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THE INFLUENCE OF BRANCHING ON INTER- AND INTRAMOLECULAR INTERACTION PARAMETERS OF POLYMER/SOLVENT SYSTEMS

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ABSTRACT

The influence of branching on inter- and intramolecular interaction parameters—as defined by Wolf for linear polymers—is discussed for starlike polystyrene and polybutadiene in good solvents. The paper proposes a method of evaluation of the interaction parameters for branched polymers starting from experimental data on A_2 and $[\eta]$ for linear chains and from the theoretical ratios $A_{2,\text{ branched}}/A_{2,\text{ linear}}$ and $[\eta]_{\text{branched}}/[\eta]_{\text{linear}}$.

INTRODUCTION

The concept of inter- and intramolecular segment contacts developed by Wolf [1] starts from the observation attesting that the dimensions of linear polymer coils increase with the addition of solvent to the pure polymer (except for theta conditions). Therefore, the intermolecular segment contacts are opened and the segments are infinitely separated; the intramolecular segment contacts are also opened, but these segments present only the extent given by their mutual distance on the polymer chain. The effects of an intermolecular contact differ from those of an intramolecular one, hence pair interaction parameters like the Flory–Huggins parameter, χ (or the second virial coefficient, A_2), can be considered as having two components, namely χ_{inter} and χ_{intra}. The evaluation of numerous literature data [2] has shown that for a large domain of molecular weights the intramolecular interaction parameters linearly depend on the intermolecular ones. Also, $\chi_{\text{inter}} = \chi_{\text{intra}} = 0.5$ only for theta conditions, and with increasing solvent quality χ_{intra} increases while χ_{inter} decreases.

Polymer properties can be significantly modified through the variation of the molecular architecture. The difference between branched and linear polymers consists in the smaller spatial volume of the first ones for the same molecular weight, the segment density of the branched molecules being higher than that of the linear ones. The effect of an increase in the number of arms of starlike polystyrene and polybutadiene on the inter- and intramolecular interaction parameters is the subject of this paper.

THEORETICAL BACKGROUND

According to the model of inter- and intramolecular interactions [1], the probability that two contacting segments separated by the addition of the solvent belong to different molecules is given by

$$P_{\text{inter}} = (1 + [\eta\theta]/[\eta])/2 \tag{1}$$

where $[\eta]$ and $[\eta\theta]$ are the intrinsic viscosities (subscript "θ" refers to the theta condition), or, by introducing the Mark–Houwink relationship ($[\eta] = K \cdot M^a$, $[\eta\theta] = K_\theta \cdot M^{0.5}$),

$$P_{\text{inter}} = [1 + (K_\theta/K)M^{-(a-0.5)}]/2 \tag{2}$$

The Flory–Huggins parameter at high dilution is given by the contribution of the two components χ_{inter} and χ_{intra}:

$$\chi = \chi_{\text{inter}} P_{\text{inter}} + \chi_{\text{intra}}(1 - P_{\text{inter}}) \tag{3}$$

The following relation holds true between the second virial coefficient A_2 and the interaction parameter χ:

$$A_2 = (0.5 - \chi)/\rho_2^2 V_1 \tag{4}$$

where ρ_2 is the polymer density and V_1 is the molar volume of the solvent. By introducing Eqs. (2) and (3) into Eq. (4), a dependence of A_2 on the molecular weight is obtained:

$$A_2 = A_2^\infty + bM^{-(a-0.5)} \tag{5}$$

where

$$A_2^\infty = [0.5 - (\chi_{\text{inter}} + \chi_{\text{intra}})/2]/\rho_2^2 V_1 \tag{6}$$

and

$$b = (1/\rho_2^2 V_1)(K_\theta/K)(-\chi_{\text{inter}} + \chi_{\text{intra}})/2 \tag{7}$$

In a previous paper [2] we discussed the inter- and intramolecular interactions in terms of phenomenological thermodynamics, based on experimental data taken from the literature. The correlation between these parameters (Eq. 8) was evaluated, the result showing a linear dependence for all the samples studied irrespective of the chemical nature of their components and the particular thermodynamic situation:

$$\chi_{\text{inter}} + \chi_{\text{intra}} \cong 1, \qquad \text{for } M > 10^5 \tag{8}$$

