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SANS Evaluation of the RPA Theory for Binary Homopolymer Mixtures

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ABSTRACT

A well characterized binary mixture of normal (protonated) and perdeuterated monodisperse 1,2 polybutenes has been studied by small-angle neutron scattering (SANS). For scattering wavevectors q greater than the inverse radius-of-gyration R_g^{-1} , the SANS intensity is quantitatively predicted by the random phase approximation (RPA) theory of deGennes over all measured values of the segment-segment interaction parameter χ . In the region $(\chi_S - \chi)\chi_S^{-1} > 0.5$ the interaction parameter determined using the RPA theory for $q > R_g^{-1}$ is greater than that calculated from the zero-angle intensity based on an Ornstein-Zernike plot, where χ_S represents the limit of single phase stability. These findings indicate a correlation between the critical fluctuation length ξ and R_g which is not accounted for by the RPA theory.

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Introduction

The advent of small angle neutron scattering (SANS) fifteen years ago heralded a new era in polymer science. Perhaps the greatest impact of this versatile technique has been felt in the area of bulk polymers, and in particular in the field of amorphous polymer melts. With the construction of several SANS spectrometers around the world, theoretical activity in molecular scale polymer physics quickened, resulting in considerable advances in the methods for interpreting small-angle scattering data. At about the time that the 30 meters SANS instrument at the National Center for Small Angle Scattering Research (NCSASR) was commissioned at Oak Ridge National Laboratory the random phase approximation (RPA) theories for binary mixtures of homopolymers, and diblock copolymers, were published in the presently used forms by deGennes⁽¹⁾ and Leibler⁽²⁾ respectively. In this paper we will evaluate the former RPA theory based on SANS data obtained using the 30m NCSASR instrument. This spectrometer is particularly well suited for such a study owing to the ability to obtain data over a wide range of scattering wavevectors without sacrificing resolution.

Although there have been a considerable number of publications dealing with multicomponent polymer melts which make use of the RPA predictions, we have found few, if any, which examine the limitations of this theory. In this article we focus on examining under what experimental conditions the RPA predictions for binary homopolymer mixtures begins to fail.

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Experimental

Perdeuterated and normal (protonated) atactic 1,2 polybutenes were prepared by hydrogenation and deuteration of atactic 1,2 polybutadienes, which were anionically polymerized using previously reported techniques.⁽³⁾ The polymers were characterized by membrane osmometry for number average degree of polymerization N_N , and by high pressure size exclusion chromatography for polydispersity N_W/N_N where N_W is the weight average degree of polymerization. The characterization results for the two polymers presently considered are listed in Table 1. A more detailed accounting of the synthesis and characterization of these materials will be given elsewhere.⁽⁴⁾

A neutron scattering sample containing 50% by volume of each polymer listed in Table 1 was prepared from a cyclohexane solution of both polymers by solvent evaporation. The dried mixture was placed in a scattering cell consisting of quartz plates separated by a 0.125 cm aluminum spacer. This assembly was then epoxied together in order to insure that the sample thickness remained constant during measurements.

SANS data were collected at sample-to-detector distances of 19, 6.9 and 2.6 meters and reduced to units of absolute intensity based on the procedures outlined elsewhere.⁽⁵⁾ The incoherent scattering intensity was approximated as the linear combination of the incoherent intensity from the pure components, and subtracted from the total intensity. A series of eight neutron scattering profiles were obtained between 26 and 100 degrees centigrade at the 19 meters detector setting. Sample temperature was controlled to within 1°C by use of a thermostated circulating fluid. These data sets will be the main focus of this paper. Two representative sets of data, obtained at the highest and lowest temperatures are presented in Ornstein-Zernicke form (inverse intensity versus q^2) in Figures 1 and 3, where $q = 4\pi\lambda^{-1} \sin(\theta/2)$ represents the scattering wavevector; $\lambda = 4.75 \text{ \AA}$ is the radiation wavelength and θ is the scattering angle. Figure 1 focuses on the intermediate region of reciprocal space available using the 19 meters detector setting while Figure 3 highlights the lowest q regime obtainable on the NCSASR SANS instrument. Data obtained at the other (higher q) detector settings, and

presently referred to, will be presented elsewhere.⁽⁴⁾

Analysis

The absolute coherent elastic scattering intensity from a binary homopolymer mixture characterized by a single segment (repeat unit) volume V is given by,

$$I = V^{-1}(b_H - b_D)^2 S(q) \quad (1)$$

where b_H and b_D presently refer to the scattering lengths of the protonated and deuterated 1,2-polybutene segments respectively.

