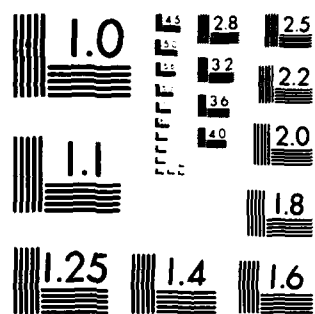END
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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

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polydispersities, the cloud point curves become flatter as the polydispersity increases. When the two polymers have similar average molecular weights but differ in their polydispersities, the cloud point curves become more skewed as the difference in the polydispersity increases. The results point out that, if the polydispersity effect is not properly accounted for, the value of X deduced from experimental cloud points is liable to be in error, especially with regard to its temperature coefficient or its concentration dependence.

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Effect of Polydisperity on the Cloud Point Curves
of Polymer Mixtures

by

Ryong-Joon Roe and Learong Lu

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University of Cincinnati

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ABSTRACT

A method is presented for the calculation of cloud point curves of polymer-polymer mixtures when the polymers involved are polydisperse. The method is based on the Flory-Huggins free energy of mixing with a concentration-independent X parameter. Numerical results are given for the cases where the molecular weight distributions are represented by the Schulz-Flory type. When the two polymers have similar average molecular weights and polydispersities, the cloud point curves become flatter as the polydispersity increases. When the two polymers have similar average molecular weights but differ in their polydispersities, the cloud point curves become more skewed as the difference in the polydispersity increases. The results point out that, if the polydispersity effect is not properly accounted for, the value of X deduced from experimental cloud points is liable to be in error, especially with regard to its temperature coefficient or its concentration dependence.

INTRODUCTION

As is well known, the solubility between two polymers is in general severely limited because of the rather small entropic gain achieved on mixing large molecules. Since the molecular weight heterogeneity modifies only the entropic term, which is already small to begin with, it could be expected that the polydispersity influences the miscibility behavior of polymers only weakly. This is certainly true when the polymers involved are all of extremely high molecular weights. In many recent studies[1-3] of thermodynamics of polymer mixtures, especially of those exhibiting UCST behavior, however, the polymers involved were of relatively low molecular weights, so that a proper consideration would have to be given to the possible effect of polydispersity. With systems exhibiting LCST behavior the phase separation is brought about usually by a change in the sign of the χ parameter accompanying a temperature change. In such cases the absolute magnitude of the χ term is small and therefore the modification of the small entropic term by the polydispersity effect, even when the molecular weights are high, may appreciably affect the observed cloud point curves.

Extensive analyses have been made, by Koningsveld,[4] Solc,[5] and others,[6] on the effect of polydispersity on phase separation of polymer solutions, i.e., solutions of a polydisperse polymer in a low molecular weight solvent. These analyses all start from the Flory-Huggins free energy of mixing (or its modification). In this work we likewise take the Flory-Huggins expression for the mixing of two polymers as the starting point, and investigate

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numerically the expected binodal curves as a function of the polydispersity of the two polymers. As has been stressed in recent years,[7] the mean-field approximation embodied in the Flory-Huggins expression is fairly satisfactory in describing the thermodynamics of polymer-polymer mixtures. A recent study by Joanny[8] of the critical behavior of polymer mixtures explicitly confirms this. This is to be contrasted with the fact that for a polymer solution the Flory-Huggins formula becomes grossly inadequate near the critical point and at dilute concentrations.

Both for polymer-solvent and polymer-polymer systems the effect of polydispersity on the spinodal curve and the critical point can be deduced fairly easily. When the χ parameter is independent of molecular weights (but may be dependent on the concentration), it has been known[9] that the spinodal curve depends only on the weight-average molecular weight and the critical point on the weight-average and z-average molecular weights. No such simple results, however, arise in the case of the binodal curve, which depends on the details of the molecular weight distribution and can therefore be deduced only numerically.

