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Second Osmotic Virial Coefficient Revisited. 2. Buildup from Contributions of Inter- and Intramolecular Contacts between Polymer Segments†

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ABSTRACT: The variation of the second osmotic virial coefficient A_2 with the molar mass M of the polymer is interpreted as the result of the thermodynamic inequality of inter- and intramolecular contacts between polymer segments. This inequality can take effect since the coil dimension (and consequently the number of intramolecular contacts) changes with concentration as M becomes larger. A model is presented in which A_2 should depend linearly on $M^{-(a-0.5)}$, where a is the exponent of the viscosity–molecular weight relationship. The evaluation of numerous literature data confirms the present concept and yields a consistent picture for the size of the inter- and intramolecular interaction parameters, their interdependence, and their variation with the thermodynamic quality of the solvent.

Introduction

In practically all cases reported so far, the second osmotic virial coefficient A_2 decreases as the molecular weight M of the polymer is raised isothermally. Recent light scattering investigations[1] with the system *tert*-butyl acetate/polystyrene have however demonstrated that $A_2(M)$ can become an increasing function for sufficiently exothermal conditions. Since this finding contradicts the results of the classical excluded volume theory[2] (according to which lim A_2 for infinite M should be 0), it was postulated[1] that (except for Θ conditions) the volume a given polymer segment excludes for the placement of a second segment depends on its belonging to the same or to a different molecule. In the present contribution this ine-

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† Affectionately dedicated to Prof. G. V. Schulz on the occasion of his 80th birthday.

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quality of inter- and intramolecular contacts is discussed in terms of phenomenological thermodynamics and substantiated by means of experimental data taken from the literature.

Theoretical Background

Comparing the behavior of a real solution with that of a perfect mixture, i.e., in terms of the thermodynamic excess functions,[3] yields

$$A_2 = -\frac{\Delta G_1^{\mathrm{E}}}{RTc_2^{\,2}V_1}\left(+\frac{V_1}{2M^2}\right) \tag{1}$$

where ΔG_1^{E} is the molar Gibbs excess energy of dilution, c_2 the concentration of the solute (mass/volume), and V_1 the molar volume of the solvent. The term placed in parentheses can be neglected for sufficiently high molar masses M of the solute. A_2 does not depend on c_2 since ΔG_1^{E} is a quadratic function of this variable; consequently A_2 measures the effect of adding 1 mol of solvent to the solution at any given constant composition within the concentration range of binary contacts. Within the framework of eq 1, these contacts concern undivided solute molecules, taken as invariable entities.

For the chain molecules of present interest the approach has to be different since the dissolved polymers normally change their coil dimensions upon dilution;[4] i.e., the solute molecules are no longer invariable. Consequently, the opening of contacts between individual polymer segments should replace that of pairs of polymer molecules. This can be achieved by taking combinatorial instead of perfect mixing, as reference behavior, yielding eq 2 by analogy with eq 1

$$\chi = \frac{\Delta G_1^{\mathrm{R}}}{RT\varphi_2^{\,2}} = \chi_0 + \chi_1\varphi_2 + \chi_2\varphi_2^{\,2} + \dots \tag{2}$$

where ΔG_1^{R} is the molar residual Gibbs energy of dilution, φ_2 is the volume fraction of the polymer, and the χ_i values are the coefficients of a power series expansion. χ measures the effect associated with the insertion of a solvent molecule between two polymer segments contacting each other. χ_0, like A_2, is independent of composition for sufficiently dilute solutions that can be described by binary intersegmental contacts. The following relation between A_2 and χ_0 holds true:[3]

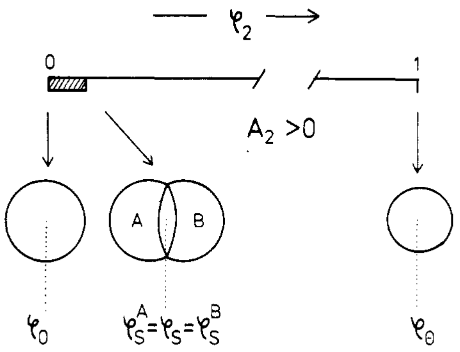
$$A_2 = \left(\frac{1}{2} - \chi_0\right)\frac{1}{\rho_2^{\,2}V_1} \tag{3}$$

where ρ_2 is the density of the polymer.

