Review

Fine characterization of oligomers and polymers in dilute solution

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Abstract

A fine characterization was made of atactic poly(\(a\)-methylstyrene) and atactic polystyrene on the basis of the helical wormlike chain model. It is found that there is a remarkable difference in chain stiffness and local chain conformation between the two polymers. Such a difference is shown to be reflected clearly in behavior of equilibrium, transport, and dynamical properties and also in the excluded-volume effects.

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Keywords: Dilute solution properties; Chain stiffness; Local chain conformation; Polystyrene; Poly(\(a\)-methylstyrene); Helical wormlike chain

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1. Introduction

Recently, a new framework of polymer solution science has been established on extensive theoretical and experimental studies of dilute solution properties of oligomers and polymers on the basis of the helical wormlike (HW) chain model [1,2]. The HW chain model is a very general continuous model applicable for both flexible and semiflexible polymers, and has already been proved to be useful for understanding behavior of almost all equilibrium conformational, steady-state transport, and dynamical properties of polymers in both the unperturbed (\(\Theta\)) and
perturbed states. In the framework, we can now obtain information about chain stiffness and local chain conformation on the basis of the HW chain model. Such a scheme of analyses of dilute solution properties is called the fine polymer molecular characterization. Such information bridges the gap between solution properties and chemical structures of polymers, and enables us to discuss how they relate to each other.

In this paper, we review our recent results of the fine characterizations carried out for two kinds of typical flexible polymers, atactic poly(α-methylstyrene) (a-PαMS) [3,4] and atactic polystyrene (a-PS) [5]. In Fig. 1 are shown the chemical structures of repeat units of a-PαMS and a-PS. As depicted in the figure, a-PαMS has a methyl group at its α-position, while a-PS has a hydrogen atom instead. Because of this difference in the chemical structure, a-PαMS and a-PS may be expected to have rather different characters from each other. The main purpose of this paper is to confirm this expectation, and further to explain how the difference is reflected in their solution behavior.

The plan of this paper is as follows: in Section 2, we give a short sketch of the HW chain model. In Section 3, we make rather detailed analyses of two kinds of equilibrium properties, i.e., the intrinsic viscosity [η] and translational diffusion coefficient D, of a-PαMS and a-PS in their respective θ states on the basis of the HW chain model, and then discuss the difference in chain stiffness and local chain conformation between the two polymers. In Section 4, we show results for two kinds of steady-state transport properties, i.e., the intrinsic viscosity [η] and translational diffusion coefficient D, of a-PαMS and a-PS in their respective θ states. In Section 5, we discuss the excluded-volume problem, i.e., the gyration-, viscosity-, and hydrodynamic-radius expansion factors zG, zη, and zH and also the second virial coefficient A2, for the two polymers. In Section 6, we refer to two topics of dynamical properties, i.e., the dynamic depolarized light scattering and first cumulant of the dynamic structure factor, of the two polymers in their respective θ states.

2. The HW chain model

The HW chain [1] is defined as an elastic wire model with both bending and torsional energies. Its total elastic energy becomes a minimum of zero when its contour becomes a regular helix, which is called the characteristic helix. The shape of the characteristic helix may be specified by the radius ρ and pitch h, which may be written in terms of characteristic helix

\[ \lambda^{-1} = \infty \]

\[ \rho = \frac{k_0}{(k_0^2 + \tau_0^2)} \]

\[ h = 2\pi \tau_0/(k_0^2 + \tau_0^2) \]

differential-geometrical curvature κ0 and torsion τ0 of the characteristic helix as

According to the HW chain model, real polymer chains in dilute solutions may be pictured as regular helices (i.e., the characteristic helices) disturbed by thermal fluctuation or as random coils retaining more or less helical portions. The extent to which the helical form may be preserved is specified by the static stiffness parameter λ−1 having the dimension of length, so that the regular helical structure is destroyed to a less extent in the chain with larger stiffness λ−1. The HW chain with λ−1 = ∞ is identical with the characteristic helix. This situation is schematically depicted in Fig. 2. A special case of the HW chain with κ0 = 0 corresponds to the Kratky–Porod (KP) wormlike chain [6] (with the torsional energy), for which the characteristic helix becomes the straight line. In addition to the parameters κ0, τ0, and λ−1, the shift factor ML, as defined as the ratio M/L of the molecular weight M of a real polymer chain to the total contour length L of the corresponding HW chain, is required in an application of HW chain.