On the other hand, as indicated in the Introduction, the degree of branching influences the behavior of polymers in solution. The effect of branching on the intrinsic viscosity is expressed by the ratio between the intrinsic viscosities of branched and linear polymers having the same molecular weight;

$$g_{[\eta]} = [\eta]_{\text{branched}}/[\eta]_{\text{linear}} \tag{9}$$

For starlike polymers, Roovers et al. [3-5] proposed useful correlations between this ratio and the number of star arms f for the theta condition (Eq. 10). Further, a semiempirical correlation of the variation of $g_{[\eta]}$ with excluded volume is described by Douglas and Freed. The $g_{[\eta]}$ ratio in good solvent conditions for $f \geq 2$ is given by Eqs. (11) and (12) [6-8].

$$g_{[\eta\theta]} = [(3f - 2)/f^2]^{0.58} \tag{10}$$

$$g_{[\eta]} = g_{[\eta\theta]}F(f) \tag{11}$$

where

$$F(f) = [1 - 0.276 - 0.015(f - 1)]/(1 - 0.276) \tag{12}$$

Also, the effect of branching on the second virial coefficient is defined by the ratio of A_2 for branched and linear polymers having the same molecular weight:

$$g_A = A_{2,\text{ branched}}/A_{2,\text{ linear}} \tag{13}$$

Renormalization group calculations [6-9] indicate that this ratio is a constant in a good solvent for a given branched structure. According to this theory, the second virial coefficients to the second order for the linear and f-arm star polymers are expressed through Eqs. (14)-(18).

$$A_{2,\text{linear}} = (2\pi N/\Lambda)^{d\nu(\eta)}\,\Lambda^{d/2}N_A(2M^2)^{-1}f_{\text{linear}}(\eta,\varepsilon) \tag{14}$$

with

$$f_{\text{linear}}(\eta,\varepsilon) = (\varepsilon/8)[\eta/(1 + \eta)] + (\varepsilon/8)^2\{(4\ln 2 - 1)[\eta/(1 + \eta)]^2 + (21/4)[\eta/(1 + \eta)]\} + O(\varepsilon^3) \tag{15}$$

and

$$A_{2,\text{star}} = (2\pi N/\Lambda)^{d\nu(\eta)}\Lambda^{d/2}N_A(2M^2)^{-1}f_{\text{star}}(\eta,\varepsilon) \tag{16}$$

with

$$f_{\text{star}}(\eta,\varepsilon) = (\varepsilon/8)[\eta/(1 + \eta)]\exp[C_{A_2}(\varepsilon/8)\eta/(1 + \eta)] + (\varepsilon/8)^2\{(4\ln 2 - 1)[\eta/(1 + \eta)]^2 + (21/4)[\eta/(1 + \eta)]\} + O(\varepsilon^3) \tag{17}$$

$$C_{A_2} = (14\ln 2 - 9\ln 3)(f - 1)^2 + (9\ln 3 - 14\ln 2)(f - 1) + 2\ln f \qquad (18)$$

where $d\nu(\eta) = 2 - (\varepsilon/2) + \varepsilon\eta/4(1 + \eta) + (O(\varepsilon^2)$, the effective exponent in the crossover region; Λ is introduced as a phenomenological length scale determined by comparison with experiment, N_A is Avogadro's number; M is the molecular weight; $\varepsilon = 4 - d$, where d is the space dimension; η is the crossover scaling variable (in good solvent condition $\eta \to \infty$); and N is the renormalized chain length of the linear chain and the total length of the sum of star branches (with arms having a length N/f), respectively.

The ratio between $A_{2,\text{star}}$ and $A_{2,\text{linear}}$, defined through Eq. (13), can be written as:

$$g_A = f_{\text{star}}(\eta,\varepsilon)/f_{\text{linear}}(\eta,\varepsilon) \qquad (19)$$

The log-log plot of $[\eta]$ versus the molecular weight shows a linear dependence with the same slope "a" for linear and star polymers. This behavior was observed for many types of star-branched polymers [10–13] and is predicted by commonly accepted theories [14, 15].

