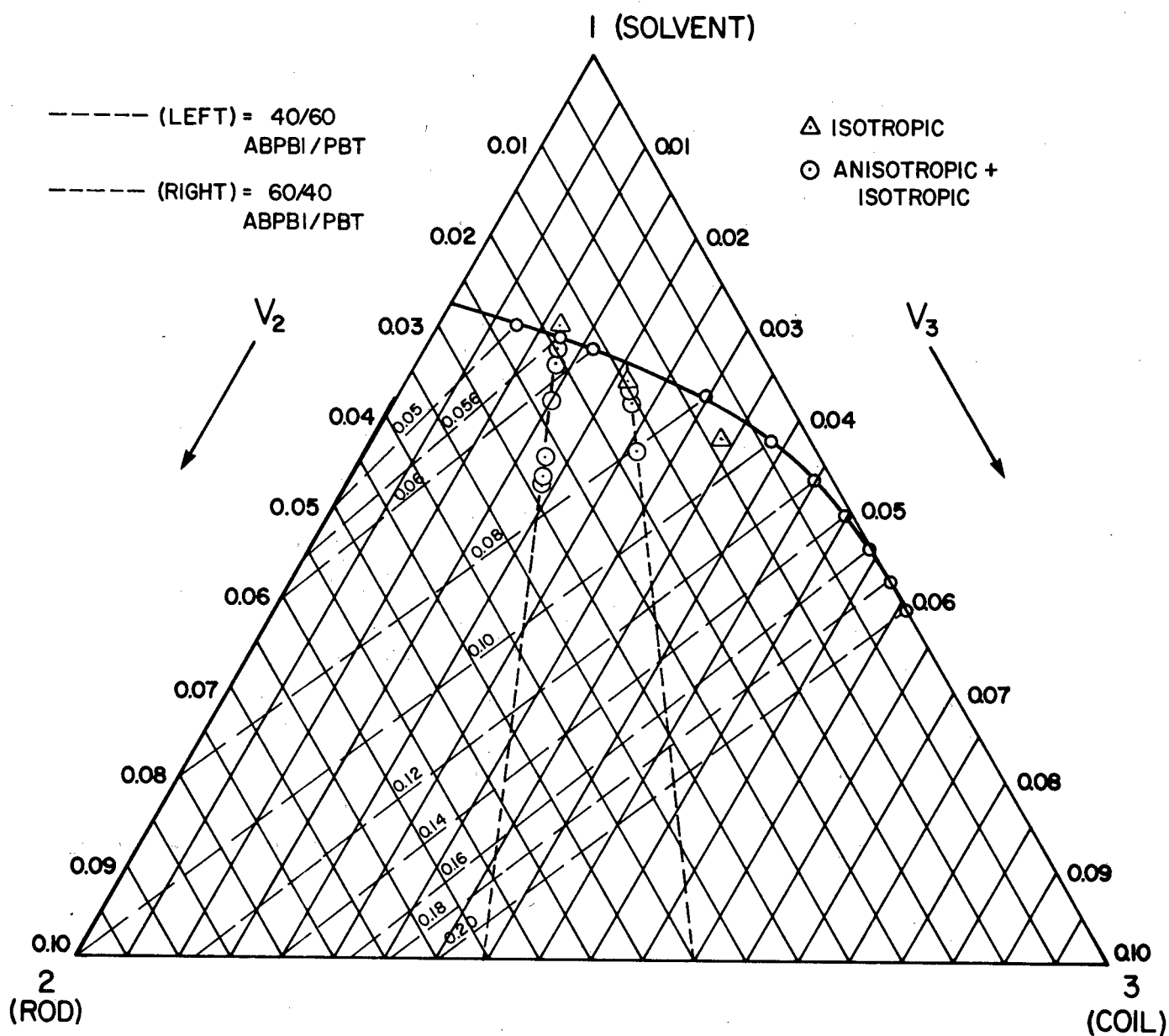


Figure 26. Theoretically Predicted Ternary Phase Diagram
With $x_2=300$, $x_3=300$.