From analyses of experimental data for dilute solution properties obtained for a series of test samples of a given polymer over a wide range of M including the oligomer region on the basis of the HW chain model, we can determine the values of the four model parameters κ0, τ0, λ−1, and ML for the polymer. Then, with the values of the parameters so determined, we can discuss the chain stiffness and local chain conformation of the polymer.
3. Equilibrium properties

3.1. Mean-square radius of gyration

In this subsection, we deal with the mean-square radius of gyration \( \langle S^2 \rangle \) for a-PzMS with the fraction of racemic diads \( f_r = 0.72 \) and for a-PS with \( f_r = 0.59 \) in their respective \( \Theta \) states. The HW model parameters of the two polymers are then determined from comparisons of the experimental values of \( \langle S^2 \rangle \) with the corresponding HW theoretical values. We note that the theoretical \( \langle S^2 \rangle \) as a function of the degree of polymerization \( x \) may be expressed in terms of the four model parameters \( k_0, \tau_0, \lambda^{-1}, \text{and } M_L \).

Fig. 3 shows the ratio \( \langle S^2 \rangle/x_w \) \( \langle S^2 \rangle \) in \( \text{Å}^2 \) plotted against the weight-average degree of polymerization \( x_w \) for a-PzMS in cyclohexane at 30.5 °C (\( \Theta \)) [3] and for a-PS in cyclohexane at 34.5 °C (\( \Theta \)) [7–9] in a semi-logarithmic manner. The experimental values of \( \langle S^2 \rangle \) have been determined from small-angle X-ray scattering measurements for the samples with \( x_w \lesssim 10^3 \) and from static light scattering measurements for those with \( x_w \gtrsim 10^5 \). In the shaded area \( (x_w \gtrsim 10^3) \) of this figure, a-PzMS and a-PS have almost the same values of \( \langle S^2 \rangle/x_w \approx (8.1 \text{Å}^2) \) independent of \( x_w \) with each other. Hence, from the conventional analyses of such data in the range of \( x_w \gtrsim 10^5 \) on the basis of the Gaussian chain model [10], any information cannot be obtained about the difference in chain stiffness and local chain conformation between the two polymers. On the other hand, the behavior of \( \langle S^2 \rangle/x_w \) for the two polymers is quite different in the oligomer region. As \( x_w \) is increased, \( \langle S^2 \rangle/x_w \) as a function of \( x_w \) for a-PS first increases monotonically and then approaches its asymptotic value, while the ratio for a-PzMS first increases steeply, then passes through a maximum at \( x_w \approx 30 \), and finally approaches its asymptotic value. The difference in the behavior of \( \langle S^2 \rangle/x_w \) in the range of \( x_w \lesssim 10^5 \) can never be explained by the Gaussian chain model and even by the Kuhn wormlike chain model.

In the figure, the solid curves represent the respective best-fit HW theoretical values calculated with the values of the HW model parameters listed in Table 1. The theoretical curves may reproduce well the respective experimental values. In Table 1 are also given the values of \( \rho \) and \( h \) calculated from Eqs. (1) and (2). From the values of \( \rho \) and \( h \), it is seen that there is a remarkable difference in shape between the characteristic helices of a-PzMS and a-PS; the value of \( \rho \) is much larger for a-PzMS than that for a-PS. In addition to this, the value of \( x^{-1} \) is about two times larger for a-PzMS than for a-PS. These results indicate that the a-PzMS chain tends to retain rather large and clearly distinguishable helical portions in dilute solution compared to the a-PS chain. In order to visualize such a difference in local chain conformation between a-PzMS and a-PS, we have generated HW Monte Carlo chains [1,11] corresponding to a-PzMS and a-PS, each with \( x = 500 \), using the above values of the HW model parameters. In Fig. 4 are depicted representative instantaneous chain contours obtained in such a way that their radii of gyration \( S \) are just equal to the respective \( \langle S^2 \rangle^{1/2} \). The shaded sphere has the radius \( S \), which is equal to 63.6 and 63.2 Å for a-PzMS and a-PS, respectively. As seen from the figure, the chain contour of a-PzMS is rather smooth with the retention of distinguishable helical portions. Further it is interesting to see that the chain contour of a-PS is much more random than that of a-PzMS, while these two polymers have almost the same asymptotic value of \( \langle S^2 \rangle/x_w \), as seen from Fig. 3.