According to Eqs. (5)–(7), it is possible to determine χ_{inter} and χ_{intra} for both linear and branched polymers by plotting A_2 versus $M^{-(a-0.5)}$. Also, by coupling these relations with Eq. (9) and (19), the influence of the degree of branching on the inter- and intramolecular interaction parameters can be evaluated.

RESULTS AND DISCUSSION

In order to verify the validity of the model of Wolf, developed for linear polymers, for star polymers, five systems (literature data) were studied, i.e., linear and 4-arm star polystyrene (PS1) in toluene at 35°C, linear and 6-arm star polystyrene (PS2) in toluene at 35°C, linear and 4-arm star polybutadiene (PBu1, PBu2)

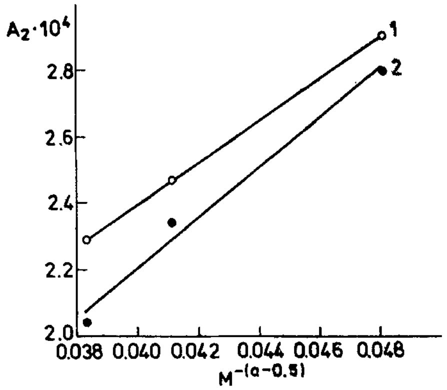

FIG. 1. A_2 vs $M^{-(a-0.5)}$ for PS1 in toluene at 35°C. Curve 1, linear; Curve 2, 4-arm star (literature data [16]).

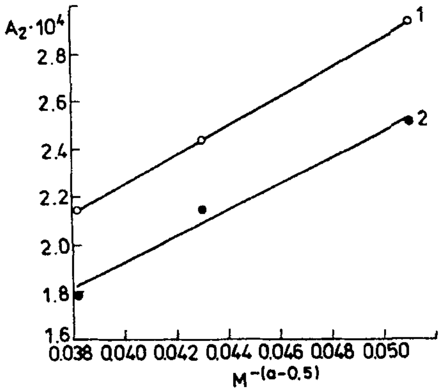

FIG. 2. A_2 vs $M^{-(a-0.5)}$ for PS2 in toluene at 35°C. Curve 1, linear; Curve 2, 6-arm star (literature data [16]).

in cyclohexane at 25°C, and linear and 18-arm star polybutadiene (PBu3) in cyclohexane at 25°C [16]. For these systems the plots A_2 versus $M^{-(a-0.5)}$ for the linear (Curve 1) and star (Curve 2) polymers are presented in Figs. 1-5. From these dependences the coefficients A_2^∞ and b were calculated according to Eq. (2). Their values are collected in Table 1. The table also presents values of χ_{inter} and χ_{intra} determined according to Eqs. (6) and (7) applied for both star and linear polymers and the ratios between their values for star and linear polymers, i.e., g_{inter} and g_{intra}.

The Mark-Houwink parameters used in these evaluations are presented in Table 2.

In order to study the influence of branching on the inter- and intramolecular interaction parameters, we propose a method using the values of the second virial coefficient and the intrinsic viscosity determined for linear polymers, as well as the theoretical values of g_A (Eq. 19) and $g_{[\eta]}$ (Eq. 9) calculated for f-arm star polymers.

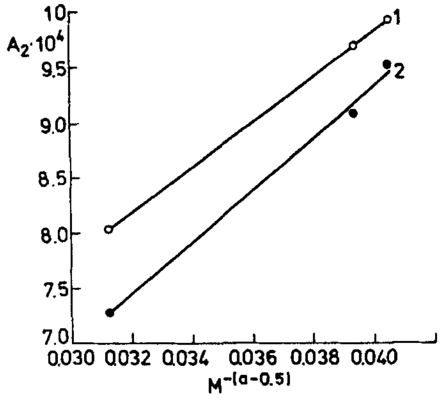

FIG. 3. A_2 vs $M^{-(a-0.5)}$ for PBul in cyclohexane at 25°C. Curve 1, linear; Curve 2, 4-arm star (literature data [16]).

