Other authors[3] found a more marked dependence of the CD spectrum on the polymer conformation in the same spectral region. The discrepancy, besides the different poly(His) sample used by the two research groups, is partly imputable to the presence of salts. In fact, in 0.02 *M* KCl we also have found that the values around 220 nm depend on the polymer conformation.

From all this discussion, it appears that in the 215–225-nm spectral region there is a strong contribution to the optical activity from the imidazole side chains and that this contribution is somewhat conformation dependent. Turning back to the interpretation of the hysteresis of the 217-nm band, a possible interpretation is that, once the polypeptide molecules have been thermally denatured, a successive lowering of the temperature does allow the folding of the peptide backbone in the original ordered conformation, while the imidazole side chains are hardly able to find the final arrangement in the ordered structure of poly(His). This hypothesis could explain the normal behavior of the 203-nm CD band (which should mainly arise from peptide contributions) and the hysteresis of the 217-nm band (which should be mainly due to side-chain contribution). Such an interpretation could also account for the slow attainment of the equilibrium value of pH in the range of the conformational transition during the potentiometric titration experiments, caused by the slow arrangement of the imidazole side chains in the growing ordered structure of poly(His).

This feature appears well reconcilable with a random coil → β pH-induced conformational change of poly(His). However, pending direct unambiguous evidence in favor of such hypothesis it appears advisable to postpone any comparison between our set of results with those few reported in the literature for supposedly similar transitions.

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A New Theoretical Approach to the Problem of Solution Behavior of Branched Polymers

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ABSTRACT: In order to explain the solution behavior of star-shaped and comb-like polymers, we have extended Flory's and Orofino's calculations, taking into account the dependence of the interaction parameter χ on the local segment concentration. These calculations have been made assuming a gaussian distribution of segments around the center of mass. We have obtained the following results: (1) at Flory's Θ temperature, the second virial coefficient is different from zero and the coil is expanded; (2) the Θ_α temperature at which $\alpha = 1$ is different from the Θ_{A_2} temperature at which $A_2 = 0$, both of them being different from Flory's Θ temperature. These theoretical results account in the case of branched polymers for most of the yet unexplained results, especially the lowering of Θ_{A_2} and the discrepancies observed by several authors between the experimental dimensions and the corresponding calculated values; these discrepancies are due to an incorrect definition of the Θ dimensions. A comparison between experimental and theoretical values of Θ_α and Θ_{A_2} performed on 25 polymers prepared and studied in different laboratories is quite satisfactory.

Recent studies[1–7] carried out on the physical properties of model star and comb polystyrenes have shown that the behavior of such polymers in dilute solution cannot be described satisfactorily by the "two-parameter" theories—the two independent parameters being statistical segment *b* and excluded volume.

In these theories,[8–12] based on the single-contact approximation, the chain is assumed to obey random-flight statistics at the Θ temperature, a temperature at which simultaneously the second virial coefficient A_2 vanishes and the expansion factor α reaches unity.

The Θ temperature[13] or Flory temperature is thus a characteristic of a given polymer–solvent system, and is independent of the molecular weight of the polymer. However, in the case of the branched polymers we are studying in this paper, there are experimental results[1–7] which seem to be well established and which are in contradiction with the abovementioned theory.

(1) The Θ temperature is always lower than that measured for linear homologs in the same solvent: it depends on the length and on the number of branches, *i.e.*, on the molecular structure of the polymer. When the degree of branching is low, there is coincidence in the values of Θ temperature for linear and branched polymers. There is only one reported exception to this rule: Berry[1] finds an increase of 2° for star polystyrenes in cyclohexane.

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(1) G. C. Berry, Preprints of Papers presented at the IUPAC meeting, Tokyo, 1966, No. VI-144; *J. Polym. Sci., Part A-2*, **9**, 687 (1971).

(2) D. Decker, *Makromol. Chem.*, **125**, 136 (1969).

(3) I. Noda, T. Horikawa, T. Kato, T. Fujimoto, and N. Nagasawa, *Macromolecules*, **3**, 795 (1970).

(4) J. C. Meunier and R. Van Leemput, *Makromol. Chem.*, **147**, 191 (1971).

(5) F. Candau and E. Franta, *ibid.*, **149**, 41 (1971); F. Candau and P. Rempp, *Eur. Polym. J.*, **8**, 757 (1972).

(6) J. G. Zilliox, *Makromol. Chem.*, **156**, 121 (1972).

(7) J. Pannell, *Polymer*, **12**, 558 (1971).

(8) B. H. Zimm, W. H. Stockmayer and M. Fixman, *J. Chem. Phys.*, **21**, 1716 (1953).

(9) T. A. Orofino, *Polymer*, **2**, 305 (1961).

(10) T. A. Orofino and F. Wenger, *J. Phys. Chem.*, **67**, 566 (1963).

(11) E. F. Casassa, *J. Chem. Phys.*, **37**, 2176 (1962).

(12) G. C. Berry and T. A. Orofino, *ibid.*, **40**, 1614 (1964).

(13) P. J. Flory, *ibid.*, **17**, 303 (1949).

(2) Neglecting excluded-volume effects, Zimm and Stockmayer[14] first, then some others,[15,16] calculated the mean-square radii of gyration of branched chains of known structure, under the assumption that each linear element obeys random-flight statistics and that the statistical segment b is the same as for linear polymers: the experimental values of the radii of gyration of branched model star-shaped or comb-like macromolecules have been shown to be systematically larger than the theoretical values, even if measured at the actual Θ temperature.

(3) A third point of discrepancy concerns the expansion of the coil, often lower than predicted by classical theories.[17] It has been established from comparisons of the molecular dimensions of branched homopolymers with those of their linear homologs that the average segment density in the coil of a branched polymer is far higher[2] than that existing in the coil of a linear one. It may therefore be necessary to take into account multiple contacts between segments to explain the above-mentioned discrepancies. This is what we intend to do in this article, in which we describe the calculation procedure and the comparisons with experiment.

To simplify the derivations, we have followed the well-known procedure of Flory,[18] in which the polymer molecule is represented by a cloud of chain segments distributed in space, with spherical symmetry, as a gaussian distribution-function. But we have introduced in the derivation previously ignored terms of the series expansion of the free energy of interaction as of function of the local segment density.

A few years ago, Orofino and Flory[19] tried to show the effect of the change of thermodynamic parameters with concentration on the dilute-solution properties of linear polymers. We have used the same method, extending it to branched polymers, and have obtained new expressions for the expansion factor α and the second virial coefficient A_2.

