

Phase Behavior of Mixtures of Tetrabromobisphenol-A Polycarbonate in Solvents and Nonsolvents

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SYNOPSIS

The relative solubility and phase relationships are presented for ternary mixtures consisting of the polymer tetrabromobisphenol-A polycarbonate in three representative good solvents and nine nonsolvents. The effects of temperature, composition, compound structure, compound molecular weight, and hydroxyl concentration upon the relative solvent power of the liquid mixtures and thus upon the phase borders separating one phase from multiphase compositions are discussed. The importance of such information for the preparation of permselective membranes is emphasized. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The polymer poly[oxy-carbonyloxy(2,6-dibromo-1,4-phenylene)(1-methylethylidene)(3,5-dibromo-1,4-phenylene)], also known as tetrabromobisphenol-A polycarbonate or TBBA-PC (*Chemical Abstracts* registry number 28774-93-8), has been described as a potentially useful material for the preparation of permselective membranes, especially for the separation of gas mixtures such as oxygen and nitrogen.^{1,2} Basic solubility characteristics of the polymer established that numerous solvent and nonsolvent combinations are potentially possible for membrane preparations with TBBA-PC using the wet process phase inversion technique.³ Pertinent phase or solubility diagrams as functions of composition and temperature may be essential in guiding such work.⁴ This paper presents several such diagrams for mixtures of TBBA-PC in various combinations of three typical solvents and nine typical nonsolvents. The relative effects of composition, compound structure and molecular weight, and temperature will be emphasized here in a qualitative fashion rather than being subjected to a more complex thermodynamic analysis based upon Flory-Huggins solution theory.⁵

EXPERIMENTAL

The polymer used has been described previously.⁶ The organic liquids were used as received without further purification except for drying over Type 4A activated molecular sieves. Mixtures of various desired compositions were prepared volumetrically from individual solutions containing 1.725 wt % of each component in methylene chloride. One or two drops of the desired mixture were placed on a 22 mm square #1½ or #2 microscope cover glass. Solvent was removed quickly at about 70–100°C on a hot plate; the residue was immediately covered with another cover glass of identical size and quenched to room temperature on a large aluminum block. Depending on the components, about 20–55 different compositions were prepared for each solubility curve. Microscopic observations were made of these specimens using a Leitz Ortholux polarizing microscope equipped with phase-contrast objectives and a Heine condenser. This equipment allowed easy and rapid interchange of brightfield, darkfield, and phase-contrast illumination as well as sample observations between crossed polarizers. Observations at room temperature were made at 100–500× magnification using objective lenses of 0.25–0.70 numerical aperture. At least two slides were examined for each composition; in compositions near phase borders, six to eight specimens were examined. Specimens

were always observed in their central area; this minimized errors due to the possible presence of moisture and/or evaporation of components. Samples for elevated temperature observations were prepared by removing the methylene chloride solvent and immediate quenching to room temperature followed by insertion into a Mettler FP80/FP82 hot stage maintained at the desired temperature. No birefringence indicative of crystallinity or another form of order was noted for any sample when it was observed between crossed polarizers.

RESULTS AND DISCUSSION

A typical experimental solubility diagram containing data points for individual compositions is shown in

Figure 1 for mixtures of TBBA-PC, 1-methyl-2-pyrrolidinone (NMP) solvent, and triethylene glycol (TEG) nonsolvent at room temperature. The open circles represent mixtures consisting of only one phase; these areas are labeled "1." The dark-shaded circles represent mixtures consisting of more than one phase, i.e., multiphase; these areas are labeled "M." Partially shaded circles indicate mixtures with borderline or indistinct phase behavior in which some slides appeared to consist of one phase, while others, of more than one phase; the degree of shading is roughly in proportion to the number of slides of each kind that was observed. The lines drawn to represent phase borders should be considered to be approximate only, nor are they meant to represent precise equilibrium conditions. They do not indicate the experimental error that includes optical reso-