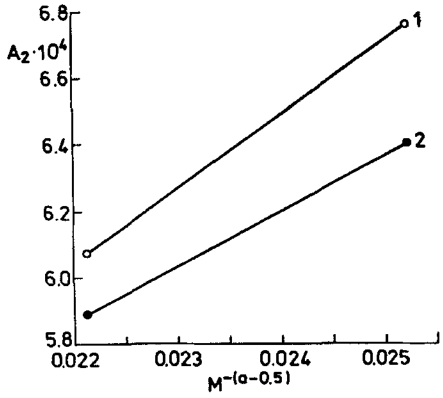

FIG. 4. A_2 vs $M^{-(a-0.5)}$ for PBu2 in cyclohexane at 25°C. Curve 1, linear; Curve 2, 4-arm star (literature data [16]).

For good solvent conditions, η tends to infinity, and for $d = 3$, i.e., $\varepsilon = 1$, Eq. (19) becomes

$$g_A = \{[\exp(c_{A_2}/8)]/8 + (4\ln 2 + 17/4)/64\}/\{(1/8) + [4\ln 2 + (17/4)]/64\} \tag{20}$$

with c_{A_2} defined through Eq. (18). The values of g_A calculated for $f = 2$ (linear polymer) and for even-branched polymers up to $f = 18$ are presented in Table 3. With these values and with the value of the second virial coefficient of the linear polymer, $A_2(f)$ corresponding to any f-arm star can be determined and plotted against $M^{-(a-0.5)}$. Plots are presented for the systems described above in Figs. 6–10, for $f = 2, 4, 6, 8, 10, 12, 14, 16$, and 18.

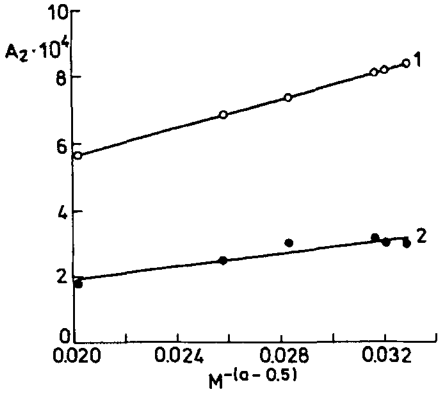

FIG. 5. A_2 vs $M^{-(a-0.5)}$ for PBu3 in cyclohexane at 25°C. Curve 1, linear; Curve 2, 18-arm star (literature data [16]).

TABLE 1. A_2^∞ and b (Eq. 5), and χ_{inter} and χ_{intra} (Eqs. 6 and 7), $g_{\text{inter}} = \chi_{\text{inter star}}/\chi_{\text{inter linear}}$, and $g_{\text{intra}} = \chi_{\text{intra star}}/\chi_{\text{intra linear}}$ Ratios for the Linear and f-Arm Star PS1 and PS2 in Toluene at 35°C and PBu1, PBu2, and PBu3 in Cyclohexane at 25°C

	Linear				f-Arm star						
Sample	$A_2^\infty \times 10^4$	b	χ_{inter}	χ_{intra}	f	$A_2^\infty \times 10^4$	b	χ_{inter}	χ_{intra}	g_{inter}	g_{intra}
PS1	−0.146	0.006	0.410	0.593	4	−0.813	0.008	0.406	0.613	0.990	1.034
PS2	−0.177	0.006	0.415	0.590	6	−0.258	0.005	0.432	0.574	1.041	0.973
PBu1	1.723	0.020	0.381	0.588	4	−0.024	0.023	0.385	0.615	1.010	1.046
PBu2	1.200	0.022	0.377	0.602	4	2.268	0.016	0.400	0.561	1.061	0.932
PBu3	1.339	0.021	0.379	0.598	18	−0.181	0.010	0.463	0.536	1.232	0.896

From Eqs. (9)–(12), the ratio $[\eta\theta]/[\eta]$ for the star polymers can be written as

$$[\eta\theta]_{\text{star}}/[\eta]_{\text{star}} = [\eta\theta]_{\text{linear}}/[\eta]_{\text{linear}}F(f)^{-1} \tag{21}$$

