Overlap Concentration of Macromolecules in Solution

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ABSTRACT: A unified approach to crossover concentrations of monodisperse random coil, wormlike, and rigid-rod macromolecules in solution from dilute to semidilute and concentrated regimes is presented. The overlap concentration is assumed to be inversely proportional to an effective volume occupied by macromolecules in solution. As wormlike chains bridge the polymer behavior from coils to rigid rods, two parameters, an effective length L^* [$=(\rho L)^{1/2}$] and an effective diameter d^* [$=(L/\rho)^{1/4}d$], are introduced to take into account the influence of flexibility, expressed in terms of the persistence length ρ of the wormlike chain. L and d are the contour length and the diameter (if the wormlike chain is a rigid rod), respectively. In comparison with available experimental data, the overlap concentrations can be predicted with remarkable precision. Inherent consistencies of overlap concentrations deduced from chains with different flexibility, from random coils to rigid rods, are discussed.

Introduction

In processing polymeric materials from solution, it is important to know the concentration dependence of static and dynamic properties of macromolecules in solution. In particular, we want to understand the conditions whereby the solution behavior changes from dilute to semidilute and concentrated regimes. In studying the viscoelastic behavior of macromolecular solutions at moderate concentrations, Graessley[1] suggested a concentration criterion between low- and high-concentration regimes for random coils in a good solvent

$$1 < C[\eta] < 10 \qquad (1)$$

where C is the polymer concentration and $[\eta]$ is the intrinsic viscosity of the polymer in solution. Berry et al.[2] studied the viscosity of moderately concentrated solutions of poly(vinyl acetate) in diethyl phthalate and cetyl alcohol. They proposed $\phi^* = 0.012/[\eta]$ to be the overlap concentration crossing over from dilute to concentrated solution regime with ϕ^* being the polymer volume fraction.

de Gennes et al.[3] presented three concentration domains for polymer random coils in solution, corresponding respectively to separated chains, overlapping chains, and a concentrated solution regime. The overlap concentration C^* is defined

$$C^* \sim N R_g^{-\mathbf{d}} \qquad (2)$$

where N and R_g are the degree of polymerization and the radius of gyration, respectively. In our case, the dimensionality $\mathbf{d} = 3$. The "$\sim$" sign in eq 2 emphasizes the order of magnitude relationship between C^* and N/R_g^3. We are not particularly concerned with the exact nature of the volume occupied by the macromolecular coil. Thus, we can use R_g^3, $4\pi R_g^3/3$, or some other criterion. Cotton and co-workers[4] predicted that the C^* value should be expressed in units of weight per volume instead of number concentration. For random coil in a good solvent, C^* could be bracketed by the condition

$$M/(N_A R_g^3) \simeq C^* \simeq 3M/(4\pi N_A R_g^3) \qquad (3)$$

in which N_A and M are Avogadro's number and the polymer molecular weight, respectively. In discussing dilute, semidilute, and concentrated solution regimes with respect to the random coil chain dimensions, Graessley[5] used

$$C^* = M/[N_A(2R_g)^3] \qquad (4)$$

For a solution of thin rod macromolecules with contour length L and diameter d and $L \gg d$, Doi and Edwards[6] have defined the semidilute concentration region to be

$$1/L^3 \ll C \ll 1/(dL^2) \qquad (5)$$

with C expressed in units of number concentration. In very dilute solutions ($C \ll 1/L^3$) the macromolecules are independent of one another, and at high concentrations ($C \gg 1/L^3$) rods are enmeshed. Then the translational motion perpendicular to the rod axis and the end-over-end rotational motion of each rod are restricted by the presence of other rods in the surroundings. Experimentally, it should also be noted that the concentration $C \ll 1/dL^2$ is far below the critical concentration of the isotropic nematic transition.