According to the random phase approximation (RPA) theory of deGennes,⁽¹⁾ the structure factor for a homogeneous (single phase) polymer mixture is,

$$S^{-1}(q) = [\Phi_H N_H g_D(R_{g,H}, q)]^{-1} + [\Phi_D N_D g_D(R_{g,D}, q)]^{-1} - 2\chi \quad (2)$$

where χ is the Flory-Huggins parameter and g_D is the Debye function

$$g_D(R_g, q) = 2[R_g^2 q^2 + e^{-R_g^2 q^2} - 1]/R_g^4 q^4. \quad (3)$$

$R_g = a(N/6)^{1/2}$ corresponds to the Gaussian coil radius of gyration based on the degree of polymerization N and statistical segment length a .

We have recently made frequent use of this RPA theory in analyzing the SANS results obtained from binary mixtures of perdeuterated and protonated amorphous polymers.⁽⁵⁻⁹⁾ In particular, the neutron scattering data obtained from such mixtures as a function of temperature, have been modelled with equation 2 in order to extract the thermodynamic parameter $\chi(T)$. Owing to the smallness of χ , for such systems, it has been necessary to study isotopic mixtures of high degree of polymerization, in order to realize a measureable variation in scattering intensity as a function of temperature. As a consequence, our previous data have been obtained over wavevectors $q \geq R_g^{-1}$ due to the limitations set by the SANS instrument. The combined effects of a small statistical segment length a (see below) and greater hydrogen-to-carbon ratio in 1,2 polybutenes versus that characterizing the previously investigated isotopic pairs has provided us with a more suitable system for evaluating the RPA theory over a wider

range of q . In order to facilitate comparison of the current results with those previously reported for isotopic mixtures we first analyze the SANS data for the 1,2 polybutene mixture for $q > R_g^{-1}$.

At large scattering wavevectors, $qR_g \gg 1$, equation 2 reduces to

$$S(q) = 12\Phi_H\Phi_D/q^2a^2 \quad (qR_g \gg 1) \quad (4)$$

so that at fixed composition the scattering intensity is determined solely by the magnitude of the statistical segment length a . Using the data obtained at detector settings of 2.6 and 6.9 meters we have verified the functional form of equation 4 and experimentally determined that $a = 5.0 \pm 0.2 \text{ \AA}$ for 1,2 polybutene. Based on this value and the weight average degree of polymerization for each component (Table 1) we have fit the SANS data obtained at each temperature, for $q > R_g^{-1}$, by adjustment of the parameter χ . In each case the agreement between the data and RPA theory for $q > R_g^{-1}$ is excellent, as exemplified by the solid curves in Figure 1. The location of the average value of the radius of gyration, $R_g = (R_{g,H} + R_{g,D})/2$, is indicated by the arrow in Figure 1.

As illustrated in Figure 2 $\chi \sim T^{-1}$ in agreement with our theoretical prediction for binary isotopic polymer mixtures.⁽⁹⁾ Further evaluation of the thermodynamics of this isotope effect will be undertaken in a separate publication. Our present analysis, which is restricted to evaluating the RPA theory, now focuses on the SANS data for $q < R_g^{-1}$.

The lower q portion of the SANS data obtained at 26 and 100°C are presented in Figure 3 where the solid curves are the RPA predictions based on the same parameters used for $q > R_g^{-1}$ (Figure 1). It is evident that the 26°C SANS data deviate significantly from the theoretical prediction for values of $q < R_g^{-1}$, whereas at 100°C there is good agreement between theory and experiment over the entire range of the experimentally accessible reciprocal space.