METHOD

We start the analysis with the Flory-Huggins free energy of mixing in the following form:

$$\Delta G_M/RT = \sum_p (\phi_{1p}/p)\ln\phi_{1p} + \sum_p (\phi_{2p}/p)\ln\phi_{2p} + \chi\phi_1\phi_2 \qquad (1)$$

where ϕ_{1p} is the volume fraction of the p-mer of polymer 1,

$$\phi_1 = \sum_p \phi_{1p}; \qquad \phi_1 + \phi_2 = 1 \qquad (2)$$

and χ is a function of temperature but is independent of ϕ. The chemical potential is derived from equation (1) as:

$$\Delta\mu_{1p}/RT = \ln\phi_{1p} + 1 - p(\phi_1/p_{1n} + \phi_2/p_{2n}) + \chi p(\phi_2)^2 \qquad (3)$$

where p_{1n} is the number-average DP of polymer 1. When two phases coexist, the chemical potentials of each species in the phases A and B are equal: $\Delta\mu_{1p}^A = \Delta\mu_{1p}^B$, and it therefore follows that:

$$\phi_{1p}^A / \phi_{1p}^B = \exp(\sigma_{1p}); \qquad \phi_{2p}^A / \phi_{2p}^B = \exp(\sigma_{2p}) \qquad (4)$$

where

$$\sigma_1 = \phi_1^A/p_{1n}^A + \phi_2^A/p_{2n}^A - \phi_1^B/p_{1n}^B - \phi_2^B/p_{2n}^B - \chi[(\phi_2^A)^2 - (\phi_2^B)^2] \qquad (5)$$

and

$$\sigma_2 = \phi_1^A/p_{1n}^A + \phi_2^A/p_{2n}^A - \phi_1^B/p_{1n}^B - \phi_2^B/p_{2n}^B - \chi[(\phi_1^A)^2 - (\phi_1^B)^2] \qquad (6)$$

At the cloud point, at which an infinitesimal volume of phase A has just separated out, the composition of phase B is essentially the same as the composition of the whole mixture:

$$\phi_{1p}^B \to \phi_{1p} \qquad \text{(cloud point)} \qquad (7)$$

Eliminating χ from (5) and (6) and using the condition (7), we find:

$$(\phi_1^A + \phi_1)\sigma_1/2 + (\phi_2^A + \phi_2)\sigma_2/2 = (\phi_1^A/p_{1n}^A + \phi_2^A/p_{2n}^A) - (\phi_1/p_{1n} + \phi_2/p_{2n}) \qquad (8)$$

If $w_1(p)$ and $w_2(p)$ are the (normalized) molecular weight

distributions (by weight) of polymer 1 and polymer 2 respectively, the quantities in equation (8) pertaining to the incipient phase A can be expressed as:

$$\phi_1^A = \phi_1 \sum_p w_1(p) \exp(\sigma_1 p) \tag{9}$$

$$\phi_1^A/p_{1n}^A = \phi_1 \sum_p (1/p) \, w_1(p) \exp(\sigma_1 p) \tag{10}$$

and similarly for ϕ_2^A and ϕ_2^A/p_2^A. Thus, equation (8) can be regarded as an implicit equation $f(\sigma_1, \sigma_2) = 0$ for two unknowns σ_1 and σ_2. Another implicit equation for σ_1 and σ_2 arises from the condition that:

$$\phi_1^A + \phi_2^A = 1 \tag{11}$$

in conjunction with equation (9). Thus, equations (8) and (11) constitute a set of two simultaneous equations which can be solved for σ_1 and σ_2 for given values of ϕ_1, $w_1(p)$, and $w_2(p)$. χ can then be evaluated from either equation (5) or (6).

For numerical calculation of the cloud point curve, we assume the molecular weight distribution $w(p)$ to be given by the so-called Schulz-Flory distribution:

$$w(p) = (a^{k+1} p^k/k!) \exp(-ap) \tag{12}$$

where the parameters a and k are related to the number average DP, p_n, and the polydispersity index, $\beta = p_w/p_n$, by

$$p_n = k/a; \qquad \beta = 1 + 1/k \tag{13}$$

The summations indicated by equations (9) and (10) can then be easily evaluated by integration. The numerical solution of the equations (8) and (11) for σ_1 and σ_2 is then straightforward.

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All results shown below were obtained with a PDP 11/23 computer.

