Experimental test of renormalization-group calculations on the universality of dilute-solution polymer dynamics

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Recent renormalization-group calculations by Wang *et al.* predict a strong coupling between the hydrodynamic and excluded-volume interactions of polymer chain dynamics in good solvents. The predictions were tested here by examining the dependences of the chain expansion factor ratios α_H/α_S, α_η^3/α_S^3 and $\alpha_\eta^3/\alpha_S^2\alpha_H$ on the excluded-volume parameter z in its large region. Well documented experimental data for five polyisoprene samples were available since the samples behaved more like a model of flexible linear polymers in dilute solution than does polystyrene. With experimental α_S^2 extending up to a value as large as 13, it was found that, contrary to the predictions, $\alpha_\eta^3/\alpha_S^2\alpha_H$ did not show a constant value, which was predicted to be universal, irrespective of polymer species and solvents used, but decreased sharply with increasing α_S^2. No draining effect was detected clearly. Rather this experimental trend could be satisfactorily compared with the result obtained from simple extrapolation of Ganazzoli *et al.*'s self-consistent Fourier configurational calculation (with non-draining limit) to large α_S.

(Keywords: excluded-volume effect; hydrodynamic interaction; universality; polymer chain dynamics; polyisoprene)

INTRODUCTION

Discrepancies between experiments and theories on the hydrodynamic radius and the intrinsic viscosity in dilute polymer solution are a serious but unsolved problem in polymer chain dynamics. Applying the renormalization-group (RG) method to the pre-averaged Kirkwood–Riseman (KR) approximate theory, Wang *et al.*[1,2] have recently examined the influence of draining and excluded volume on the dynamic properties of polymers in dilute good solution. They have found that the exponents describing the molecular-weight dependence of the intrinsic viscosity $[\eta]$ and the hydrodynamic radius R_H in good solvents are sensitive functions of the hydrodynamic interaction because the hydrodynamic interaction couples strongly with the excluded-volume interaction. This finding naturally followed the observation that the discrepancies[3] found so far between experiments and theories in the chain expansion ratios α_H/α_S and α_η^3/α_S^3 ($=\Phi/\Phi_0$, subscript S denotes the radius of gyration R_G) may be explainable through the partial draining effect. In good solvents these ratios are not universal functions of excluded volume alone and rather universality should be observed only in the context that the ratio $\alpha_\eta^3/\alpha_S^2\alpha_H$ is nearly constant, independent of polymer and solvent and of whether the limiting good solvent dynamic molecular-weight exponents agree with or depart from the naive scaling predictions[3]. If this finding was consistent with the experimental facts, we might be able to draw a clear picture of the polymer chain dynamics in dilute solution. In the present paper, this RG theory of partial draining is checked through experimental data in good solvents for carefully prepared monodisperse polyisoprene (PIP). In this case, our very recent data[4–6] are effective because α_S and α_H have values large enough to find out the draining and excluded-volume effects on polymer dynamics clearly. It is the first test of these effects in such large region of α_S^2 as 13, hitherto the maximum being limited to ~6.

SUMMARY OF RENORMALIZATION-GROUP THEORY

The partial draining expression of RG theory to first order ε is summarized for the expansion factors on $[\eta]$ and R_H in three dimensions as follows[1]:

$$\alpha_\eta^3=[\eta](\xi_\eta,\zeta)/[\eta](\xi_\eta,\zeta=0)$$
$$=[H(\xi_\eta)\lambda_{\xi\eta}/H(\infty)](1-13\lambda_\zeta/96)(1+0.224\lambda_{\xi\eta}\lambda_\zeta)^{-1}$$
$$(2\pi N/\Lambda)^{(2+\lambda_{\xi\eta})\lambda_\zeta/16} \tag{1}$$

