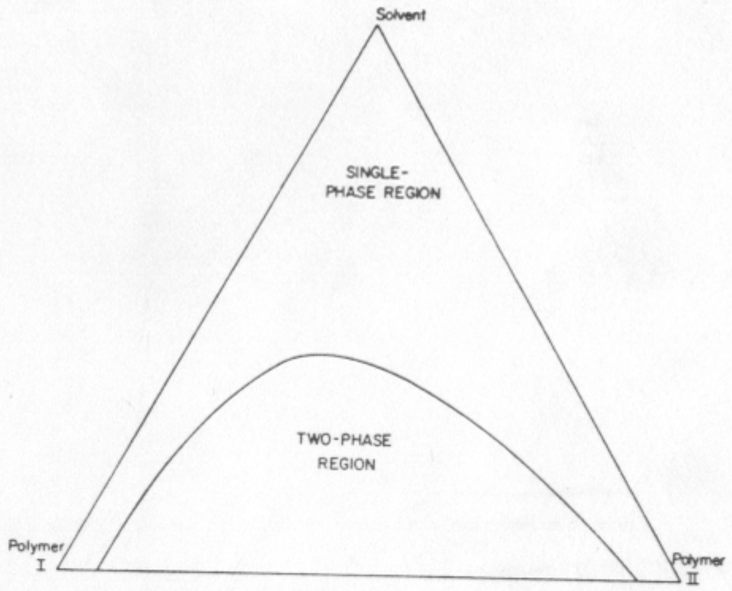


Fig. 4a

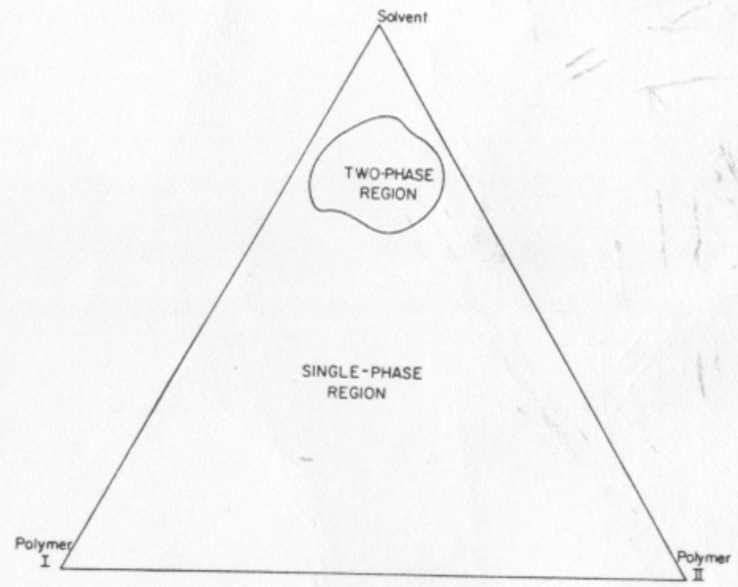
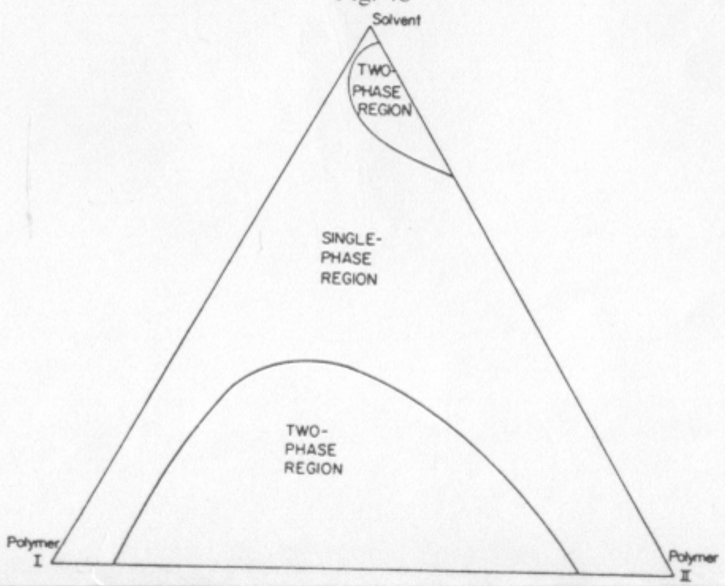