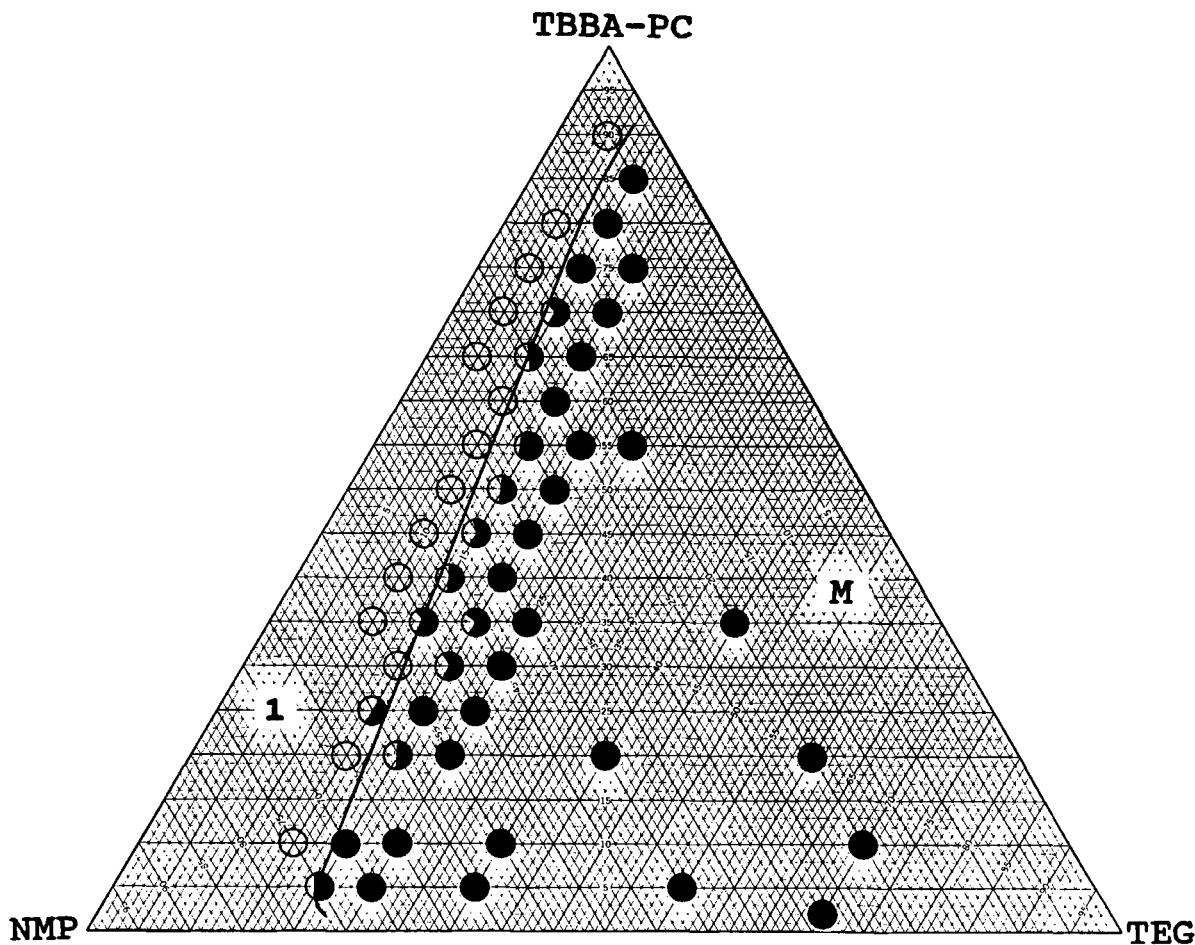


Figure 1 Solubility behavior of mixtures of TBBA-PC, NMP solvent, and TEG nonsolvent at room temperature.