By means of eq 3 the influence of M on A_2 can be looked upon in a new way, taking into account that (i) not only inter- but also intramolecular contacts between polymer segments are normally ($A_2 \neq 0$) opened upon dilution due to the already-mentioned change in coil dimensions and that (ii) the effects associated with the opening of inter- or intramolecular contacts, $\chi^{)(}$ or $\chi^{()}$, are normally different from each other.

The soundness of item i is beyond doubt, while that of item ii can be rationalized by bearing in mind that the segments of an intermolecular contact can separate indefinitely when solvent is added, whereas those of an intramolecular contact can only reach a maximum mutual distance given by their position within the polymer chain. Consequently at least the entropy parts of $\chi^{)(}$ and $\chi^{()}$ should be different, but most likely also the enthalpy parts, because of a general interrelation[5] between the entropies and enthalpies of dilution. The question now arises how $\chi^{)(}$ and $\chi^{()}$ contribute to χ_0 in the case of different molecular weights; the model considerations presented in the next section serve to find the answer.

Scheme I



Model Considerations

Scheme I serves the purpose of visualizing the influence of the volume fraction φ_2 of the polymer on its coil dimensions and introduces the variables used in the present approach. For the concentration regime of interest (the hatched region in this scheme), it suffices to focus attention on a pair of polymer molecules. Ω, the degree of overlap of molecule A and B, can then be introduced according to

$$\Omega = k(\varphi_2/\varphi_s) \tag{4}$$

Naturally Ω increases as φ_2 is raised, but in different ways depending on the particular thermodynamic situation. This fact is primarily taken into account by φ_s, the volume fraction of segments of either molecule A or B in the overlap region of a binary contact. For constant φ_2 and a given molar mass of the polymer, Ω will become larger with increasing solvent quality, since the coils expand and reduce φ_s. Furthermore, the thermodynamics of a given solvent/polymer system will also be reflected in the value of the constant k, which accounts for the average geometry of the overlap region and its changes with solvent power.

Let N be the total number of segments of polymer molecule A or B; then $N^{)(}$, the number of segments of one molecule in contact with segments of the other, will be proportional to $N^\nu\Omega$, the number of segments of A contained in the overlap region, and to φ_s, the volume fraction of segments of B in this area

$$N^{)(} = k'N^\nu\Omega\varphi_s = k''N^\nu\varphi_2 \tag{5}$$

where ν is a constant of the order of 0.5–0.7.

$N^{()}$, the number of segments contacting other segments of the same molecule *in excess of the number at infinite dilution*, on the other hand, is given by

$$N^{()} = k'N^\nu\Omega(\varphi_s - \varphi_0) = k''N^\nu(1 - \varphi_0/\varphi_s)\varphi_2 \tag{6}$$

the difference in parentheses, and consequently $N^{()}$, becoming zero in the case that the coil dimension does not change with polymer concentration.

The probability $P^{)(}$ that two contacting segments, separated by the addition of solvent, belong to different molecules is given by

$$P^{)(} = (\partial N^{)(}/\partial\varphi_2)/(\partial N^{)(}/\partial\varphi_2 + \partial N^{()}/\partial\varphi_2)$$

which yields (eq 5 and 6)

$$P^{)(} = \left(2 - \frac{\varphi_0}{\varphi_s} - \frac{\partial(\varphi_0/\varphi_s)}{\partial\varphi_2}\varphi_2\right)^{-1} \tag{7}$$

In order to calculate $P^{)(}$, one needs to know the volume fractions of segments φ_0 and φ_s in the isolated coil and in the overlap region. There arises no problem with φ_0, which represents the ratio of v_2 (the specific volume of the pure (glassy) polymer) and the intrinsic viscosity $[\eta]$, i.e., the specific (hydrodynamic) volume of the isolated polymer coils. The situation is, however, more complicated with φ_s.