To define satisfactorily the additional terms of the series expansion of the free energy parameter, we have assumed that

$$\chi = \chi_0(1 + a\phi_2 + b\phi_2^2 + \ldots) \qquad (1)$$

with $a = (1/\chi_0)(\partial\chi/\partial\phi_2)_{\phi_2=0}$ and $b = (1/2\chi_0)(\partial^2\chi/\partial\phi_2^2)_{\phi_2=0}$. In this expression, ϕ_2 is the volume fraction of the polymer and χ is defined by the well-known expression of total free energy of mixing given by Flory[18]

$$\Delta G_M = kT(n_1 \log \phi_1 + n_2 \log \phi_2 + \chi n_1 \phi_2) \qquad (2)$$

(I) Expansion of the Coil

Assuming that the distribution of segments around the center of mass is gaussian and that the unperturbed mean-square radius of gyration has the value $\overline{R_{0b}^2}$, we obtain for the expansion of the coil the expression

$$\alpha^5 - \alpha^3 = 2C_{M,l}\psi\left(1 - \frac{\theta}{T}\right)M^{1/2}g^{-3/2} + (2/3)\,\frac{C'_{M,l}}{\alpha^3}\,g^{-3} \qquad (3)$$

$$C_{M,l} = (1/16)\left(\frac{3}{\pi}\right)^{3/2}\left(\frac{\bar{v}^2}{N_A V_1}\right)\left(\frac{b^2}{6m}\right)^{-3/2} \qquad (3a)$$

$$C'_{M,l} = (3^{5/2}/2^3)\left(\frac{A}{\pi^3}\right)\left(\frac{\bar{v}^3}{N_A{}^2 V_1}\right)\left(\frac{b^2}{6m}\right)^{-3} \qquad (3b)$$

In these expressions $\bar{v}$ is the partial specific volume of polymer, V_1 the molar volume of solvent, N_A Avogadro's number, and m the mass of a statistical segment, the length of which is b. The parameter g characterizes the effect of branching on the unperturbed mean-square radius of a polymer molecule. It is defined as the ratio of the mean-square radii of branched and linear chains of the same mass[14]

$$g = \overline{R_{0b}^2}/\overline{R_{0l}^2}$$

The new parameter A is defined by the relation

$$(1/6) + \chi_0(b - a) = A$$

The quantities $C_{M,l}$ and $C'_{M,l}$ are independent of the molecular weight of the sample and are constant for any given polymer–solvent system.

In order to simplify the following discussion, one can write

$$K = 4C_{M,l}\psi\left(1 - \frac{\theta}{T}\right)\frac{M^{1/2}}{\alpha^3 g^{3/2}} \qquad (4a)$$

$$K' = \frac{2C'_{M,l}}{\alpha^6 g^3} \qquad (4b)$$

Hence, the expansion factor α may be written

$$\alpha^5 - \alpha^3 = \alpha^3\left(\frac{K}{2} + \frac{K'}{3}\right) \qquad (5)$$

Owing to our definition of the variation of χ as function of ϕ_2, our notations are different from those of Orofino and Flory,[19] who begin with the relation

$$\mu_1 - \mu_{1,0} = RT\left[\log(1 - \phi_2) + \left(1 - \frac{1}{x}\right)\phi_2 + \sum_{i=1}\chi_i\phi_2^{\,i+1}\right]$$

Our a, b, and A parameters are then related to their χ_1 and χ_2 parameters by the relations

$$\chi_0(1 - a) = \chi_1$$

$$2\chi_0(a - b) = \chi_2$$

$$2A = (1/3) - \chi_2$$

Discussion. From eq 3 and 5, it appears that the expansion factor α can be calculated for linear ($g = 1$) and for branched ($g < 1$) polymers, when T, A, g, ψ, and Θ are known. It has to be emphasized that the correction involved by the additional term is the more important, the smaller α is (poor solvent) and the smaller g is (more branched polymer).

Furthermore, the most significant result arising from our relation 3 is that α is not equal to unity when $T = \Theta$.

If we call Θ_α the temperature at which α equals unity, the preceding eq 3 yields

$$\frac{\Theta}{\Theta_\alpha} - 1 = \frac{C'_{M,l}g^{-3/2}}{3C_{M,l}\psi M^{1/2}} \qquad (6)$$

The second term of this equation characterizes the perturbation resulting from the high segment density: decreasing the molecular weight or increasing the grafting ratio will further remove the Θ_α temperature with respect to Flory's Θ temperature.

It seems necessary to assume a positive value for A, since in the other case the solution would be unstable. In this case, Θ_α is always lower than Θ, becoming equal to Θ only when M is infinite.

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(14) B. H. Zimm and W. H. Stockmayer, *J. Chem. Phys.*, **17**, 1301 (1949).

(15) E. F. Casassa and G. C. Berry, *J. Polym. Sci., Part A-2*, **4**, 881 (1966).

(16) G. C. Berry, *ibid.*, **6**, 1551 (1968).

(17) W. H. Stockmayer and M. Fixman, *Ann. N. Y. Acad. Sci.*, **57**, 334 (1953).

(18) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

(19) T. A. Orofino and P. J. Flory, *J. Chem. Phys.*, **26**, 1067 (1957).

An interesting consequence is that values of the radius of gyration measured at Flory's temperature are not really unperturbed values: the corresponding α is higher than unity. This result may explain why the observed values of $\overline{R_0}^2$ are found to be systematically larger than the values calculated according to Orofino's equation.[1-7]

If we consider the expansion factor α at Flory's temperature, a simple relation is obtained from eq 3

$$\alpha_\Theta^8 - \alpha_\Theta^6 = (2/3)C'_{M,l}g^{-3} \qquad (7)$$

We may note that α_Θ does not depend on molecular weight but solely on g. This relation can be used to evaluate $C'_{M,l}$, and thus A.

(II) Second Virial Coefficient A_2

According to Flory's procedure, when taking into account the variation of χ with the concentration, we obtain for the second virial coefficient the following expression

$$A_2 = \left(\frac{2^4}{3^{3/2}}\right)(N_A\pi)\left(\frac{g^{3/2}\alpha^3}{M^{1/2}}\right)\left(\frac{b^2}{6m}\right)^{3/2}\int_0^\infty [1 - \exp(-Ke^{-y^2} - K'e^{-4/3y^2})]y^2\mathrm{d}y \qquad (8)$$

where

$$y = \left(\frac{l}{2^{1/2}}\right)\left(\frac{3}{2\overline{R}^2}\right)^{1/2}$$

l being the distance between the center of gravity of the two polymer molecules.

Since this integral unfortunately cannot be evaluated in terms of classical functions, we have considered only two special cases which allow fruitful comparisons with experimental data. These two cases are the temperature at which A_2 is equal to zero, Θ_{A_2}, and the Flory Θ temperature, at which A_2 would be equal to zero in the single contact approximation; it has in fact a nonzero value, which we shall call $A_{2\Theta}$.

(1) The Temperature Θ_{A_2}

Since Θ_{A_2} is not far from Flory's temperature, the quantity $(1 - (\Theta/T))$ and therefore the K term is small enough to allow an expansion of A_2 in powers of K. The detailed derivation is reported in the appendix.

We have obtained thus a general expression of the second virial coefficient which is only valid when K^2 is negligible.

$$A_2 = \pi^{3/2}N_A\left(\frac{b^2}{6m}\right)^{3/2}\left[\frac{C'_{M,l}}{M^{1/2}\alpha^3g^{3/2}}J(K') + \frac{2^4}{3^{3/2}}C_{M,l}\psi\left(1 - \frac{\Theta}{T}\right)G(K') + \ldots\right] \qquad (9)$$

The slowly decreasing functions $J(K')$ and $G(K')$ have been computed and they are shown in Figure 1.