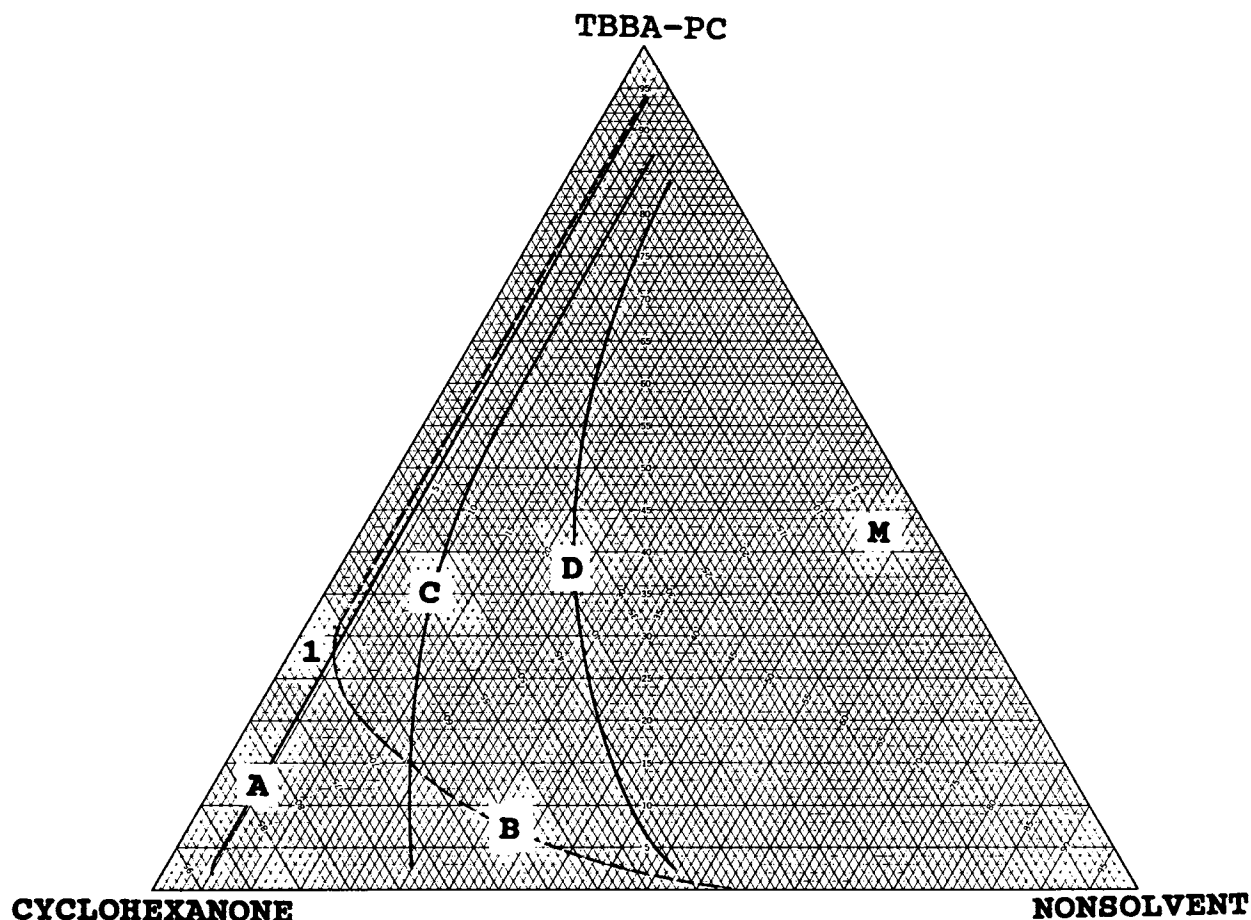


Figure 2 Composite diagram of the solubility behavior of mixtures of TBBA-PC, cyclohexanone solvent, and (A) TEG, (B) hexadecane, (C) dodecane, and (D) diethylene glycol dibutyl ether nonsolvents at room temperature.

lution, operator judgment, and composition reproducibility. Higher precision would require, among other things, the examination of a larger number of various compositions, especially those near the phase-transition regions. The present precision is sufficient for differentiating among and selecting of various membrane spinning compositions. The effects of the kinetics of phase transformations can be important in membrane formation, but they are not rigorously addressed by the present experimental technique. Figures 2-7 are composite diagrams in which the individual experimental points have been deliberately omitted to enhance clarity of presentation. For membrane preparative operations, only those compositions containing intermediate concentrations of polymer are usually of importance, e.g., in the range of about 25-65% polymer. Those

containing higher concentrations are more difficult to prepare and handle and may require excessively high temperatures to spin because of the higher viscosities. Those mixtures containing lower concentrations of polymer may require lower spinning speeds and lower temperatures and are harder to fabricate into a fiber with sufficient integrity for handling. Flat-sheet membrane preparations or coating operations may employ compositions lower in polymer concentration. Comparisons for the present work will be essentially limited to the middle concentration ranges.

It is known that a number of variables can affect the phase behavior of certain polymers, e.g., cellulose triacetate and polyamides, in liquid mixtures used for preparing membranes; these include the chemical structure and composition of the solvent-nonsolvent