In order to more quantitatively evaluate and compare this behavior for all eight measurement temperatures, we have calculated the measured value of χ based on the zero-angle intensity $I(0)$. This can be determined from a linear extrapolation of the low q results

based on the classical critical scattering expression,⁽¹⁾

$$S(q) = \frac{S(0)}{1 + q^2\xi^2} \quad (5)$$

where ξ corresponds to the composition fluctuation length. Such an extrapolation is illustrated by the dashed line in Figure 3. In general⁽¹⁾

$$S^{-1}(0) = \frac{\partial^2 F}{\partial \Phi^2} \quad (6)$$

where, according to Flory-Huggins theory,

$$\frac{F}{k_B T} = \frac{\Phi_H}{N_H} \ln \Phi_H + \frac{\Phi_D}{N_D} \ln \Phi_D + \Phi_H \Phi_D \chi \quad (7)$$

leading to

$$\chi_{I(0)} = 1/2 \left\{ (N_H \Phi_H)^{-1} + (N_D \Phi_D)^{-1} - VI(0)(b_H - b_D)^{-2} \right\}. \quad (8)$$

In Figure 4 we compare the ratio of the Flory-Huggins parameters as determined using the RPA theory ($qR_g > 1$) with those determined from $I(0)$, as a function of the reduced parameter $(\chi_S - \chi_{RPA})\chi_S^{-1}$, where

$$\chi_S = [(N_H \Phi_H)^{-1} + (N_D \Phi_D)^{-1}]/2 \quad (9)$$

corresponds to the limit of thermodynamic stability. These results indicate a statistically significant systematic disparity between the RPA theory and the SANS determined composition fluctuations for $q < R_g^{-1}$ and $(\chi_S - \chi)\chi_S^{-1} < 0.5$. This finding is discussed in the following section.

Discussion

Mixtures of perdeuterated and normal (protonated) amorphous polymers have recently been shown by us to be characterized by an upper critical solution temperature.^(5,9) Such mixtures represent ideal substrates with which to investigate in detail the theoretical predictions for the small-angle scattering from multicomponent polymer melts. The thermodynamic interactions

which drive these systems to segregate are sufficiently small so as to allow the investigation of relatively large polymers in the homogeneous state. Furthermore, as recently shown,⁽⁹⁾ the interactions derive from classical van der Waal's forces thus avoiding the awkward necessity of dealing with polymer mixtures characterized by complicated and poorly understood attractive forces such as hydrogen bonding. By synthesizing the presently discussed polymers by means of anionic polymerization we have been able to investigate a truly model system consisting of highly monodisperse components which interact via simple and well understood interactions.⁽⁹⁾

We have focused this report on the small-angle neutron scattering obtained from a single 1,2 polybutene isotopic mixture in order to eliminate any uncertainties which might result from comparing different mixtures. Systematic errors attributable to the SANS intensity calibration or polymer molecular weight determinations will affect each set of data equally. Therefore, we are confident that the systematic differences between the RPA theory and the SANS data for $q < R_g^{-1}$ and $(\chi - \chi_S)\chi_S^{-1} < 0.5$ are real, and not artifacts of the experiments.

What then accounts for the experimental results summarized in Figure 4? Our first suspicion is that the mean-field assumption inherent in the RPA theory might be breaking down. However, as shown in Figure 5, the zero-angle intensity increases as a function of reduced temperature $T - T_S$ with a mean-field critical exponent $\gamma = -1.01 \pm 0.04$, where T_S refers to the temperature intercept in the plot of $I^{-1}(0)$ versus T . This is in accordance with the calculations of Binder,⁽¹⁰⁾ which indicate that deviations from mean-field behavior for this mixture should not be apparent except very near the critical point.

Although we have no fundamental explanation for the results summarized in Figure 5, the following observations can be made. The composition fluctuation length predicted by the mean-field RPA theory is as follows,⁽¹⁾

$$\xi_{RPA} = \frac{R_g}{\sqrt{2}} \left(\frac{\chi_S - \chi}{\chi_S} \right)^{-1/2} \quad (10)$$

While we have not measured $\chi_{II(0)}/\chi_{RPA}$ for $(\chi_S - \chi)\chi_S^{-1} > 0.5$ in the present work, numerous other studies have found excellent agreement between the RPA theory and experiments in this

region of phase space. Therefore, based on the results of Figure 5, we believe there exists a crossover in the composition fluctuation behavior at $(\chi_s - \chi)\chi_s^{-1} \cong 0.5$. This corresponds to the point at which the composition fluctuation length equals the polymer radius of gyration according to equation 10. As previously noted, it is also at $q = R_g^{-1}$ that these effects become apparent in the SANS experiments (Figures 1 and 3). Thus there appears to be an additional correlation between ξ and R_g which is not accounted for by the RPA theory. We are quite surprised at how well defined this correlation appears to be, and hope these experimental results will stimulate further theoretical work regarding critical fluctuations in binary homopolymer mixtures.