Introducing this relation in Eqs. (1)–(7), the following dependence of the second virial coefficient of the f-arm star polymer on the molecular weight is obtained:

$$A_2(f) = A_2^\infty + b(f)M^{-(a-0.5)} \tag{22}$$

where

$$A_2^\infty(f) = (1/\rho_2^2 V_1)[0.5 - (\chi_{\text{inter}}(f) + \chi_{\text{intra}}(f))/2] \tag{23}$$

and

$$b(f) = (1/\rho_2^2 V_1)[(-\chi_{\text{inter}}(f) + \chi_{\text{intra}}(f))/2]\,(K_{\theta,\,\text{linear}}/K_{\text{linear}})F(f)^{-1} \tag{24}$$

From the dependences presented in Figs. 6–10 and from Eqs. (23) and (24), the inter- and intramolecular interaction parameters for the considered f-arm star polymers and also the ratios defined through Eqs. (25) and (26):

$$g_{\text{inter}}(f) = \chi_{\text{inter}}(f)/\chi_{\text{inter}}(f = 2) \tag{25}$$

$$g_{\text{intra}}(f) = \chi_{\text{intra}}(f)/\chi_{\text{intra}}(f = 2) \tag{26}$$

TABLE 2. Mark–Houwink Parameters Used in the Evaluation of the Inter- and Intramolecular Interaction Parameters for the Samples from Table 1 and Figs. 1–5

		Linear		f-Arm star		
Sample	a	$K \times 10^3$	$K_\theta \times 10^3$	$K \times 10^3$	$K_\theta \times 10^3$	Ref.
PS1	0.73	10.4	83	7.400	63.1	17
PS2	0.726	10.2	83	5.800	52.4	18
PBu1	0.77	12	205	8.760	155.8	16, 19
PBu2	0.77	12	205	8.760	155.8	16, 19
PBu3	0.77	12	205	2.76	71.75	16, 19

TABLE 3. g_A Values Calculated According to Eqs. (18) and (20) for $f = 2$ to 18

f	2	4	6	8	10	12	14	16	18
g_A	1	0.932	0.804	0.671	0.570	0.510	0.482	0.472	0.469

which represents the effect of branching on the inter- and intramolecular interaction parameters calculated.

The dependence of χ_{inter} and χ_{intra} on f are presented in Fig. 11.

Good agreement between these values and the values obtained from experimental data (Table 1) is observed, except for samples PS1 and PBu1. The divergent behavior of these two samples is easily explained by analyzing the experimental data given in Figs. 1 and 3, respectively.

The interdependence of the inter- and intramolecular interaction parameters expressed through Eq. (8) for linear polymers is also valid for branched chains, irrespective of the number of arms, i.e.:

$$\chi_{inter}(f) + \chi_{intra}(f) \cong 1, \qquad \text{for } M > 10^5 \tag{27}$$

With the increase of the number of arms, χ_{inter} increases while χ_{intra} decreases, and it seems that for f tending to infinity, $\chi_{inter} = \chi_{intra} = 0.5$. This condition is obtained for linear polymers in the theta condition. Accordingly, it appears that for a branched polymer possessing a high number of arms, the segment density is equivalent to that of the linear polymer in the theta condition.

The curves in Fig. 11 (in the limit of experimental errors) were obtained for three different thermodynamic conditions, i.e., for $a = 0.726$, $a = 0.73$, and $a =$

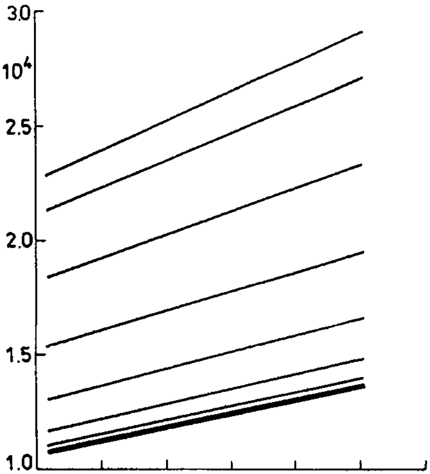

FIG. 6. A_2 vs $M^{-(a-0.5)}$ for f-arm star PS1 in toluene at 35°C, with $f = 2, 4, 6, 8, 10, 12, 14, 16$, and 18 from top to bottom.