Dynamic properties of macromolecules for both random coils and rodlike chains[7-10] tend to change rather abruptly in crossing over from dilute to semidilute regimes. Nevertheless, when experimental results are compared with the overlap concentrations calculated from the theoretical equations mentioned above, obvious discrepancies, as listed in Table III, arise. For random coils in solution, the overlap concentration from $C^* \sim M/(N_A R_g^3)$ is higher than that obtained from experimental data. For wormlike chains, the C^* value obtained from eq 5 is underestimated.[11] It should also be noted that the Doi-Edwards theory is applicable to rigid rods only. In reality, even very stiff polymer chains have some flexibility.[10,12,13] Thus, a breakdown of the Doi-Edwards prediction to wormlike chains is to be expected. Jain and Cohen[14] postulated an effective length L_e equal to $0.15L$, which is much shorter than the real length L, while Odijk[15] introduced a deflection length to consider the motion of one wormlike chain within a network. In this paper, we consider the influence of chain flexibility on the dynamic behavior of macromolecules in order to define overlap concentrations that are in close agreement with experimental data. In order to provide a more unified approach to the concept of overlap concentrations for monodisperse random coils, wormlike chains, and rigid rods, an effective length L^* and an effective diameter d^*, in terms of the physical dimensions of the macromolecules and the persistence length ρ, are introduced.

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Crossover from Dilute to Semidilute Regimes

A. Random Coil. The overlap concentration C^* from dilute to semidilute regimes is defined as the concentration at which the polymer coils touch one another. The crucial criterion is to consider the magnitude of the volume occupied by a random coil at C^*. We identify the volume occupied by a macromolecular coil to be $(h_0/2)^3$, where h_0 is the root-mean-square end-to-end distance of the macromolecular coil at infinite dilution, i.e.

$$C^*_{\text{coil}} \simeq M/[N_A(h_0/2)^3] \tag{6}$$

According to the Flory and Fox equation,[16] the intrinsic viscosity $[\eta]$ depends on the macromolecular chain dimension

$$[\eta] = \phi(h_0)^3/M \tag{7}$$

where ϕ is Flory's viscosity factor in a good solvent. Then eq 6 can be rewritten as

$$C^*_{\text{coil}} \simeq (\phi/N_A)(2^3/[\eta]_{\text{coil}}) \simeq (\phi/N_A)(1/[\eta]^*_{\text{coil}}) \tag{8}$$

for polymer coils in a good solvent, where $[\eta]^*_{\text{coil}} = [\eta]_{\text{coil}}/2^3$. Under Θ-condition, the overlap concentration in a Θ-solvent C^* has the form

$$C_\Theta^* \simeq (\phi_0/N_A)(2^3/[\eta]_\Theta) \tag{9}$$

where ϕ_0 and $[\eta]_\Theta$ are respectively Flory's viscosity factor and intrinsic viscosity under Θ-condition. Equations 8 and 9 show that C^* is inversely proportional to $[\eta]$.

B. Wormlike Chain. The overlap concentration of wormlike chains C^*_{wormlike} from dilute to semidilute solution can be written

$$C^*_{\text{wormlike}} \simeq (\phi/N_A)(2^3/[\eta]_{\text{wormlike}}) \tag{10}$$

where we have followed the same reasonings as those of eq 8 and 9. Yamakawa and Fujii[17] derived an expression for the intrinsic viscosity of unperturbed wormlike chains

$$[\eta] = \phi L_R^{3/2}/(\lambda^3 M) \tag{11}$$

with

$$L_R = \lambda L = \lambda(M/M_L) \tag{12}$$

$$M_L = M/L \tag{13}$$

$$\rho \sim 1/(2\lambda) \tag{14}$$

L_R, λ^{-1}, and ρ are the reduced contour length, the Kuhn statistical length, and the persistence length, respectively. Substituting eq 12–14 into eq 11, we have

$$[\eta] = \phi(2)^{3/2}(\rho L)^{3/2}M^{-1} \tag{15}$$

Thus, putting eq 15 into eq 10 gives C^*_{wormlike} of the form

$$\begin{aligned} C^*_{\text{wormlike}} &\simeq (2^3\phi/N_A)(1/[\eta]_{\text{wormlike}}) \\ &\simeq (2^{3/2}M)/[N_A(\rho L)^{3/2}] \end{aligned} \tag{16}$$

If we let

$$L^* = (\rho L)^{1/2} \tag{17}$$

we obtain

$$C^*_{\text{wormlike}} \simeq 2^{3/2}[M/(N_A L^{*3})] \tag{18}$$

If $\rho \geq L$, $L^* = L$. Then eq 18 can be rewritten for rigid rods as

$$C^*_{\text{rod}} \simeq 2^{3/2}[M/(N_A L^3)] \tag{19}$$

which is similar to the Doi–Edwards condition as expressed in eq 5.