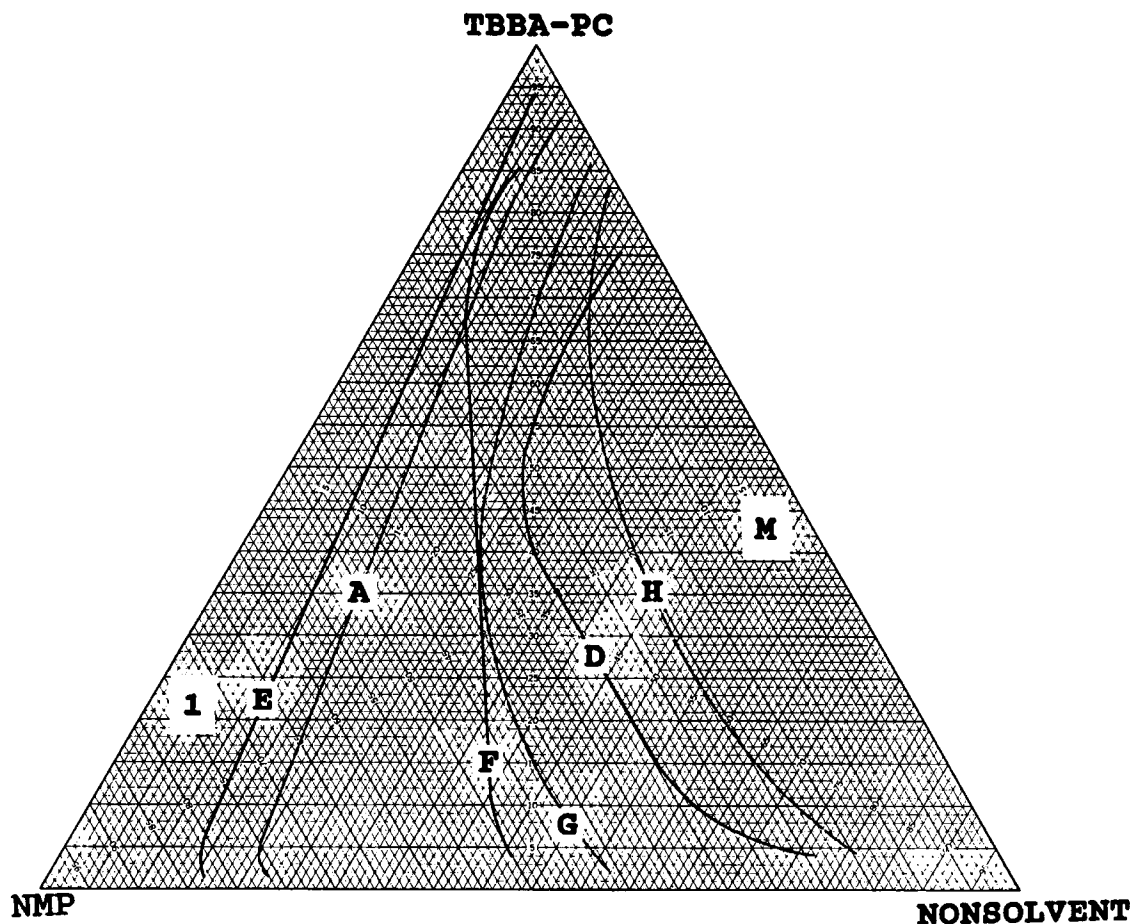


Figure 3 Composite diagram of the solubility behavior of mixtures of TBBA-PC, NMP solvent, and (E) DEG, (A) TEG, (F) PEG 1450, (G) PEG 400, (D) diethylene glycol dibutyl ether, and (H) 2-ethoxyethanol nonsolvents at room temperature.

mixture, the polymer concentration, and the temperature.^{3,7} This is also true for TBBA-PC mixtures. Figure 2 shows room-temperature solubility curves for mixtures containing cyclohexanone solvent and four nonsolvents: TEG, diethylene glycol dibutyl ether (commonly known as butyl diglyme), dodecane, and hexadecane. Hydrocarbons and alcohols are nonsolvents for the polymer. Hexadecane (mol. wt. 226) is a better nonsolvent (poorer solvent) for the polymer than is the lower molecular weight hydrocarbon dodecane (mol. wt. 170); this behavior difference cannot be readily explained by their solubility parameters that differ by only about 0.3 MPa^{1/2}.⁸ TEG, which has the lowest molecular weight of the four nonsolvents, 150, has about the same nonsolvent behavior as does hexadecane. The

two hydroxyl groups that account for a relatively large portion of the molecular weight (about 23%) are responsible for its effectiveness as a nonsolvent. Butyl diglyme is the least effective nonsolvent shown even though its molecular weight, 218, is the largest; the butyl groups compose over one-half of the molecular weight of this molecule. By contrast, the analogous compound bis(2-methoxyethyl)ether (diglyme) is a good solvent for TBBA-PC, as are tri- and tetraethylene glycol dimethyl ethers. The subtle and combined effects of molecular weight, hydroxyl concentration, and structure on solvent/nonsolvent ability are apparent here.

Figure 3 is a similar composite of room temperature solubility diagrams for mixtures of polymer, NMP solvent, and six nonsolvents: diethylene glycol