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Table i

1,2 Polybutene Characterization Data

Sample	^a N _N × 10 ³ (± 2%)	^b N _W /N _N
(C ₄ H ₈) _N	1.29	1.03
(C ₄ D ₈) _N	1.67	1.03

^a Number average degree of polymerization as determined by membrane osmometry.

^b Polydispersity as determined by high pressure size exclusion chromatography.

FIGURE LEGENDS

- Figure 1. Ornstein-Zernike plot of the SANS data obtained from a binary mixture of perdeuterated and protonated 1,2 polybutenes at two representative temperatures. The solid curves are the predictions of the RPA theory, which were determined by adjustment of the segment-segment interaction parameter χ in order to obtain a best-fit for $q^2 > R_g^{-2}$.
- Figure 2. Temperature dependence of the segment-segment interaction parameters obtained by fitting the RPA theory to the SANS data for $q > R_g^{-1}$.
- Figure 3. Low q SANS data for two representative temperatures. The solid curves have been calculated using the RPA theory based on the χ parameters determined at $q > R_g^{-1}$ (Figure 1). The dashed line represents the linear extrapolation from which the zero-angle intensity is obtained.
- Figure 4. Ratio of the interaction parameters as determined from the zero-angle intensity $I(0)$ and the RPA theory for $q > R_g^{-1}$, as a function of the relative distance from the single phase stability limit χ_S .
- Figure 5. Critical plot based on the stability temperature T_s and zero-angle intensity $I(0)$. The exponent $\gamma = -1.01$ is consistent with the mean-field assumptions of the RPA theory.