C^* equations for random coils, wormlike chains, and rigid rods are summarized in Table I.

Table I
Equations for C^* of Random Coils, Wormlike Chains, and Rigid Rods

	eq	eq no.
random coils	$2^3M/(N_Ah_0^3)$	6
wormlike chains	$2^{3/2}M/(N_AL^{*3})$ $L^* = (\rho L)^{1/2}$	18
rods	$2^{3/2}M/(N_AL^3)$	19

Crossover from Semidilute to Concentrated Regimes

A. Overlap Concentration C^{**} Crossover from Semidilute to Concentrated Regime. From semidilute to concentrated solution regimes, it should be noted that the entangled polymer coils, if they are dissolved in a good solvent, continue to contract toward the unperturbed size limit. The convergence of the hydrodynamic volume is one measure of the crossover between semidilute and concentrated solution regimes.

Graessley[5] pointed out that the overlap concentration from semidilute to concentrated regimes, C^{**}, is independent of molecular weight and can be estimated from the equation

$$C^{**} = 0.77/[\eta]^{**} \tag{20}$$

where the parameter $[\eta]^{**}$ is defined as the intrinsic viscosity corresponding to the molecular weight limit M^{**} at which $[\eta] = [\eta]_\Theta$.

Following the same formalism as C^* between dilute and semidilute regimes, we can write C^{**} as

$$\begin{aligned} C^{**}_{\text{coil}} &\simeq (\phi_0/N_A)(2^3/[\eta]_c) \\ &\simeq (\phi_0/N_A)(1/[\eta]^{**}) \end{aligned} \tag{21}$$

where

$$[\eta]^{**} = [\eta]_c/2^3 \propto (h^{**}/2)^3 \tag{22}$$

with h^{**} being the end-to-end distance of the macromolecular chain with molecular weight M^{**} at C^{**}.

Comparing eq 21 with eq 20 as derived by Graessley,[5] we see that ϕ_0/N_A is a constant and $[\eta]^{**}$ represents the intrinsic viscosity value where $[\eta]$ and $[\eta]_\Theta$ first begin to diverge. From eq 22, we note that $[\eta]^{**}$ should be related to an equivalent volume whose size is proportional to $(h^{**}/2)^3$. Equation 21 may be used to represent both random and wormlike chains as indicated below.

$$C^{**} \simeq (\phi_0/N_A)(1/[\eta]^{**}) \tag{23}$$

B. Equivalent Volume Occupied by a Macromolecule at the Crossover Concentration between Semidilute and Concentrated Solution Regimes. 1. Random Coil. The dimensions of a random coil macromolecule in solution depend on both the solvent quality and the macromolecular concentration. In a good solvent, the coil size decreases with increasing concentration, eventually reaching a contraction limit corresponding to the unperturbed chain dimension.[4] In a Θ-solvent, the coil size maintains the unperturbed value at all concentrations.[3] At $C \approx C^{**}$, macromolecular chains are entangled and the screening length of entangled polymer chains may be approximated by the chain length between entanglement points. Let M^{**} and h_Θ^{**} be respectively the polymer molecular weight between two entanglement points and the unperturbed root-mean-square end-to-end distance of such a polymer segment having a molecular weight of M^{**}. Then $[\eta]^{**}$ denotes the intrinsic viscosity of an equivalent hard sphere with molecular weight M^{**} and size $h_\Theta^{**}/2$.

According to the equation for intrinsic viscosity of isolated hard spheres,[18] $[\eta]^{**}$ is given by

$$[\eta]^{**} = (2.5N_A/M^{**})V_e \tag{24}$$

where V_e is the equivalent volume of a hard sphere with radius $h_\Theta^{**}/2$, i.e.