The second virial coefficient is equal to zero when K equals K_{A_2}, given by

$$K_{A_2} = -K_{A_2}'\left(\frac{3^{3/2}}{2^3}\right)H(K') \qquad (10)$$

where

$$H(K') = \frac{J(K')}{G(K')} \qquad (11)$$

H(K') is an increasing function, always equal to/or greater than unity: it is also shown in Figure 1. The Θ_{A_2} temperature may then be expressed by eq 12 in a similar way as it was done for Θ_α in the preceding section (eq 6)

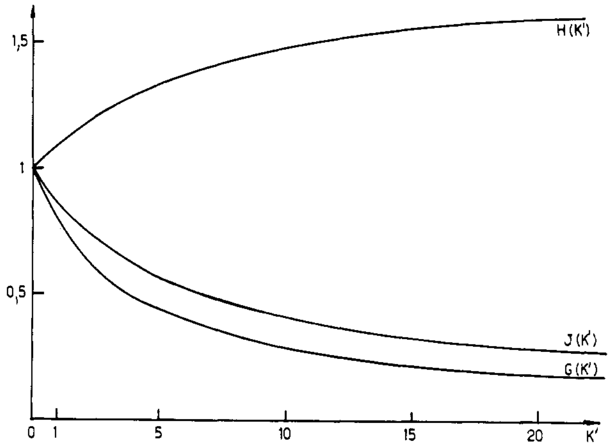

Figure 1. The functions $J(K')$, $G(K')$, $H(K')$ plotted against K'.

$$\frac{\Theta}{\Theta_{A_2}} - 1 = \frac{3^{3/2}}{2^4}\frac{C'_{M,l}}{C_{M,l}}\frac{1}{\psi M^{1/2}}H(K')\frac{1}{\alpha^3g^{3/2}} \qquad (12)$$

(2) Flory's Θ Temperature

When $T = \Theta$, it is possible to simplify eq 9. Finally, we get for the second virial coefficient the expression

$$A_{2\Theta} = \pi^{3/2}N_A\left(\frac{b^2}{6m}\right)^{3/2}\frac{C'_{M,l}}{\alpha^3g^{3/2}}\frac{J(K')}{M^{1/2}} \qquad (13)$$

$A_{2\Theta}$ is then different from zero at Flory's temperature, if the dependence of χ on concentration is taken into account. $A_{2\Theta}$ has the sign of A and, curiously enough, its expression is very similar to Flory's classical relation.[18] As opposed to the molecular weight independence of α_Θ, $A_{2\Theta}$ decreases with increasing molecular weight. By setting $g = 1$ into these expressions, one should get the same results as Orofino and Flory.[19] This is effectively the case, the only difference being the approximation we are using for the calculation of the second virial coefficient.

Discussion. The relationships 6 and 12 yielding respectively Θ_α and Θ_{A_2} are very similar, but not identical. We may thus conclude the existence of two characteristic temperatures, the Θ_α temperature at which $\alpha = 1$ and the Θ_{A_2} temperature at which $A_2 = 0$, both of them being different from Flory's temperature.

If we call $\Delta\Theta_\alpha$ and $\Delta\Theta_{A_2}$ the differences $(\Theta - \Theta_\alpha)$ and $(\Theta - \Theta_{A_2})$, respectively, we get for their ratio

$$\frac{\Delta\Theta_{A_2}}{\Delta\Theta_\alpha} = \frac{3^{5/2}}{2^4}\frac{H(K')}{\alpha_{A_2}{}^3} \qquad (14)$$

This relation shows that $\Delta\Theta_\alpha$ and $\Delta\Theta_{A_2}$ have the same sign; $\Delta\Theta_{A_2}$ and $\Delta\Theta_\alpha$ are both positive when A is positive. In the most general case, this expression cannot tell whether $\Delta\Theta_\alpha$ is larger or smaller than $\Delta\Theta_{A_2}$. However, if one assumes that A (*i.e.*, K') is small, the right-hand side of eq 14 is lower than unity and $\Delta\Theta_\alpha$ is larger than $\Delta\Theta_{A_2}$. Still assuming that A is positive, the three temperatures Θ_α, Θ_{A_2}, and Θ obey the following inequality

$$\Theta_\alpha < \Theta_{A_2} < \Theta$$

(III) Comparison with the Theory of Vrij and Casassa

Very recently, Vrij[20] and then Casassa[21] have proposed, as a

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(20) A. Vrij, *J. Polym. Sci., Part A-2*, 7, 1627 (1969).
(21) E. F. Casassa, *ibid.*, 8, 1651 (1970).

TABLE I
STRUCTURAL CHARACTERISTICS OF BRANCHED POLYSTYRENES

Series	$M_w \times 10^{-6}$	$M_w \times 10^{-5}$ (backbone)	$M_w \times 10^{-4}$ (one branch)	p	f	g_{th}
I[a] M 2A	2.05		1.9	10.7		0.263
M 2E	2.95		1.9	15.5		0.185
P 2C	2.35		1.9	12.3		0.230
M 5E	5.00		5.7	8.7		0.318
II[b] 24 B_4	0.240		6.73	4		0.625
23 B_6	0.573		9.73	6		0.445
III[c] 1457 f_1	1.59	3.75	0.685	195	12	0.165
1457 f_2	1.22	2.73	0.685	150	12	0.168
1427 f_1	3.82	3.00	1.60	219	14	0.0948
1427 f_2	2.80	2.25	1.60	161	14	0.0989
1591 f_1	2.27	2.55	1.76	115	22	0.135
1406 f_1	11.70	6.80	2.32	475	14	0.0648
1406 f_2	7.50	4.80	2.32	305	14	0.0679
1406 f_3	4.63	2.60	2.32	188	14	0.0732
1428 f_1	3.70	3.10	3.60	94	33	0.111
1428 f_2	2.70	2.30	3.60	79	33	0.123
IV[d] H 6′	2.43	0.97	12.90	18.1	54	0.16
V[e] 2 A	1.50	7	4	20	344	0.53
3 A	3.52	7	4	70	95	0.232
4 A	8.50	7	4	195	36	0.098
1 B	1.07	7	1.1	33	204	0.67
2 B	1.83	7	1.1	100	68	0.406
3 B	2.60	7	1.1	165	43	0.282
4 B	3.38	7	1.1	234	31	0.22

[a] Reference 6. [b] Reference 4. [c] Reference 2. [d] Reference 3. [e] Our results.

refinement of Flory's theory, to take into consideration interfacial energies between the coil and the surrounding solvent. Their theory predicts the temperature at which the chain obeys random-flight statistics to be lower for a branched chain than for a linear one. It was therefore interesting to compare their results with ours.

Vrij and Casassa have written the results of their calculation concerning α in the following way

$$\frac{\Delta\Theta_\alpha}{\Theta} = \frac{5}{4} l^2 \left(\frac{\overline{R_0^2}}{M}\right)^{-1} \frac{1}{Mg} \tag{15}$$

l being the characteristic length defined by Debye.[22] This expression has to be compared to eq 6, which may be written as

$$\frac{\Delta\Theta_\alpha}{\Theta} = \frac{2A\bar{v}}{\pi^{3/2}N_A\psi} \frac{1}{M^{1/2}g^{3/2}} \left(\frac{\overline{R_0^2}}{M}\right)^{-3/2} \tag{16}$$

These two relations are similar in so far as both show a decrease in $\Delta\Theta_\alpha$ when g and M—*i.e.*, the density of segments in the coil—increase, but the exponents of g and M are different.