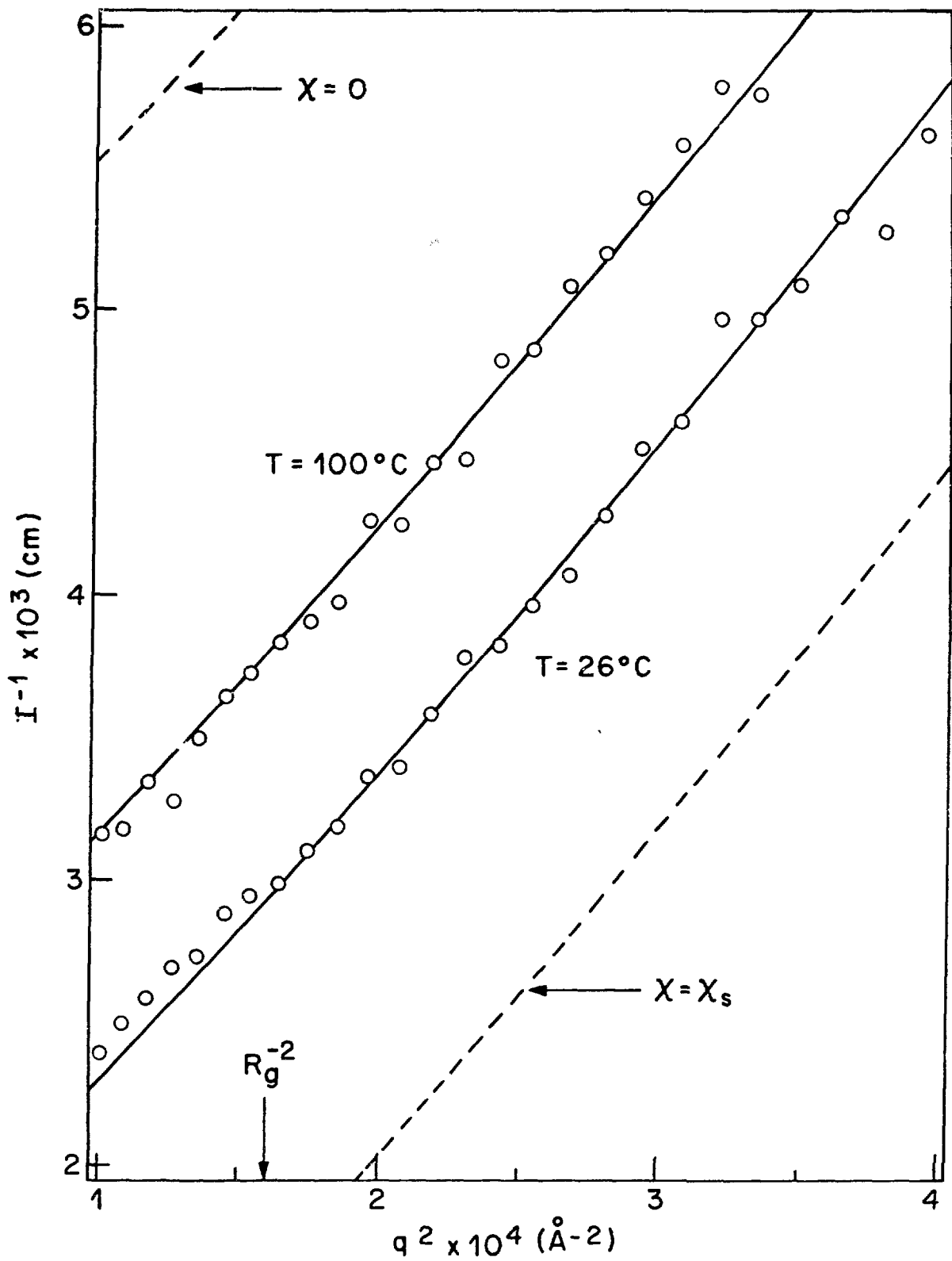


Figure 1