$$V_e \sim (4\pi/3)(h_\Theta^{**}/2)^3 \tag{25}$$

Then

$$[\eta]^{**} \sim (2.5N_A/M^{**})[(4\pi/3)(h_\Theta^{**}/2)^3] \tag{26}$$

By the definition given by Graessley,[5] i.e., $[\eta]^{**}$ is the value where $[\eta]$ and $[\eta]_\Theta$ first begin to diverge, M^{**} can be estimated from the molecular weight dependence of $[\eta]$ and $[\eta]_\Theta$. In a good solvent, the molecular weight dependence of $[\eta]$ is given by

$$[\eta] = K_\eta M^\alpha \tag{27}$$

with $\alpha = {}^3/_4$. In a Θ-solvent, $\alpha = 0.5$ and eq 27 becomes

$$[\eta]_\Theta = K_{\eta\Theta}M^{1/2} \tag{28}$$

The root-mean-square end-to-end distance has the form

$$h_\Theta = K_\Theta^{1/2}M^{1/2} \tag{29}$$

Then at $C = C^{**}$

$$K_\eta M^{**(3/4)} = K_{\eta\Theta}M^{**(1/2)} \tag{30}$$

yielding

$$M^{**(1/2)} = (K_{\eta\Theta}/K_\eta)^2 \tag{31}$$

By combining eq 23, 26, and 29 and by taking $\phi_0 = 2.87 \times 10^{23}$ for flexible polymer chains in a Θ-solvent and $\phi_0/N_A = 0.477$, we obtain the relation

$$C^{**}_{\text{coil}} \simeq 0.477/[\eta]^{**} \tag{32}$$

$$C^{**}_{\text{coil}} \simeq B'[K_\eta^2/(N_A K_\Theta^{3/2}K_{\eta\Theta}^2)] \tag{33}$$

where B' is a constant. In this limit, the polymer coils are assumed to behave hydrodynamically as rigid spheres. The constant term in eq 32 is smaller than the value proposed by Graessley (eq 20); however, from eq 33 (similar to eq 7 in the Graessley[5] paper), C^{**}_{coil} can be expected to be independent of molecular weight, in agreement with the conclusion pointed out by Graessley[5] and noted experimentally by Nemoto and co-workers.[19]

2. Wormlike Chain. Properties of wormlike chains bridge between those of random coils and rigid rods. The influence of flexibility on the effective volume of wormlike chains is our basic concern. We introduce the concept of an effective length (L^*) and an effective diameter d^* which are controlled by the persistence length: the more flexible the chain, the shorter the effective length and the larger the effective diameter.

To proceed with our discussion of the equivalent volume occupied by a wormlike chain, we first recall eq 17, which related L^* as a function of $L\rho$. Now we shall discuss d^*. If we take the molar volume of a rod macromolecule with length L and diameter d to be $\pi(d/2)^2L$ and assume a constant molecular volume when the rod molecule becomes flexible, then the wormlike chain with contour length L and diameter d has an effective length L^* and diameter d^* such that

$$\pi(d/2)^2L = \pi(d^*/2)^2L^* \tag{34}$$

Substiting eq 17 into eq 34, we get

$$d^* = (L/\rho)^{1/4}d \tag{35}$$

If we insist on the same form for C^{**}_{wormlike} as for C^{**}_{coil} of eq 23, we then have

$$C^{**}_{\text{wormlike}} \simeq (\phi_0/N_A)(1/[\eta]^{**}) \tag{36}$$

where similar to eq 24

$$[\eta]^{**} = (2.5N_A/M)V_e \tag{37}$$

with V_e being the equivalent volume occupied by a rod macromolecule with molecular weight M. From the Doi–Edwards idea for rigid rods, the volume occupied by one wormlike chain at $C \simeq C^{**}_{\text{wormlike}}$ is

$$V_e \sim \pi(L^*/2)^2d^* \tag{38}$$

Substituting eq 17, 35, 37, and 38 into eq 36 and combining constant terms, we have

$$C^{**}_{\text{wormlike}} \simeq 0.243\{M/[N_A(L^*)^2d^*]\} \tag{39}$$

or

$$C^{**}_{\text{wormlike}} \simeq 0.243[M/(N_A\rho^{3/4}L^{5/4}d)] \tag{40}$$

With $\rho \geq L$ as the limit for a rod macromolecule, $L^* \simeq L$ and $d^* \simeq d$, and eq 39 is reduced to

$$C^{**}_{\text{rod}} \simeq 0.243[M/(N_AL^2d)] \tag{41}$$

which is the C^{**} expression for rigid rods. Equations of C^{**} for random coils, wormlike chains, and rigid rods are listed in Table II.