It is obvious that φ_s has to lie somewhere between φ_0 and φ_Θ (the value at the Θ condition prevailing at $\varphi_2 = 1$) even in the limit of $\varphi_2 \to 0$. Assuming that the concentration influences on φ_s can be neglected as long as A_2 suffices to describe the thermodynamic situation (i.e., Ω remains well below unity) and taking into account that φ_s has to become equal to φ_Θ for $A_2 = 0$, one may propose the following simple expression:

$$\varphi_s = (\varphi_0 + \varphi_\Theta)/2 \tag{8}$$

(The assumption of the geometric mean instead of the arithmetic would yield φ_s values only a few percent lower as long as $\varphi_0 > 0.5\varphi_\Theta$ but a very unhandy analytical expression for $P^{)(}$.)

From eq 7 and 8 one obtains

$$P^{)(} = \tfrac{1}{2}(1 + \varphi_0/\varphi_\Theta) \tag{9}$$

and by substituting $\varphi_0 = v_2/[\eta]$ and using the viscosity–molecular weight relationship

$$\frac{\varphi_0}{\varphi_\Theta} = \frac{[\eta]_\Theta}{[\eta]} = \frac{K_\Theta}{K} M^{-(a-0.5)} \tag{10}$$

where K and a are the Kuhn–Mark–Houwink parameters.

By means of eq 9 one can now calculate χ_0, the average interaction parameter at high dilution, from the individual contributions $\chi^{)(}$ and $\chi^{()}$ according to

$$\chi_0 = P^{)(}\chi^{)(} + (1 - P^{)(})\chi^{()} \tag{11}$$

and arrive at

$$\chi_0 = \frac{\chi^{)(} + \chi^{()}}{2} + \frac{\chi^{)(} - \chi^{()}}{2}\,\frac{\varphi_0}{\varphi_\Theta} \tag{12}$$

With the aid of eq 3 and 10 the following relation results:

$$A_2 = A_2^{\infty} + bM^{-(a-0.5)} \tag{13}$$

in which

$$A_2^{\infty} = \left(\frac{1}{2} - \frac{\chi^{)(} + \chi^{()}}{2}\right)\frac{1}{\rho_2^2 V_1} \tag{14}$$

and

$$b = \frac{\chi^{()} - \chi^{)(}}{2}\,\frac{K_\Theta}{K}\,\frac{1}{\rho_2^2 V_1} \tag{15}$$

According to these considerations it should be possible to determine $\chi^{)(}$ and $\chi^{()}$ by means of plots of A_2 vs. $M^{-(a-0.5)}$ from A_2^{∞}, the intercept for infinite molecular weight, and from the slope b.

Before such an evaluation is performed, a few tests are made to check whether the results are reasonable. First of all, $P^{)(}$ has to approach unity for Θ conditions, where the coil dimensions do not vary with concentration. As can be seen from eq 9, this is actually the case. Furthermore, $P^{)(}$ should tend toward 0.5 as M is raised in the case of thermodynamically good solvents, since all intramolecular contacts between segments will be opened upon dilution, just like intermolecular contacts, because of the infinitely large coil expansion. Again this reasoning is in

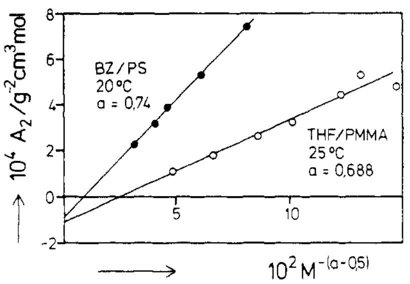


Figure 1. Evaluation of $A_2(M)$ according to eq 13 for the systems tetrahydrofuran/poly(methyl methacrylate)[6] (THF/PMMA, a = 0.688 from ref 7) and benzene/polystyrene[8] (BZ/PS).