RESULTS AND DISCUSSION

Fig. 1 shows the cloud point curves calculated for the case where $P_{1w} = P_{2w} = 1000$ and $\beta_1 = \beta_2 = 1.0$, 1.1, and 2.0 respectively. The three curves go through the common critical point at $\phi_1 = 0.5$. When χ is independent of composition, the spinodal curve is given by:

$$1/P_{1w}\phi_1 + 1/P_{2w}\phi_2 = 2\chi \tag{14}$$

and the critical point by:

$$1/\phi_{2c} = 1 + P_{2w}P_{1z}^{\frac{1}{2}}/P_{1w}P_{2z}^{\frac{1}{2}} \tag{15}$$

and

$$2\chi_c = (1/P_{1z}^{\frac{1}{2}} + 1/P_{2z}^{\frac{1}{2}})(P_{1z}^{\frac{1}{2}}/P_{1w} + P_{2z}^{\frac{1}{2}}/P_{2w}), \tag{16}$$

from which it can easily be shown that the three curves should share the critical point. For polymer pairs having P_{1w} (and P_{2w}) different from 1000 the curves remain the same if χ values are suitably rescaled. This can be seen from the fact that the structure of the Flory–Huggins equation remains unaltered when all the molecular lengths are reduced by a constant factor and χ, at the same time, is multiplied by the same factor.

The most interesting feature of Fig. 1 is that as the polydispersity index β is increased, the cloud point curves become flatter. In other words, at compositions away from $\phi_1 = 0.5$, phase separation occurs more readily (i.e., at a lower value of χ) as the polymers become more polydisperse. To

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understand why this happens, we analyze the composition of the minority phase (or phase A) which just begins to come out as a separate phase at the cloud point. Fig. 2 shows the calculated values of ϕ_1^A vs. χ (the so-called shadow curve) for $p_{1w} = p_{2w} = 1000$ and $\beta_1 = \beta_2 = 2.0$. The cloud point and the spinodal curves are also shown there. The horizontal line ties a point on the shadow curve with a point on the cloud point curve, indicating that these two points correspond to the compositions of the coexisting phases at the given value of χ. Fig. 3 shows the weight-average p_{1w}^A of polymer 1 in phase A separated out from the principal phase of composition ϕ_1. Thus, when a mixture containing, say, 20% of polymer 1 is brought to the condition of incipient phase separation, the minority phase that is being formed contains 68.67% of polymer 1, instead of 80% as would be expected if both polymers were monodisperse. The polymer 1 in phase A consists predominantly of higher molecular weight fractions of the original polymer so that its weight-average DP is now equal to 1853. Thus, this fractionation, in favor of the higher molecular weight end of the distribution, is responsible for the separation occurring prematurely at a value of χ smaller than otherwise.

For the polymers having the Schulz-Flory distribution considered here, the polydispersity index of the polymers separating out in the minority phase is not different from that in the principal phase. This is so, since from equations (4), (7) and (12), we have:

$$w^A(p) = (a^{k+1}p^k/k!) \exp [-(a-\sigma)p] \tag{17}$$

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showing that the index $\beta = 1 + 1/k$ is unaltered. The same conclusion is reached even when one of the components involved is a low molecular weight solvent. Thus, in the case of a polymer having the Schulz-Flory distribution, the width of the distribution cannot be made narrower by fractional precipitation.[5a]

Figs. 4 and 5 show the cloud point curves calculated for the cases where $p_{1w} = p_{2w} = 1000$ but $\beta_1 \neq \beta_2$. The cloud point curves develop assymmetry as the polydispersity indices of the two polymers deviate from each other. The distortion of the curve away from the symmetrical shape is in the same direction as one would have found if one had made the p_w of one of the polymers larger, instead of making its distribution broader.

One of the most practical ways of determining χ parameters between polymer pairs is to determine the cloud points experimentally and then find the best value of χ which brings the observed values in agreement with the cloud point curves calculated in accordance with the Flory-Huggins expression. In such a procedure, the effect of polydispersity is normally neglected because of computational difficulties. The present results show that unless the polymers employed have fairly narrow distributions, the χ values thus obtained could entail an appreciable error. When the two polymers are symmetrical with respect to p_w and β, the error is more likely to affect the temperature coefficient of the χ parameter, while when the two polymers differ in their polydispersity, the error is more likely to affect the concentration dependence of the χ parameter.

In the analysis of the cloud point curves of polymer-solvent systems, it was shown[5] that a computational difficulty arises when the molecular weight distribution is a "divergent" type (for example, log-normal distribution), and also that in the vicinity of the critical point a more complicated phase relations, sometimes leading to a coexistence of three phases, could be encountered. Analogous situations are expected to arise in the case of polymer-polymer systems as well, but we have not investigated these subtleties in this work.