$$\alpha_H=R_H(\xi_D,\zeta)/R_H(\xi_D,\zeta=0)$$
$$=[H(\xi_D)\lambda_{\xi D}/H(\infty)](1+0.075\lambda_{\xi D}\lambda_\zeta)^{-1}(2\pi N/\Lambda)^{\lambda_{\xi D}\lambda_\zeta/16} \tag{2}$$

$$\alpha_S^2=R_G^2(\zeta)/R_G^2(\zeta=0)=(1-13\lambda_\zeta/96)(2\pi N/\Lambda)^{\lambda_\zeta/8} \tag{3}$$

$$H(\xi)=\Gamma(2-\lambda_\xi/2)/(4-\lambda_\xi)^{1/2}\Gamma(3/2-\lambda_\xi/2) \tag{4}$$

$$\lambda_\xi=\xi/(1+\xi) \qquad \lambda_\zeta=\zeta/(1+\zeta) \tag{5}$$

$$\xi=(16/315)(f/\pi\eta_s l)(2\pi n)^{1/2} \tag{6}$$

Here ξ is related to the usual draining parameter $h=[f/(12\pi^3)^{1/2}\eta_s l]n^{1/2}$ with f the friction coefficient of a monomer, n the number of Kuhn units of length l ($N=nl$) and η_s the solvent viscosity. The case $\xi\to\infty$ corresponds to the non-draining and $\xi\to 0$ to the free-draining limits. The variable ζ describes the crossover between the Gaussian ($\zeta\to 0$) and self-avoiding ($\zeta\to\infty$) chain regimes and is transformed to the excluded-volume parameter z ($=(3/2\pi l^2)^{3/2}\beta n^{1/2}$) with β the binary cluster integral. Λ is a length that characterizes the excluded-volume interaction along the chain. In equations (1) and (2), it

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is assumed that Gaussian chains are non-draining; $\xi_\eta(\zeta=0)\to\infty$ and $\xi_{\mathrm{D}}(\zeta=0)\to\infty$ at Θ state.

Combination of equations (1)–(3) yields:

$$\alpha_\eta^3/\alpha_{\mathrm{S}}^2\alpha_{\mathrm{H}}=(1+0.075\lambda_\zeta\lambda_\xi)/(1+0.224\lambda_\zeta\lambda_\xi) \tag{7}$$

$$\lambda_\zeta=(32/3)z/[1+(32/3)z] \qquad (z<0.15)$$

$$\lambda_\zeta=1 \qquad (z>0.75) \tag{8}$$

on the condition that $\lambda_{\xi\eta}=\lambda_{\xi\mathrm{D}}$, which is achieved at $\xi>20$–30 since $\xi_{\mathrm{D}}=(32/13)\xi_\eta$. Owing to cancellation of $\alpha_{\mathrm{H}}/\alpha_{\mathrm{S}}$ by $\alpha_\eta^3/\alpha_{\mathrm{S}}^3$, the quantity $\alpha_\eta^3/\alpha_{\mathrm{S}}^2\alpha_{\mathrm{H}}$ becomes constant and independent of the excluded-volume effect at $z>0.75$. The value depends only on the degree of draining; it has the free-draining value 1.0 as its upper bound and has the non-draining good-solvent limit value $(\alpha_\eta^3/\alpha_{\mathrm{S}}^2\alpha_{\mathrm{H}})_{\mathrm{nD,good}}=0.878$ as its lower bound. On the other hand, complicated crossover behaviour is observed on $\alpha_{\mathrm{H}}/\alpha_{\mathrm{S}}$, $\alpha_\eta^3/\alpha_{\mathrm{S}}^3$ and $\alpha_{\mathrm{H}}/\alpha_\eta$ because of the strong coupling between the draining and the excluded-volume effects. When $z>0.75$, that is, $\alpha_{\mathrm{S}}^3>1.93$, the z representation of N, Λ and ζ in equations (1)–(3) yields:

$$\alpha_{\mathrm{H}}/\alpha_{\mathrm{S}}=[(1-13/96)^{1/2}(1+0.075\lambda_{\xi\mathrm{D}})]^{-1}F(\lambda_{\xi\mathrm{D}}) \times(6.441z)^{0.1836(\lambda_{\xi\mathrm{D}}-1)} \tag{9a}$$

$$\alpha_\eta^3/\alpha_{\mathrm{S}}^3=[(1-13/96)^{1/2}(1+0.224\lambda_{\xi\eta})]^{-1}F(\lambda_{\xi\eta}) \times(6.441z)^{0.1836(\lambda_{\xi\eta}-1)} \tag{9b}$$

$$\alpha_{\mathrm{H}}/\alpha_\eta=(1+0.224\lambda_{\xi\eta})^{1/3}[(1-13/96)^{1/3}(1+0.075\lambda_{\xi\mathrm{D}})]^{-1} \times F^{2/3}(\lambda_{\xi\mathrm{D}})(6.441z)^{0.1224(\lambda_{\xi\eta}-1)} \tag{9c}$$

$$F(\lambda_\xi)=3^{1/2}H(\lambda_\xi)\lambda_\xi/\Gamma(3/2) \tag{10}$$

and these plots against z produce a family of curves having the following non-draining limit values as the upper bound: $(\alpha_{\mathrm{H}}/\alpha_{\mathrm{S}})_{\mathrm{nD,good}}=1.00$, $(\alpha_\eta^3/\alpha_{\mathrm{S}}^3)_{\mathrm{nD,good}}=0.878$ and $(\alpha_{\mathrm{H}}/\alpha_\eta)_{\mathrm{nD,good}}=1.044$.

EXPERIMENTAL

The methods of characterization for our PIP samples have already been reported in detail[4–6]. We give here only a brief summary, which will give information about degree of data quality. Integrated scattering intensity was measured with our laboratory-made computer-operated photogoniometer at angles from 5° to 150°. Molecular weights and mean-square radius of gyration of the samples were usually estimated by the method of 'square-root plots'. Especially for high-molecular-weight samples of $M_{\mathrm{w}}>10^6$, another method proposed by Fujita was also used to check the consistency of the R_{G} and M_{w} values with those from the square-root plots. The scattering intensity autocorrelation function $A(\tau)$ was measured with our laboratory-made time-interval correlator (512 channels) at six fixed scattering angles at $\theta=10°$, 30°, 60°, 90°, 120° and 150°. Translational diffusion coefficients at finite polymer concentration $D(c)$ were estimated by fitting the $A(\tau)$ data in the range $qR_{\mathrm{G}}<0.4$ to a single-exponential decay curve using a weighted least-squares algorithm ($\theta=10°$–30° for L-14, L-12 and L-15, $\theta=10°$ for L-11). For sample L-16, the histogram method combined with a weighted non-linear least-squares algorithm was applied to $A(\tau)$ data at $\theta=10°$ ($(qR_{\mathrm{g}})^2=0.45$). The $D(c)$ values thus estimated were linearly extrapolated to zero concentration to obtain the diffusion coefficient at infinite dilution D_0, which is related to the hydrodynamic radius R_{H} through the Einstein–Stokes relation. Viscosity measurements were made with a conventional Ubbelohde capillary viscometer of shear rate 990 s^{-1} for lower-molecular-weight samples. For higher-molecular-weight samples a Cannon–Fenske type of four-bulb spiral capillary viscometer (shear rate 15–105 s^{-1}) was used in order to estimate the intrinsic viscosity at zero shear rate.