Correlation of Wormlike Chain with Random Coil and Rod

The basic concept in defining the overlap concentrations is geometrical in nature. There are no fundamental differences in expressing the volume occupied by a macromolecule, irrespective of chain shapes. Thus, overlap concentrations of random coils, wormlike chains, and rigid rods are closely related. It is reasonable to expect that the chain flexibility plays an important role in defining the effective volume and in controlling properties from coils to rigid rods, with coils and rods being the two limiting cases of wormlike chains. Therefore, there is inherent consistency in those equations describing the overlap concentrations.

A. Overlap Concentration between Dilute and Semidilute Regimes. The root-mean-square end-to-end distance of a Gaussian chain is given by[20]

$$h_0 = N^{1/2}b \tag{42}$$

and

$$\rho \approx b/2 \tag{43}$$

where b [$\equiv\lambda^{-1}$] is the Kuhn statistical length. Combining eq 42 and 43 with eq 17, we get

$$L^{*3} = (1/2)^{3/2}h_0^3 \tag{44}$$

Then eq 18 can be rewritten as

$$\lim_{\rho\to(b/2)} C^*_{\text{wormlike}} \simeq (2^3M)/(N_Ah_0^3) \tag{45}$$

which is identical with eq 6, the C^* expression for random coils. On the other hand, for $\rho \geq L$, eq 19 describes the overlap concentration of wormlike chains in the rigid-rod limit.

B. Crossover Concentration between Semidilute and Concentrated Solution Regimes. As the flexibility of wormlike chains is increasing, it is appropriate to assume that L^* decreases and d^* increases. In other words, as ρ decreases, $d^* \to L^*$ and $d^*L^{*2} \propto L^{*3}$. Then

$$d^*L^{*2} = BL^{*3} \tag{46}$$

where B is a proportionality constant. It has been noted

Table II
Equations for C^{**} of Random Coils, Wormlike Chains, and Rigid Rods

	eq	eq no.	comments
random coils	$0.477/[\eta]^{**}$	32	independent of molecular weight
wormlike chains	$0.243M/(N_A d^* L^{*2})$ $L^* = (\rho L)^{1/2}$ $d^* = (L/\rho)^{1/4} d$	39	relatively independent of molecular weight
rods	$0.243M/(N_A d L^2)$	41	dependent on molecular weight

that at C^{**} the molecular size has essentially an unperturbed dimension. The relationship between the rod length L and the radius of gyration R_g of a thin rod is given by

$$L^2 = 12R_g^2 \tag{47}$$

and the end-to-end distance of a random coil is

$$h^2 = 6R_g^2 \tag{48}$$

Thus, as the chain becomes more flexible, we may write

$$L^* = 2^{1/2}h_\Theta \tag{49}$$

At $C = C^*$

$$h_\Theta = K_\Theta^{1/2}M^{1/2} \tag{29}$$

By substituting eq 46, 49, and 29 into eq 39, we then have

$$\lim_{L^* \to h_\Theta} C^{**}_{\text{wormlike}} \simeq [0.243/(2^{3/2}B)][1/(N_A K_\Theta^{3/2} M^{1/2})] \tag{50}$$

where $M \approx M^{**}$. Combining eq 31 with eq 50, we finally obtain

$$\lim_{L^* \to h_\Theta} C^{**}_{\text{wormlike}} \simeq B'[K_\eta^2/(N_A K_\Theta^{3/2} K_{\eta\Theta}^2)] \tag{51}$$

where B' is a constant. Equation 51 retrieves eq 33 and

Table III
C^{**} Comparison of Calculated Overlap Concentrations with Experimental Data

C^{**} (Wormlike Macromolecules)