Acknowledgment

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Legends to Figures

Figure 1. Cloud point curves calculated for the symmetrical cases: $P_{1w} = P_{2w} = 1000$ and $\beta_1 = \beta_2 = 1.0$, 1.1 and 2.0 as indicated.

Figure 2. The cloud point curve (labeled c_1) and the spinodal curve (broken line), calculated for the case where $P_{1w} = P_{2w} = 1000$ and $\beta_1 = \beta_2 = 2.0$. The curve labeled ϕ_1^A is the "shadow" curve giving the composition of the incipient minority phase A. The horizontal lines tie pairs of points giving the composition c_1 of the principal phase and the composition c_1^A of the minority phase which coexist at the cloud point.

Figure 3. The ordinate gives the weight-average DP, p_{1w}^A, of polymer 1 in the incipient minority phase A which coexists with the principal phase of composition c_1, calculated for the case where $P_{1w} = P_{2w} = 1000$ and $\beta_1 = \beta_2 = 2.0$.

Figure 4. Cloud point curves for $P_{1w} = P_{2w} = 1000$, $\beta_1 = 2.0$ and $\beta_2 = 1.0$, 1.1 and 2.0 respectively. As the polydispersities of the two polymers deviate more from each other, the curves become more unsymmetrical. It is as if the molecular weight of the broader polymer has become much higher, even though in fact the weight-average DP's of the two polymers are the same.