As shown in Fig. 5, the two successive skeletal bond angles in the main chain of a-PzMS are appreciably different.

Table 1

Values of the HW model parameters and characteristic helix parameters for a-PzMS and a-PS

| Polymer   | \( \lambda^{-1} \) | \( \lambda^{-1} \) | \( \lambda^{-1} \) | \( M_L \) (Å⁻¹) | \( \rho \) (Å) | \( h \) (Å) |
|-----------|-------------------|-------------------|-------------------|----------------|-------------|----------|
| a-PzMS    | 3.0               | 0.9               | 46.8              | 39.8           | 14.3        | 27.0     |
| a-PS      | 3.0               | 6.0               | 20.6              | 35.8           | 1.37        | 17.3     |

Fig. 3. Plots of \( \langle S^2 \rangle/x_w \) against log \( x_w \) for a-PzMS and a-PS. The solid curves represent the HW theoretical values.

Fig. 4. Representative instantaneous contours of HW Monte Carlo chains corresponding to the a-PzMS and a-PS with \( x = 500 \).
from each other because of the steric hindrance between its side groups. In addition to this, its main chain tends to adopt a trans-zigzag (planar) conformation because of a predominance of the trans-trans conformation for its racemic diads, which are numerically superior to the meso diads. For these reasons, the a-PzMS chain tends to retain the large and clearly distinguishable helical portions. On the other hand, as for a-PS, the two successive skeletal bond angles in the main chain are almost identical with each other because the steric hindrance is small. Furthermore, the a-PS chain includes many C–C bonds adopting the gauche conformation because its \( f_g \) is not so large, so that the chain tends to bend sharply at various places. Therefore, its contour becomes much more random than that of a-PzMS. As stated above, there is a clear difference in chain stiffness and local chain conformation between the a-PzMS and a-PS chains, and it is reflected in the difference in the behavior of \( \langle S^2 \rangle \).

3.2. Mean-square optical anisotropy

In this subsection, we make a study of another equilibrium property, the mean-square optical anisotropy \( \langle \Gamma^2 \rangle \), of a-PzMS and a-PS in their respective \( \Theta \) states. The quantity \( \langle \Gamma^2 \rangle \) depends on the optical anisotropy of the repeat unit as well as the polymer chain conformation, and it can be determined experimentally from anisotropic light scattering measurement with a set of a polarizer and an analyzer having very small extinction ratios. We note that the HW theoretical \( \langle \Gamma^2 \rangle \) as a function of \( x \) may be expressed in terms of the four basic model parameters \( \kappa_0, \tau_0, \lambda^{-1}, \) and \( M_L \) and the local polarizability tensor \( \alpha_0 \) of the repeat unit of the polymer [1,12].

Fig. 6 shows plots of \( \langle \Gamma^2 \rangle / x_w \) (in \( \text{Å}^6 \)) against log \( x_w \) for a-PzMS [13] and a-PS [5,14] in their respective \( \Theta \) states. As seen from the figure, the values of \( \langle \Gamma^2 \rangle / x_w \) for the two polymers for very small \( x_w \) are in rather good agreement with each other. As \( x_w \) is increased, \( \langle \Gamma^2 \rangle / x_w \) for a-PzMS increases more steeply than that for a-PS and approaches the asymptotic value \( 100 \text{Å}^6 \) appreciably larger than the value \( 61 \text{Å}^6 \) for a-PS. Since the optical anisotropies of the \( \text{C}^\alpha-\text{CH}_3 \) part of a-PzMS and of the \( \text{C}^\alpha-\text{H} \) part of a-PS are both much smaller than that of the \( \text{C}^\beta \)-phenyl part, the optical anisotropy of the repeat unit itself of a-PzMS may be considered to be almost identical with that of a-PS, as confirmed by the above-mentioned agreement in the range of very small \( x_w \). Therefore, the difference in the behavior of \( \langle \Gamma^2 \rangle / x_w \) for large \( x_w \) between the two polymers may be regarded as arising from those in chain stiffness and local chain conformation mentioned in the preceding subsection. In the figure, the solid curves represent the HW theoretical values calculated with the values of the model parameters listed in Table 1 along with those of the tensor \( \alpha_0 \) estimated from the chemical structures of a-PzMS and a-PS. It is clearly seen that the HW theory may explain satisfactorily that difference in the behavior of \( \langle \Gamma^2 \rangle / x_w \).

