

Macromolecular Conformations in Solutions. II. Thermodynamics of Interactions

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The model of polymeric chains in solution developed in the preceding paper (this issue) is examined. Results of some numerical calculations are reported. Predictions of chain behavior are derived from the model in terms of the exchange interaction energy parameter X_{12} , polymer concentration, number of segments in a bundle, molecular mass, and temperature.

KEY WORDS: Chain flexibility; macromolecular conformations; thermodynamics of polymer solutions; polymer structure.

1. INTRODUCTION

In the preceding paper⁽¹⁾ the structure of a macromolecule in solution has been characterized in terms of a number of parameters. Further, we have characterized the solution in terms of the coordination number z . Moreover, parameters representing pair interaction energies have been introduced. In each macromolecular chain concomitant existence of two kinds of sequences differing in rigidity, called compact and extended bundles, was assumed. Statistical mechanics was used to derive relations involving structural as well as interactional parameters. To see what the model so constructed tells us, numerical calculations were necessary to study effects of various parameters upon chain conformations. The present paper reports some results of such calculations.

2. BASIC RELATIONS

A monodisperse system of polymeric chains without branches was treated in Part I.⁽¹⁾ Both polydispersity and branching can be included.

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The combinatorial factors for molecular size distribution in random polyfunctional condensation have been derived by Falk and Marcotte,⁽²⁾ and their relations represent generalizations of earlier equations of Stockmayer⁽³⁾ and Flory,⁽⁴⁾ Further, distribution functions of molecular masses for results of an arbitrary polymerization process have been studied by Sicotte.^(5,6) Under certain conditions specified by Sicotte⁽⁶⁾ the Gram-Charlier series expansion with the Laguerre polynomials provides a very good fit. However, taking into account branching and polydispersity would necessitate introduction of further structural parameters. Therefore, we continue with a monodispersive system of nonbranched polymers in the interest of perspicuity.

With the solvent represented by index 1 and the polymer by 2, we have three parameters characterizing pair interaction energies: η_{12} , η_{11} , and η_{22} . This is still relatively complex, so we now introduce one parameter characterizing the energetic situation in solution. Following Flory^(7,8) we define

$$X_{12} = \frac{z(\eta_{11} + \eta_{22} - 2\eta_{12})}{2v^{*2}} \quad (1)$$

where v^* is the segmental hard-core volume and z the liquid coordination number.³ The original definition^(7,8) of X_{12} was in terms of the surface parameter s_1 , but in the present Eq. (1) we have used Eq. (21) from Part I.⁽¹⁾ It is worth reminding that the range of possible values of z in the liquid state is⁽⁹⁾

$$4 \leq z \leq 11 \quad (2)$$

Given Eq. (1), we now rewrite Eqs. (12) and (13) in Part I as

$$\ln \frac{b_c(b - b_c - N_{ce}/2)}{(b - b_c)(b_c - N_{ce}/2)} + \frac{\beta r_b(z - \xi)v^{*2}}{zv} \\ \times \left[v_m - 2 \left(\frac{N_{ce}/2}{b_c + N_{ce}/2} \right)^2 (v_m - v_t) \right] X_{12} = 0 \quad (3)$$

$$\ln \frac{(b_c - N_{ce}/2)(b - b_c - N_{ce}/2)}{(N_{ce}/2)^2} \\ - \frac{2\beta r_b(z - \xi)v^{*2}}{zv} \left(\frac{b_c}{b_c + N_{ce}/2} \right)^2 (v_m - v_t) X_{12} = 0 \quad (4)$$

³ In some earlier work (W. Brostow, unpublished) X_{12} proportional to $(2\eta_{12} - \eta_{11} - \eta_{22})$ was used. The original definition has now been reinstated.

Parameters featured in Eqs. (3) and (4) have been defined in Part I⁽¹⁾ and we do not repeat the definitions here. We only reiterate that the pair of unknowns to be evaluated are the number of compact bundles b_c and the number N_{ce} of pairs of nearest neighbor bundles such that one of them is compact and the other extended.

The number of factors affecting the structure of polymeric chains in solution is reflected by the number of parameters which appear in Eqs. (3) and (4). We cannot possibly study the role of each of these parameters separately. Rather, we want to acquire the basic understanding of the model represented by these equations. To do this, we introduce a terminology for comparing two solvents for the same polymer: we shall call more *favorable* the solvent which has a lower value of

$$F = \frac{\beta r_b (z - \zeta) v^{*2} (v_m - v_t) X_{12}}{zv} \quad (5)$$

Note that the function F corresponds to the second term in Eq. (4) divided by the factor which depends on b_c and N_{ce} . Since z , v , v^* , r_b , and $(v_m - v_t)$ are always positive, F can be negative only when X_{12} is negative. F can be equal to zero (a) when all polymer segments are tetrafunctional, that is $\zeta = 4$, and simultaneously we are at the liquid-vapor critical point of the solvent—see the lower limit in inequality (2); (b) when $X_{12} = 0$. Otherwise, F is a positive function.