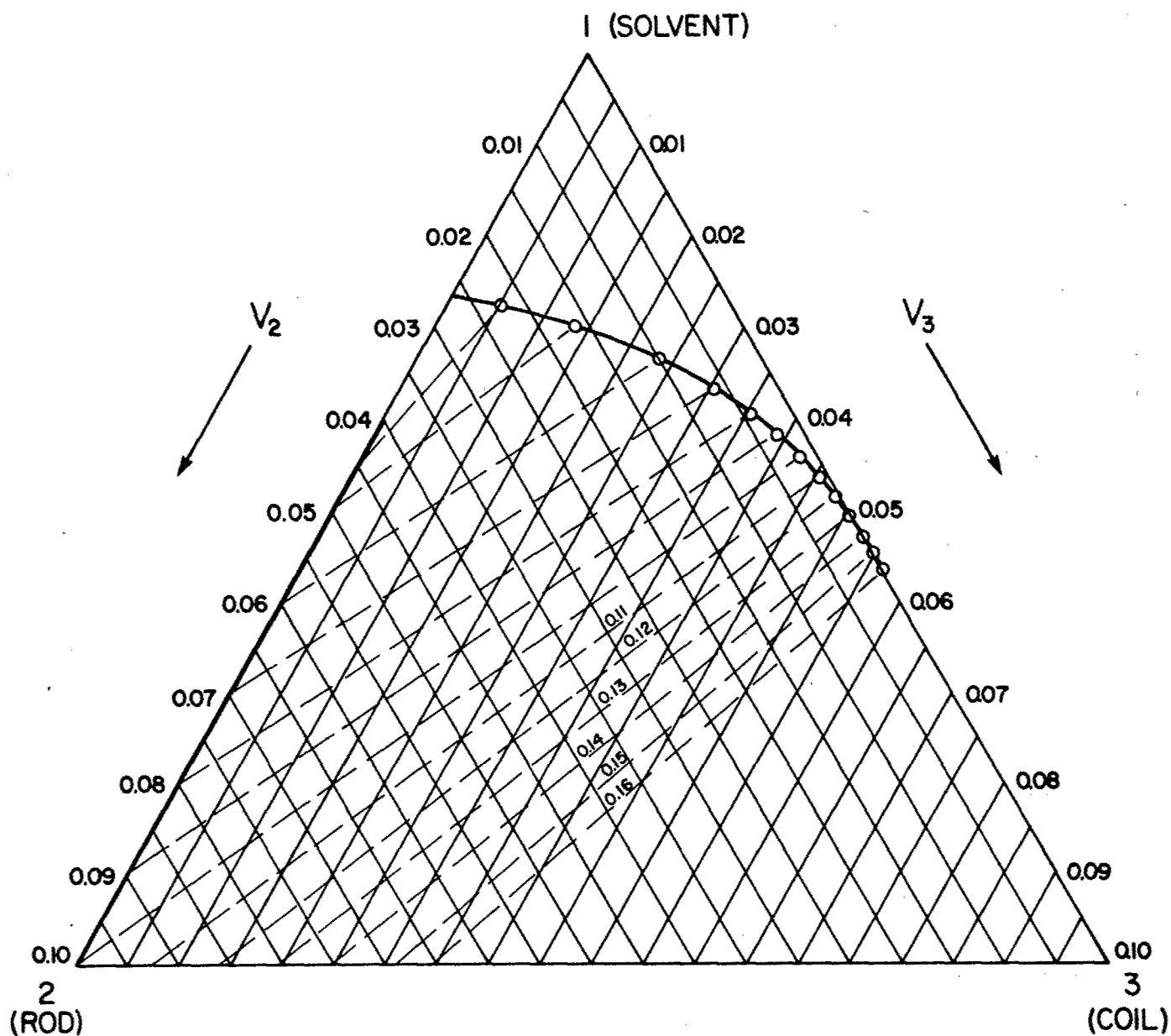


Figure 27. Theoretically Predicted Ternary Phase Diagram
With $x_2=300$, $x_3=1000$.

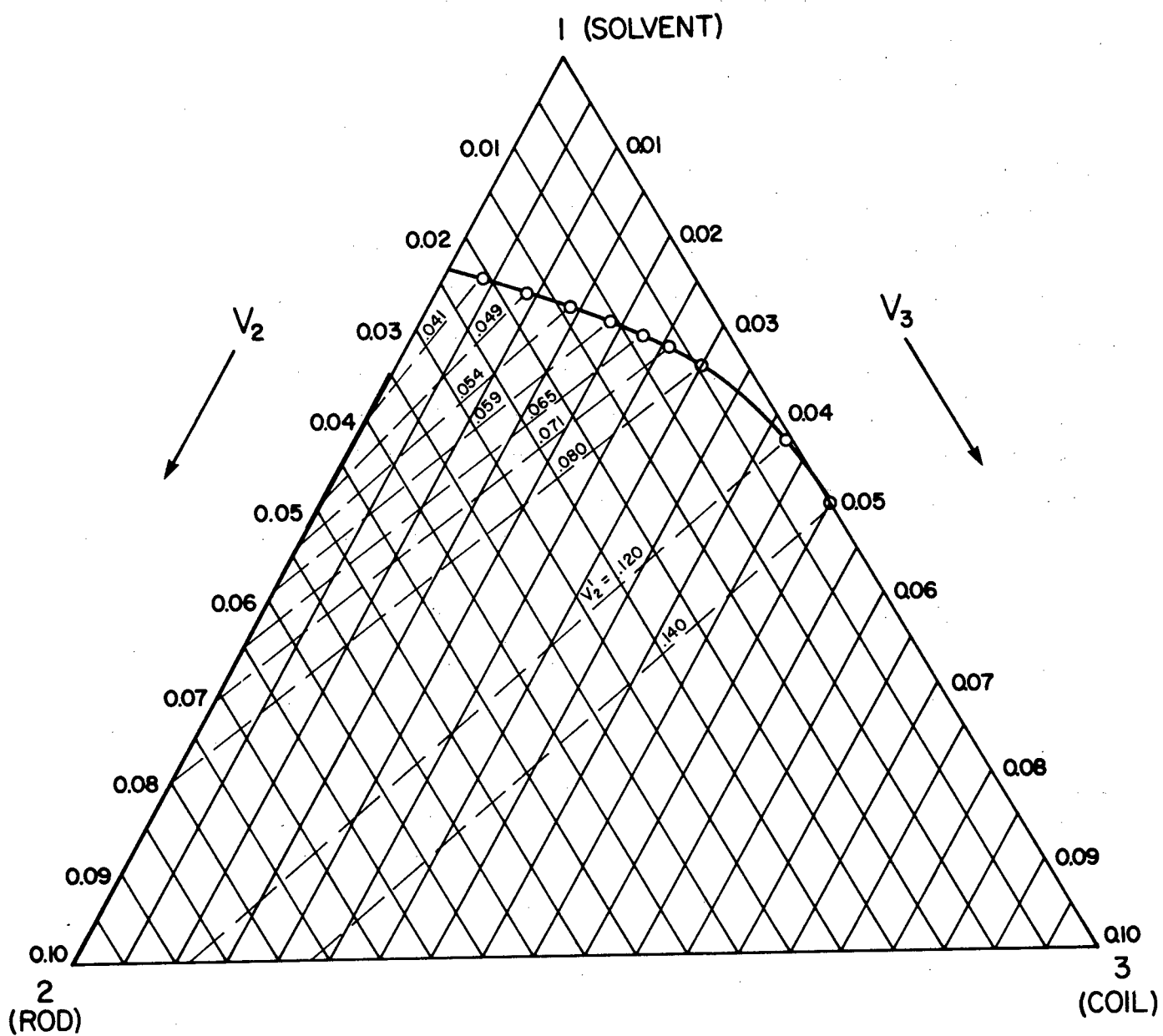


Figure 28. Theoretically Predicted Ternary Phase Diagram
With $x_2=350$, $x_3=300$.