Figure 5. Cloud point curves for $P_{1w} = P_{2w} = 1000$, $\beta_1 = 1$ and $\beta_2 = 1.0$, 1.1 and 2.0 respectively. See the caption for Figure 4.
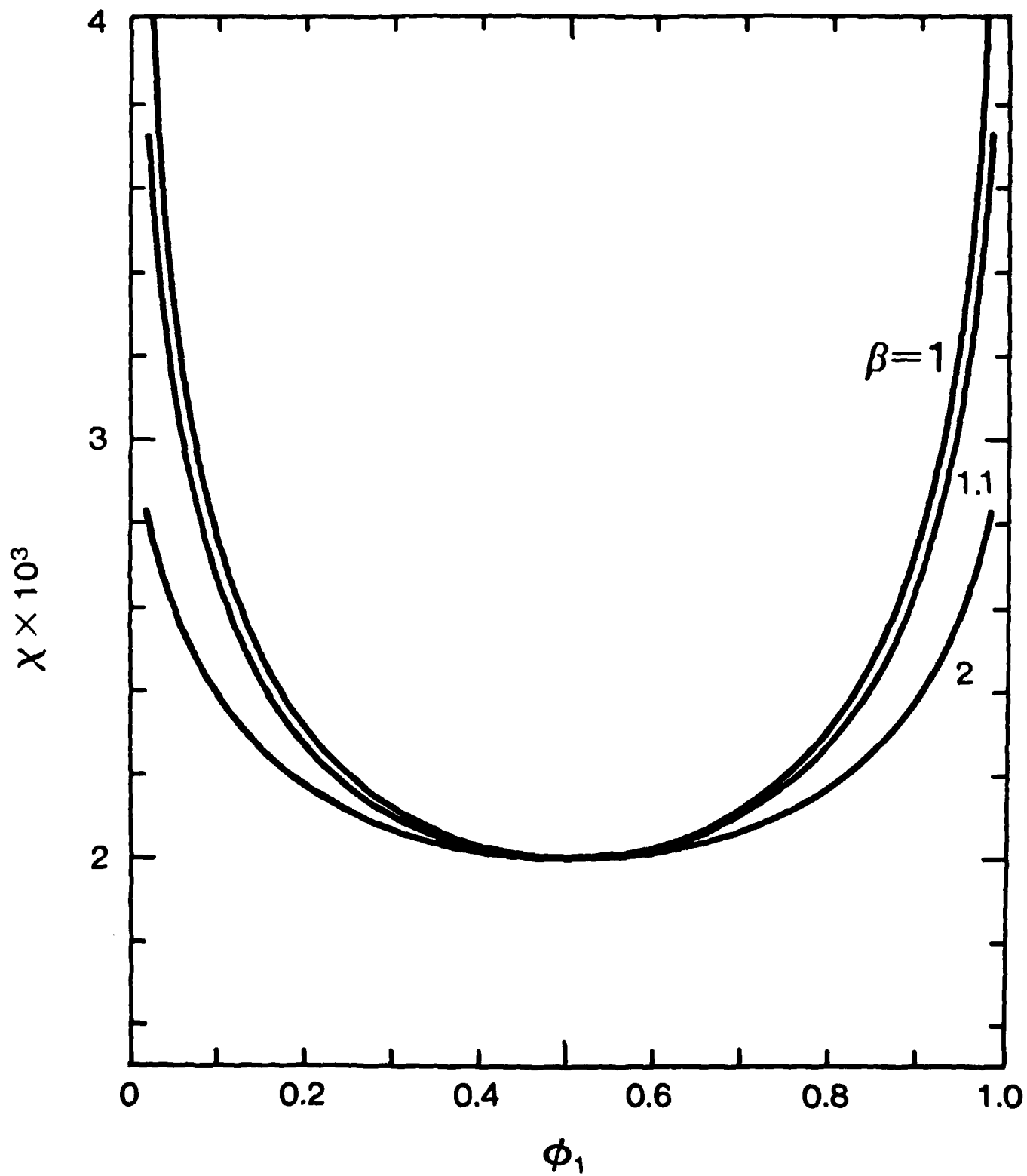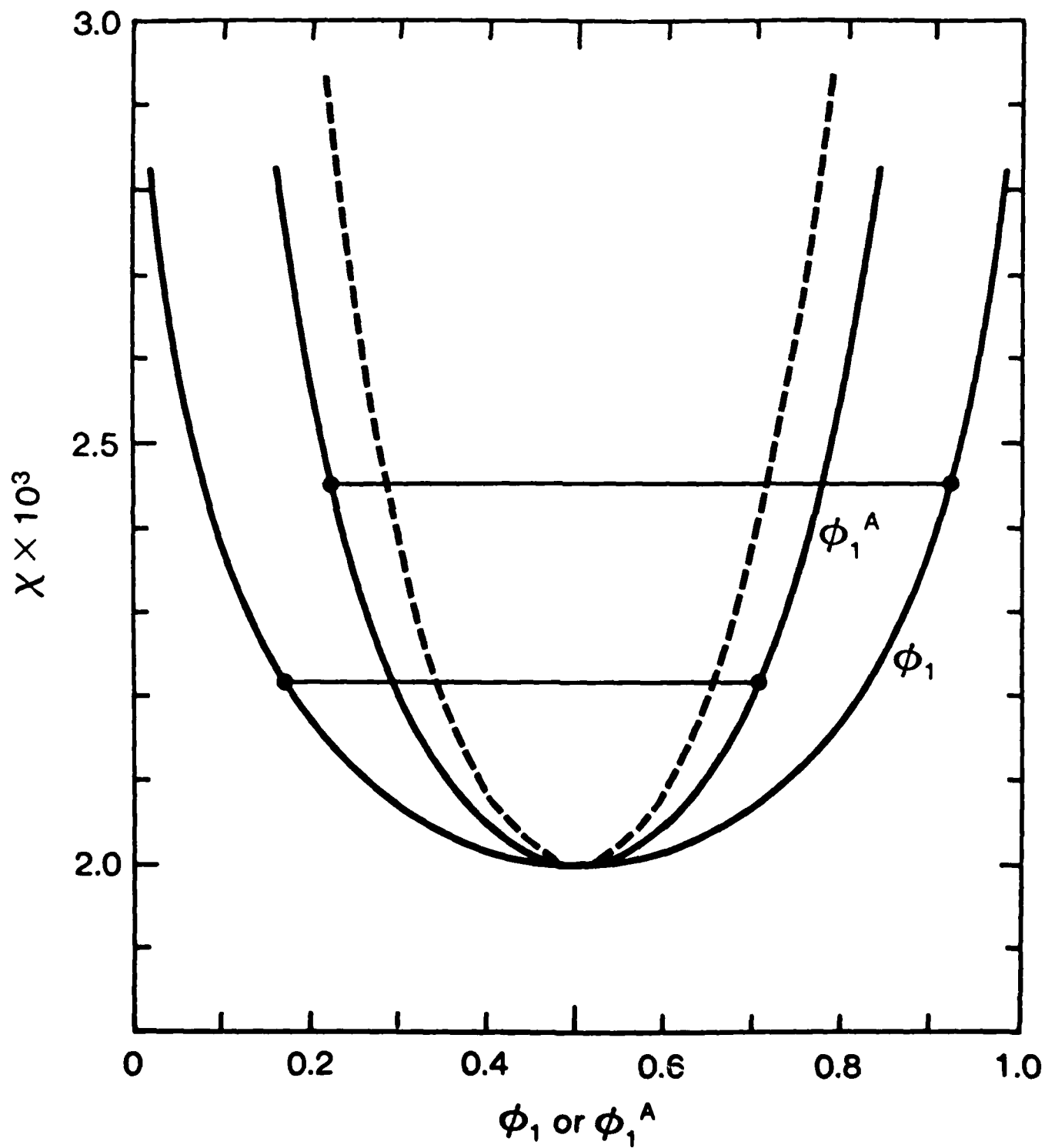