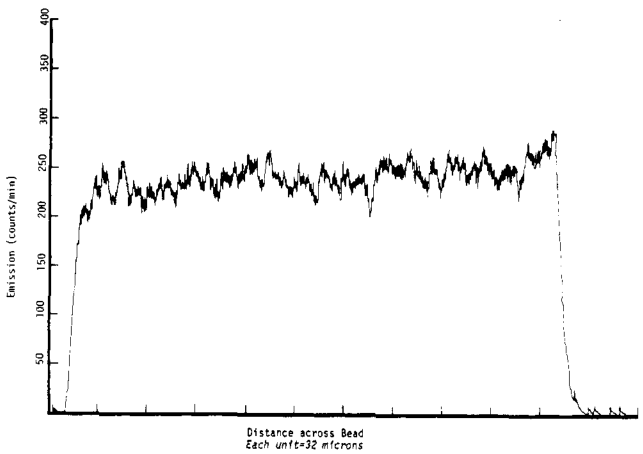

Figure 1. Phosphorous spectrum of phosphinated copolymer.

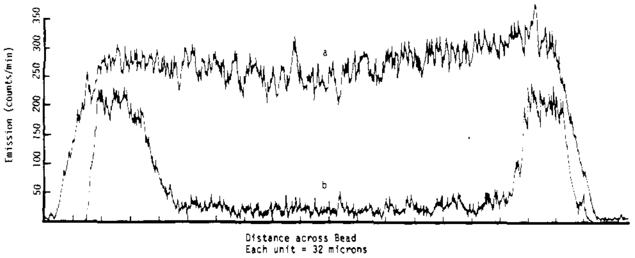

Figure 2. (a) Rhodium microprobe spectrum of Rh(I)-attached complex from $(Ph_3P)_3ClRh$. (b) Rhodium spectrum of Rh(I)-attached complex from deficiency of $[Rh(COE)_2Cl]_2$.

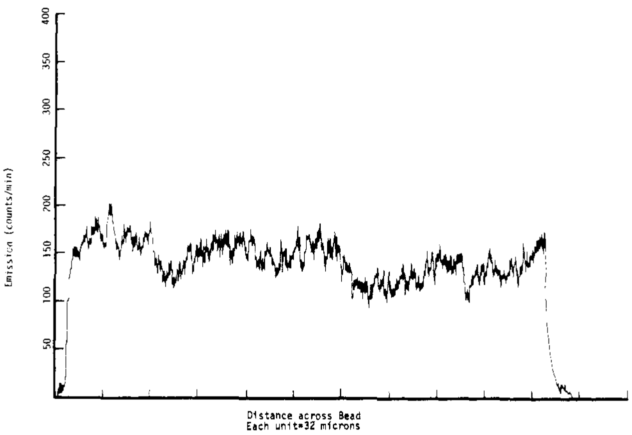

Figure 3. Rhodium spectrum from Rh(I)-attached complex from excess $[Rh(COE)_2Cl]_2$.

(to itself) as a function of position within the bead. Relative density comparison between elements, *i.e.*, Rh, P, and Cl, was not attempted. Direct comparison of X-ray intensities between elements is not a valid indication of their relative densities.

Beads were scanned by moving the stage at constant speed on a path corresponding to a diameter across the bead.[7] X-Ray intensities were recorded on the *Y* axis of an *X–Y* recorder driven at constant speed. Thus distance on the chart is directly related to the distance across the bead, and the relative elemental density can be determined as a function of distance from the edge of the bead.

Results and Discussion

A sample of 2% divinylbenzenepolystyrene beads (30–80 mesh μ) was chloromethylated by the procedure of Pepper and Paisley.[8] A portion of these beads, containing 0.67 mequiv Cl/g was phosphinated with lithiodiphenylphosphine.[2] These phosphinated beads were then equilibrated with chlorobis(cyclooctene)rhodium(I) dimer or chlorotris(triphenylphosphine)rhodium(I) under the conditions presented in Table I. After removal of the nonattached complex the samples were dried and then shown to be active hydrogenation catalysts. Random beads were selected from the phosphinated and the three samples of Rh(I)-attached copolymer. Individual beads were imbeded in epoxy and sectioned with a microtome. The cross sections of the beads were examined under a microscope for major surface flaws and to check the centering of the cut. Each of the four samples was subjected to electron microprobe analysis. Plots of X-ray emission *vs.* distance across the cross section are presented in Figures 1–3. Since good standards for each of the elements in a representative matrix were difficult to obtain, and the only interest at this stage of analysis was the relative distribution within each bead, the spectra were not corrected or normalized.