4. Transport properties

In Section 3, we have seen that there is a clear difference in chain stiffness and local chain conformation between the a-PzMS and a-PS chains. It may be expected that such a difference is also reflected in the behavior of steady-state transport properties, such as the intrinsic viscosity \( [\eta] \) and translational diffusion coefficient \( D \). Therefore, we further determine the two transport properties from viscosity and dynamic light scattering measurements for a-PzMS and a-PS, and compare the results with the HW theory in order to confirm whether the above expectation is true or not. We note that for the theoretical evaluation of the transport properties for flexible polymers on the basis of the HW chain model, we need another parameter, i.e., the bead diameter \( d_b \), to express the hydrodynamic chain thickness of the HW model in addition to the four basic model parameters [1,15,16].

Fig. 7 shows double-logarithmic plots of \( [\eta] \) (in dL/g) against weight-average molecular weight \( M_w \) for a-PzMS [17] and a-PS [8,18,19] in their respective \( \Theta \) states. Fig. 8 shows double-logarithmic plots of \( \eta_0 M_w D / k_B T \) (in cm\(^{-1} \)) against \( M_w \) for a-PzMS [17] and a-PS [8,16,20] in their
respective $\Theta$ states, where $\eta_0$ is the viscosity coefficient of the solvent, $k_B$ the Boltzmann constant, and $T$ the absolute temperature. In these figures, the dotted lines represent the respective asymptotic straight lines of slope $\frac{1}{2}$, representing the values evaluated for the unperturbed Gaussian chain in the nondraining limit [10]. As for a-PS, both the data points of $[\eta]$ and $\eta_0 M_w D/k_B T$ follow the respective asymptotic straight lines over a wide range of $M_w \approx 5 \times 10^5$. On the other hand, as for a-PzMS, the data points of $[\eta]$ deviate definitely upward from the asymptotic straight line for $M_w \approx 2 \times 10^5$ and form an inverse S-shaped curve as a whole, while those of $\eta_0 M_w D/k_B T$ deviate downward from the asymptotic straight line for $M_w \approx 2 \times 10^5$ and form an S-shaped curve as a whole. In Figs. 7 and 8, the solid curves represent the respective best-fit HW theoretical values. The theoretical values are seen to reproduce satisfactorily the data points. The values of the HW model parameters so determined are listed in Table 2.

Table 2. Values of the HW model parameters for a-PzMS and a-PS determined from transport properties

| Polymer | $\chi^{-1} k_0$ | $\chi^{-1} \ell_0$ | $\chi^{-1}$ (Å) | $M_L$ (Å$^{-1}$) | $d_0$ (Å) | OBSD quantity |
|---------|----------------|-----------------|----------------|----------------|---------|---------------|
| a-PzMS  | 3.0            | 1.2             | 43.0           | 42.3           | 10.3    | $[\eta]$     |
|         | 3.0            | 1.2             | 56.2           | 38.0           | 10.7    | $D$           |
| a-PS    | 3.0            | 6.0             | 23.5           | 42.6           | 10.1    | $[\eta]$     |
|         | 3.0            | 6.0             | 27.0           | 35.0           | 9.5     | $D$           |

5. Excluded-volume effects

5.1. Gyration-radius expansion factor

In the preceding two sections, we made the experimental studies on the equilibrium and transport properties of a-PzMS and a-PS in their respective $\Theta$ states. Following the well-established procedures by means of the HW theories, the data for $\langle S^2 \rangle$, $\langle T^2 \rangle$, $[\eta]$, and $D$ were analyzed to show that the a-PzMS chain tends to retain rather large and clearly distinguishable helical portions while the a-PS chain does not. Such a difference in chain stiffness and local chain conformation between the two polymer chains was discussed in comparison with that in the chemical structure. With the above results of the fine characterization for a-PzMS and a-PS in their $\Theta$ states, we now proceed to investigate the excluded-volume problems for the two polymers. In this subsection, we investigate the gyration-radius expansion factor $\zeta_S$ defined by

$$\langle S^2 \rangle = \langle S^2 \rangle_0 \zeta_S^2.$$  \hspace{1cm} (3)

In this section, the subscript 0 indicates the unperturbed value.