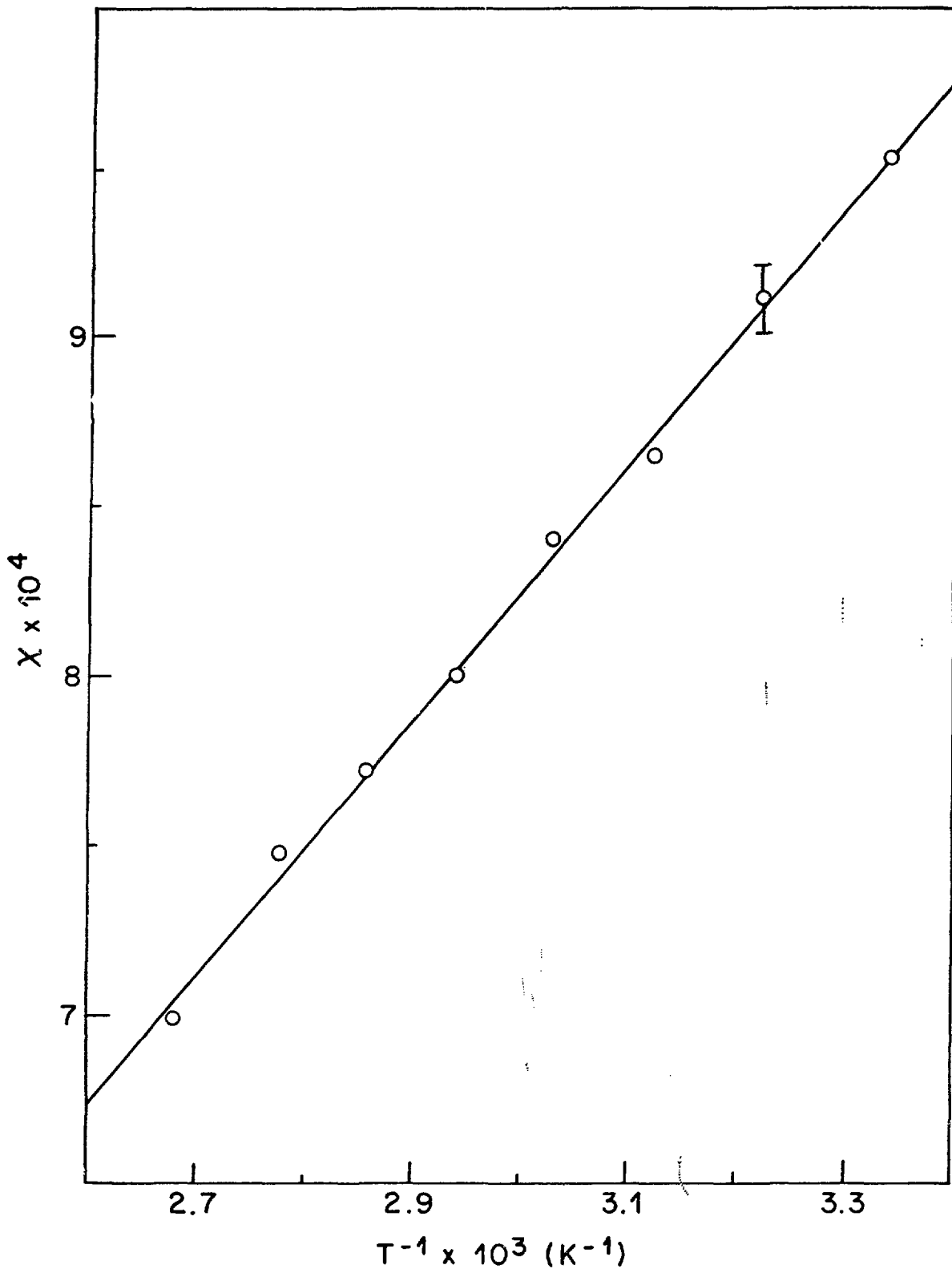


Figure 2

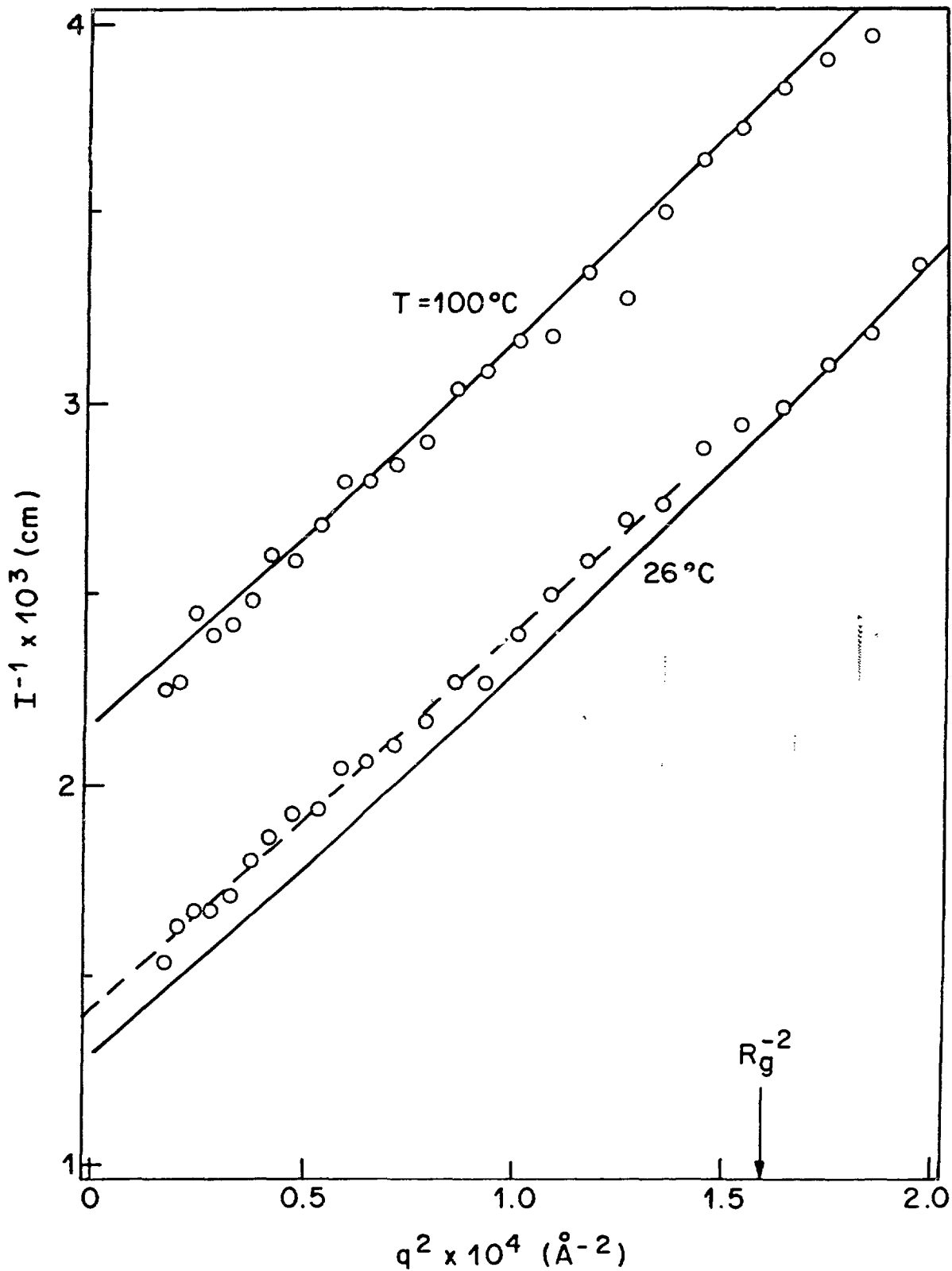