(ii) As the rod length, x_2 , increases, the phase segregation phenomenon is enhanced; i.e., it occurs at lower and lower concentrations of solutes as x_2 becomes larger and larger, for any composition of the two polymer solutes.

(iii) For any set of x_2 and x_3 values, as more flexible-coiled polymers are introduced; i.e., as ratio v_3/v_2 increases, the phase segregation will occur at higher concentration of polymer solutes as can be seen from the downward slope of the binodial curves. However, when it does occur, the volume fraction of the rod-like polymers in the anisotropic phase will be higher (larger v_2' value) and the rod-like polymer molecules are more aligned (smaller y value) in that phase. In other words, as more flexible coiled polymers were added into the solution (v_3 increased), the volume (on lattice sites) available for rod-like polymers decreases so that the rod-like polymers have to be more efficiently packed, and thus more aligned, in the anisotropic domains.

(iv) For such a ternary system, the effect of the chain length of the flexible coiled polymers, x_3 , on the phase diagrams is not as marked as the effect of x_2 . As can be seen through comparisons between Figures 22 through 24 and between Figures 25 through 27, for certain value of x_2 , the phase diagrams for various x_3 are similar. The dominant quantitative difference between them is that the binodial curves for systems with larger x_3 follow a course somewhat above that for systems with smaller x_3 ; i.e., phase segregation occurs at somewhat lower concentrations of polymer solutes for systems with larger x_3 values.

Thus, for such ternary systems, as long as the axis or aspect ratio of the rigid rod-like polymer and the chain length of the flexible coiled polymer can be determined, a theoretical phase diagram can be composed; and from which critical concentrations for any blends of coil-like/rod-like polymers can be predicted, the compositions of such blends can be determined, and the degree of orientations (y values) of the rod-like polymer molecules in the anisotropic domains can be inferred.

The experimentally critical concentrations of four ABPBI/PBT blends in 97 MSA/3 CSA are summarized in Table 2. Also listed in Table 2 are theoretically calculated C_{cr} values for $x_2 = 300$ and various x_3 values. The aspect ratio of PBT molecules was estimated to be $293\text{\AA}$ from model compound calculation by using repeat unit length of $12.2\text{\AA}$, repeat unit width of $4.691\text{\AA}$, and polymer molecular weight of 30,000. Thus, the adopted value of $x_2 = 300$ throughout these calculations seems to be justified.

For the purpose of comparisons, the experimental data are inserted onto the theoretically determined phase diagram for $x_2 = 300$, $x_3 = 300$ (Figure 26). The triangular points are the critical concentration points for the four blends studied.

As it is shown in Figure 26 and Table 2, the experimental results are (within the experimental errors) in excellent agreement with the theoretically predicted results. The difference between the units of weight percent and volume percent are not significant for this particular ternary system, since the densities of the three components are about the same. The major difference is between the experimentally determined critical concentration points and the theoretically predicted binodial curve. As can be seen in Figure 26, the downward trend of the slope of the experimental curve is more drastic than that of the theoretical one.

As mentioned before, the rigid rod-like polymers form liquid crystalline solutions due to their inherent rigid chain conformation. They are lyotropic. Some lyotropic systems may also be thermotropic; i.e., they become isotropic on heating. PBT polymers have been shown^[18] to form nematic liquid crystalline solution in MSA/CSA solvent systems, and they become totally isotropic at certain temperatures which may be called the Nematic-Isotropic transition temperature, T_{N-I} .

For the ABPBI/PBT blends, such thermotropic behavior was also observed. The experimental T_{N-I} data for the 40/60 ABPBI/PBT blends are summarized in Table 3 while that for the

TABLE 2

CRITICAL CONCENTRATIONS OF ABPBI/PBT BLENDS IN
97 MSA/3 CSA AT ROOM TEMPERATURE (22°C-25°C)

ABPBI/PBT Composition	C_{cr} , exp (wt %)	C_{cr} , theo (Vol %)		
		$x_2=300, x_3=300$	$x_2=300, x_3=200$	$x_2=300, x_3=1000$
80/20	4.24	3.75	3.88	3.61
70/30	4.05	3.57	3.64	3.34
60/40	3.58	3.42	3.48	3.16
40/60	3.00	3.12	3.22	2.95

TABLE 3

CRITICAL THERMOTROPIC BEHAVIOR
OF ABPBI/PBT BLENDS

Concentration (wt %)	Viscosity (Relative) *	T _{N-I} (°C)	Y	v ₂ '	(v ₂ /v ₃) **	(v ₃ '/v ₂ ') ⁻¹	% Total Rods in the Anisotropic Phases
4.74	Decreasing	147.6	28.90	0.074	0.359	2.13x10 ⁻⁶	76.0
4.62	Decreasing	126.8	29.36	0.073	0.392	2.62x10 ⁻⁶	73.9
4.40	Decreasing	107.2	30.83	0.070	0.463	5.34x10 ⁻⁶	69.1
3.79	Decreasing	70.9	35.54	0.062	0.832	3.01x10 ⁻⁵	44.5
3.43	Decreasing	56.5	38.54	0.058	1.146	6.82x10 ⁻⁵	23.6
3.27	Decreasing	36.5	39.80	0.056	1.475	9.31x10 ⁻⁵	1.7
3.00 (C _{cr})	Maximum	R.T.	---	---	---	---	---
2.70	Decreasing	----	---	---	---	---	---
1.80	Decreasing	----	---	---	---	---	---

* Solution viscosity was not measured; it, however, was qualitatively determined from the observation of the stirring speed of the magnet in solution.