RESULTS AND DISCUSSION

The RG predictions summarized above were checked with the data obtained by both us[4–6] and Davidson *et al.*[7] for well characterized monodisperse PIP ($M_{\mathrm{w}}/M_{\mathrm{n}}<1.01$) in good solvents. PIP, a typical rubbery polymer, has much higher chain flexibility than polystyrene has and shows[4–6] more desirable model-like behaviour of flexible linear polymers in dilute solution. When selecting the data, we set a criterion: for the given polymer, the data in both good and Θ solvents should be obtained by the same authors with the same series of homologous fractions. This criterion will help to produce reliable expansion factors for a given polymer–solvent system. The good solvent–Θ solvent pairs thus selected are cyclohexane at 25°C[4,6]/1,4-dioxane at 34.7°C[5,6] and cyclohexane at 23° and 25°C[7]/1,4-dioxane at 34°C[8,9]. In these good solvents, we have the characteristic relations that $R_{\mathrm{G}}=1.35\times10^{-9}M_{\mathrm{w}}{}^{0.61\pm0.01}$ cm, $R_{\mathrm{H}}=9.03\times10^{-10}M_{\mathrm{w}}{}^{0.61\pm0.01}$ cm and $[\eta]=1.80\times10^{-2}M_{\mathrm{w}}{}^{0.74\pm0.02}$ cm^3 g^{-1} for the former and that $R_{\mathrm{G}}=2.84\times10^{-9}M_{\mathrm{w}}{}^{0.545}$ cm, $R_{\mathrm{H}}=1.23\times10^{-9}M_{\mathrm{w}}{}^{0.584}$ cm and $[\eta]=2.05\times10^{-2}M_{\mathrm{w}}{}^{0.730}$ cm^3 g^{-1} for the latter. The extremely low exponent on R_{G} vs. M_{w} in the latter (Davidson *et al.*[7]) should be noticed[*]. In the present checks, special attention was paid to the data at $\alpha_{\mathrm{S}}^3>4$ because they usually show good solvent limit-like behaviour at $\alpha_{\mathrm{S}}^3>4$ and because the larger z makes the check more strict. *Table 1* is a summary of these checks.

First we examine α_{S}^3 dependences of $\alpha_\eta^3/\alpha_{\mathrm{S}}^2\alpha_{\mathrm{H}}$. This is done in *Figure 1*. Opposed to the RG prediction, $\alpha_\eta^3/\alpha_{\mathrm{S}}^2\alpha_{\mathrm{H}}$ decreases drastically with increasing α_{S}^3, as is represented by the data-fitted full curve T, which is drawn with the empirical relation[6] $\alpha_\eta^3/\alpha_{\mathrm{S}}^2\alpha_{\mathrm{H}}=1.15\alpha_{\mathrm{S}}{}^{-0.8354}$ at $\alpha_{\mathrm{S}}^3>4$. To make matters worse, the values are far below[†] the theoretical lower bound of non-draining good-solvent limit, 0.878 (full line WDF,nD). Consequently, the draining effect makes no sense for the present PIP data. No remarkable cancellation of $\alpha_\eta^3/\alpha_{\mathrm{S}}^3$ by $\alpha_{\mathrm{H}}/\alpha_{\mathrm{S}}$ occurs and the predicted constancy of $\alpha_\eta^3/\alpha_{\mathrm{S}}^2\alpha_{\mathrm{H}}$ at $\alpha_{\mathrm{S}}^3>1.93$ is not observed on PIP data in the large α_{S} region. These results will be assessed later in more detail by discussing individual behaviour of $\alpha_{\mathrm{H}}/\alpha_{\mathrm{S}}$, $\alpha_\eta^3/\alpha_{\mathrm{S}}^3$ and $\alpha_{\mathrm{H}}/\alpha_\eta$ against α_{S}^3.