Besides, for Vrij, $\Delta\Theta_\alpha$ is always a positive quantity, whereas according to our results, $\Delta\Theta_\alpha$ has the same sign as A.

A much more important difference concerns the comparison of the Θ_{A_2} expressions. Although both yield similar g and M dependence, they mainly differ by their sign. According to Vrij and Casassa, Θ_{A_2} is always larger than Θ. The three temperatures are then in the following order: $\Theta_\alpha < \Theta < \Theta_{A_2}$, whereas according to our derivations $\Delta\Theta_\alpha$ and $\Delta\Theta_{A_2}$ have the same sign, being both positive when A is positive.

As we shall see later, our theoretical conclusions are confirmed by all experimental results, suggesting that our theory gives a better fit with experimental data. (It is of interest to note that Casassa[21] in the same paper remarked that higher order terms in the expansion of the free energy in the segment density could be of equal importance to the interfacial energy terms, and predicted a term proportional to R^{-3}. The theoretical results used in the present paper are in accordance with eq 20 of Casassa's paper, but they have the advantage of easy comparison with experiments.)

(IV) Comparison with Experiment

In the theoretical relations established above, the parameters which have appeared are related to the thermodynamic characteristics of the polymer–solvent system.

Fortunately, the system we have studied—polystyrene in cyclohexane—is a very classical one and has been described in many articles.[23-25]

Moreover, in the past few years several authors have investigated dilute-solution properties of various branched polystyrenes in cyclohexane.[1-7] A comparison of our results with experiments is therefore possible. The discussion will be conveniently presented in two sections: in the first part, we shall compare theoretical and experimental values of the expansion factor α, and in the second part, those concerning the second virial coefficient.

Table I summarizes data on several star- and comb-branched polystyrenes which have been studied in various laboratories, and the properties of which have been investigated in cyclohexane.

In this table, p stands for the number of branches and f is the average number of segments between two subsequent branches along the backbone. Polymers of series I and II are star-shaped polystyrene samples. Those of the series I were synthesized by Zilliox using anionic block copolymerization of styrene and DVB.[6] The samples of the series II were prepared by Meunier by electrophilic deactivation of a living polystyrene with a polyfunctional deactivator.[4] The other polymers are comb-shaped polystyrenes; some of them are our own samples,[5] others were prepared by different methods, described by Decker[2] and Noda, *et al.*[3]

(A) Expansion Factor α near the Θ Temperature. Two experimental methods are available for the determination of the expansion factor α: light scattering and viscosity measurements. The latter is much simpler to handle, but the relation between the viscosimetric expansion factor α_η thus measured and the geometrical expansion α we are concerned with is not well established, especially in the case of branched polymers.

This is the reason that we preferred light-scattering measurements, even though this method is sensitive to polydispersity and its use limited to polymers of rather high molecular weight.

Knowing the structural characteristics of the polymer samples listed in Table I, we may calculate their radii of gyration from Orofino's equation.[9] For star-shaped polystyrenes, this expression can be written as

$$\overline{R^2}_{0*} = \frac{N_b b^2}{6}\left(\frac{3p-2}{p}\right) \tag{17}$$

where $\overline{R^2}_{0*}$ is the unperturbed mean-square radius of gyration of a star-shaped polystyrene having p equal branches with N_b segments in each of them. For comb-shaped polystyrenes,

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(22) P. Debye, *J. Chem. Phys.*, 31, 680 (1959).

(23) T. G. Fox and P. J. Flory, *J. Amer. Chem. Soc.*, 73, 1915 (1951).

(24) T. G. Scholte, *Eur. Polym. J.*, 6, 1063 (1970).

(25) S. H. Maro and C. A. Daniels, *J. Macromol. Sci., B*, 2, 743 (1968).

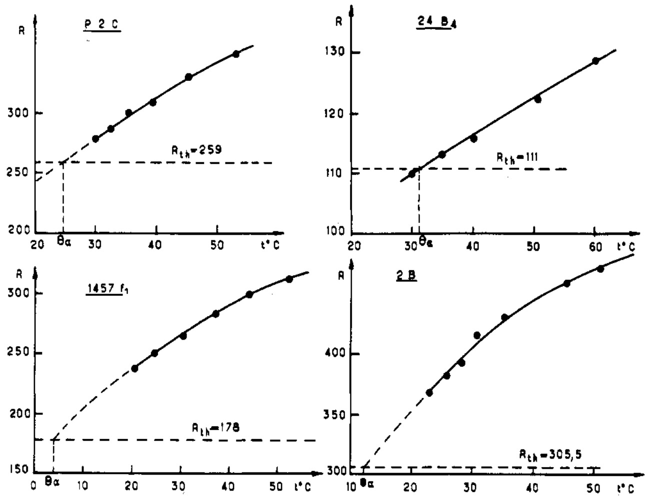

Figure 2. Plots of the mean-square radius of gyration of several star and comb polymers *vs.* temperature. For the sake of simplicity, we have called R the measured z average of $(R^2)^{1/2}$. The dotted lines refer to the extrapolation of the curves to the theoretical R value.

the mean-square radius of gyration $\overline{R^2}_{0b}$ is given by the following expression

$$\overline{R^2}_{0b} = \frac{b^2}{6}\left[N_S + 3N_G\left(\frac{r}{1+r}\right)\right] \tag{18}$$

N_S and N_G are respectively the number of segments of the backbone and of the branch. The parameter r is the ratio between the number of segments in a graft and the distance between two branches $r = N_G/f$.

To obtain the expansion factor α, one usually measures the dimensions of the molecule in a given solvent at temperature T and the dimensions of the same molecule at the Θ temperature. As our derivations have shown that Θ_α, *i.e.*, the temperature at which $\alpha = 1$, is not necessarily equal to Θ, nor even to Θ_{A_2}, we have defined here α as the ratio between the radius of gyration at temperature T and the value calculated according to Orofino[9] using for b the value obtained for linear polystyrene in cyclohexane. We postulate that

$$\alpha^2 = \overline{R^2}_{0b}/\overline{R^2}_{0\text{th}} \tag{19}$$

There are, however, two difficulties to be considered. The first is related to the fact that experimental values of the radius of gyration are Z average, whereas the theoretical values are based on M_w measurements. The comparisons are only satisfactory for samples of low polydispersity. The second difficulty is related to the fact that the $\overline{R^2}_{0b}$ and $\overline{R^2}_{0s}$, radii of gyration of the individual branch and of the backbone, respectively, are taken at the Θ temperature and not at the actual Θ_α temperature.

(1) The Θ_α Temperature. We have been able to determine the Θ_α temperature—at which $\alpha = 1$—by two different methods.