As mentioned in the opening paragraph, the HW model may explain the behavior of dilute solution properties of real polymer chains also in the perturbed state (good-solvent condition) in which the excluded-volume effect plays an important role. The conventional theory of the excluded-volume effect, i.e., the two-parameter (TP) theory [10] based on the Gaussian chain model, has been confirmed to be valid only in a restricted range of extremely large $M$ where effects of chain stiffness on the excluded-volume effect is not important. On the other hand, the theory [1,21–23] based on the HW model, which takes account of both effects of excluded-volume and chain stiffness, may be valid over a wide range of $M$ including the oligomer region. Within the framework of the HW theory, all the expansion factors (intramolecular excluded-volume effect) including $\zeta_S$ may be described by the quasi-two-parameter (QTP) theory, which claims that they are
functions only of the (intramolecular) scaled excluded-volume parameter \( \hat{z} \). In the TP theory, on the other hand, all the expansion factors are functions only of the conventional excluded-volume parameter \( z \) \([10]\). The parameter \( \hat{z} \) is related to \( z \) by the equation \( \hat{z} = \langle z \rangle K(\lambda L)z \), where \( K \) is a function of the reduced contour length \( \lambda L \) of the HW chain. \( K \) becomes \( \frac{4}{3} \) and 0 in the limits of \( \lambda L \rightarrow \infty \) and 0, respectively, so that the QTP theory becomes identical with the TP theory in the former (random coil) limit. In the latter (rigid rod) limit, all the expansion factors become unity and the intramolecular excluded-volume effect vanishes. The main purpose of this subsection is to confirm the validity of the above QTP theory for \( z_S \) of a-PzMS and a-PS.

Fig. 9 shows double-logarithmic plots of \( \langle S^2 \rangle /x_w \) against \( x_w \) for a-PzMS \([24]\) and a-PS \([9, 25]\) in three kinds of good solvents, i.e., toluene, 4-tert-butylationuene, and \( n \)-butyl chloride. There are also plotted the data for the two polymers in their respective \( \Theta \) states, which have been reproduced from Fig. 3. As seen from the figure, for each polymer, the data in the good solvents agree well with those in the \( \Theta \) state in the range of \( x_w \leq 30 \) and then deviate upward progressively from the latter with increasing \( x_w \) in the range of \( x_w \geq 30 \) because of the intramolecular excluded-volume effect. The value of \( x_w \) at which the effect appears is somewhat larger for a-PzMS than for a-PS, because the former chain is stiffer than the latter. For each of the polymers, the agreement in the range of \( x_w \leq 30 \), where the intramolecular excluded-volume effect may be ignored, enables us to evaluate the values of \( z_S \) from Eq. (3) by adopting the values of \( \langle S^2 \rangle \) in the \( \Theta \) state as the unperturbed values \( \langle S^2 \rangle_0 \) in the good solvents. In Fig. 10 are shown double-logarithmic plots of \( x_w^2 \), so evaluated, against \( \hat{z} \) for a-PzMS and a-PS. The symbols have the same meanings as in Fig. 9. The values of \( \hat{z} \) have been calculated from the value of \( M_w \) for each sample with those of \( \lambda^{-1} \), \( M_L \), and an additional parameter, i.e., the reduced excluded-volume strength \( \lambda B \) \([1]\), to express the solvent quality. In Table 3 are listed the values of \( \lambda B \) for the respective polymer-solvent systems. It is seen from the figure that the data points for a-PzMS in the three different good solvents along with those for a-PS form a single-composite curve. This result confirms the validity of the QTP prediction that \( z_S \) is a function only of \( \hat{z} \) irrespective of the differences in polymer species (chain stiffness and local chain conformation) and solvent condition.

5.2. Viscosity- and hydrodynamic-radius expansion factors

In this subsection, we proceed to make a study of the viscosity- and hydrodynamic-radius expansion factors \( z_\eta \) and \( z_H \). As in the case of \( z_S \), \( z_\eta \) and \( z_H \) are defined by

\[
[\eta] = [\eta]_0 \hat{z}_\eta^3,
\]

\[
R_H = R_H(0) z_H,
\]

where \( R_H \) is the hydrodynamic radius defined by

\[
R_H = k_B T / 6 \pi \eta_0 D.
\]

The QTP theory predicts that \( z_\eta \) and \( z_H \) as well as \( z_S \) are functions only of \( \hat{z} \) irrespective of polymer species (chain stiffness and local chain conformation) and solvent condition.