To explain the usefulness of the function F , let us return to the definition of X_{12} . Equation (1) tells us that an increase in strength of the solvent-polymer interaction η_{12} (when the respective potential well is deeper) produces a decrease in X_{12} . This is so because η_{12} is a positive quantity by definition (unless external pressure is so high that repulsion dominates). Qualitatively, we would therefore expect that a decrease of X_{12} (by going from one solvent to another, or by manipulating concentration in a mixed solvent) should produce a better solvent. Consequently, more bundles should become extended ones. Such a reasoning, however, would represent a gross oversimplification. The Flory theory of the liquid state^(7,8) and consequences of its various applications^(8,10,11) have taught us that the energetic parameters do not dominate alone the situation in polymer solutions. Not to mention combinatorial entropy contributions, the equation-of-state contribution of Flory, represented by molar volume V , isobaric expansivity α , and isothermal compressibility κ_T , is quite important. To give just one example, Orwoll and Flory⁽¹²⁾ have calculated the enthalpies of mixing H^E of binary n -alkanes from the Flory theory. For hexane and hexadecane at 293.15 K they have found that the energetic contribution (proportional to X_{12}) is the largest, and H^E is positive. As temperature increases, a negative equation-of-state contribution becomes dominant, and

this explains the otherwise puzzling experimental fact of the change of sign of H^E .⁽¹³⁾ Thus, if two solvents for a given polymer have widely different V , α , and κ_T , a lower value of X_{12} does not necessarily guarantee a better solvent. When, however, volumetric characteristics of two (or more) solvents are comparable, then the most favorable solvent according to our definition is also the best one.

3. SPECIAL CASES

Before attempting numerical solutions, let us consider some specific configurations. Assuming $X_{12} = 0$, from Eqs. (3) and (4) [or (14) and (15) in Part I⁽¹⁾] and from the definitions of the quantities involved we obtain

$$b_c = b_e = b/2 = N_{ce} = 2N_{cc} = 2N_{ee} \quad (6)$$

Denoting as before the two kinds of bundles by, respectively, letters c and e we can write down some possible configurations which fulfill the condition (6). For instance, for $b = 25$ we can have

$$eccccccccccccccccccce \quad (7)$$

We see that (7) obeys (6) within ± 1 ; the tolerance ± 1 results from the fact that the sequence (6) is relatively short; note that b is odd and see the second and third member in Eq. (4) in Part I.⁽¹⁾ More important, we observe that writing configurations fulfilling (6) we ought to take into account the dynamics of chains in solution. Thus, instead of (7) consider

$$eeeecccccccccccccccee \quad (8)$$

The sequence (8) has exactly the same set of parameters b , b_c , b_e , N_{ce} , N_{cc} , and N_{ee} . From the point of view of the equilibrium statistical mechanics, they are both equally acceptable given our model and the condition $X_{12} = 0$. Elementary considerations of chain dynamics suggest, however, that (8) should prevail: chain ends have here more mobility with respect to solvent molecules and with respect to the middle part of the chain.

Returning now to the stage of constructing the model in Ref. 1, we find that both b_c and N_{ce} have to be employed in the specification of chain conformations. Imagine the model in Part I developed in terms of b_c alone. Take the same values of the b -type parameters as before, that is $b = 25$, $b_c = 12$, and $b_e = 13$. Now, among others, the following two configurations would become acceptable too:

$$eeeeeeeeeeeeccccccccccc \quad (9)$$

$$eeeeeececececcccccccccc \quad (10)$$

While (10) is better than (9), both sequences violate the condition (6). At the same time, since each bundle contains a number r_b of polymer segments, the usual Gaussian statistics (in terms of the radius of gyration, for instance) should be obeyed. From this point of view, we arrive at the same conclusion: the sequences (9) and (10) both have to be rejected, although (10) is better than (9). Thus, various approaches coincide. Among the sequences displayed above, it is the sequence of the type (8) that will be found in a real solution in which X_{12} is small.

4. CALCULATIONS

Equations (3) and (4) have been solved varying a number of parameters. While we have two equations in two unknowns, the relations are anything but linear with respect to b_c and N_{ce} . Solutions were obtained by using an IBM 370 Model 168 machine belonging to the UNI-COLL Corp. When other parameters were kept constant and only X_{12} changed (for instance from 5 to 10 J cm⁻³), the preceding solution was inserted to initialize the unknowns in the next evaluation. Typically, a solution was accepted when the right-hand sides of (3) and (4) became $O(E - 9)$ or $O(E - 10)$.