** Remember that the original blend has a v₂/v₃ ratio of 1.5.

60/40 blends are summarized in Table 4. The temperature-concentration phase diagram for the above two blends is shown in Figure 29. Also listed in Tables 3 and 4 are calculated v_2' , v_3' values for each concentration and the observations of the relative viscosity made for each solution. In Table 3, the phase compositions in the anisotropic phase and in the isotropic phase, v_2/v_3 , v_3'/v_2' , are also listed.

The viscosity observations made for the two ABPBI/PBT blends were qualitative. They did, however, indicate the presence of maximum viscosity at the critical concentration, and the generally decreasing trend of viscosity as the concentration of polymers increases or decreases from C_{cr} as one would have expected from the behavior of rod-like polymers in solution (see Figure 3). Also, the 60/40 blends are generally more viscous than the 40/60 blends when they are compared at the same polymer concentration.

The temperature-concentration phase diagram of the ternary systems shown in Figure 29 exhibits a similar behavior as that of a binary system illustrated in Figure 2; i.e., there is the sharp increase in T_{N-I} as the concentration of the polymers increases.

The phase segregation behavior in a ternary system with $C > C_{cr}$ as predicted from Flory's theory is illustrated in Table 3. As seen in Table 3, the calculated v_2/v_3 ratio in the isotropic phase decreases sharply as the concentration of the solution increases, while the v_3'/v_2' ratio ($<10^{-4}$) stays negligibly small at all concentrations; i.e., in the biphasic region, the coil-like polymers are excluded altogether from the anisotropic phase while the isotropic phase retains a non-negligible amount of rod-like polymers. Having the calculated values of the v_2/v_3 , v_3'/v_2' (remember that the coil-like polymers remain in the isotropic phase exclusively) and the original composition of the two polymeric components (e.g., for 40/60 ABPBI/PBT blend, $v_2^0/v_3^0 = 1.5$), the percentage of rod-like polymers remaining in the isotropic phase and that which goes into the anisotropic phase can be calculated. The calculated results are listed in Table 3.

TABLE 4
SOME CHARACTERISTICS OF 60/40 ABPBI/PBT
SOLUTIONS IN 97 MSA/3 CSA

Concentration (wt %)	Viscosity (Relative)	T _{N-I} (°C)	v' 2	Y
4.34	Decreasing	125.6	0.081	26.02
3.81	Decreasing	85.5	0.072	29.83
3.70	Decreasing	56.9	0.070	31.09
3.58 (C _{cr})	Maximum	Room Temperature	----	----