**Table 3**

| Polymer | Solvent          | Temp (°C) | \( \lambda B \) |
|---------|------------------|-----------|------------------|
| a-PzMS  | Cyclohexane      | 30.5      | 0                |
|         | toluene          | 25.0      | 0.43             |
|         | 4-tert-butylationuene | 25.0 | 0.12             |
|         | \( n \)-butyl chloride | 25.0 | 0.080            |
| a-PS    | Cyclohexane      | 34.5      | 0                |
|         | toluene          | 15.0      | 0.26             |
|         | 4-tert-butylationuene | 50.0 | 0.10             |
The purpose of this subsection is to confirm this prediction for a-PzMS and a-PS.

Figs. 11 and 12 show double-logarithmic plots of $\alpha_H$, respectively, against $\xi$ for a-PzMS [26] and a-PS [19,20] in the good solvents. The values of $\alpha_H$ for the two polymers may be evaluated by adopting the values of [\(\eta\)] and $R_H$ in their respective $\Theta$ states as the unperturbed values $[\eta]_0$ and $R_{H,0}$ in the good solvents, respectively. As seen from these figures, the data points for each expansion factor form a single composite curve. These results indicate that the QTP theory is valid for $\alpha_H$ as well as $\alpha_S$.

5.3. Second virial coefficient

In the preceding two subsections, we investigated the expansion factors, which are concerned with the intramolecular excluded-volume effect. In this subsection, we proceed to study the behavior of the second virial coefficient $A_2$, which is concerned with the intermolecular excluded-volume effect. The conventional TP theory [10] of $A_2$ predicts the interpenetration function $\Psi$ appearing in $A_2$ to be a function only of $\xi$, as in the cases of the expansion factors. On the other hand, the theory [1,27,28] of $A_2$ based on the HW chain model predicts that $\Psi$ is not a function only of $\xi$ nor $\tilde{\xi}$ because of chain stiffness, and also that the dependence of $A_2$ on $M$ is remarkably affected, especially for small $M$, by a chemical difference of the chain ends from the inner parts of the chain. The main purpose of this subsection is to confirm the validity of the HW theory of $A_2$ for a-PzMS and a-PS.

According to the HW theory [1,27,28], $A_2$ may then be written as

$$A_2 = A_2^{(HW)} + A_2^{(E)},$$

(7)

where $A_2^{(HW)}$, the part of $A_2$ without the effects of chain ends, and $A_2^{(E)}$ represents their contribution to $A_2$. The first term $A_2^{(HW)}$ may be written as

$$A_2^{(HW)} = 4\pi^{3/2}N_A(\langle S^2 \rangle^{3/2}/M^2)\Psi \quad \text{(in good solvents)},$$

(8)

where $N_A$ is the Avogadro constant and the term $A_2^{(HW)}$ represents possible effects of three-segment interactions. At the $\Theta$ temperature, $\Psi$ vanishes for all values of $M$, while the term $A_2^{(HW)}$ may remain finite for finite $M$. The contribution of $A_2^{(HW)}$ may be ignored for good-solvent system.

Fig. 13 shows double and semi-logarithmic plots of $A_2$ (in cm$^3$ mol/g$^2$) against $M_w$ for a-PzMS in toluene at 25.0°C [29] and in cyclohexane at 30.5°C ($\Theta$) [29]. Fig. 14 shows similar plots for a-PS in toluene at 15.0°C [25] and in cyclohexane at 34.5°C ($\Theta$) [30,31]. These experimental values of $A_2$ have been determined from static light scattering measurements. In these figures, the solid curves represent the HW theoretical values of $A_2 = A_2^{(HW)} + A_2^{(E)}$, and the dashed and dotted curves represent...
Agreement between theory and experiment is seen to be rather satisfactory. It is clearly seen that, for all the systems, the effects of the chain ends on $A_2$ remain appreciable up to $M_w = 10^4–10^5$.