As follows, the PIP data compare rather satisfactorily with the simple extrapolation of Ganazzoli *et al.*'s calculations[10,11] to large α_{S} without introducing any draining effect to polymer chains. There, the elastic part

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[*] As described in the experimental section of ref. 7, their R_{G} values were estimated with the Berry method using the scattering intensities at angles above 30°. However, it is widely accepted that, if the intensities were not measured down to below 30° for the samples of $M>10^6$, the Berry method would give underestimated values of both R_{G} and M_{w}. Taking these into consideration, we can easily obtain a new R_{G}–M_{w} relation, $R_{\mathrm{G}}=1.71\times10^{-9}\,M^{0.586}$ cm, using their data on samples B–H, for which M never exceeds 10^6. This new exponent is very close to ours, as was described in the text

[†] The larger $\alpha_\eta^3/\alpha_{\mathrm{S}}^2\alpha_{\mathrm{H}}$ values in figure 1 of Davidson *et al.*[7] might be attributed to the low exponent in their R_{G} vs. M_{w} relation

Table 1 Ratios of chain expansion factors for polyisoprene in cyclohexane

Sample code	$M_w \times 10^{-6}$	α_S^3	$\alpha_\eta^3/\alpha_S^2\alpha_H$	α_S/α_H	α_H/α_η	α_η^3/α_S^3
L-14[a]	0.326	4.53	0.707	1.14	1.03	0.622
L-12[a]	0.568	5.07	0.752	1.13	1.02	0.661
L-15[a]	0.578	4.97	0.768	1.14	1.00	0.681
L-11[a]	2.44	8.10	0.651	1.18	1.03	0.551
L-16[a]	7.24	12.70	0.554	1.15	1.11	0.482
PI-II[b]	0.0620	3.02	0.863	1.31	0.878	0.658
DSP/GVS-1[b]	0.156	3.38	0.931	1.26	0.880	0.742
PLS-305[b]	0.302	3.63	0.942	1.23	0.890	0.768
PI-12[b]	0.581	4.42	0.927	1.23	0.893	0.753
PI-LFI[b]	0.920	4.17	1.05	1.20	0.874	0.878
PI-L17[b]	1.67	4.49	0.995	1.10	0.941	0.907
DSP/GVS-3[b]	3.42	4.93	0.975	1.07	0.966	0.914

[a,b] Combinations of good solvent and theta solvent are: (a) cyclohexane at 25°C/1,4-dioxane at 34.7°C[4–6]; (b) cyclohexane at 23 and 25°C/1,4-dioxane at 34°C[7–9]

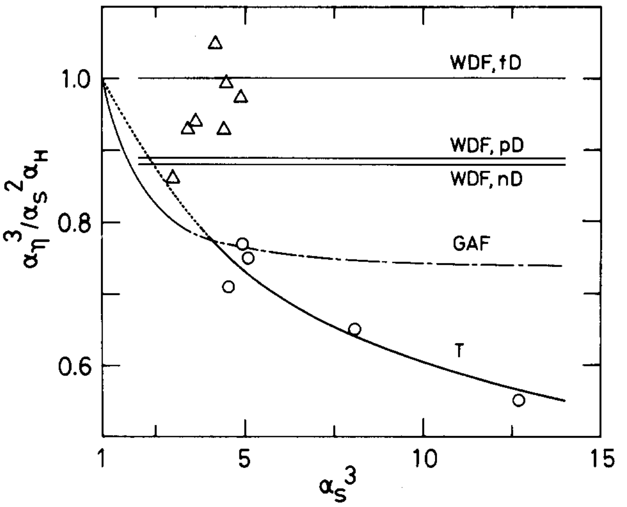

Figure 1 The combined expansion ratio $\alpha_\eta^3/\alpha_S^2\alpha_H$ plotted against the 'mean-square radius of gyration' expansion ratio α_S^3 for polyisoprene in cyclohexane: (○) Tsunashima *et al.*[4–6]; (△) Davidson *et al.*[7–9]. The full curve T represents our empirical relation[6] $\alpha_\eta^3/\alpha_S^2\alpha_H = 1.15\alpha_S^{-0.8354}$ at $\alpha_S^3 > 4$. The full and chain curve GAF represents the results of calculations by Ganazzoli *et al.*[10,11] with non-draining hydrodynamic interaction ($\alpha_S^3 \leqslant 3.5$) and its extrapolation ($\alpha_S^3 > 3.5$), respectively. The other full horizontal lines, WDF,fD, WDF,nD and WDF,pD represent the results of the RG calculations by Wang, Douglas and Freed[1,2] with the free-draining, non-draining and partial draining ($\lambda_\xi = 0.9$) hydrodynamic interaction, respectively, for $\alpha_S^3 > 1.93$