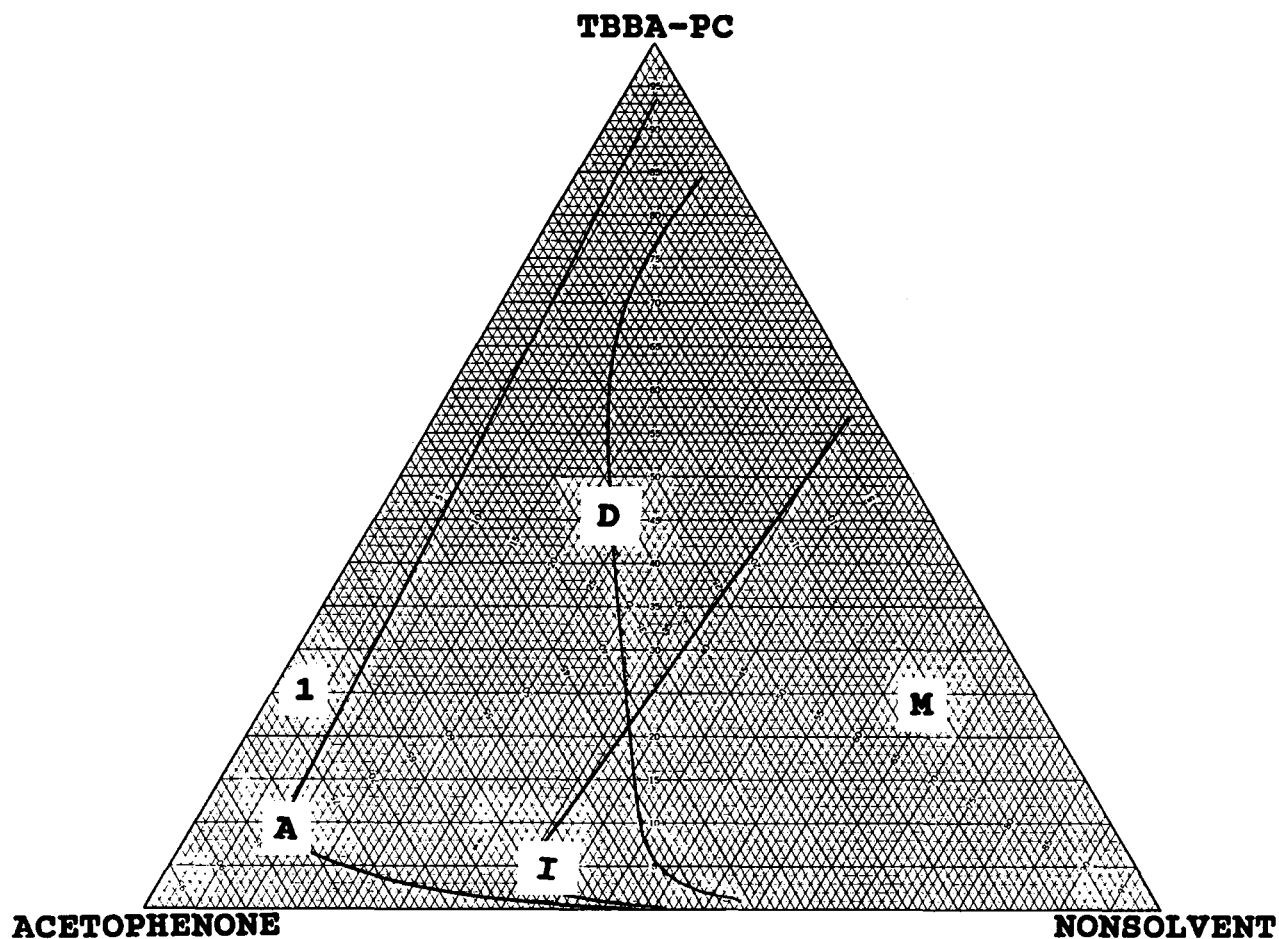


Figure 4 Composite diagram of the solubility behavior of mixtures of TBBA-PC, acetophenone solvent, and (A) TEG, (D) diethylene glycol dibutyl ether, and (I) dioctyl phthalate nonsolvents at room temperature.

(DEG), TEG, polyethylene glycols PEG 400 and PEG 1450, butyl diglyme, and 2-ethoxyethanol. Similar effects of nonsolvent are shown using NMP solvent as were noted above with cyclohexanone. DEG, which is the lowest molecular weight glycol and which contains the highest concentration of hydroxyl groups, is the best nonsolvent of the six compounds shown. Increasing the molecular weight of the glycol, i.e., TEG and PEG 400, progressively dilutes the concentration of OH groups and results in decreasing nonsolvent effectiveness. By further increasing the glycol molecular weight, one might expect that the compound would become a better nonsolvent. This is not observed to occur in this molecular weight range; it is evident that the concentration of OH groups is of greater effectiveness in determining the solvent-nonsolvent behavior than is the glycol molecular weight. A further in-

crease in glycol molecular weight with an accompanying decrease in OH concentration, i.e., PEG 1450, does not further decrease the nonsolvent power of the glycol; PEG 400 and PEG 1450 have about the same nonsolvent power. It appears that the OH groups have been sufficiently diluted so that the molecular weight of the glycol becomes dominant. A further increase in glycol molecular weight might be expected to move the phase line further to the left, i.e., reflecting better nonsolvent ability. The effect of dilution of the OH group concentration is further shown by DEG, butyl diglyme, and 2-ethoxyethanol. Replacement of one OH group in DEG by a hydrogen atom results in the compound 2-ethoxyethanol that has a comparable molecular weight but only about one-half the concentration of OH groups. This results in 2-ethoxyethanol being a much poorer nonsolvent than is DEG. Butyl diglyme is intermediate