Figure 1 shows that the reaction of the bulky, ionic lithiodiphenylphosphine with the chloromethyl groups proceeds throughout the polymer bead and gave a smooth distribution of phosphine groups across the cross section.

The metal distribution could be controlled by the choice of conditions used in the attachment reaction. When the attached catalysts were prepared by ligand substitution, using a deficiency of the complex, the metal was distributed in the first 180 μ of the polymer bead with no metal in the center of the bead. Using an excess of either Rh(I) complex gave an attached catalyst which showed a distribution of rhodium which was similar to the distribution of the phosphine.

These results confirm the earlier assumptions concerning the metal distribution in the polymer and demonstrate that the reactions of the catalyst must be occurring within the polymer matrix.[2]

Experiments to determine the change in catalytic properties with metal distribution are now in progress.

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The Limiting Critical Behavior in Polymer Solutions at Infinite Chain Length

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Kennedy[1] has studied the chain-length dependence of the critical point in strictly binary polymer solutions obeying a generalized Flory–Huggins relation[2] for the free energy of mixing

$$\Delta G_M/RT \equiv G = (1 - \phi)\ln(1 - \phi) + \phi m^{-1}\ln\phi + \Gamma(\phi, T) \qquad (1)$$

where ϕ is the volume fraction of polymer, m is the number of "monomer" units per chain (the ratio of molar volumes of polymer and solvent), and the function Γ is specified initially only to the extent that it is not dependent on m or pressure. Kennedy concludes that if a critical point (critical composition ϕ_c, critical temperature T_c) exists at $\phi = 0$, it can only be as $m \rightarrow \infty$ and, further, that at the limit

$$\lim_{\phi_c \rightarrow 0} (\mathrm{d}T_c/\mathrm{d}\phi_c) = 0 \qquad (2)$$

A practical consequence of eq 2 is to put into question certain extrapolations of experimental critical temperatures to obtain the limiting T_c for infinite m (*i.e.*, the Θ temperature[2]). For an upper critical separation, $\mathrm{d}T_c/\mathrm{d}\phi_c$ is always found to be negative in the experimentally accessible range, and the limiting T_c might therefore be overestimated. However, we contend that eq 2 is incorrect, as we propose to demonstrate in the following.

Kennedy's procedure is a standard one[3] of differentiating G four times with respect to ϕ

$$G' = -\ln(1 - \phi) - 1 + m^{-1} + (\ln\phi)/m + \Gamma' \qquad (3)$$

$$G'' = (1 - \phi)^{-1} + (m\phi)^{-1} + \Gamma'' \qquad (4)$$

$$G''' = (1 - \phi)^{-2} - (m\phi^2)^{-1} + \Gamma''' \qquad (5)$$

$$G'''' = 2(1 - \phi)^{-3} + 2(m\phi^3)^{-1} + \Gamma'''' \qquad (6)$$

and imposing the conditions for a critical point: *i.e.*, the condition for the spinodal

$$G'' = 0 \qquad (7)$$

the additional condition for a critical point

$$G''' = 0 \qquad (8)$$

and the stability criterion

$$G'''' > 0 \qquad (9)$$

By straightforward manipulations of $G''(T,\phi,m)$ and $G'''(T,\phi,m)$ Kennedy derives, without approximation

$$-\left(\frac{\partial T}{\partial\phi}\right)_{G'',G'''} = \frac{[2/(1 - \phi)^3] + [2/m\phi^3] + \Gamma''''}{(1/\phi)(\partial\Gamma''/\partial T)_{\phi,m} + (\partial\Gamma'''/\partial T)_{\phi,m}} \qquad (10)$$

Kennedy interprets eq 9 as requiring G'''' to be everywhere finite. It follows from this that $(m\phi^3)^{-1}$ is always finite, that the numerator of the right-hand side of eq 10 is finite, and hence that eq 2 holds as $\phi_c \rightarrow 0$ and $m \rightarrow \infty$.

In taking a different approach to the limiting behavior of the critical point, we note that the troublesome indeterminate forms in G and its derivatives at the limit arise from the circumstance that the total derivative of the free energy of mixing with respect to composition ϕ is essentially the difference of chemical potentials of solute and solvent, and as $\phi \rightarrow 0$, the solute potential necessarily varies as $\ln\phi$. Since the potentials in a two-component system are related by the Gibbs–Duhem equation, the derivatives of either individually contain equivalent information, and it should therefore be possible to avoid any ambiguity associated with the limiting process discussed by Kennedy by dealing directly with the solvent potential μ_1, which is well behaved at $\phi = 0$. Accordingly we take as our starting point, the logarithm of the solvent activity[2] corresponding to eq 1

$$\mu \equiv (\mu_1 - \mu_1^0)/RT = \ln(1 - \phi) + (1 - m^{-1})\phi + \Psi(\phi, T) \qquad (11)$$