sample	10^{-4} M_w	10^{-3} L_w, Å	10^{-2} ρ, Å	d, Å	L_w/ρ	C^{**}, $\times 10^{-3}$ g/mL exptl	C^{**}, $\times 10^{-3}$ g/mL calcd[a]	C^{**}, $\times 10^{-3}$ g/mL DE[b]
			PPTA–H_2SO_4[12]					
5	4.83	2.56	2.90	6	8.8	2.50	2.54	2.04
4	3.84	2.03	2.90	6	7.0	2.1	2.69	2.58
2	1.59	0.84	2.90	6	2.9	1.8	3.38	6.24
1	1.45	0.77	2.90	6	2.7	2.4	3.41	6.77
			PPTA–H_2SO_4–K_2SO_4 (0.005 M)[12]					
4	3.03	1.60	2.00	6	8.0	~4	3.79	3.28
			PPTA–H_2SO_4–K_2SO_4 (0.05 M)[14]					
4	2.98	1.58	2.00	6	7.9	~4.5	3.77	3.30
			Xanthan (H_2O + 0.02% NaN_3)[13,21]					
	220	15.0	~3.50	20	4.3	0.6–1.0	0.59	0.81
			~2.00				0.90	
			~1.00				1.50	
			PBLG–1,2-Dichloroethane[10]					
	15	1.03	14.0	15	0.73	~5	3.1	15.7
	17	1.16			0.83		3.0	13.9
	21	1.44			1.03		2.8	11.2
	15	1.03	9.00	15	1.03		4.2	
	17	1.16			1.29		4.1	
	21	1.44			1.60		3.9	

C^* (Wormlike Macromolecules)

10^{-4} M_w	10^{-3} ρ, Å	10^{-4} L_w, Å	C^*, $\times 10^{-3}$ g/mL exptl	C^*, $\times 10^{-3}$ g/mL calcd[c]	C^*, $\times 10^{-3}$ g/mL DE[d]
		Xanthan (H_2O + 0.02% NaN_3)[13,21]			
220	~3.50[22]	1.50	0.13–0.25	0.027	0.001
	~1.00			0.18	

C^* (Random Coil Macromolecules)

10^{-5} M_w	10^{-2} R_g, Å	10^{-2} h_0, Å	C^*, $\times 10^{-2}$ g/g exptl	C^*, $\times 10^{-2}$ g/g calcd[c]	C^*, $\times 10^{-2}$ g/g DE
		PS-Benzene[7]			
0.78	1.18	2.90	4	4.86	9.0
2.71	2.48	6.07	1.5	1.83	3.35
5.99	3.97	9.72	0.75	0.98	1.59
7.54	4.55	11.15	~0.7	0.82	1.33
		PS-Benzene[23]			
2.45			1.6[e]	1.75[e]	3.2[e]
		PS–*trans*-Decalin[24]			
1.79	130	318	~0.1	0.083	0.153

[a] C^{**}_{calcd} calculated from eq 39 for wormlike macromolecules. [b] C^{**}_{DE} calculated from the Doi–Edwards inequality (eq 5). [c] C^{*}_{calcd} calculated from eq 6 for random coils and from eq 18 for wormlike chains. [d] C^{*}_{DE} calculated from $C^* \simeq M/(N_A R_g^3)$. [e] In units of $\times 10^{-2}$ g/mL.

confirms the fact that C^{**}_{coil} is independent of molecular weight. In order to compare with available experimental data, the overlap concentrations between dilute and semidilute regimes and the crossover concentrations between semidilute and concentrated regimes were computed according to eq 6, 9, 18, and 40. The results are listed in Table III.

In comparing our approach with experiments, it should be emphasized that experimental values for the overlap concentrations are very difficult to obtain, especially for C^{**}. We have some confidence in our own experimental estimates for poly(1,4-phenyleneterephthalamide) (PPTA) in concentrated sulfuric acid and polystyrene (PS) in *trans*-decalin. Using forced Rayleigh light-scattering methods, Leger and co-workers[7] reported C^* values for the PS-benzene system (except the value of C^* of the highest molecular weight sample $M_w = 7.54 \times 10^5$, which was estimated from Figure 5 in ref 7), which are in very good agreement with the calculated C^* values. The xanthan results are rough approximations and are included to provide additional experimental evidence. As the values of persistence length of xanthan from the literature[13,21] were either estimated or calculated from the Kuhn statistical length, three different C^{**}_{calcd} values, as listed in Table III, could be presented. Nevertheless, the C^{**}_{calcd} values are within, or close to, the range of experimental estimates reported. The same predictions for the poly(γ-benzyl L-glutamate) (PBLG)-1,2-dichloroethane system are shown in Table III, where we have used two different ρ values (140 and 90 mn) to compute the C^{**}_{calcd} values, while $C^{**}_{\text{exptl}} \sim 5 \times 10^3$ g/mL for $M_w \sim 1.5 \times 10^5$. The overall agreement between experiment and theory is indeed remarkable. Further confirmation awaits additional experimental data.