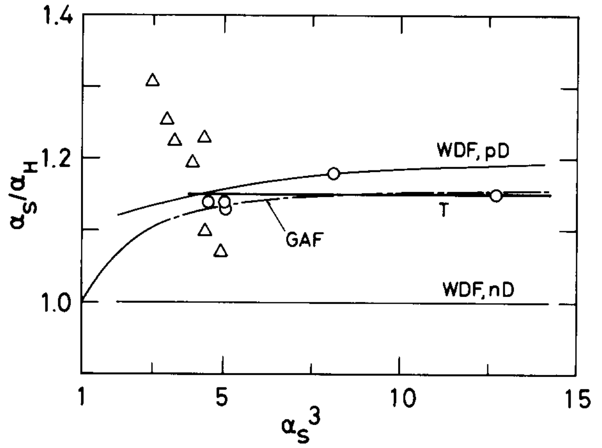

Figure 2 The expansion ratio α_S/α_H plotted against α_S^3 for polyisoprene in cyclohexane. The full line T represents the empirical relation[6] $\alpha_S/\alpha_H = 1.15$ at $\alpha_S^3 > 4$. The other lines and symbols have the same meaning as in *Figure 1*

of the configurational free energy of a perturbed chain was decomposed in Fourier normal modes within the Gaussian approximation and the energy was minimized over all the degrees of freedom in a self-consistent way. With pre-averaged hydrodynamic interaction, the expansion factors in the intermediate region of $z \leqslant 2$ were obtained as follows:

$$\alpha_S = (1 + 67z/7 + 18z^2 + 55z^3)^{1/15}$$
$$\alpha_H = (1 + 4.16z + 3.2z^2)^{1/10}$$
$$\alpha_\eta = (1 + 3.64z + 3.10z^2)^{1/10} \qquad (0 \leqslant z \leqslant 2) \qquad (11)$$

The equations produce a $\alpha_\eta^3/\alpha_S^2\alpha_H$ vs. α_S^3 relation. It is shown in *Figure 1* by thin full line GAF at $\alpha_S^3 \leqslant 3.5$. The extended chain line at $\alpha_S^3 > 3.5$ represents its simple extrapolation under the assumption that equation (11) holds in this α_S region too. This extrapolation may be open to question[12] since the GAF calculation supposes the Gaussian distribution for the perturbed interatomic mean-square distances. However, its initial trend at $\alpha_S^3 < 3.5$, which is rigorous within the GAF calculations, is of great interest in predicting a downward feature of $\alpha_\eta^3/\alpha_S^2\alpha_H$ with increase of α_S^3.

Next, we discuss the behaviour of the constitutive elements of $\alpha_\eta^3/\alpha_S^2\alpha_H$, i.e. α_S^3 dependences of α_S/α_H, α_η^3/α_S^3 and α_H/α_η. *Figure 2* shows plots of α_S/α_H against α_S^3. The data indicate a rough constancy, $\alpha_S/\alpha_H = 1.15$, at $\alpha_S^3 > 4$ as shown by the empirical full line T. Theoretically, the data can also be represented well by the GAF extrapolation curve with non-draining limit. Moreover, the data seem to be explainable, for this figure only, with the RG theory of partial draining, i.e. with the full curve WDF,pD of the draining parameter $\lambda_\xi = 0.9$. On the other hand, plots of α_η^3/α_S^3 against α_S^3 in *Figure 3* reveal that the degree of draining $\lambda_\xi = 0.9$ (curve WDF,pD) is not sufficient to describe the experimental data at large α_S^3, which are represented by the empirical relation[6] $\alpha_\eta^3/\alpha_S^3 = \alpha_S^{-0.8354}$ (curve T). Again, the GAF non-draining curve is relatively closer to the data. Going to the final plot, that is, plots of the expansion ratio defined by two kinds of dynamic properties α_H/α_η against α_S^3 in *Figure 4*, the effect of draining on this ratio becomes unclear to