5. RESULTS AND DISCUSSION

An increase in, say, $\nu_m - \nu_t$ in Eq. (5) can be compensated by a simultaneous decrease of, for instance, v^* . This is the reason why we have made calculations in series. In each series X_{12} was varied, while other parameters kept constant.

In one such series we have taken the degree of polymerization $r = 6000$; number of segments in a bundle $r_b = 10$; $T = 300.0$ K; the coordination number $z = 6$; $\zeta = 2$ (i.e., an unbranched chain or a chain without cycles, see Ref. 1); $\nu_m = 0.020$ and $\nu_t = 0.010$, that is a solution fairly dilute in which the approximation $\nu_e = 0$ is applicable. Values of $v^*/(\text{cm}^3 \text{g}^{-1})$ at 298.15 K are: 0.8860 for benzene;⁽¹⁴⁾ 0.9342 for natural rubber;⁽¹⁴⁾ 0.8098 for polystyrene;⁽¹⁵⁾ and 1.000 for polymethylene.⁽¹⁶⁾ Therefore, we have taken as a representative value $v^* = 0.90 \text{ cm}^3 \text{g}^{-1}$. The corresponding values of $v/(\text{cm}^3 \text{g}^{-1})^{(14-16)}$ are 1.1444, 1.0952, 0.9336, and 1.182. We have chosen $v = 1.08 \text{ cm}^3 \text{g}^{-1}$. The relative molecular mass of the monomer $M_u = 100.00$ (neither M_u nor r appears explicitly in Eqs. (3) and (4); but note the units of the volumetric parameters and Eq. (2) in Part I⁽¹⁾).

The results of calculations for a series of X_{12} values are listed in Table I; $1 \text{ J cm}^{-3} = 1 \text{ MPa}$ exactly.

Table I. Chain Characteristics in Function of the Interaction Energy Parameter X_{12} for $r = 6000$, $r_b = 10$, $\nu_m = 0.020$, and $\nu_t = 0.010$. Other Parameters Listed in the Text

$\frac{X_{12}}{\text{J cm}^{-3}}$	$\frac{N_{ce}}{2}$	$\frac{b_c}{b}$
0	150.0	0.5000
0.1	150.0	0.5001
0.2	150.0	0.5002
0.5	150.0	0.5004
1.0	149.9	0.5009
2.0	149.9	0.5018
5.0	149.7	0.5045
10.0	149.3	0.5090
15.0	148.9	0.5136
20.0	148.4	0.5183
25.0	148.0	0.5230
30.0	147.5	0.5278
50.0	145.1	0.5475
100.0	136.5	0.6014
200.0	106.1	0.7280
300.0	63.3	0.8561
400.0	0	1

We postpone any discussion of Table I until more results are displayed. An important parameter which affects the conformation of an average chain is the polymer concentration c . When more chains in a unit volume are present, ν -type parameters increase. Accordingly, we report in Table II results of another series of computations, with $\nu_m = 0.240$ and $\nu_t = 0.110$, while all other parameters were the same as in the series presented above.

Looking at Tables I and II we note, first of all, that in both series an increase in X_{12} leads ultimately to the disappearance of ce pairs of nearest neighbors and to conversion of all bundles into compact ones. From Eq. (1) we see that an increase in X_{12} corresponds to greater relative strength of interactions in pure components as compared to the mixed interactions. Clearly, when the affinity of polymer segments, as represented by η_{22} , increases, so does the tendency for compact conformations. Therefore, the fraction b_c/b does symbatically with X_{12} .

By comparing Tables I and II the effect of polymer concentration c can be assessed. We find that, for a given value of X_{12} , increase of c produces a decrease of N_{ce} and a higher value of b_c/b . The result is expected, but it is also important. By producing a higher degree of compactness, a higher polymer concentration results in a smaller volume

Table II. Chain Characteristics in Function of X_{12} for $r = 6000$, $r_b = 10$, $\nu_m = 0.240$, and $\nu_l = 0.110$. Other Parameters Listed in the Text.

$\frac{X_{12}}{\text{J cm}^{-3}}$	$\frac{N_{ce}}{2}$	$\frac{b_c}{b}$
0.0	150.0	0.5000
0.1	149.9	0.5011
0.2	149.8	0.5021
0.5	149.4	0.5022
1.0	148.8	0.5108
2.0	147.5	0.5220
5.0	142.2	0.5586
10.0	128.0	0.6304
15.0	105.7	0.7168
20.0	76.5	0.8101
25.0	47.8	0.8900
30.0	27.0	0.9419
33.0	0	1

pervaded by each chain, that is, in a smaller radius of gyration R_g . Thus, for higher c complete compactness is reached at a lower value of the interchange energy parameter X_{12} .