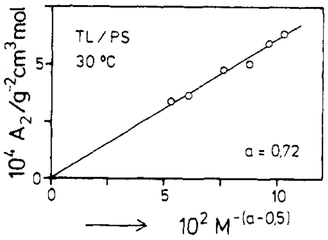


Figure 2. As in Figure 1 except for the system toluene/polystyrene[9] (TL/PS).

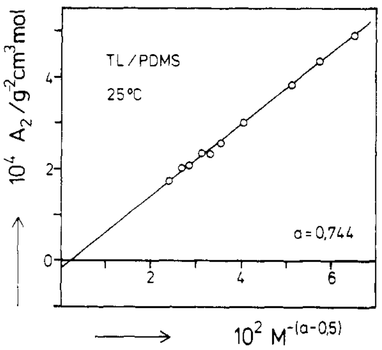


Figure 3. As in Figure 1 except for the system toluene/poly(α-methylstryene)[10] (TL/PDMS).

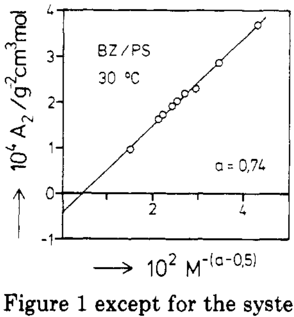


Figure 4. As in Figure 1 except for the system benzene/polystyrene[11] (TL/PS).

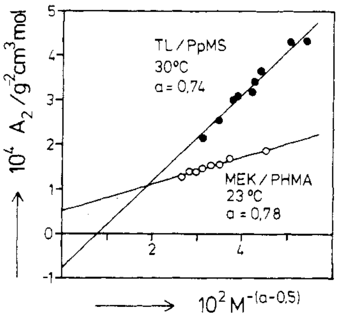


Figure 5. As in Figure 1 except for the systems toluene/poly(p-methylstyrene)[12] (TL/P$_p$MS) and methyl ethyl ketone/poly(hexyl methacrylate)[13] (MEK/PHMA).

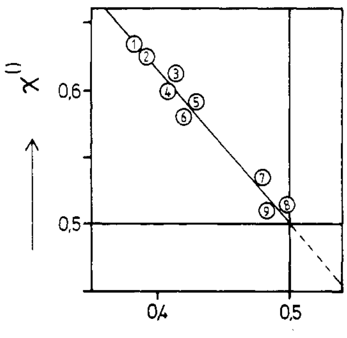


Figure 6. Dependence of the intramolecular interaction parameter $\chi^{()}$ on the intermolecular interaction parameter $\chi^{)(}$ (eq 7 and 11). The numbers stand for the following systems: (1) toluene/poly(*p*-methylstyrene);[12] (2) benzene/polystyrene;[8] (3) methyl ethyl ketone/poly(methyl methacrylate);[13] (4) toluene/poly(α-methylstyrene);[10] (5) carbon tetrachloride/polychloroprene;[15] (6) toluene/polystyrene;[9] (7) cyclohexane/polystyrene;[16] (8) toluene/poly(*p*-bromostyrene);[12] (9) methyl ethyl ketone/poly(hexyl methacrylate).[18]

accord with the present results, as can be seen from eq 9 and 10.

Results and Discussion

Figures 1–5 show plots according to eq 13. In all cases the experimentally observed variation of A_2 with M can very well be represented by straight lines in these diagrams.

The most striking feature of the present evaluation is the general occurrence of negative A_2^{∞} values. Although it had to be expected from the present model that this quantity differs from zero, the result is puzzling at first sight, since it implies that $A_2 = 0$ at some characteristic molecular weight of the polymer, even in thermodynamically good solvents, and this has not been reported so far to the knowledge of the author. On closer examination the discrepancy vanishes, however, since all the characteristic M values lie considerably above 10^8 according to the present results, i.e., well outside the molecular weight region normally investigated.