In the first method we merely use the experimental plot of $\overline{R^2}$ *vs.* temperature for each of our samples. Extrapolating this curve to $\overline{R^2}_{0\text{th}}$, we can directly evaluate Θ_α. In some cases this extrapolation is obvious, in a few other cases it is rather unprecise. Some of these curves are shown in Figure 2. The second process takes advantage of eq 3 which may be written

$$\alpha^8 - \alpha^6 = 2C_{M,l}\psi\alpha^3\left(1 - \frac{\Theta}{T}\right)M^{1/2}g^{-3/2} + (2/3)\frac{C'_{M,l}}{g^8} \tag{20}$$

A plot of $(\alpha^8 - \alpha^6)$ *vs.* $\alpha^3(1 - (\Theta/T))$ should thus define a straight line. The parameters ψ and A can be evaluated from the slope and from the intercept of this line, respectively. Its intersection with the x axis provides the Θ_α temperature.

We have applied eq 20 to our data for all the samples. Figure 3 shows that good straight lines are obtained, which is a strong argument in favor of our theoretical treatment. The Θ_α values obtained by these two different methods are collected in Table II. Let us briefly comment on these results.

TABLE II

EXPERIMENTAL AND THEORETICAL VALUES OF THE Θ_α AND Θ_{A_2} TEMPERATURES; CALCULATED VALUES OF THE A AND ψ PARAMETERS FOR VARIOUS BRANCHED POLYMERS

Sample	g_{th}	Θ_α[a]	Θ_α[b]	$A_2 \times 10^2$	$\psi \times 10^2$	Θ_{A_2}[c]	Θ_{A_2}[d]
M 2A	0.263	28	28	0.55	3.6	29	29.5
M 2E	0.185	24	25.5	0.6	3.1	29	28
P 2C	0.23	25	27	0.5	3	30	28.5
M 5E	0.318	33	33	0.4	2.9	33	31.5
24 B_4	0.625	31	32	0.5	8.9	32.5	30
23 B_6	0.445	33	32.5	0.25	2.6	33.9	29.5
1457 f_1	0.165	4	0	5.8	10.7	25	30
1457 f_2	0.168					25	29
1427 f_1	0.0948	7	6	2	7.5	27.5	28
1427 f_2	0.0989					27.5	26
1591 f_1	0.135	14	12	2.3	8.3	28	28
1406 f_1	0.0648					28.5	30
1406 f_2	0.0679	13	7	3.5	8.4	28.5	29.5
1406 f_3	0.0732	10	7	2.6	9.1	28.5	27
1428 f_1	0.111	20	23	0.43	3.3	31	25
1428 f_2	0.123					31	24.5
H 6′	0.16	18	Curve			32.4	32.5
2A	0.53	25	25	10	13.5	33	32.5
3A	0.232	21	20	5.9	11.2	28.5	32
4A	0.098	12	7	6.7	12	26.5	28.5
1B	0.67	25.5	27	7	12.5	28	32.5
2B	0.406	12	9	27	17	22.5	32.5
3B	0.282	4	0	23	15	20	32
4B	0.22	5	Curve			19	32.5

[a] By extrapolating the curve $R(t)$ to the theoretical value. [b] By extrapolation of the $(\alpha^8 - \alpha^6)$ *vs.* $\alpha^3(1 - (\Theta/T))$ plot. [c] Measured by light scattering. [d] From calculated values according to eq 12.

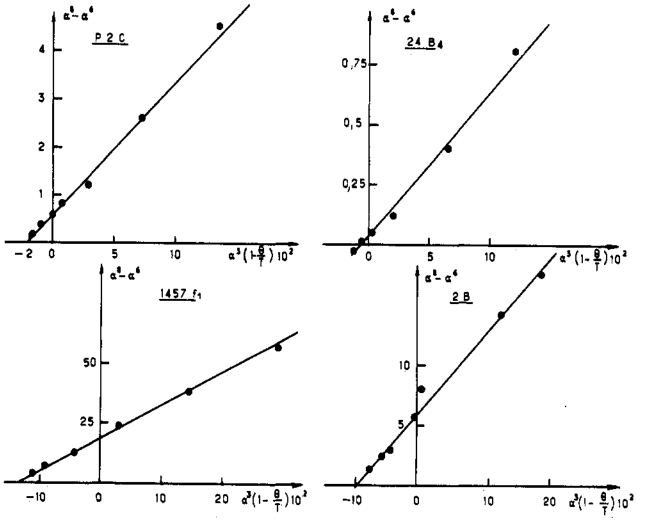

Figure 3. Determination of the θ_α temperature by extrapolating the curve $\alpha^8 - \alpha^6 = f[(\alpha^3(1 - (\theta/T))]$ for several star- and comb-shaped polymers.

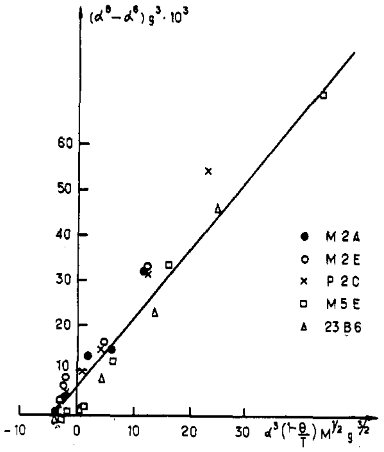

Figure 4. Plots of $(\alpha^8 - \alpha^6)g^3$ *vs.* $\alpha^3(1 - (\theta/T))M^{1/2}g^{3/2}$ for star-shaped polystyrenes in cyclohexane (eq 20).

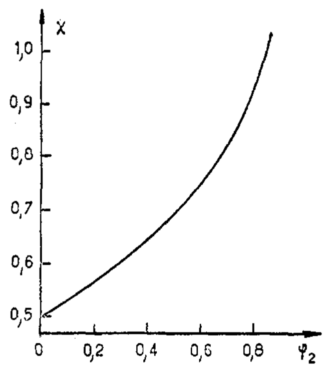

Figure 5. Plot of the interaction parameter χ *vs.* volume fraction of polystyrene–cyclohexane mixtures. The diagram is taken from T. G. Scholte, *J. Poly. Sci.*, **8**, 841 (1970).

(a) The Θ_α values obtained for one given sample by the two methods are in satisfactory agreement, in spite of the rather low precision of the second procedure. Besides, for star-shaped polystyrenes, the Θ_α values are obtained without any ambiguity from the curve $R = f(t)$, since measurements have been carried out down to temperatures very close to Flory's Θ temperature. The good agreement between the two Θ_α temperatures confirms the validity of the results.

(b) All the Θ_α values obtained are lower than Flory's Θ temperature. This was to be expected, since it follows from our theoretical results that Θ_α and Θ_{A_2} have to be simultaneously lower than Θ if A is positive, which, as it has been shown experimentally and theoretically, should be the case.

(c) From a qualitative point of view, there is also a good correlation between the difference $(\Theta - \Theta_\alpha)$ and the degree of branching of the polymer. $(\Theta - \Theta_\alpha)$ increases, as expected from our theory, when g decreases.

(d) The difference between Flory's temperature and the Θ_α values thus obtained is in some cases very important, and this explains the discrepancies observed between the geometrical radii of gyration measured by light scattering at Flory's temperature and the calculated values.