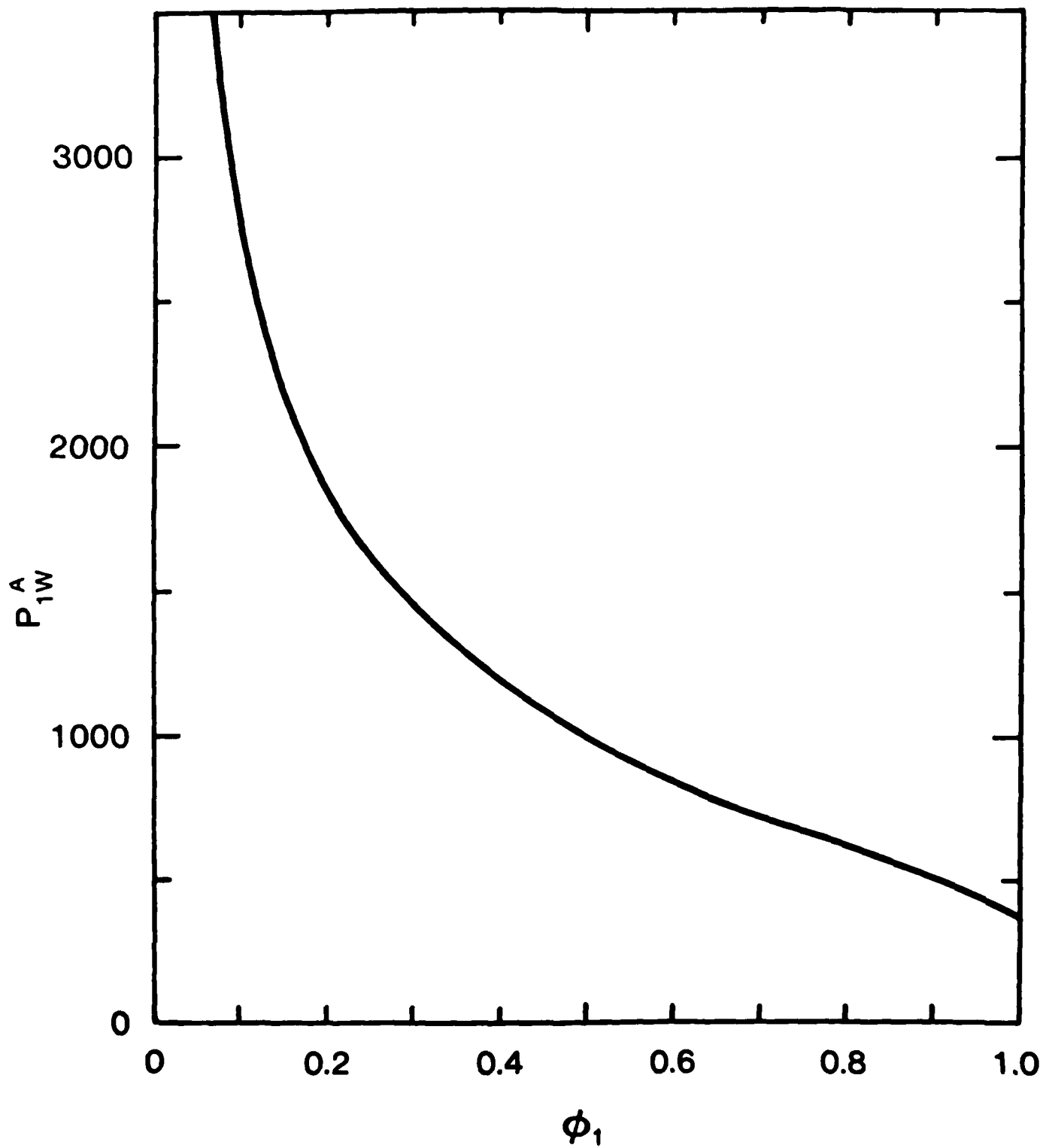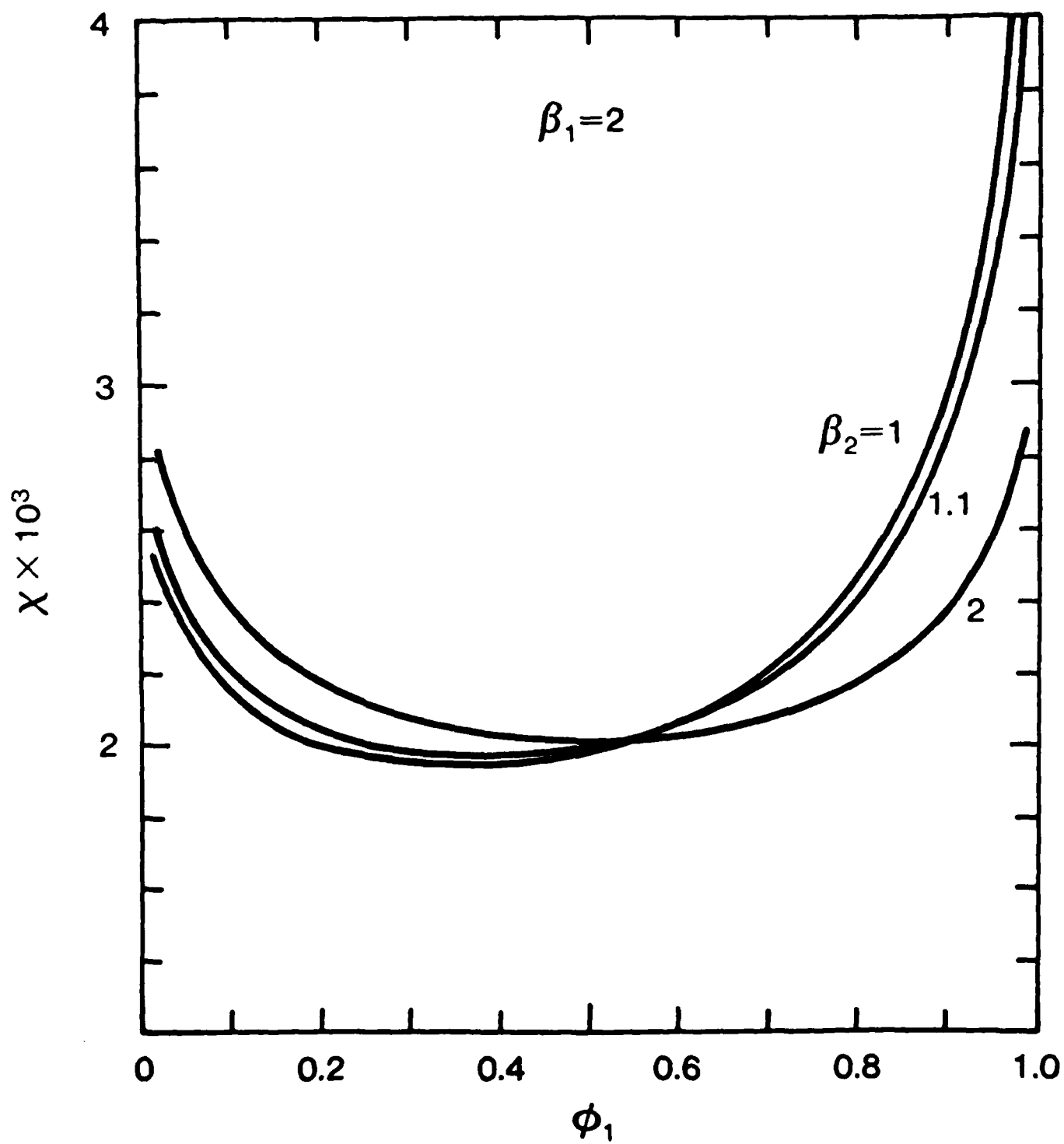
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