Figs. 15(a) and 16(a) show plots of the experimental values of $\Psi$, which have been evaluated from the experimental values of $A_2$ by subtraction of the contributions of $A_2^{(E)}$, against $\alpha_3^S$ for a-PaMS [29] and a-PS [25], respectively, in the three good solvents, i.e., toluene, 4-tert-butyltoluene, and n-butyl chloride. The solid and dashed curves represent the HW theoretical values.

The dotted curves connect smoothly the data points at constant $B$ (solvent condition) and $M_w$, respectively. The dotted curves represent the TP theory values. As seen from the figures, $\Psi$ as a function of $\alpha_3^S$ depends separately on $M_w$ and $B$ and deviates appreciably upward from the TP prediction. In Figs. 15(b) and 16(b), the HW theoretical values of $\Psi$ as a function of $\alpha_3^S$ are plotted for a-PaMS and a-PS, respectively. The solid curves represent the values for which $\lambda L$ (or $M$) is changed at constant $\lambda B$, while the dashed curves represent the values for the case in which $\lambda B$ is changed at constant $\lambda L$ (or $M$). From a comparison of Figs. 15(b) and 16(b) with Figs. 15(a) and 16(a), there seems to be semiquantitative agreement between theory and experiment. For the calculation of the theoretical values of $\Psi$, the intermolecular scaled excluded-volume parameter is necessary in addition to $z$ and $\bar{z}$ [1,27]. These results indicate that $\Psi$ is not a function only of $z$ nor $\bar{z}$.
6. Dynamical properties

6.1. Dynamic depolarized light scattering

This section is devoted to a discussion of dynamical properties of a-PzMS and a-PS in their respective Θ states. As seen in the preceding sections, there is a clear difference in chain stiffness and local chain conformation between the a-PzMS and a-PS chains. Such a difference is naturally expected to have a great influence on behavior of dynamical properties of the two polymers. In the present and following subsections, we investigate two kinds of dynamical properties of polymer chains, i.e., the power spectrum \( J_\Gamma \) of the excess depolarized component of the dynamic light scattering intensity and the first cumulant \( \Omega(k) \) of the dynamic structure factor, for a-PzMS and a-PS.

From a frequency-domain dynamic depolarized light scattering measurement for a test sample, we can determine the (excess) power spectrum \( J_\Gamma \) due to the solute polymer molecule as a function of the difference \( \Delta \omega \) between the angular frequencies of the scattered and incident light waves. We can then determine a relaxation time \( \tau_\Gamma \), associated with local rotational motions of the polymer chain, defined as the reciprocal of the half-width at half-maximum of \( J_\Gamma \) thus determined. The asymptotic value \( \tau_{\Gamma,\infty}/\tau_\Gamma^0 \) of the ratio \( \tau_\Gamma \) to its value \( \tau_\Gamma^0 \) for the monomer in the limit of \( M \to \infty \) represents the degree of restriction on the local motion of the isolated motional unit (monomer) due to its incorporation into the long enough polymer chain, and may be regarded as a measure of dynamic chain stiffness [1,32].

Fig. 17 shows double-logarithmic plots of \( \tau_\Gamma/\tau_\Gamma^0 \) against \( x_w \) for a-PzMS in cyclohexane at 30.5 °C (Θ) [33] and a-PS in cyclohexane at 34.5 °C (Θ) [34], where \( \tau_\Gamma^0 \) is the \( \tau_\Gamma \) of the monomer of each of a-PzMS and a-PS. From this figure, it is seen that \( \tau_\Gamma/\tau_\Gamma^0 \) for each of the polymers first increases with increasing \( x_w \) and seems to level off in the limit of \( x_w \to \infty \), in contrast to the theoretical prediction based on the spring-bead model (i.e., dynamic version of the Gaussian chain model) [35]. In the limit of \( x_w \to \infty \), the value of the ratio for a-PzMS is larger than that for a-PS, confirming the conclusion on the basis of the dynamic HW model that there is good correlation between dynamic and static chain stiffness [1,32]. We note that the value of static chain stiffness \( \lambda^{-1} \) is larger for a-PzMS than for a-PS, as seen in Sections 3 and 4. The heavy solid and dashed curves represent the theoretical values calculated on the basis of the dynamic HW chain model [36] with the parameter values determined from \( \langle S^2 \rangle \) and proper values of the dynamic model parameters for a-PzMS and a-PS, respectively. The light solid and dashed curves represent the values for the rigid sphere model [34] for a-PzMS and a-PS, respectively. The behavior of the data points for \( x_w \leqslant 10 \) may be explained well by the rigid sphere model while those for \( x_w \geqslant 10 \) deviate downward from the theoretical values for the rigid sphere model, indicating that the orientation of the polarizability tensor affixed to each repeat unit relaxes due to the rotation of the entire chain for the oligomer with \( x_w \leqslant 10 \) but the former becomes independent of the latter for \( x_w \geqslant 10 \). For \( x_w \geqslant 10 \), the dynamic HW theory may explain well the asymptotic behavior of the data points and also the difference in \( \tau_{\Gamma,\infty}/\tau_\Gamma^0 \) between a-PzMS and a-PS, although agreement between theory and experiment is only semiquantitative for a-PzMS.