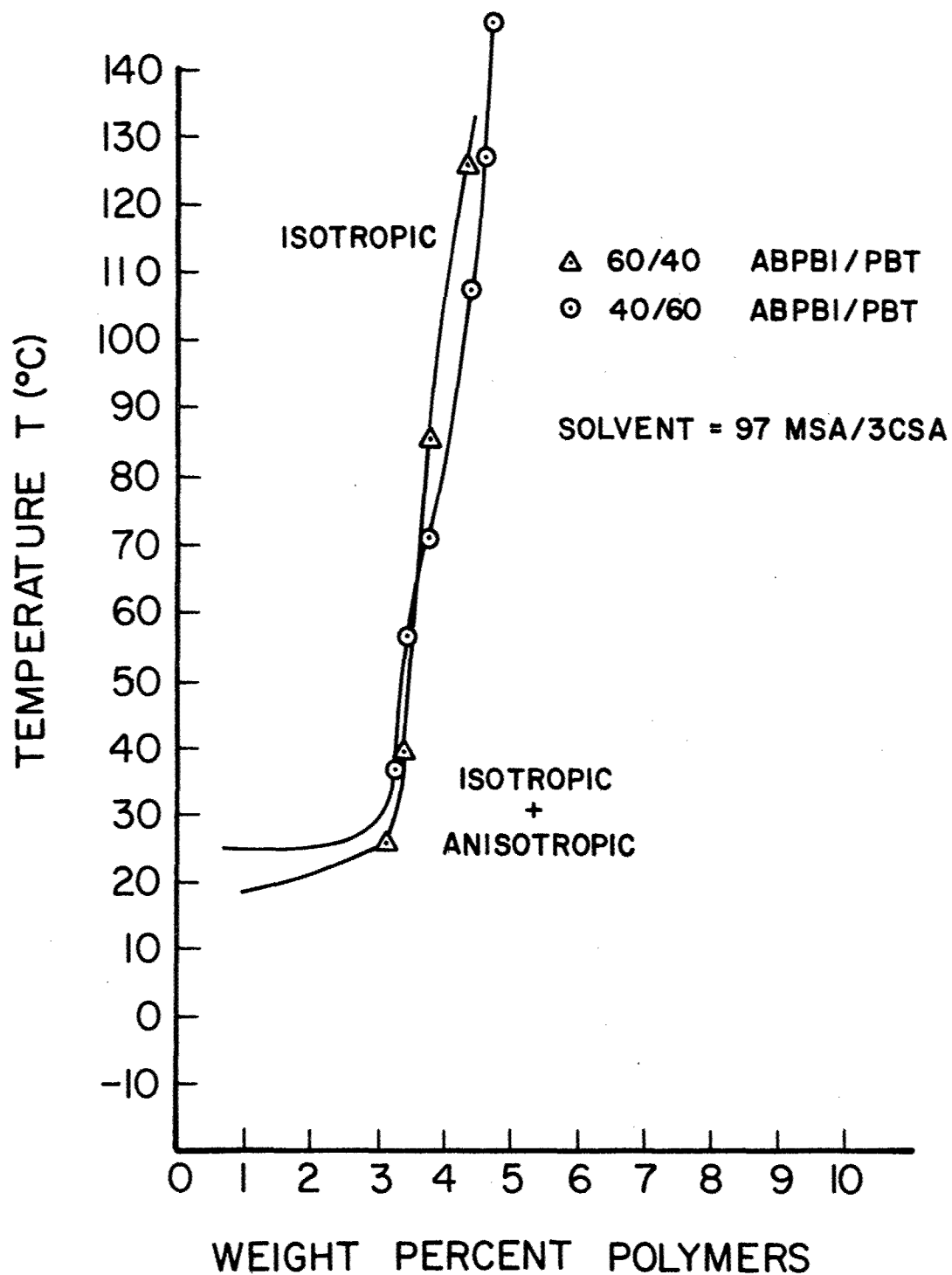


Figure 29. Temperature-Composition Phase Diagram of 97 MSA/3 CSA ABPBI/PBT Ternary Solutions.

There seems to be some sort of correlations (as shown in Tables 3 and 4) between the experimentally determined T_{N-I} values and the calculated y values; i.e., when the concentration of the polymers is higher, T_{N-I} is higher and the value of y is lower. At first glance, this correlation (between y and T_{N-I}) seems to be fictitious, since the derivation of all the Flory equations for the phase relationships of the ternary system are based on the "athermal" condition. In other words, the solution behaviors of such systems are independent of temperature so that the thermotropic behavior (the existence of T_{N-I}) of our ABPBI/PBT systems are not expected with the athermal geometric lattice model of Flory. However, the athermal restriction is only meant to simplify the theoretical treatment and to facilitate the derivation of equations for numerical analysis, while fundamental features predicted from the theory are preserved. Thus, one may view y simply as a characteristic of the state of the solution. Any thermal energetic consideration is implicitly contained in y which defines the degree of orientation (or alignment) of the rod-like polymer molecules in the anisotropic phases. The smaller the y value, the higher is the degree of orientation. Hence, for a particular composition of ABPBI/PBT (e.g., 40/60), the thermal energy (obtained by heating) required to disrupt the alignment of rod-like polymers of a higher concentrated solution would be expected to be higher than that of a lower concentrated solution. Thus the T_{N-I} of a more concentrated solution would be expected to be higher than that of a less concentrated solution, when the measurements are taken at the same heating rate. The experimental data of T_{N-I} and the calculated values of y listed in Tables 3 and 4 seem to prove the validity of the above postulations. Recall that the higher the concentration the smaller the value of y .

In conclusion, the solution behaviors of the ABPBI/PBT systems are in quantitative (or at least semi-quantitative) agreement with Flory's theory.

V. CONCLUSIONS AND RECOMMENDATIONS

The following principal conclusions may be drawn from this research study.

- (1) For the [(97% MSA/3% CSA)/ABPBI/PBT] ternary systems, which are (solvent/coil-like polymer/rod-like polymer) systems, there indeed exists a critical concentration for each of the blends being investigated; and at the critical concentration the solution viscosity of the blend is the highest.
- (2) When the critical concentrations of polymers are higher than the critical concentration, the solutions segregate into isotropic and anisotropic phases; and film specimens prepared from such optically anisotropic solutions are macroscopically separated inhomogeneous systems.
- (3) The experimental phase behaviors of these ternary systems are in excellent agreement with that as predicted from Flory's Theory.
- (4) These ternary systems are also thermotropic; i.e., the originally anisotropic solutions become totally isotropic when heated to a so-called nematic-isotropic transition temperature, T_{N-I} .
- (5) The close relationship between the experimentals observable such as T_{N-I} and the theoretically calculated parameter such as γ illustrates what one can infer from the "athermal" geometrical model of Flory in relation to real thermal systems.
- (6) The general downward trend of the slopes of the experimental and the theoretical binodial curves (see Figure 27) implies that an ABPBI/PBT solution with higher PBT in composition at its critical concentration; e.g., sheared quenched films prepared from an 80/20 ABPBI/PBT solution at its critical concentration would be more uniaxially oriented (orientations between PBT molecules) than that prepared from the corresponding 70/30 ABPBI/PBT solution. Some preliminary SAXS^[18] and WAXD^[20] data do indicate such a trend.

- (7) The dilute solutions offer none of the advantages of the orientations of rod-like polymers in solutions.
- (8) The significance in the application of Flory's theory to a real ternary system such as ours lies not at its calculated "numerical values" in the superficial sense. Rather, the significance lies in the "physical" implications and relative trends that one can derive from those numbers and apply them to the elucidation and hence the understanding of the solution behaviors of a real system.

For our present solvent/ABPBI/PBT system, such calculations offer us the insight of the important parameters such as concentration, composition, and achievable orientations of the solution which are critical in the processing of composite films.

From the findings and conclusions indicated above, the following are recommendations for obtaining composite films having good physical properties. These are based upon the criteria that an acceptable molecular composite, processed from solution, must have aligned rod-like molecules and in order to have reinforcement of the matrix (or host flexible polymer), aggregates of the rod-like polymer should not be present.

- (1) In order to achieve these criteria the following is recommended:
 - (a) Composite films should be processed from solutions at the critical concentrations, since at this point the solution is still isotropic but the rod-like polymers can be oriented by external shear stresses (remember that the critical concentration point is the onset of the alignments rod-like polymers which lead to phase segregation).
 - (b) Composite films may be processed from highly concentrated anisotropic solutions at their T_{N-I} , since here the solution is isotropic and the high concentration ensures easier alignment of the rod-like polymers by external shear stresses.