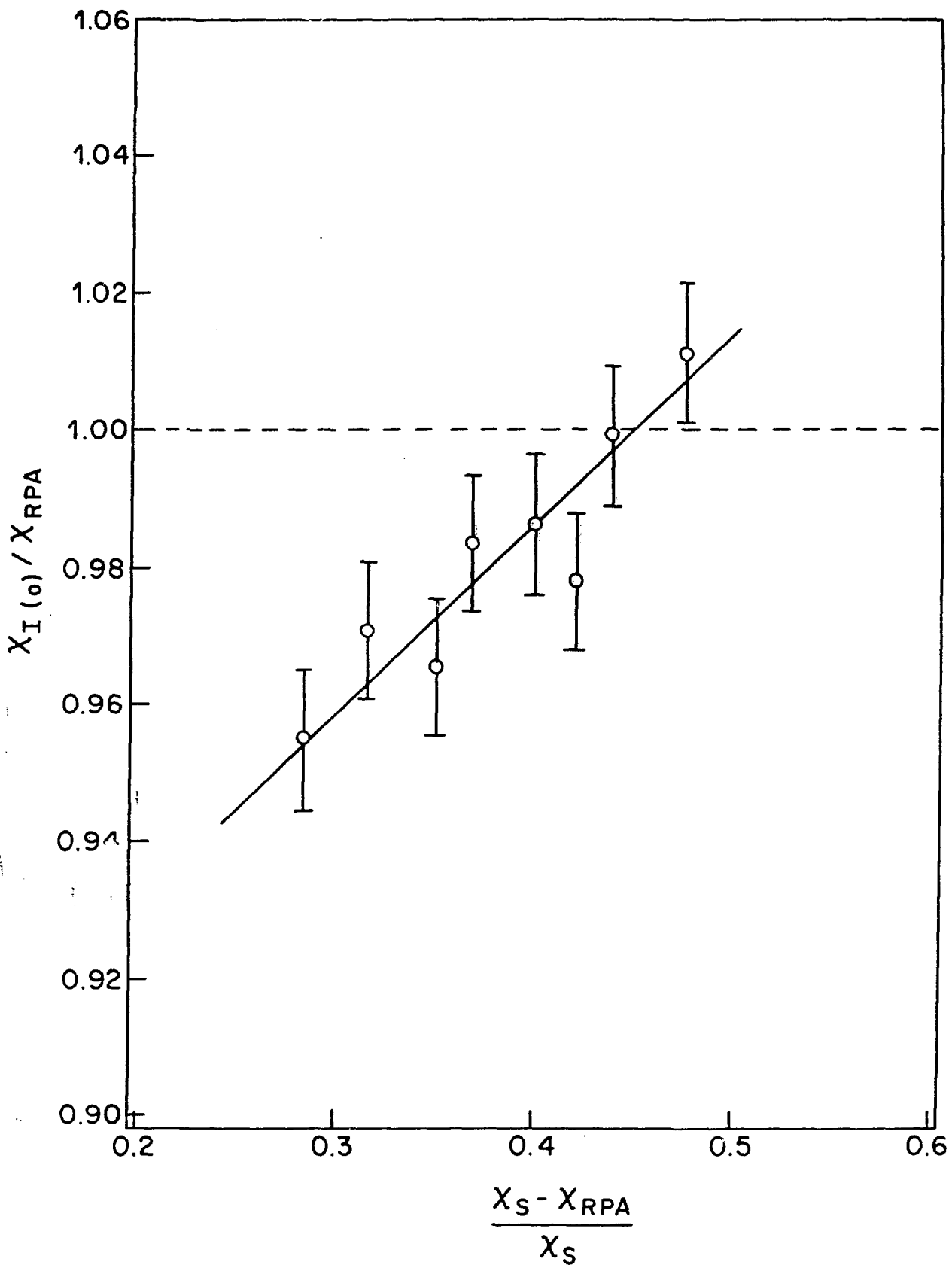