(2) General Diagram for Star-Shaped Polystyrenes. Another test for the validity of eq 20 consists in plotting $(\alpha^8 - \alpha^6)g^3$ *vs.* $\alpha^3(1 - (\Theta/T))M^{1/2}g^{3/2}$, since the g parameter and the molecular weight are known for each of the samples considered. Such a representation should provide a straight line with a slope equal to $2C_{M,t}\psi$. Figure 4 is relative to star-shaped polystyrenes. The straight line thus obtained confirms once more the possibility of using eq 20 for these polymers. However, points relative to comb-like polystyrenes do not lie on the same line. This shows the limitation of our present theory for this type of structure and will be discussed later.

(3) Determination of the A coefficient. It has been previously shown that the A coefficient is defined by the following expression

$$A = (1/6) + \chi_0(b - a)$$

On plotting $(\alpha^8 - \alpha^6)$ against $\alpha^3(1 - (\Theta/T))$, the intercept of the line yields $C'_{M,t}$ and thus A, as mentioned above. The A values have been determined for all the samples. They are also listed in Table II. The following results can be seen.

(a) For star-shaped polystyrenes, the A values are not far from the average value 5×10^{-3}.

(b) For comb-like polystyrenes the A values are much more scattered. It appears thus that our equations give better account of the properties of star-shaped polystyrenes than of those of comb-like polystyrenes.

A trivial explanation would be to assume that polydispersity affects comb-like much more than star-shaped polymers.

Zilliox[26] has shown that the polydispersity does not affect the radius of gyration of star-shaped polymers, provided that it originates solely from fluctuations in the number of branches.

On the other hand, for comb polymers with few grafts, even if the backbone and the grafted chain are monodisperse, some polydispersity is due to fluctuations in the number of grafted chains. The effect of polydispersity therefore could be much more important in this case.

Even for series III, where the number p is large, polydispersity can be important, since the backbone was prepared by radical polymerization.[2]

More than polydispersity, the molecular model adopted may be subject to discussion. The model we have used to make our calculations assumes a gaussian distribution of spherical symmetry of segments around the center of mass.

It is known that this model is not correct for linear chains. Fortunately, this hypothesis is much more justified for star-shaped polystyrenes, since this type of distribution is obtained for a large number of branches. For comb-like polymers, it can be far from reality. If these results are confirmed, they will show that the g parameter only cannot suffice for describing the behavior of comb polymers. One has to take into account their detailed structure which cannot be described only by two parameters, as for instance g and M.

(c) Comparison may be made with the A value obtained for linear polystyrenes. Our initial assumption concerning the concentration dependence of the interaction parameter was based on experimental results[27–30] obtained for the system polystyrene–cyclohexane at various temperatures, over a concentration range 0–80 wt %. As segment densities within the coils of branched polymers may reach 10 g/100 ml,[2] it is obvious that in this concentration range, χ notably depends on polymer concentration (Figure 5). Moreover, it has been shown very recently that for linear polymers χ also depends slightly on molecular weight of the polymer.[24]

The numerical value of A may be deduced from Figure 5 by calculating the a and b coefficients [$A = 1/6 + \chi_0(b - a)$],

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(26) J. G. Zilliox, Thesis, Strasbourg, 1970.

(27) W. R. Krigbaum and D. O. Geymer, *J. Amer. Chem. Soc.*, **81**, 1859 (1959).

(28) E. C. Baugham, *Trans. Faraday Soc.*, **44**, 495 (1948).

(29) K. Smoll and E. Senkel, *Z. Elektrochem.*, **60**, 756 (1956).

(30) T. G. Scholte, *J. Polym. Sci., Part A-2*, **8**, 841 (1970).

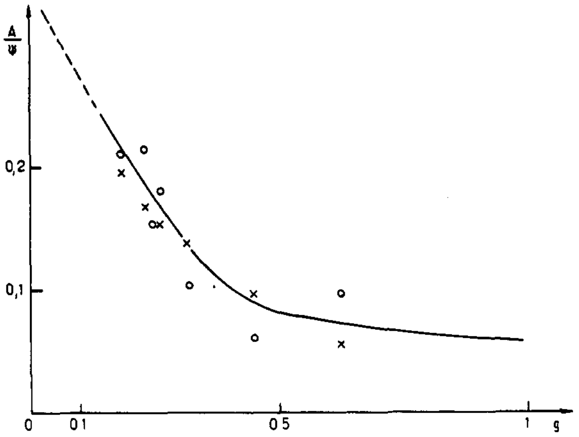

Figure 6. Plot of the A/ψ ratio *vs.* the g parameter for star-shaped polystyrenes: (O) A/ψ determination from the curve $R = f(t)$, (X) A/ψ determination from the curve $\alpha^8 - \alpha^6 = f[(\alpha^3(1 - (\theta/T)]$.

but the obtained value depends on how we draw the tangent to the curve at the origin, *i.e.*, for $\chi = {}^1/_2$. Since this operation cannot be performed without any ambiguity, the comparison loses some of its value. We can, however, conclude that the order of magnitude is about the same, showing that there is no contradiction between our results and the variation of χ with concentration measured by classical techniques. It should be pointed out that the Krigbaum and Geymer[27] curve we have used for the determination of A could have a complicated behavior near the origin when one is going from a region of uniform density of segments (high concentration) to a region where the solution may be considered as a dispersion of clouds of segments separated by regions of pure solvent.

If our treatment is valid for branched polymers, it should also be valid for linear polymers. We have tried to calculate the lowering of the Θ point starting from eq 12 for a linear polystyrene of $M_w = 50{,}000$. For this purpose, we have used our A value, *i.e.*, 5×10^{-3} and $H(K') \sim 1$. As will be discussed later, we have found, as have other authors,[1,10] that ψ depends on the structure of the polymer. Using for linear polymers $\psi = 0.36$, we find the difference between infinite M_w and 50,000 to be 0.5°. This is within the experimental error, and it would be interesting to check with precise measurements on small molecular weights whether this effect can be detected.

(4) Entropy Parameter Determination. Even for linear polystyrenes in cyclohexane, the value of the entropy parameter ψ is not very well known. Values obtained from measurements of precipitation temperature, of the intrinsic viscosity, and of second virial coefficient differ by a large factor, since the different methods are giving respectively 1.06, 0.13, and 0.36.[31]

From Table II, it appears that the ψ values obtained from the slope of the straight lines defined by eq 20 for branched polymers are systematically lower than the smallest value ($\psi = 0.13$) obtained for linear polystyrenes.[31]

This is in good agreement with results published by Orofino, *et al.*,[10] who have observed for star-shaped polystyrenes of very low density of branching a value which is lower by a factor of 1.5 than that for a linear polystyrene.

Moreover, the ψ values are different for each sample. As a first approximation it seems that ψ is an increasing function of the structural parameter g. In Figure 6, we have plotted for star-shaped polystyrenes, the ratio A/ψ determined by the two previously described methods.