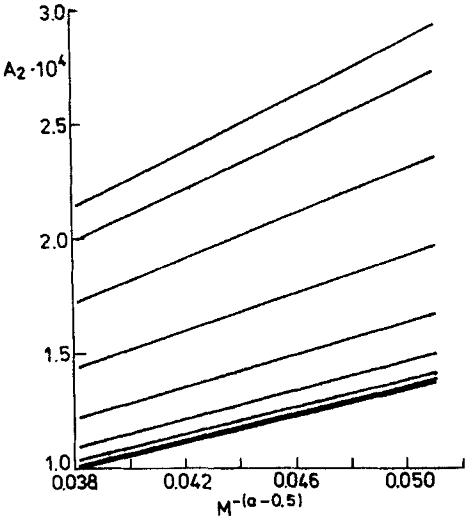

FIG. 7. A_2 vs $M^{-(a-0.5)}$ for f-arm star PS2 in toluene at 35°C, with f = 2, 4, 6, 8, 10, 12, 14, 16, and 18 from top to bottom.

0.77. It appears that a dependence of $\chi_{\text{inter}}(f)$ and $\chi_{\text{intra}}(f)$ on solvent quality for any given f-arm star polymer is obtained, as in the case of linear polymers, i.e., with an increase of solvent quality, $\chi_{\text{intra}}(f)$ increases and $\chi_{\text{inter}}(f)$ decreases.

The effect of branching on the inter- and intramolecular interaction parameters, defined in Eqs. (25) and (26), are plotted against the number of arms, f, in Fig. 12.

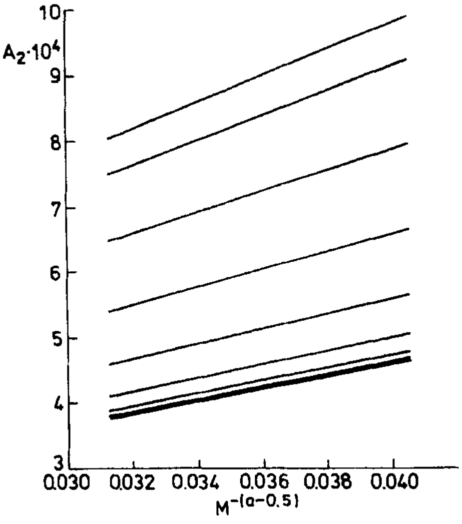

FIG. 8. A_2 vs $M^{-(a-0.5)}$ for f-arm star PBu1 in cyclohexane at 25°C, with f = 2, 4, 6, 8, 10, 12, 14, 16, and 18 from top to bottom.

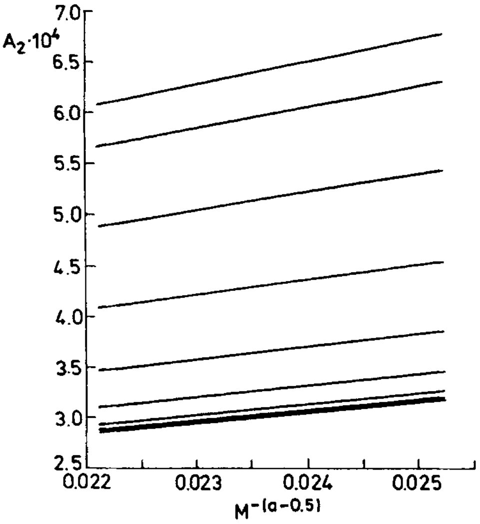

FIG. 9. A_2 vs $M^{-(a-0.5)}$ for f-arm star PBu2 in cyclohexane at 25°C, with f = 2, 4, 6, 8, 10, 12, 14, 16, and 18 from top to bottom.