- (c) Composite films may be processed from mechanically homogenized highly concentrated solutions, in which good dispersion of rod-like polymer aggregates may be achieved and the high degree of rod-like polymers is intrinsically present in the solutions.
- (2) The effects of molecular weight and molecular weight distributions of the rod-like polymers on the solution behaviors, and thus the physical properties of the composite films, should be studied in the future.
- (3) The property/morphology/processing correlations of the ABPBI/PBT films as processed according to (1) are currently underway and will be reported in the next technical report.
- (4) Preliminary processings and mechanical testings indicate that films prepared from the method as indicated in (1-a) are optically transparent (without aggregation) and have moderate high initial modulus (e.g., for 80/20 ABPBI/PBT film, prepared by shear quenching on glass slide has initial modulus of 5.56 GPa. It should be cautioned that this film was prepared by hand and is rather defective).
- (5) Finally, it should be mentioned that a SAXS technique to study the ordering processes (orientations) of PBT molecules in the ABPBI/PBT dope solutions under various processing conditions (e.g., shear rate, total shear, etc.) and thus to determine the best processing conditions of ABPBI/PBT composite films, is currently being developed in the light of a model recently being put forward by Sjöberg.^[27]

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APPENDIX A

COMPUTER PROGRAM LISTING

```

00010      EXTERNAL F9
00020      REAL F9
00030      EXTERNAL V2SOLVE
00040      REAL V2SOLVE
00050      EXTERNAL V3SOLVE
00060      REAL V3SOLVE
00070      COMMON/V3DATA/V3STRT,V3STOP,ITER
00080      COMMON V1,V2,V3,X2,X3,V1P,V2P,V3P,Y,A,B
00090      READ,NI,X2,X3,TOL1
00100      READ START,STOP
00110      READ,V3STRT,V3STOP,ITER
00120      DELTA=START-STOP
00130      DELTA=DELTA/NI
00140      NJ=NI+1
00150      WRITE(2,101)
00160      DO 500 J=1,NJ
00170          V2P=START-(J-1)*DELTA
00180 C      WE HAVE CHOSEN V2P
00190 C      SOLVE NOW FOR Y
00200          SET=-1.+V2P
00210          Y1=0.
00220          DO 15 JT=1,40
00230              YT=X2-X2/40.*(40-JT)
00240              F=F9(YT)
00250              IF(F*SET.LT.0.)Y1=YT
00260 15      CONTINUE
00270          Y0=0
00280          IF(Y1.EQ.0.)GOTO500
00290          CALL BISEK2(Y0,Y1,TOL1,IFLAG1,1)
00300          Y=(Y0+Y1)/2.
00310          IF(Y.GT.X2)GOTO500
00320          IF(IFLAG1.GT.0)GOTO500
00330 C      SOLVE FOR V3 (THIS SOLVES FOR V2)
00340          ISTEP=0
00350          CALL SOLVE(ISTEP)
00360          IF(ISTEP.GT.0)GOTO500
00370          WRITE(2,10)Y,V1,V2,V3,V1P,V2P,V3P
00380 10  FORMAT(' ',6F11.6,E11.3)
00390 101  FORMAT('0',5X,'Y',9X'V1'9X'V2'9X'V3'10X'V1''8X'V2''8X'V3''
00400          GOTO500
00410 500  CONTINUE
00420          STOP
00430          END
00440 C
00450 C
00460 C
00470 C
00480      FUNCTION F9(R)
00490      COMMON V1,V2,V3,X2,X3,V1P,V2P,V3P,Y,A,B
00500      IF(R.EQ.0)(F9=-1.+V2P;RETURN;)
00510      F9=EXP(-2./R)-1.+V2P*(1.-R/X2)
00520      Y=R
00530      RETURN
00540      END
00550 C
00560 C
00570 C

```

```

01770 C
01780 FUNCTION V2SOLVE(W)
01790 COMMON V1,V2,V3,X2,X3,V1P,V2P,V3P,Y,A,B
01800 A=W*(1.-1./X2)+V3*(1.-1./X3)
01810 ASUP=LOG(V2P/W*(X2/Y)**2)
01820 ASUP=ASUP+2.*(1.-X2/Y)
01830 IF(X3/X2*ASUP.LT.-100)ASUP=X2/X3*(-50.)
01840 IF(X3/X2*ASUP.GT.100.)ASUP=X2/X3*50.
01850 V3P=V3*EXP((X3/X2)*ASUP)
01860 B=V2P*(Y-1.)/X2+V3P*(1.-1./X3)
01870 V2SOLVE=LOG(V2P/W)-(A-B)*X2+2.*LOG(X2/Y)+2.
01880 RETURN
01890 END
01900 C
01910 C
01920 FUNCTION V3SOLVE(V)
01930 COMMON V1,V2,V3,X2,X3,V1P,V2P,V3P,Y,A,B
01940 V1P=1.-V2P-V3P
01950 V1=V1P*EXP(-A+B+2./Y)
01960 V3SOLVE=1.-V1-V2-V3
01970 RETURN
01980 END
01990 C
02000 C
01490 C
01500 SUBROUTINE BISEK3(A,B,XTOL,IFLAG)
01510 IFLAG=0
01520 N=-1
01530 CALL F2(A,K)
01540 FA=V3SOLVE(A)
01550 CALL F2(B,K)
01560 FB=V3SOLVE(B)
01570 IF(FA*FB.LT.0.)GOTO5
01580 IFLAG=2
01590 5 ERROR=ABS(B-A)
01600 6 ERROR=ERROR/2.
01610 IF(ERROR.LE.XTOL)RETURN
01620 XM=(A+B)/2.
01630 IF(XM+ERROR.EQ.XM)GOTO20
01640 CALL F2(XM,K)
01650 FM=V3SOLVE(XM)
01660 N=N+1
01670 IF(FA*FM.LE.0.)GOTO9
01680 A=XM
01690 FA=FM
01700 GOTO6
01710 9 B=XM
01720 GOTO6
01730 20 IFLAG=1
01740 RETURN
01750 END
01760 C