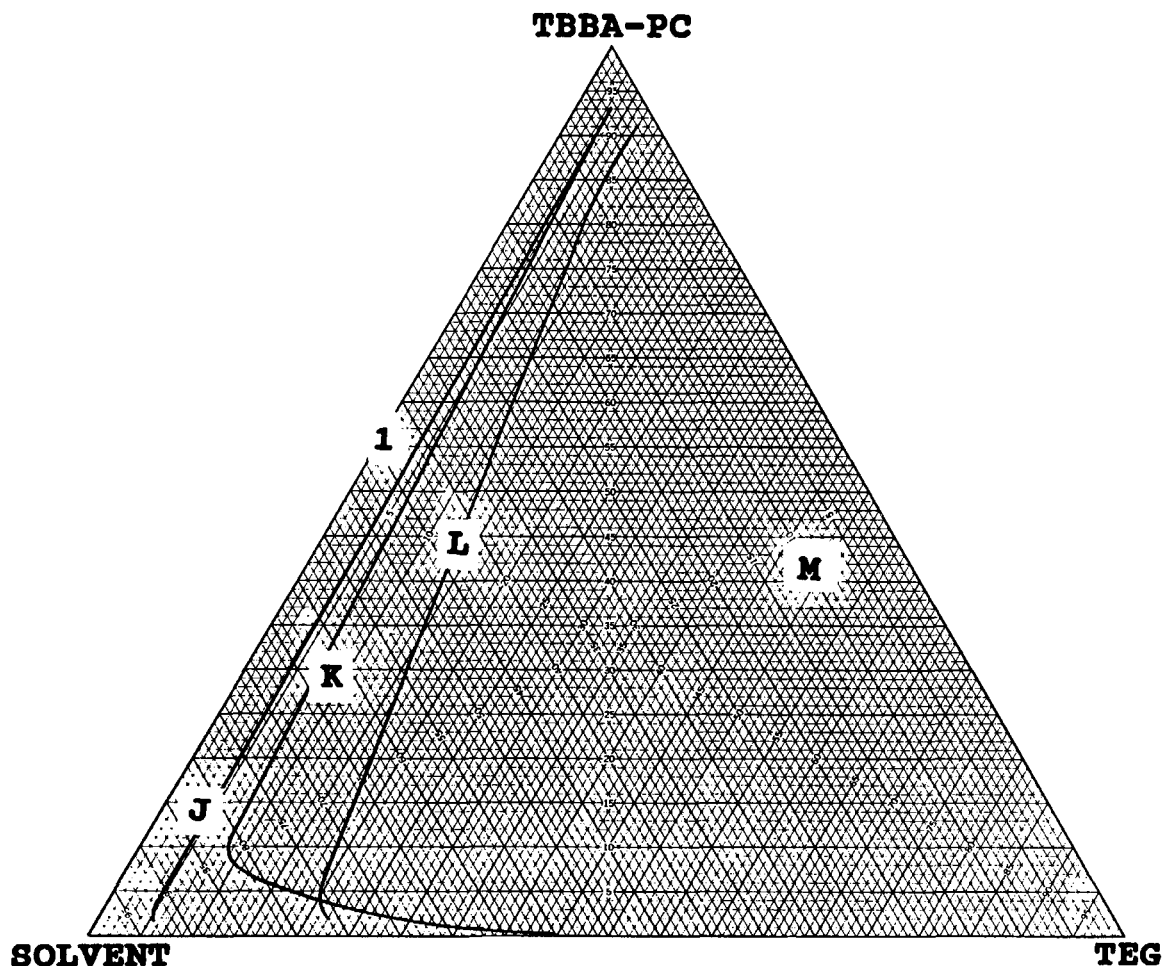


Figure 5 Composite diagram of the solubility behavior of mixtures of TBBA-PC, TEG nonsolvent, and (J) cyclohexanone, (K) acetophenone, and (L) NMP solvents at room temperature.

in effectiveness as a nonsolvent between DEG and 2-ethoxyethanol; here the lack of any OH groups tends to move the phase line to the right, but the increase molecular weight and hydrocarbonlike butyl groups have the opposite and apparently more dominant effect. The presence of water being the ultimate nonsolvent must be carefully excluded or controlled for reproducible results.