Figure 3



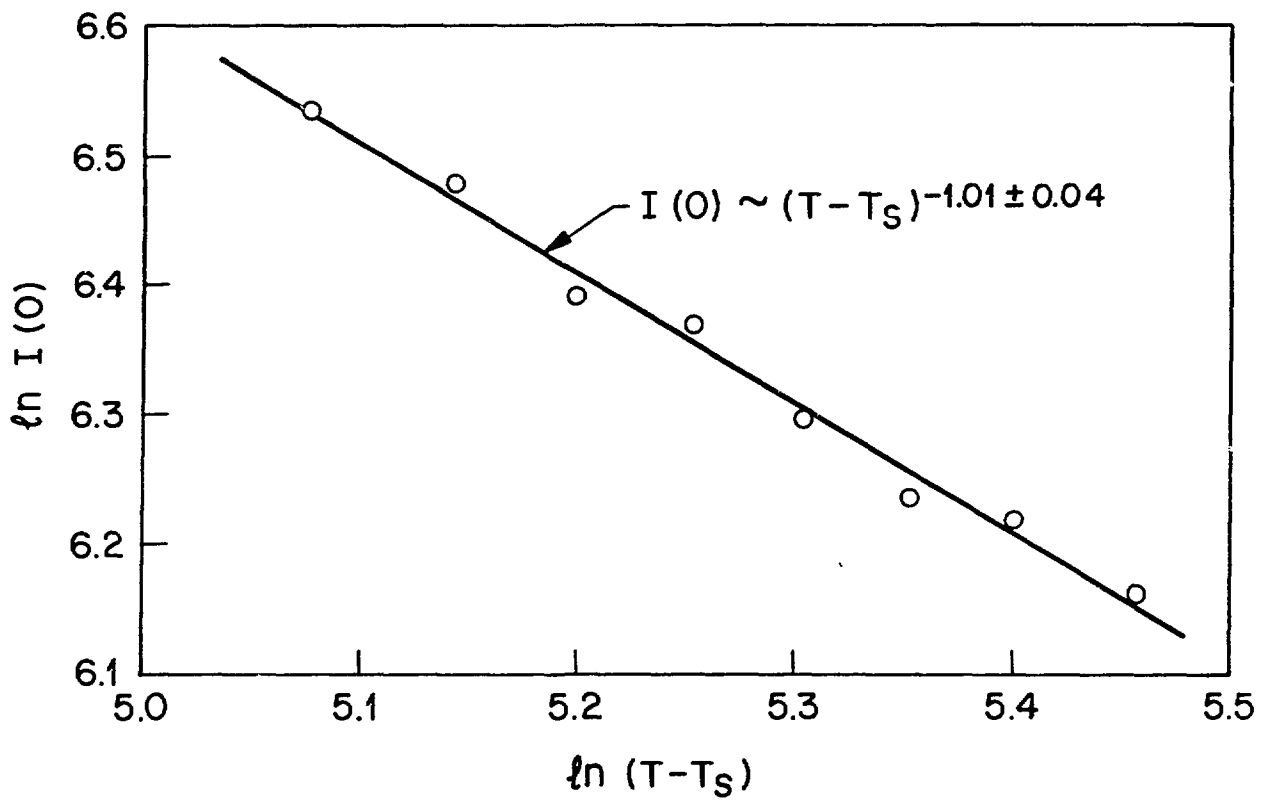


Figure 5