```

```

01220      SUBROUTINE BISEK2(A,B,XTOL,IFLAG,K)
01230      IFLAG=0
01240      N=-1
01250      IF(K.EQ.1)FA=F9(A)
01260      IF(K.EQ.2)FA=V2SOLVE(A)
01270      IF(K.EQ.1)FB=F9(B)
01280      IF(K.EQ.2)FB=V2SOLVE(B)
01290      IF(FA*FB.LT.0.)GOTO5
01300      IFLAG=2
01310 5      ERROR=ABS(B-A)
01320 6      ERROR=ERROR/2.
01330      IF(ERROR.LE.XTOL)RETURN
01340      XM=(A+B)/2.
01350      IF(XM+ERROR.EQ.XM)GOTO20
01360      IF(K.EQ.1)FM=F9(XM)
01370      IF(K.EQ.2)FM=V2SOLVE(XM)
01380      N=N+1
01390      IF(FA*FM.LE.0.)GOTO9
01400      A=XM
01410      FA=FM
01420      GOTO6
01430 9      B=XM
01440      GOTO6
01450 20     IFLAG=1
01460      RETURN
01470      END
01480 C

00580 C
00590 C
00600      SUBROUTINE F2(V,IFLAG)
00610      COMMON V1,V2,V3,X2,X3,V1P,V2P,V3P,Y,A,B
00620      IFLAG=0
00630      V3=V
00640      AA=.0000001
00650      FA=V2SOLVE(AA)
00660      AB=1
00670      FB=V2SOLVE(AB)
00680      IF(FA*FB.GT.0.)GOTO7
00690      X0=AA
00700      X1=AB
00710      CALL BISEK2(X0,X1,1E-6,K,2)
00720      V2=(X1+X0)/2.
00730      RETURN
00740 7      IFLAG=1
00750      RETURN
00760      END
00770 C

```

```

00780 C
00790      SUBROUTINE SOLVE(KSTEP)
00800      COMMON V1,V2,V3,X2,X3,V1P,V2P,V3P,Y,A,B
00810      COMMON/V3DATA/V3STRT,V3STOP,ITER
00820      REAL Z(1000),LOW,X(1000)
00830      DV3=(V3STRT-V3STOP)/ITER
00840      ISTOP=ITER+1
00850      DO 1 J=1,ISTOP
00860 C      X=V3, TRIAL VALUE
00870      X(J)=V3STRT-(J-1)*DV3
00880 C      FIND CORRESPONDING V2 VALUE
00890      CALL F2(X(J),IFLAG)
00900      IF(IFLAG.GT.0)GOTO7
00910      Z(J)=V3SOLVE(X(J))
00920      GOTO1
00930 7      Z(J)=1E40
00940 1      CONTINUE
00950      LOW=-1.E40
00960      HIGH=1.E40
00970      ISET=0
00980      JSET=0
00990      DO 2 J=1,101
01000      IF(Z(J).LT.0..AND.Z(J).GT.LOW)GOTO10
01010      IF(Z(J).GT.0..AND.Z(J).LT.HIGH)GOTO20
01020      GOTO2
01030 10      ISET=J
01040      LOW=Z(J)
01050      GOTO2
01060 20      JSET=J
01070      HIGH=Z(J)
01080 2      CONTINUE
01090      IF(ISET.EQ.0.OR.JSET.EQ.0)KSTEP=10
01100      IF(ISET.EQ.0.OR.JSET.EQ.0)RETURN
01110 C      PICK UPPER AND LOWER VALUES
01120 C      AND ITERATE
01130      S0=X(ISET)
01140      S1=X(JSET)
01150      X0=MIN(S0,S1)
01160      X1=MAX(S0,S1)
01170 C      HERE BISEK3 WILL HAVE TO CALL F2
01180      CALL BISEK3(X0,X1,1E-6,KI)
01190      V3=(X1+X0)/2.
01200      RETURN
01210      END

```

APPENDIX B

COMPUTED VALUES FOR SELECTED

AXIAL RATIOS x_2/x_3

$X_2 = 300, X_3 = 200$

Y	V ₁	V ₂	V ₃	V' ₁	V' ₂	V' ₃
4.203344	0.911581	0.000001	0.088408	0.616000	0.384000	.155E-35
4.701601	0.916230	0.000001	0.083760	0.648000	0.352000	.286E-31
4.986321	0.918574	0.000001	0.081416	0.664000	0.336000	.321E-29
5.299652	0.920956	0.000001	0.079033	0.680000	0.320000	.319E-27
5.646230	0.923376	0.000003	0.076631	0.696000	0.304000	.282E-25
6.031773	0.925758	0.000005	0.074228	0.712000	0.288000	.110E-23
6.463362	0.928214	0.000009	0.071767	0.728000	0.272000	.559E-22
6.949879	0.930707	0.000016	0.069267	0.744000	0.256000	.243E-20
7.502714	0.933272	0.000030	0.066689	0.760000	0.240000	.100E-18
8.136559	0.935830	0.000053	0.064111	0.776000	0.224000	.355E-17
8.870827	0.938479	0.000096	0.061416	0.792000	0.208000	.110E-15
9.731674	0.941214	0.000173	0.058603	0.808000	0.192000	.324E-14
10.755196	0.944074	0.000318	0.055615	0.824000	0.176000	.847E-13
11.992714	0.946949	0.000569	0.052490	0.840000	0.160000	.204E-11
13.519699	0.949990	0.001044	0.048975	0.856000	0.144000	.438E-10
15.451935	0.953098	0.001884	0.045010	0.872000	0.128000	.849E-09
17.976837	0.956397	0.003429	0.040166	0.888000	0.112000	.144E-07
21.419601	0.959825	0.006095	0.034072	0.904000	0.096000	.213E-06
26.399582	0.963459	0.010623	0.025908	0.919997	0.080000	.254E-05
34.270538	0.967217	0.017100	0.015674	0.935978	0.064000	.221E-04
34.270538	0.967228	0.017163	0.015614	0.935978	0.064000	.219E-04
38.884308	0.068797	0.020293	0.010915	0.942357	0.057600	.431E-04
44.937210	0.971135	0.028832	0.000000	0.948800	0.051200	.355E-10