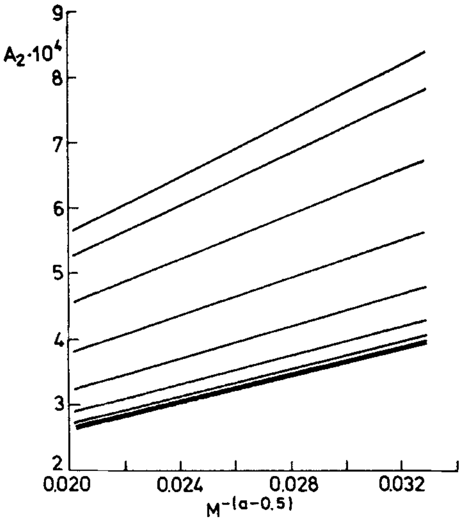

FIG. 10. A_2 vs $M^{-(a-0.5)}$ for f-arm star PBu3 in cyclohexane at 25°C, with f = 2, 4, 6, 8, 10, 12, 14, 16, and 18 from top to bottom.

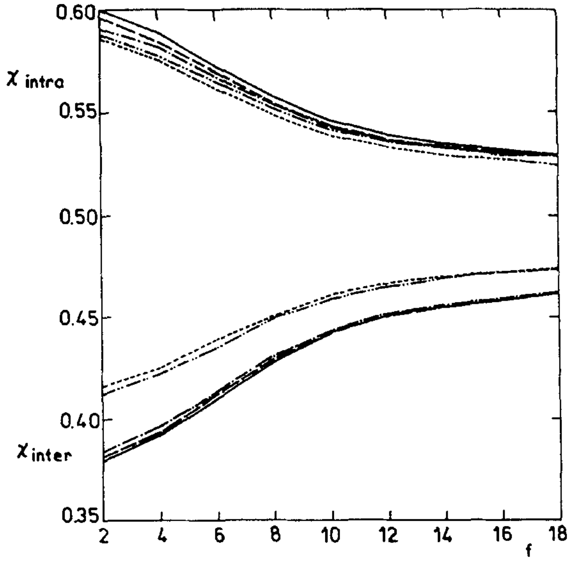

FIG. 11. The inter- and intramolecular interaction parameters according to Eqs. (23) and (24), plotted against the number of arms star, f: (-··-) PS1 sample in toluene at 35°C, a = 0.726; (·····) PS2 sample in toluene at 35°C, a = 0.73; (-·-·) PBu1 in cyclohexane at 25°C, a = 0.77; (——) PBu2 in cyclohexane at 25°C, a = 0.77; (---) PBu3 in cyclohexane at 25°C, a = 0.77.

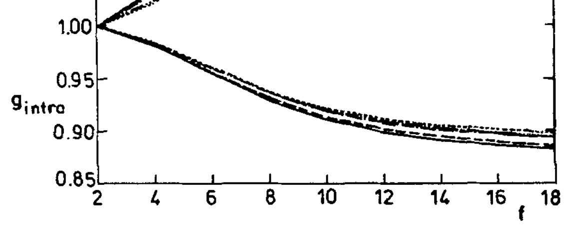

FIG. 12. Plots of g_{inter} and g_{intra} calculated with the values from Fig. 11, according to Eqs. (25) and (26), against the number of arms star, f: (-··-) PS1 in toluene at 35°C, a = 0.726; (·····) PS2 in toluene at 35°C, a = 0.73; (-·-·) PBu1 in cyclohexane at 25°C, a = 0.77; (——) PBu2 in cyclohexane at 25°C, a = 0.77; (---) PBu3 in cyclohexane at 25°C, a = 0.77.

One observes that $g_{\text{inter}}(f) > 1$ and $g_{\text{intra}}(f) < 1$. For f tending to infinity, g_{inter} and g_{intra} tend to a limit which depends on the thermodynamic conditions. In the case of other parameters, the theoretical investigations lead to functions of a single variable, f. For g_{inter} and g_{intra}, a mathematical expression must take into account both variables f and a. However, more experimental data are necessary for this purpose.

CONCLUSIONS

The analysis presented in this paper has shown that so far as interaction parameters are concerned, the behavior of star polymers in dilute solution can be described starting from experimental data on their linear homologs. More detailed conclusions require a greater amount of experimental data obtained from extensive, careful measurements on a large number of well-characterized polymer samples covering a wide range of molecular masses, chemical structures, and solvents.

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