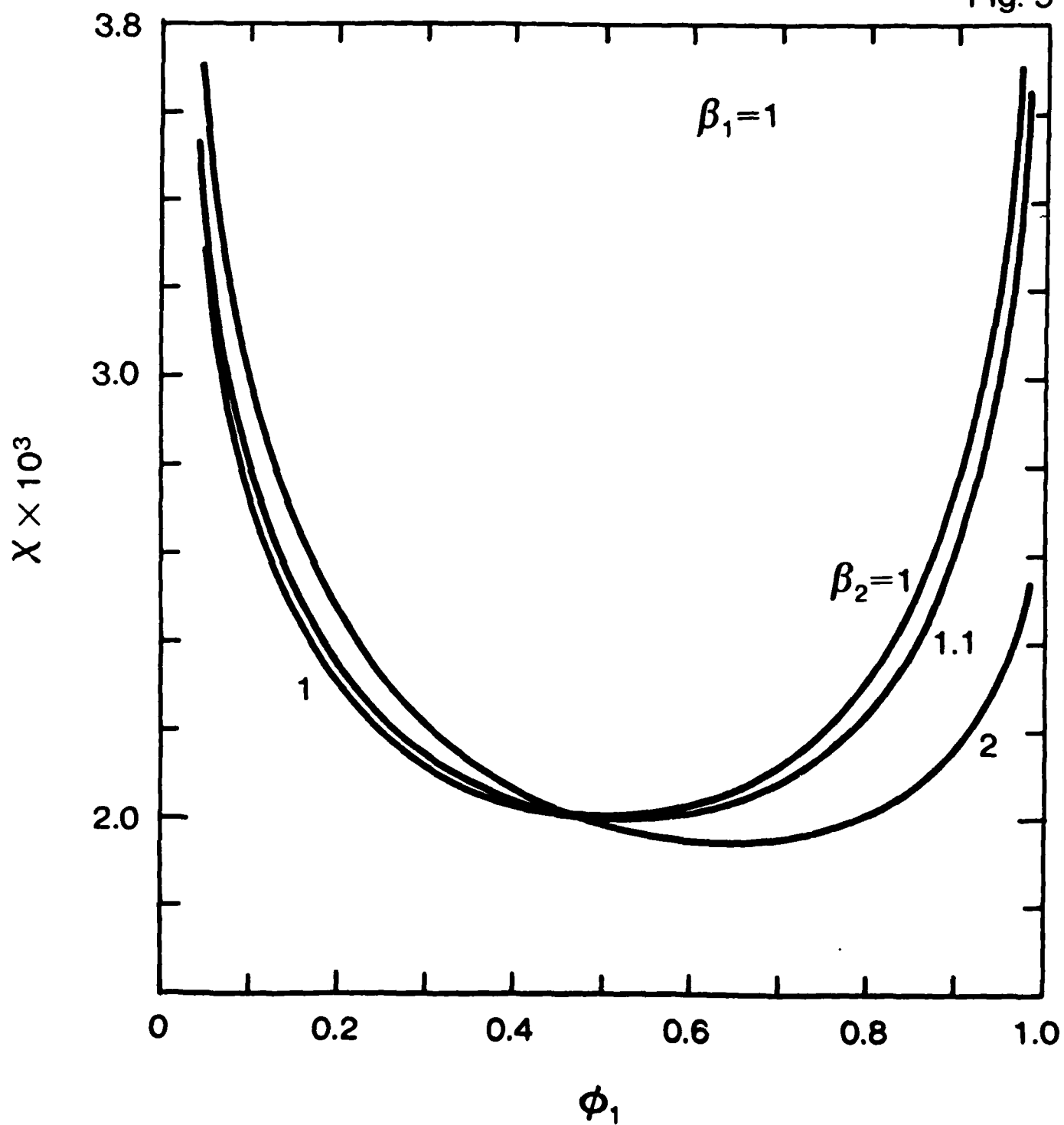
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