Fig. 4b



Scott [58] and Tompa [59] were the first to apply the Flory [60, 61]–Huggins [62, 63] theory of polymer solutions to mixtures of polymers, with or without added solvent. Scott [58] obtained essentially the following expression for the Gibbs free energy of mixing a total volume V of two polymers:

$$\Delta G_{mix} = (RTV/V_r)[(\phi_A/x_A)\ln\phi_A + (\phi_B/x_B)\ln\phi_B + \chi_{AB}\phi_A\phi_B] \quad (1)$$

where V_r is a reference volume which is taken as close to the molar volume of the smallest polymer repeat unit as possible, ϕ_A and ϕ_B are the volume fractions of polymers A and B, respectively, x_A and x_B are the degrees of polymerization of polymer A and polymer B in terms of the reference volume V_r, respectively, and χ_{AB} is related to the enthalpy of interaction of the polymer repeat units, each of molar volume V_r (see Eq. 12).

Scott found the critical conditions in such a system; these can be found from Eq. (1) by letting [3] (at constant T and p)

$$\partial^2 \Delta G_{mix}/\partial\phi_A{}^2 = \partial^3 \Delta G_{mix}/\partial\phi_A{}^3 = 0 \quad (2)$$

The critical conditions are

$$(\chi_{AB})_{cr} = \tfrac{1}{2}[1/x_A^{1/2} + 1/x_B^{1/2}]^2 \quad (3a)$$

$$(\phi_A)_{cr} = \frac{x_B^{1/2}}{x_A^{1/2} + x_B^{1/2}} \quad (3b)$$

$$(\phi_B)_{cr} = \frac{x_A^{1/2}}{x_A^{1/2} + x_B^{1/2}} \quad (3c)$$

Scott noted, using these equations, that $(\chi_{AB})_{cr}$ would be very small for two polymers having appreciable degrees of polymerization, and that polymers of infinite molecular weight would be incompatible if there were any positive heat of mixing at all.

The equation for the spinodal (at constant T and p) is calculated from

$$\partial^2 \Delta G_{mix}/\partial\phi_A{}^2 = 0 \quad (4)$$

and is equal to

$$(\chi_{AB})_{sp} = \tfrac{1}{2}[1/x_A(\phi_A)_{sp} + 1/x_B(\phi_B)_{sp}] \quad (5)$$

Fig. 4 Phase diagrams for Polymer I–Polymer II–solvent mixtures. (a) Polymers are incompatible in bulk but each is miscible with the solvent, such as polystyrene–polypropylene–toluene [55]. (b) Components are miscible in all proportions when taken two at a time but phase separation occurs at some compositions when all three components are mixed, such as benzene–butyl rubber–EPDM rubber or diphenyl ether–atactic polypropylene–polyethylene [52]. (c) Phase diagram that may be observed when polymers are incompatible in bulk and only one of the polymers is miscible with solvent in all proportions [56].

The equations for the binodal are calculated by setting the chemical potential of both polymer A and polymer B equal in the two coexisting phases.

Using primes to designate one phase, and double primes the other phase, the binodal equations for a mixture of two polymers are

$$\ln \phi_A' + (1 - x_A/x_B)\phi_B' + x_A \chi_{AB}(\phi_B')^2 = \ln \phi_A'' + (1 - x_A/x_B)\phi_B'' + x_A \chi_{AB}(\phi_B'')^2 \quad (6a)$$

$$\ln \phi_B' + (1 - x_B/x_A)\phi_A' + x_B \chi_{AB}(\phi_A')^2 = \ln \phi_B'' + (1 - x_B/x_A)\phi_A'' + x_B \chi_{AB}(\phi_A'')^2 \quad (6b)$$

All equations for binodals contain a mix of logarithmic and nonlogarithmic terms and the number of equations to be solved simultaneously equals the number of components times the number of coexisting phases minus one. (The maximum number of coexisting phases that are not vapor or crystalline expected at any temperature and pressure equals the number of components in the mixture.) For this reason, equations for binodals are very difficult to solve even with a computer, and very few such equations are given in this chapter.

Scott [58] also discussed mixtures of two polymers in the presence of a solvent—a three-component mixture. He obtained equations that led to a Gibbs free energy of mixing

$$\Delta G_{mix} = RTV/V_S[\phi_S \ln \phi_S + (\phi_A/x_A) \ln \phi_A + (\phi_B/x_B) \ln \phi_B + \chi_{AB}\phi_A\phi_B + \chi_{AS}\phi_A\phi_S + \chi_{BS}\phi_B\phi_S] \quad (7)$$

where V_S, the reference volume, is equal to the molar volume of the solvent, and x_A, χ_{AB}, χ_{AS}, and χ_{BS} must be considered in terms of reference volume V_S; χ_{AS} and χ_{BS} are the interaction parameters between polymers A and B, respectively, and the solvent. The equation for the spinodal in a three-component system is [3]

$$(\partial^2 \Delta G_{mix}/\partial \phi_A^2)(\partial^2 \Delta G_{mix}/\partial \phi_B^2) = (\partial^2 \Delta G_{mix}/\partial \phi_A\, \partial \phi_B)^2 \quad (8)$$

leading to a complex equation that has been discussed by Tompa [3].