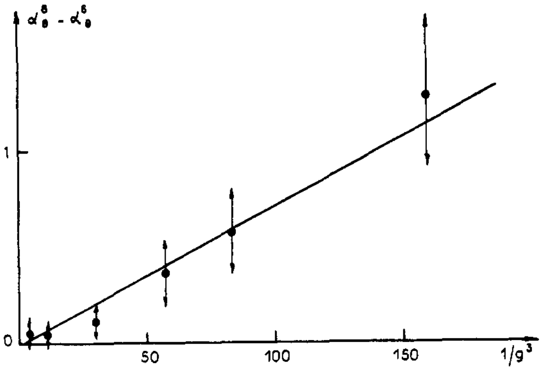

Figure 7. Plot of ($\alpha_\Theta^8 - \alpha_\Theta^6$) *vs.* $1/g^3$ for star-shaped polystyrenes.

This g dependence of the entropy parameter is rather surprising if we keep its definition in mind. ψ characterizes the interaction between two segments, independent of the length and the structure of the chains to which they belong. Owing to this definition it should be therefore independent of the structure of the chain. This weakness of the theory is not due to our model since, as we have said, this effect has already been found. Neither our calculations nor other available theoretical treatments are able to explain these variations.

(5) Expansion Factor α at the Θ Temperature. We have already discussed the relative simplicity of eq 7 at Flory's temperature

$$\alpha_\Theta^8 - \alpha_\Theta^6 = (2/3)C'_{M,t}g^{-3}$$

The quantity ($\alpha^8 - \alpha^6$) should be proportional to g^{-3}. It is shown in Figure 7 that the experimental points are fitted satisfactorily by a straight line passing through the origin. The slope provides once more the average value 5×10^{-3}. We want to emphasize here that, using this method, the determination of A does not depend on the value of ψ, which makes this representation very interesting.

(6) Expansion Factor in a Good Solvent (Benzene). Here again, the expansion factor α is defined as the ratio between the radius of gyration of the branched molecule in the considered solvent and the unperturbed value $\overline{R^2}_{0\text{th}}$, calculated according to Orofino.[9]

Some authors[4,6] have observed that in benzene at 25° the expansion factors α are of the same order of magnitude for linear and for branched polymers. These results disagree with Orofino's[12] and Stockmayer's[17] theories, which may be due to an incorrect definition of the Θ dimensions.

All the preceeding authors have assumed that the unperturbed dimensions can be measured at Flory's temperature. Since, as we have shown, at this temperature the molecules are already expanded, it is obvious that their α values are too low.

In Figure 8, the expansion factor α is plotted *vs.* the molecular weight of each sample. The dotted line is for linear polymers; the two others have been drawn somehow arbitrarily. One of them is for star-shaped polystyrenes and comb-like polystyrenes with very few branches, the other is for highly comb-like branched polystyrenes.

We must note that the new values of the expansion factor are in all cases higher than those for linear chains, as expected theoretically. Moreover, as a first approximation, these three lines seem to be roughly parallel, which indicates that

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(31) W. R. Krigbaum, *J. Amer. Chem. Soc.*, 76, 3758 (1954).

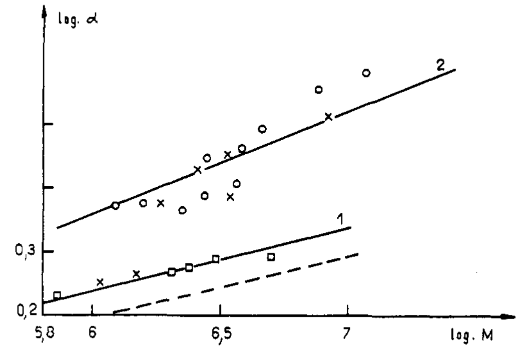

Figure 8. Plots of the expansion factor α *vs.* the molecular weight for linear and branched polystyrenes: (1) star-shaped polystyrenes and comb-like polystyrenes with few branches ($f > 200$), (□) Zilliox, (×) our results; (2) highly branched polystyrenes, (○) Decker[2], (×) our results.

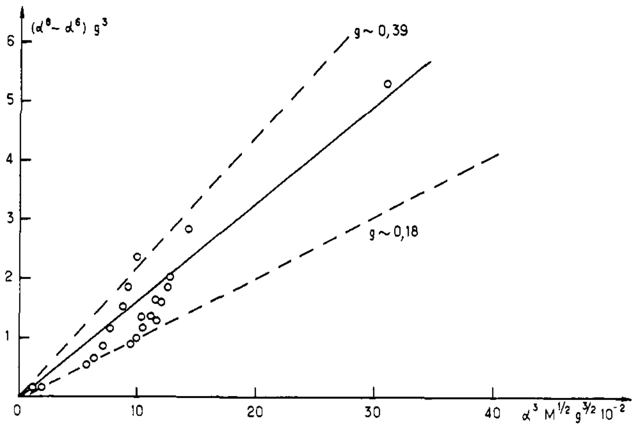

Figure 9. Plot of $(\alpha^8 - \alpha^6)g^3$ *vs.* $\alpha^3M^{1/2}g^{3/2}$ for star-shaped polystyrenes in benzene (eq 20).

the expansion coefficient increases when g decreases. However, it is impossible to establish a general relation. This indicates the difficulty in completely describing the properties of branched polymers using only g to characterize their structures.

Another representation clearly demonstrates the influence of branching upon the expansion of the coil.

We have said that in a good solvent, the second term on the right-hand side of eq 3 must be negligible; this equation may thus be written

$$(\alpha^8 - \alpha^6)g^3 = 2C_{M,l}\psi\left(1 - \frac{\Theta}{T}\right)\alpha^3M^{1/2}g^{3/2}$$

Therefore, plotting $(\alpha^8 - \alpha^6)g^3$ as function of $\alpha^3M^{1/2}g^{3/2}$ one should obtain a straight line going through the origin, if our approximation is correct.

This is approximately the case (Figure 9) for fractionated star-shaped samples prepared by Zilliox.[26] We have drawn two dotted lines which correspond to extreme g values. Let us remark that the smaller the g value, the higher the slope, showing again the dependence of ψ on the parameter g.

(B) Second Virial Coefficient. We will now critically examine the results concerned with the second virial coefficient.

It has been demonstrated above that the Θ_α temperature is lower than Flory's temperature.

We have also shown that if A is small (and positive) the inequality $\Theta_\alpha < \Theta_{A_2} < \Theta$ holds for all the samples. This is also verified by our results, which are listed in Table II.

More quantitatively, we can calculate Θ_{A_2} from eq 12. For this purpose, we need the ratio A/ψ and the A constant implicitly included in $C'_{M,l}$. The A/ψ ratio varies somewhat with g, but rather than taking for each sample its true value, which may be in some cases erroneous, we have preferred to take an average A/ψ value of 0.17, and the average A value of 5×10^{-8} previously found.

Comparison between experimental and calculated Θ_{A_2} values is reported in Table II. The satisfactory agreement between these values supports the validity of our initial assumptions.

It is noteworthy that such an agreement has been obtained starting from simple theoretical calculations based on Flory's treatment.

However, a comparison between theoretical and experimental A_2 values at Flory's temperature is less successful, because of experimental difficulties for accurate A_2 measurements.

Conclusions

In this paper we have presented an interpretation of the dilute-solution properties of branched polymers. Experimental evidence has been obtained, from our results as well as from data of other laboratories, that the Θ conditions depend on the structure of the branched molecules and do not characterize anymore a given polymer–solvent system. These experimental facts seem to rest on solid ground, but they cannot be explained using the so-called "two-parameter" theories.