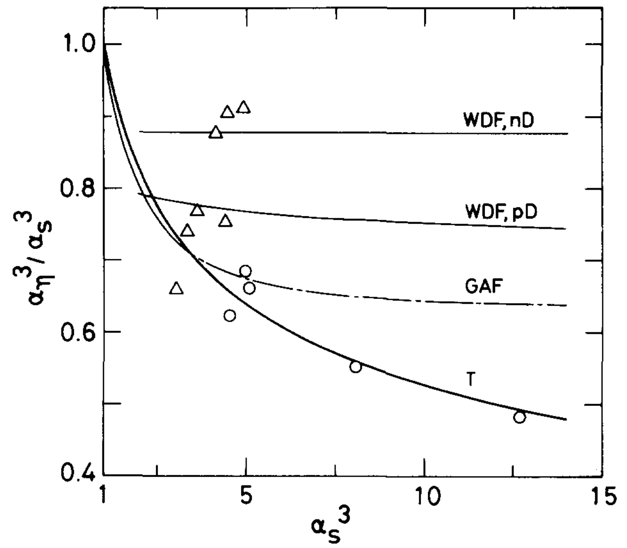

Figure 3 The ratio of the viscosity constant α_η^3/α_S^3 plotted against α_S^3 for polyisoprene in cyclohexane. The full curve T represents the empirical relation[6] $\alpha_\eta^3/\alpha_S^3 = \alpha_S^{-0.8354}$. The other lines and symbols have the same meaning as in *Figure 1*

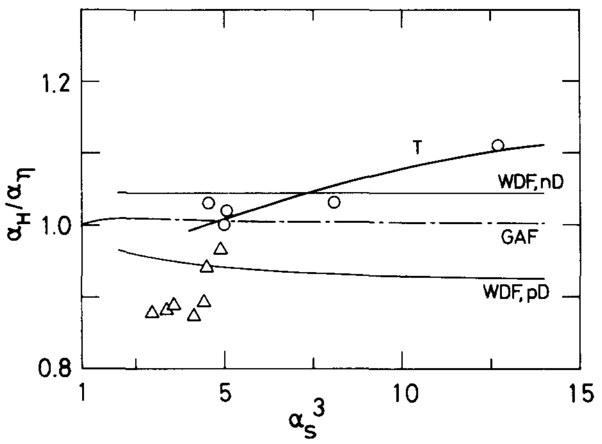

Figure 4 The expansion ratio of two dynamic variables α_H/α_η plotted against α_S^3 for polyisoprene in cyclohexane. The full curve T represents the empirical relation[6] $\alpha_H/\alpha_\eta = \alpha_S^{0.2784}/1.15$ at $\alpha_S^3 > 4$. The other lines and symbols are the same as in *Figure 1*

some extent. However, the figure indicates that the partial draining is inadequate to explain the data in the large α_S region.

In conclusion, it is found that the data which spread up to $\alpha_S^3 = 13$ do not support the constancy of $\alpha_\eta^3/\alpha_S^2\alpha_H$, whose value was predicted from the draining-effect sensitive RG theory to be universal, irrespective of polymer and solvent. Recently, Shiwa and Oono[13] have claimed that the RG theory is not adequate to describe the partial draining: the partial draining is describable only by introducing into the basic kinetic equation a new parameter which characterizes the coupling strength between the chain conformation and the solvent velocity field. Using the modified KR–RG calculation to order ε, they have predicted that the ratio $[\eta]/R_G{}^2R_H$ becomes a true universal function of α_S in the context that it is not affected by polymer and solvent. We may need further experimental work.

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