Scott [58] calculated some binodals for special cases; one example is that in which $\chi_{AS} = \chi_{BS}$ and $x = x_A = x_B$, that is, the case in which polymers of comparable degree of polymerization are dissolved in a solvent that has the same interaction parameter with each of the two polymers. Scott called this the "symmetrical" case. He found an equation for the binodal:

$$\ln \theta_A' + x\chi_{AB}(1 - \phi_S)(\theta_B')^2 = \ln \theta_B' + x\chi_{AB}(1 - \phi_S)(\theta_A')^2 \quad (9)$$

where $\theta_A = \phi_A/(\phi_A + \phi_B)$ and $\theta_B = \phi_B/(\phi_A + \phi_B)$. Equation (9) looks exactly like Eqs. (6a) and (6c) when both polymers have the same degree of polymerization, $x = x_A = x_B$, that is,

$$\ln \phi_A' + x\chi_{AB}(\phi_B')^2 = \ln \phi_B' + x\chi_{AB}(\phi_A')^2 \quad (10)$$

except that in Eq. (9) $\chi_{AB}(1 - \phi_S)$ takes the place of χ_{AB} in Eq. (10); θ_A and θ_B refer to relative volume fractions of polymers A and B in the polymer portion of the three-component mixture, and are therefore exactly analogous to ϕ_A and ϕ_B in the binary mixture.

Scott noted that the binodal Eq. (9) in the symmetrical case, did not depend on χ_{AS} or χ_{BS} and that the presence of solvent served only to diminish the effective interaction parameter between the polymers, that is, $\chi_{AB}(1 - \phi_S)$ can be considered the effective interaction parameter between the polymers in this case. When there is a great deal of solvent present, that is, when $\phi_S \simeq 1$, the effective interaction parameter between the two polymers approaches zero, and the whole system will form a single phase. These conclusions can be restated as follows: *No matter how incompatible two polymers may be, it is always possible to make a very dilute solution containing both polymers, as long as a solvent that dissolves both polymers exists.* For this reason it is possible to obtain light-scattering data on very dilute solutions of polymer mixtures, even for polymers that are very incompatible in the absence of solvent.

Scott used the exact result he calculated for the symmetrical case to reach some approximate general conclusions for all polymer–polymer–solvent systems. He calculated an approximate plait point, which is analogous to the critical point in binary mixtures of polymers:

$$(\chi_{AB})_{pl} = \tfrac{1}{2}\{1/x_A^{1/2} + 1/x_B^{1/2}\}^2\{1/1 - \phi_S\} \quad (11a)$$

$$(\theta_A)_{pl} = x_A^{1/2}/(x_A^{1/2} + x_B^{1/2}) \quad (11b)$$

$$(\theta_B)_{pl} = x_B^{1/2}/(x_A^{1/2} + x_B^{1/2}) \quad (11c)$$

These equations are exactly like Eqs. (3a)–(3c) if we remember that θ_A and θ_B are volume fractions of polymer A and B in the polymer portion of the mixture, and if we use $\chi_{AB}(1 - \phi_S)$ as the effective interaction parameter between the polymers in the presence of solvent. Equations (11a)–(11c) allow calculation of the minimum volume fraction of solvent necessary to "compatibilize" the two polymers, that is, the minimum volume fraction necessary to form a single-phase solution; this minimum volume fraction of solvent will depend on the degree of polymerization of each polymer and on the interaction parameter between the polymers. Equations (11a)–(11c) indicate that the same minimum volume fraction of any solvent that dissolves each polymer separately will give a single phase in the three-component system. This prediction is not strictly true, as we shall see below, but it serves as a reasonably accurate rule for most systems.

Since the advent of high-speed computers, it is no longer necessary to consider only the symmetrical case $\chi_{AS} = \chi_{BS}$, and several workers have taken advantage of this. Zeman and Patterson [64] calculated spinodals for systems where $\chi_{AS} \neq \chi_{BS}$ and actually predicted phase diagrams like Fig. 4b.