The slope (b in eq 13) of all lines is positive, as has to be the case with systems exhibiting a decrease of A_2 with increasing M; $b > 0$ implies (eq 15) $\chi^{()} > \chi^{)(}$ and is thus in accord with the expectation that the opening of intermolecular contacts between segments is in most cases thermodynamically more favorable than the opening of intramolecular ones. Only if additional effects (not discussed in the present context) turn up can the situation be reversed, as has been demonstrated[1] in the case of pronounced free volume effects, leading to an increase of A_2 with rising M, i.e., to $\chi^{()} < \chi^{)(}$.

The interaction parameters $\chi^{)(}$ and $\chi^{()}$, or equivalently the residual Gibbs energy of dilution for inter- and intramolecular contacts between segments, cannot be independent of each other; they only differ as a result of the spatial constraint in the case of $\chi^{()}$. Indeed such a correlation is obtained, as can be seen from Figure 6, where the results of the evaluation shown in Figures 1–5 fall on a common line for all systems, irrespective of the chemical nature of their components and the particular thermodynamic situation. The data needed to calculate the individual interaction parameters (eq 14 and 15) were taken from the literature;[14] for the systems denoted by a circled 1 and circled 5, the ratio K/K_Θ had to be estimated from the known a values by means of the general correlation that results if one evaluates literature data[14] of this ratio and of a.

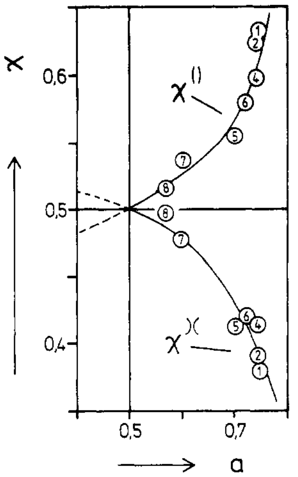


Figure 7. Variation of the intramolecular interaction parameter $\chi^{()}$ and of the intermolecular interaction parameter $\chi^{)(}$ with the thermodynamic quality of the solvent as measured by a, the exponent of the viscosity–molecular weight relationship. The symbols are the same as in Figure 6.

The observed interrelation demonstrates that $\chi^{()} = \chi^{)(}$ only for Θ conditions, where both parameters become 0.5 and consequently $A_2 = 0$, due to a very specific buildup of these quantities from the corresponding enthalpy and entropy contributions. As the separation of intermolecular contacts becomes thermodynamically more favorable, i.e., as $\chi^{)(}$ decreases, $\chi^{()}$ ascends. This finding can be rationalized by bearing in mind that the spatial constraints, which hinder the segments of a polymer molecule from distributing uniformly throughout the solution, become more effective as the tendency to surround the segments by solvent molecules becomes larger, i.e., as $\chi^{)(}$ becomes smaller.

The thermodynamic influence on $\chi^{)(}$ and $\chi^{()}$ can be examined by plotting these quantities as a function of a, the exponent of the viscosity–molecular weight relationship. The dependences resulting for different systems from a variation in temperature have to be expected to differ, and consequently the data points for different systems need not fall on a common line, in contrast to the situation encountered in plots of $\chi^{()}$ vs. $\chi^{)(}$, where chemical or structural particularities of the molecules involved largely cancel, since they influence both interaction parameters likewise. Nevertheless clear-cut results are obtained if the comparison is restricted to solutions of polystyrene and its derivatives and of poly(methyl methacrylate), as can be seen from Figure 7.

The finding clearly demonstrates that an improvement in the thermodynamic quality of the solvent only reduces $\chi^{)(}$, whereas it raises $\chi^{()}$. This observation is in accord with the reasoning concerning the interrelation of $\chi^{)(}$ and $\chi^{()}$.

In conclusion it can be stated that the interpretation of the molecular weight dependence of the second osmotic virial coefficient in terms of normally unequal interaction parameters for inter- and intramolecular contacts between segments yields a consistent and intelligible picture. Further tests of the present concept are under way.