Figure 4 is a composite diagram showing the effects of three nonsolvents on the room-temperature behavior of mixtures of polymer and acetophenone solvent. Nonsolvent power decreases in the following order: TEG > butyl diglyme > dioctyl phthalate (DOP). This figure shows that the solubility of polymer in DOP is less than about 1–2%; this is consistent with its observed solubility of less than about 4.7% polymer at room temperature and at

100°C. The relatively large composition area of one phase behavior shown in this figure suggests that DOP may be a better solvent than reported from common solubility measurements that measure the solubility of *polymer in liquid*. However, normal solubility measurements do not record the solubility of *liquid in polymer*, which appears here to be about 40%. TBBA-PC is not significantly soluble in DOP, but DOP is significantly soluble as a plasticizer in the polymer.

The relative solvent powers of NMP, cyclohexanone, and acetophenone in the presence of TEG and butyl diglyme at room temperature are shown in Figures 5 and 6, respectively. In both cases, the order of relative solvent ability is NMP > acetophenone > cyclohexanone.

The effect of temperature in changing the solution

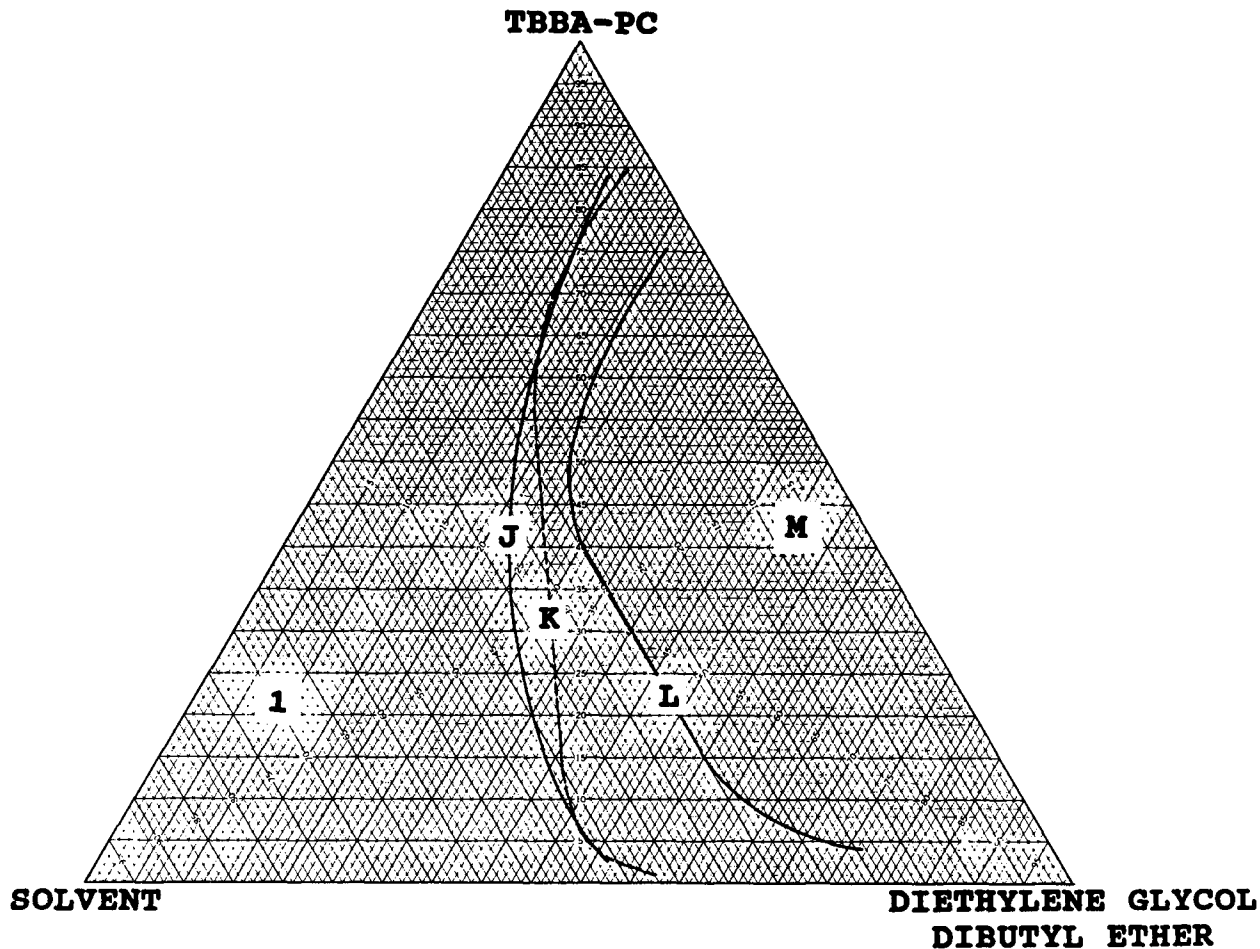


Figure 6 Composite diagram of the solubility behavior of mixtures of TBBA-PC, diethylene glycol dibutyl ether nonsolvent, and (J) cyclohexanone, (K) acetophenone, and (L) NMP solvents at room temperature.

behavior of mixtures of NMP solvent and TEG nonsolvent is shown in Figure 7. The data are for mixtures at room temperature and at 100°C consisting of 25–75% polymer. These are the approximate concentration ranges of interest for many membrane preparations. Increasing temperature increases the one-phase region significantly.