To take account of the high segment density within the polymer coil, we have suggested taking three terms in the series expansion of the interaction coefficient between segments. This assumption led us to an additional term in the expansions of the thermodynamical functions, depending on the third power of the segment concentration. We have been able to show that this additional term does not vanish when the second virial coefficient is zero: we had thus to disregard the superposition principle.

From these results it follows that the Θ point has really no physical meaning anymore, since the temperature Θ_α at which the expansion coefficient α is unity, and the temperature Θ_{A_2}, at which the A_2 coefficient is equal to zero, are not identical, and are both different from the Θ point as defined by Flory.

It follows from these results that neither at the temperature Θ_α at which $\alpha = 1$, nor at Θ_{A_2}, at which $A_2 = 0$, does the molecule behave entirely according to the gaussian statistics: depending on the local segment concentration in the coil, there are parts which are more expanded and others which are less expanded than in the unperturbed state. This theoretical approach led us to a new definition of the expansion factor α. This definition seems to be more satisfactory than the previously used ratio, which implied that $\alpha = 1$ and $A_2 = 0$ at the same temperature.

We have been able to explain most of the thus far unexplained results without being obliged to assume deviations from the gaussian behavior of the linear chain elements of the molecule—the hypothesis used by Orofino for his calculations. The average gaussian segment distribution around the center of mass of the molecule has also been retained in our theoretical treatment. The fit between theoretical and experimental results is more satisfactory for star-shaped polymers than for comb-like polymers. It is possible that some of the shortcomings of our theory in the case of comb polymers is due to the fact that assuming a gaussian distribution of segments around the center of mass is not quite justified here, thus obliging us to use more than two parameters for the description of this type of branched polymers. However, as already pointed out by Casassa,[21] considerable caution should be involved in the choice of models meant to give account of experimental results. All we can say is that the assumption we have made in this paper concerning multiple contacts between segments in the region of high segment density leads to very plausible and self-consistent results.

Appendix

Equation 8 may also be written

$$A_2 = \left(\frac{2^4}{3^{3/2}}\right)\pi N_\mathrm{A}\left(\frac{b^2}{6m}\right)^{3/2}\frac{g^{3/2}\alpha^3}{M^{1/2}} \times \int_0^\infty [1 - \exp(-K'e^{-4/3y^2})\exp(-Ke^{-y^2})]y^2\mathrm{d}y \quad \text{(A1)}$$

If K is small enough, we may obtain by limiting the development of $\exp(-Ke^{-y^2})$ to the first two terms

$$A_2 = \left(\frac{2^4}{3^{3/2}}\right)\pi N_\mathrm{A}\left(\frac{b^2}{6m}\right)^{3/2}\frac{g^{3/2}\alpha^3}{M^{1/2}}\left\{\int_0^\infty [1 - \exp(-K'e^{-4/3y^2})]y^2\mathrm{d}y + K\int_0^\infty \exp(-y^2) \times \exp(-K'e^{-4/3y^2})y^2\mathrm{d}y\right\} \quad \text{(A2)}$$

The first term on the right-hand side of this expression stands for the A_2 value when K is equal to zero, *i.e.*, the A_2 value at Flory's Θ temperature, namely $A_{2\Theta}$.

By introducing y' as new variable, $y' = (2/\sqrt{3})y$, it is possible to write $A_{2\Theta}$ in terms of the function $J(X)$ which has been calculated by Flory

$$J(X) = 4\pi^{-1/2}(X^{-1})\int_0^\infty [1 - \exp(-Xe^{-y^2})]y^2\mathrm{d}y$$

then

$$A_{2\Theta} = \frac{N_\mathrm{A}}{2}\pi^{3/2}\left(\frac{b^2}{6m}\right)^{3/2}\frac{g^{3/2}\alpha^3}{M^{1/2}}K'J(K')$$

The integral which appears in the second term of the right-hand side of eq A2 can be expanded in the following way

$$\int_0^\infty [\exp(-y^2)\exp(-K'e^{-4/3y^2})]y^2\mathrm{d}y = \int_0^\infty \exp(-y^2)y^2\mathrm{d}y + \sum_{p=1}^{\infty}\frac{(-1)^p}{p!}K'^p \times \int_0^\infty \exp\left[-y^2\left(1 + \frac{4p}{3}\right)\right]y^2\mathrm{d}y$$

Then, after integration, we get the final expression for A_2

$$A_2 = \pi^{3/2}N_\mathrm{A}\left(\frac{b^2}{6m}\right)^{3/2}\left[\frac{C'_{M,l}}{\alpha^3 g^{3/2}}\frac{J(K')}{M^{1/2}} + \left(\frac{2^4}{3^{3/2}}\right)C_{M,l}\psi\left(1 - \frac{\Theta}{T}\right)G(K')\right]$$

whereby the function $G(K')$ has been computed and is given by the following expression

$$G'(K') = \sum_{p=0}^{\infty}\frac{(-1)^p}{p!}\frac{K'^p}{\left(1 + \frac{4p}{3}\right)^{3/2}}$$

Creep Behavior of Polymer Solutions. III. Creep Compliance of Concentrated Polystyrene Solutions

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ABSTRACT: The creep compliance $J(t)$ of polystyrene solutions in chlorinated diphenyl was measured at various temperatures (−20 to 30°). The ranges of molecular weight M and concentration c were 9.7×10^4–1.8×10^6 and 10–60 g/dl, respectively. The temperature coefficient of the fractional free volume as evaluated from a_T, the shift factor obtained from the time–temperature reduction method, was approximately equal to that for undiluted polystyrene over the whole range of concentration investigated. The time–concentration reduction method was applied to the creep compliance in the transition region, giving the shift factor a_c which is proportional to the segmental friction coefficient. The viscosity divided by the segmental friction coefficient was proportional to the 3.4th power of the product cM. The time–concentration reduction method was not applicable to the relaxation modulus calculated from $J(t)$ in the flow and the plateau regions. This result indicates that the strength of one or a few relaxation mechanisms at the longest time end are proportional to the third or a higher power of c, in contrast to that in the plateau region which was found to be proportional to c^2.

In previous papers of this series, we reported an apparatus for measurements of creep and creep recovery and the experimental results of the viscosity η and steady-state compliance J_e^0 obtained for polystyrene solutions in chlorinated diphenyl.[2] It has been found that J_e^0 is independent of the molecular weight M and inversely proportional to the third power of the concentration c at large values of M and c. This behavior is in contrast to the so-called Rouse–Zimm behavior, $J_\mathrm{e}^0 \propto M/c$, which is found to be valid up to a certain concentration depending on M. The inverse N-shaped transition from the c^{-1} dependence of J_e^0 to the c^{-3} dependence occurs in a limited range of concentration adjacent to the critical concentration.

The study of J_e^0 and η as functions of M and c is essential

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(1) (a) Institute for Chemical Research; (b) Department of Industrial Chemistry.

(2) (a) K. Osaki, Y. Einaga, M. Kurata, and M. Tamura, *Macromolecules*, 4, 82 (1971); (b) Y. Einaga, K. Osaki, M. Kurata, and M. Tamura, *ibid.*, 4, 87 (1971).