Conclusions

Overlap and crossover concentrations (C^* and C^{**}) are geometric problems controlled merely by effective volumes, irrespective of particle shape. If we take the persistence length as a fundamental parameter and assume that the molecular volume remains a constant, independent of chain flexibility, we can then correlate the overlap crossover concentrations from random coils to rigid rods with the effective length $L^* \simeq (\rho L)^{1/2}$ and the effective diameter $d^* \simeq (L/\rho)^{1/4} d$ for wormlike chains.

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References and Notes

(1) Graessley, W. W. *Adv. Polym. Sci.* **1974**, *16*, 1.
(2) Berry, G. C.; Nakayasu, H.; Fox, T. G. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1825.
(3) Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C.; de Gennes, P.-G. *Macromolecules* **1975**, *8*, 804.
(4) Cotton, J. P.; Nierlich, M.; Boue, F.; Daoud, M.; Farnoux, B.; Jannink, G.; Duplessix, R.; Picot, C. *J. Chem. Phys.* **1976**, *65*, 1101.
(5) Graessley, W. W. *Polymer* **1980**, *21*, 258.
(6) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 560, 918.
(7) Leger, L.; Hervet, H.; Rondelez, R. *Macromolecules* **1981**, *14*, 1732.
(8) Maguire, J. F.; McTague, J. P. *Phys. Rev. Lett.* **1980**, *45*, 1891.
(9) Ying, Q.; Chu, B.; Qian, R.; Bao, J.; Zhang, J.; Xu, C. *Polymer* **1985**, *26*, 1401.
(10) Zero, K. M.; Pecora, R. *Macromolecules* **1982**, *15*, 87.
(11) Kubota, K.; Chu, B. *Biopolymer* **1983**, *22*, 1461.
(12) Ying, Q.; Chu, B. *Macromolecules* **1986**, *19*, 1580.
(13) Southwick, J. G.; Jamieson, A. M.; Blackwell, J. *Macromolecules* **1981**, *14*, 1728.
(14) Jain, S.; Cohen, C. *Macromolecules* **1981**, *14*, 759.
(15) Odijk, J. *Macromolecules* **1983**, *16*, 1340.
(16) Flory, P. J.; Fox, T. G., Jr. *J. Am. Chem. Soc.* **1951**, *73*, 1904.
(17) Yamakawa, H.; Fujii, M. *Macromolecules* **1974**, *7*, 128.
(18) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University: Ithaca, NY, 1953; Chapter XIV, p 606.
(19) Nemoto, N.; Landry, M. R.; Noh, I.; Kitano, T.; Wesson, J. A.; Yu, H. *Macromolecules* **1985**, *18*, 308.
(20) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University: Ithaca, NY, 1953; Chapter X, p 413.
(21) Jamieson, A. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1982**, *23*(1), 69.
(22) Aharoni, S. M. *Macromolecules* **1983**, *16*, 1722.
(23) Hervet, G.; Leger, L.; Rondelez, R. *Phys. Rev. Lett.* **1979**, *42*, 1681.
(24) Chu, B.; Nose, T. *Macromolecules* **1979**, *12*, 599.

Self-Consistent Field Theory for the Adsorption of Ring Polymers from Solution

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ABSTRACT: The self-consistent field polymer adsorption theory of Scheutjens and Fleer has been extended for the case of ring macromolecules. This is achieved by enumerating the chain conformations in three dimensions while maintaining a mean field approximation to calculate the different interaction enthalpies. A comparison of the adsorption of rings and linear chains shows that under certain physical conditions the adsorbed amount of rings is higher, whereas in other cases the reverse is true. The volume fraction of segments in trains and loops is calculated as are the RMS thickness and bound fractions for different values of the adsorption energy and for a variety of different solvency conditions.

Introduction

One of the most interesting phenomena in the adsorption of polymers at the solid-solution interface is the prediction that segments of adsorbed molecules can exist in extended "tails".[1] The Scheutjens-Fleer theory,[2,3] in particular, predicts that at high adsorbed amounts very long tails are formed. This prediction has been corroborated experimentally by hydrodynamic thickness measurements.[4,5]

One way of investigating the influence of tails on adsorption properties is to study a system that only has segments in loops and trains. An ideal system from this

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