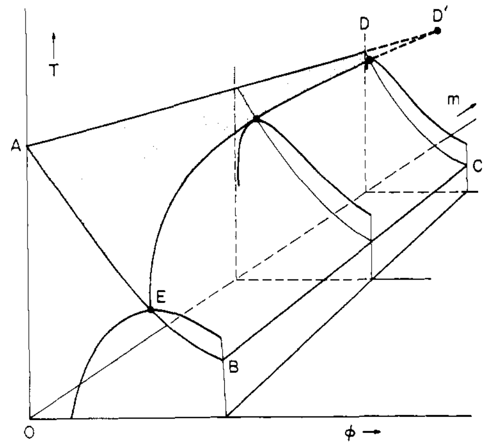

Figure 1. Schematic representation of the surface $\mu''(T,\phi,m) = 0$ and the locus (line ED') of critical points. Three spinodals are shown with their maxima intersecting ED'.

where

$$\Psi = \Gamma - \phi\Gamma' \qquad (12)$$

Now the critical conditions[3-5] are obtained from the first three derivatives of μ with respect to ϕ

$$\mu' = -(1 - \phi)^{-1} + 1 - m^{-1} + \Psi' \qquad (13)$$

$$\mu'' = -(1 - \phi)^{-2} + \Psi'' \qquad (14)$$

$$\mu''' = -2(1 - \phi)^{-3} + \Psi''' \qquad (15)$$

by requiring

$$\mu' = 0 \qquad (16)$$

for the spinodal, together with

$$\mu'' = 0 \qquad (17)$$

$$\mu''' < 0 \qquad (18)$$

The equivalence (apart from behavior as $\phi \rightarrow 0$) of eq 7 and 16 is confirmed by dividing the right-hand side of eq 13 by ϕ and combining two terms. Equations 8 and 17 do not define the same surface in T,ϕ,m space, but the two surfaces must cut the spinodal surface in a common line defining the locus of critical points.

A schematic drawing is shown as Figure 1. The surface ABCD is part of the surface $\mu'' = 0$. The maxima of the spinodal curves, $\mu'(\phi,T) = 0$ at constant m, define ED' the line of critical points traced on ABCD. Equations 16 to 18 afford critical conditions in particularly simple form: the chain length m does not appear in derivatives of μ beyond the first, and if the derivatives of Ψ are well behaved, there are no potentially divergent terms to contend with at $\phi = 0$. The nondependence of μ'' on m means that cross sections through the surface $\mu'' = 0$ (or any surface of constant μ'') at fixed m are the same for all m. Consequently, the projection of ED' on the T,ϕ coordinate plane is just AE, and $\mathrm{d}T/\mathrm{d}\phi$ along the critical line can be had directly from eq 14. We can write

$$\left(\frac{\partial T}{\partial\phi}\right)_{\mu',\mu''} = \left(\frac{\partial T}{\partial\phi}\right)_{\mu'',\mathrm{m}} = -\frac{(\partial\mu''/\partial\phi)_T}{(\partial\mu''/\partial T)_\phi} = \left[\frac{2}{(1 - \phi)^3} - \Psi'''\right] \Bigg/ \left(\frac{\partial\Psi''}{\partial T}\right)_\phi \qquad (19)$$

If there is a critical point at $\phi = 0$, it follows that

$$\lim_{\phi_c \rightarrow 0}\left(\frac{\mathrm{d}T_c}{\mathrm{d}\phi_c}\right) = \left[(2 - \Psi''') \Big/ \frac{\partial\Psi''}{\partial T}\right]_{\phi=0} \qquad (20)$$

and there is no basis for expecting the right-hand side of this expression to vanish at the limit.

For concreteness we suppose that

$$\Psi = \chi_1\phi^2 + \chi_2\phi^3 + O(\phi^4) \tag{21}$$

where the coefficients χ_i are functions of temperature alone. This is equivalent to assuming the validity of a virial expansion of the chemical potential

$$-(\mu_1 - \mu_1^0)/RT = \frac{\phi}{m} + (\tfrac{1}{2} - \chi_1)\phi^2 + (\tfrac{1}{3} - \chi_2)\phi^3 + \dots \tag{22}$$

where the coefficients of ϕ^2 and ϕ^3 are the second and third virial coefficients. Then as $\phi \rightarrow 0$, eq 17 and 18 are satisfied if

$$\chi_1 = \tfrac{1}{2} \tag{23}$$

$$\chi_2 < \tfrac{1}{3} \tag{24}$$

and eq 20 becomes

$$\lim_{\phi_c \to 0}\left(\frac{dT_c}{d\phi_c}\right) = (1 - 3\chi_2)\Big/\frac{d\chi_1}{dT} \tag{25}$$