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Block Copolymers near the Microphase Separation Transition. 3. Small-Angle Neutron Scattering Study of the Homogeneous Melt State

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ABSTRACT: A model set of six homogeneous (disordered) 1,4-polybutadiene–1,2-polybutadiene diblock copolymers containing perdeuterated 1,4-polybutadiene blocks have been examined by small-angle neutron scattering (SANS). Each of the SANS spectra exhibits a peak in the scattering intensity $I(q^*)$ at wave vector q^*, which diverges upon approaching the microphase separation transition (MST). These findings are in close agreement with the MST theory of Leibler, which predicts that $I(q^*)$ should depend on the product of the degree of polymerization N and interaction parameter χ; this provides a new, sensitive method of determining χ for polymer pairs. The theory fails to account for "domain" scattering, which results in an unpredicted increase in the level of $q < q^*$ scattering as $\chi N \rightarrow (\chi N)_{\mathrm{MST}}$ in samples containing 18–25% 1,4-polybutadiene. This investigation corroborates our previous findings concerning the rheological properties of block copolymers near the MST.

Introduction

The combined effects of advances in quantitative theory, experimental techniques, and elegant synthetic chemistry over the past decade have brought about a revolution in the study of polymer–polymer thermodynamics. This synergistic, cross-disciplinary growth has been particularly evident in the area of block copolymers. Nevertheless, the limited availability of appropriate polymer pairs has focused most structure–property investigations of block copolymers on a select class of materials consisting of polystyrene and polydiene diblock and triblock copolymers. The inherent incompatibility of polystyrene and polydienes, together with the intrinsic differences in segment electron densities and chemical reactivities toward heavy metal oxidizing agents, and the availability of deuterated monomers make such copolymers useful substrates for studying the microphase-separated state by X-ray and neutron scattering and electron microscopy.[1-6] Furthermore, the elevated glass-transition temperature of polystyrene (~100 °C) imparts commercially important physical properties to these materials and an obvious motivation for understanding the structure–property relationships that govern their behavior.[7,8] The above-stated attributes that make polystyrene–polydiene block copolymers attractive candidates for studying microphase (ordered) structure and properties are largely detrimental in their application to the investigation of the microphase separation transition (MST). Chemical dissimilarity, which renders X-ray contrast and differential oxidizability utilized in obtaining phase contrast for electron microscopy, also leads to a large Flory interaction parameter ($\chi \cong 10^{-1}$) and a correspondingly low critical degree of polymerization for microphase separation ($N_c \cong 10^2$). The elevated glass-transition temperature that provides desirable mechanical properties limits any investigation of melt transitions to temperatures greater than ~100 °C. This greatly reduces the range of available experimental space and can lead to spurious and complicating chemistry. Nevertheless, several investigators have identified rheological[9-11] and X-ray scattering[12] phenomena in styrene–butadiene and styrene–isoprene block copolymers at elevated temperatures, which have been attributed to the microphase separation transition (MST). Yet it is apparent that the theoretical treatment[13] concerning the MST has far outdistanced our ability to quantitatively study such phenomena with conventional polystyrene–polydiene systems. This has motivated us to develop a more suitable model set of diblock copolymers with which to examine the detailed theoretical predictions and physical properties associated with this class of polymers near the MST.

The first of this series of papers[14] described the preparation and physical characteristics of a model set of 1,4-polybutadiene–1,2-polybutadiene diblock copolymers near the MST. Owing to a coupling between the structural order parameter and molecular diffusion, the phase state of these materials can be determined from rheological properties, as detailed in a second publication.[15] In the present and third report of this series, we address in detail the issue of structure in the homogeneous (disordered) melt state as determined by small-angle neutron scattering (SANS); the initial findings of this investigation have been published separately.[16] These results in large part corroborate the theoretical findings of Leibler[13] concerning disordered diblock copolymers, although the predicted scattering correlation function cannot account for all the

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