CONCLUSIONS

This work shows the large variation in solubility and phasic behavior that may be expected upon making relatively minor changes in the composition

and the temperature for ternary mixtures of TBBA-PC and various solvents and nonsolvents. This knowledge plus the identification of numerous solvent and nonsolvent compounds together with the options of membrane preparation from one-phase isotropic or multiphase mixtures offer the membrane specialist a large range of synthetic choices. Opportunities for varying the ultimate membrane properties can also be reasonably expected as a result. The determination of phase diagrams for potential membrane spinning mixtures at room temperature and at least one elevated temperature can thus prove to be helpful and should be made before extensive fabrication operations are undertaken.

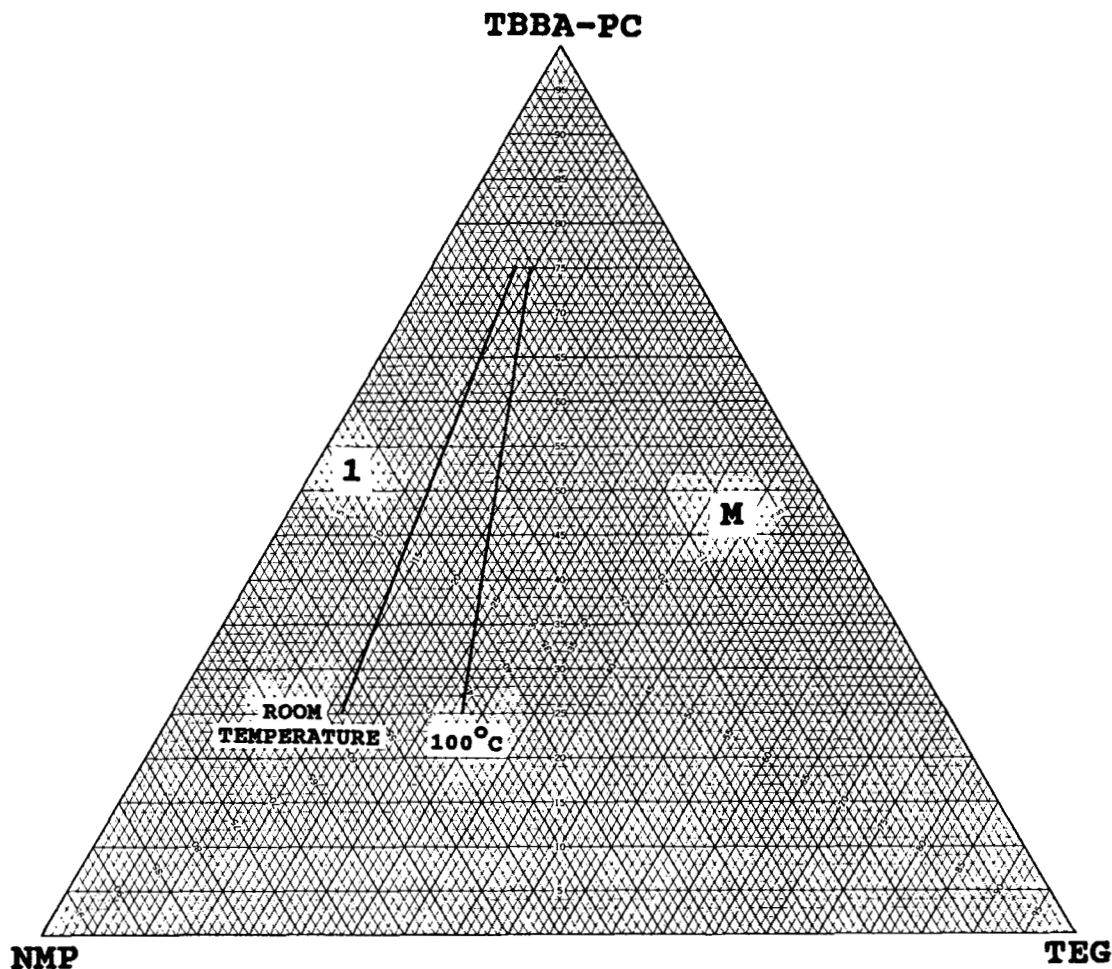


Figure 7 Composite diagram of the solubility behavior of mixtures of TBBA-PC, NMP solvent, and TEG nonsolvent at room temperature and at 100°C.

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