$$X_2 = 300, X_3 = 300$$

Y	V ₁	V ₂	V ₃	V ₁ '	V ₂ '	V ₃ '
9.283455	0.938372	0.000081	0.061539	0.800000	0.200000	.987E-22
9.849846	0.940121	0.000117	0.059754	0.810000	0.190000	.234E-20
10.481590	0.941854	0.000169	0.057969	0.820000	0.080000	.513E-19
11.190804	0.943666	0.000247	0.056079	0.830000	0.170000	.107E-17
11.992729	0.945481	0.000358	0.054154	0.840000	0.160000	.210E-16
12.906952	0.947378	0.000524	0.052106	0.850000	0.150000	.385E-15
13.958992	0.949333	0.000774	0.049901	0.860000	0.140000	.664E-14
15.182770	0.951272	0.001113	0.047609	0.870000	0.130000	.110E-12
16.624374	0.953335	0.001639	0.045019	0.880000	0.120000	.168E-11
16.624374	0.953341	0.001643	0.045010	0.880000	0.120000	.168E-11
18.348099	0.955488	0.002431	0.042087	0.890000	0.110000	.236E-10
20.446503	0.057655	0.003526	0.038826	0.900000	0.100000	.315E-09
23.057968	0.959998	0.005237	0.034758	0.910000	0.090000	.374E-08
26.399612	0.962406	0.007646	0.029955	0.920000	0.080000	.403E-07
30.833527	0.964940	0.011075	0.023992	0.930000	0.070000	.375E-06
37.016174	0.967691	0.016124	0.016192	0.939997	0.060000	.267E-05
41.133759	0.060040	0.018779	0.012178	0.944994	0.055000	.649E-05
46.291138	0.970564	0.022552	0.006878	0.949989	0.050000	.111E-04
52.967850	0.972047	0.026006	0.001952	0.954990	0.045000	.961E-05
62.027054	0.973269	0.026742	0.000000	0.960000	0.040000	.606E-10

$$X_2 = 300, X_3 = 1000$$

Y	V ₁	V ₂	V ₃	V' ₁	V' ₂	V' ₃
10.825607	0.940635	0.000104	0.059262	0.825000	0.175000	.114E-22
11.190765	0.941549	0.000127	0.058324	0.830000	0.170000	.112E-22
11.579033	0.942475	0.000152	0.057373	0.835000	0.165000	.111E-22
11.992706	0.943377	0.000182	0.056441	0.840000	0.160000	.109E-22
12.434372	0.944310	0.000220	0.055469	0.845000	0.155000	.107E-22
12.906898	0.945290	0.000270	0.054440	0.850000	0.150000	.105E-22
13.413795	0.946219	0.000325	0.053455	0.855000	0.145000	.103E-22
13.959023	0.947194	0.000394	0.052412	0.860000	0.140000	.590E-43
14.546913	0.948162	0.000474	0.051365	0.865000	0.135000	.688E-41
15.182716	0.949204	0.000579	0.050216	0.870000	0.130000	.734E-39
15.872780	0.950217	0.000701	0.049082	0.875000	0.125000	.759E-37
16.624359	0.951263	0.000856	0.047880	0.880000	0.120000	.721E-35
17.445953	0.952310	0.001035	0.046655	0.885000	0.115000	.678E-33
18.348114	0.953419	0.001269	0.045312	0.890000	0.110000	.579E-31
19.343185	0.954493	0.001529	0.043979	0.895000	0.105000	.496E-29
20.446487	0.955626	0.001866	0.042507	0.900000	0.100000	.382E-27
21.676895	0.956791	0.002280	0.040929	0.905000	0.095000	.278E-25
23.057953	0.958026	0.002826	0.039149	0.910000	0.090000	.181E-23
24.619385	0.959242	0.003448	0.037310	0.915000	0.085000	.116E-21
26.399551	0.960494	0.004207	0.035301	0.920000	0.080000	.696E-20
28.448669	0.961847	0.005246	0.032905	0.925000	0.075000	.356E-18
30.833496	0.963226	0.006494	0.030280	0.930000	0.070000	.172E-16
33.646057	0.964625	0.007974	0.027401	0.935000	0.065000	.775E-15
37.016144	0.966214	0.010128	0.023598	0.940000	0.060000	.268E-13
41.133789	0.967851	0.012965	0.019178	0.945000	0.055000	.807E-12
46.291107	0.969664	0.017030	0.013312	0.950000	0.050000	.168E-10
46.291107	0.969690	0.017163	0.013150	0.950000	0.050000	.162E-10
52.967880	0.971696	0.023250	0.005861	0.955000	0.045000	.150E-09
62.027023	0.973269	0.026742	0.000000	0.960000	0.040000	.407E-14
75.281418	0.974358	0.025668	0.000000	0.965000	0.035000	.240E-12
98.012787	0.975462	0.02457				