6.2. First cumulant of the dynamic structure factor

The first cumulant \( \Omega(k) \), which is defined as the initial decay rate of the dynamic structure factor \( S(k,t) \) as a function of the magnitude \( k \) of the scattering vector and time \( t \), may be determined from time-domain dynamic (isotropic) light scattering measurements on dilute polymer solutions. As is well known, \( \Omega(k) \) reflects the translational motion of the entire polymer chain in the range of \( \langle S^2 \rangle^{1/2} \leqslant 1 \), while it reflects the internal motions of the chain in the range of \( \langle S^2 \rangle^{1/2} \geqslant 1 \). For long enough, flexible polymer chains without excluded volume, it was considered on the basis of the Gaussian chain model that the plot of \( \eta_0 \Omega(k)/k_BTk^3 \) against \( \langle S^2 \rangle^{1/2} \) is universal, or the plot, especially its height in an intermediate range of \( k \), is independent of the polymer–solvent system [37–39]. On the other hand, it has been shown on the basis of the HW chain model that the above plot may depend on the kind of polymer even for large molecular weight (\( \sim 10^7 \)) [40]. The main purpose of the present subsection is to confirm this prediction for a-PzMS and a-PS, which are clearly different in chain stiffness and local chain conformation from each other.

Fig. 18 shows plots of \( \eta_0 \Omega(k)/k_BTk^3 \) against \( \langle S^2 \rangle^{1/2} \) for a-PzMS (with \( M_w = 3.22 \times 10^6 \) and \( 5.46 \times 10^6 \) in
properties between a-P and explain well the differences in the behavior of those effects. Then, it has been shown that the HW theory may
dynamical properties and also in the excluded-volume
reflected in the behavior of the equilibrium, transport, and polymers. We have also seen how such a difference is
made it clear that there is a remarkable difference in chain
P
realized.
realization and therefore that the universality cannot in general be
slightly on both chain stiffness and local chain conforma-
tional quantitative. The qualitative agreement between
agreement between theory and experiment is not comple-
what downward from the corresponding data points and
flexible polymers with very large
k
3-region cannot
be realized even for such large Mw. In the figure, the solid
and dashed curves represent the HW theoretical values [40]
calculated with the model parameters determined from (S)
and proper values of the dynamic model parameters along
with the experimental values of the reduced hydrodynamic radius ρ−1 for a-PzMS and a-PS, respectively. As seen from
the figure, the HW theory may correctly predict the order
of the height of the plateau in the k3-region for a-PzMS and a-PS, although the theoretical curves deviate somewhat downward from the corresponding data points and agreement between theory and experiment is not completely quantitative. The qualitative agreement between
theory and experiment indicates that the height of the
k3-region for flexible polymers with very large Mw depends
slightly on both chain stiffness and local chain conformation
and therefore that the universality cannot in general be
realized.

7. Conclusion

As we have seen, a fine characterization carried out for a-PzMS and a-PS on the basis of the HW chain model has
made it clear that there is a remarkable difference in chain stiffness and local chain conformation between the two
polymers. We have also seen how such a difference is reflected in the behavior of the equilibrium, transport, and
dynamical properties and also in the excluded-volume effects. Then, it has been shown that the HW theory may
explain well the differences in the behavior of those properties between a-PzMS and a-PS, while the conven-
tional theory based on the Gaussian chain model cannot. Thus, it may be concluded that all the results presented so
far confirm the foundation of the new framework of polymer solution science.

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