We remark that the simple form of the Flory–Huggins theory[2] corresponds to a special case of eq 21 with $\chi_i = 0$ for $i \geq 2$. Assuming a temperature dependence

$$\chi_1 = \beta_0 + \beta_1/T \tag{26}$$

with β_0 and β_1 positive constants, which implies merely the resolution of the free energy quantity $RT\chi_1$ into entropic and enthalpic components in the region of an upper critical separation, we have for this case a result

$$\lim_{\phi_c \to 0}(dT_c/d\phi_c) = -T^2/\beta_1 \tag{27}$$

that unequivocally contradicts eq 2. Furthermore, if eq 16 to 18 and the succeeding development are beyond question, eq 27 effectively refutes the corollary of eq 2 that would deem the classical Flory–Huggins model thermodynamically inadmissible.

Continuing with Ψ described by the single χ parameter, we can easily see what is needed to resolve the discrepancy. We have

$$\Gamma = \chi_1\phi(1 - \phi) \tag{28}$$

whence

$$\Gamma'' = -2\chi_1 \tag{29}$$

$$\Gamma''' = \Gamma'''' = 0 \tag{30}$$

and the critical conditions of eq 7 to 9 reduce to

$$(1 - \phi)^{-1} + (m\phi)^{-1} - 2\chi_1 = 0 \tag{31}$$

$$(1 - \phi)^{-2} - (m\phi^2)^{-1} = 0 \tag{32}$$

$$(1 - \phi)^{-3} + (m\phi^3)^{-1} > 0 \tag{33}$$

At $\phi = 0$, eq 32 can only be satisfied if

$$\lim_{\phi \to 0}(1/m\phi^2) = 1 \tag{34}$$

which means that $(m\phi^3)^{-1}$ must simultaneously pass to infinity. Now eq 31 to 34 are in complete accord with eq 16 to 18, and we conclude finally that the condition on G'''', eq 9, must be amended to include

$$\lim_{\phi \to 0}(G'''') = \infty \tag{35}$$

The same conclusion is reached if Γ contains terms of higher order than quadratic in ϕ.

In support of eq 2 Kennedy cites an analysis[6] of phase-separation data of Koningsveld, Kleintjens, and Shultz[7] on the system polystyrene + cyclohexane, to give a Θ temperature near 30°, at least 3° below fairly concordant values found in a number of earlier studies. We cannot fault the data of Koningsveld, *et al.*, but we think two remarks are pertinent. (A) There is no reason to suppose, but rather the converse, that phase-separation measurements lead to values of the Θ temperature more reliable than those established by the vanishing of the second virial coefficient,[2] and measurements of the latter kind[8] on polystyrene + cyclohexane have usually yielded values between 34° and 35°. (B) Conventional extrapolations of critical temperatures to infinite molecular weight are based on the premise that a plot of T_c^{-1} *vs.* $m^{-1/2}$ becomes linear as $m \rightarrow \infty$, and not on direct use of $dT_c/d\phi_c$. This dependence is easily shown to obtain for a system obeying eq 26, 31, and 32. More significantly perhaps, it is also confirmed by a less specific derivation[9] requiring only that a virial expansion be applicable in the neighborhood of a critical point in dilute solution.

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Glass Transition of the Polymer Microphase

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Studies of block copolymer behavior showed that the properties of the finely dispersed microphase are not the same as those of the polymer in bulk. Hendus, Illers, and Ropte[1] observed that the glass transition temperature of the styrene component in SBS systems is lowered for more finely dispersed microphase. The decrease of the glass transition temperature of the hard component with decreasing concentration of its blocks was also observed by Cooper and Tobolsky.[2] Ductility of the polystyrene microphase was observed at lower temperatures than predictable[3-5] from the values of the bulk material. Fischer and Henderson[6] found the T_g of polystyrene blocks in the SBS system at about 70° which is a low limit compared to bulk polystyrene for which $T_g \approx$ 90–100° at reasonably high molecular weights. The two-phase system poly[(ethylene-*co*-propylene)-*g*-vinyl chloride] was found by us to exhibit a lower glass transition temperature of the PVC microphase according to both dilatometric and stress relaxation measurements.[7] Fischer and coworkers[8,9] did not find any significant decrease of the glass transition temperatures of the amorphous microphase in semicrystalline polybutene and polyethylene. It follows from these experimental data[1-9]