We can express the volume v_2 occupied by one polymeric chain in terms of the volume of a compact bundle v_c and the volume of an extended bundle v_e :

$$v_2 = b_c v_c + b_e v_e \quad (11)$$

By introducing the symbol

$$v_e/v_c = \gamma \quad (12)$$

we can rewrite (11) as

$$v_2 = b v_c [\gamma - (\gamma - 1) b_c/b] \quad (13)$$

with $\gamma > 1$ by definition, we see how v_2 decreases linearly with an increase of b_c/b .

To see the concentration effect somewhat more in detail, we show in Fig. 1 curves of b_c/b vs. ν_m for three values of X_{12} . In each case $\nu_l = \nu_m/2$, while other parameters are the same as before. We see that for very small values of X_{12} the relation deviates only slightly from a straight line. More important, in favorable solvents (for the two lower X_{12} values) the changes of b_c/b with concentration are quite slow. For $X_{12} = 20.0 \text{ J cm}^{-3}$, however, a definite concave curvature is obtained.

In a series of papers Rudin and collaborators⁽¹⁷⁻¹⁹⁾ have treated the problem of hydrodynamic volume, effectively occupied by polymer mole-

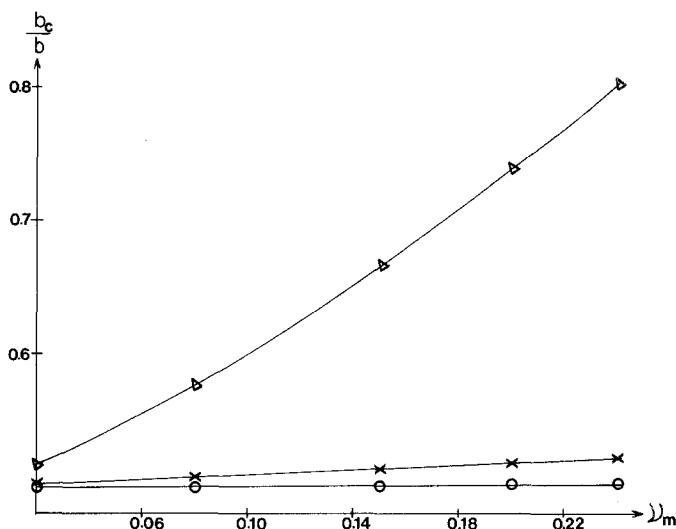


Fig. 1. Effect of concentration—in terms of the ν_m parameter—on the fraction of compact bundles b_c/b for $X_{12} = 0.2$ (circles), $X_{12} = 2.0$ (crosses), and $X_{12} = 20.0 \text{ J cm}^{-3}$ (triangles). Other parameters are listed in the text.

cules. Rudin's treatment is in terms of dimensionless swelling factor $\epsilon = \alpha^3$, where α is the Flory expansion factor. By assuming

$$\alpha^3 = \frac{\epsilon_0}{1 + (\epsilon_0 - 1/c_\theta)c} \quad (14)$$

where ϵ_0 is a constant and c_θ the polymer concentration at the theta point, Rudin and Wagner⁽¹⁹⁾ made good predictions of effects of solvent and concentration on elution volumes in gel permeation chromatography. We expect to deal with the problem of hydrodynamic volumes in a separate paper. But let us at least signal now that our model provides a reason for the success of the simple equation (14): the term $\gamma - (\gamma - 1)b_c/b$ in Eq. (13) can be with good approximation represented by the right-hand side of (14). We have found this to be the case for the top curve ($X_{12} = 20.0 \text{ J cm}^{-3}$) in Fig. 1.

Each model of polymeric structures has a built-in dependence on the molecular mass M . In this respect, predictions from the present model are quite simple. An increase in M produces a proportional increase of b , b_c , b_e , and of N_{yy} , parameters. Thus, b_c/b remains the same. These conclusions will be used to advantage elsewhere⁽²⁰⁾ in the explanation of mechanical degradation in flow.

Return now to the definition (1). There is nothing in the definition itself to exclude the possibility of negative values of X_{12} . Accordingly, we

have also made calculations which included $X_{12} < 0$. We have covered the entire span of values of b_c/b from zero to unity. The results are reported in Table III for $\nu_m = 0.200$ and $\nu_t = 0.100$, with other parameters the same as before.

We find in Table III that the function N_{ce} vs. X_{12} exhibits a maximum around $X_{12} = -10 \text{ J cm}^{-3}$. Posing the zero value of X_{12} we have found [Eq. (6)] that $b_c = b_e$. When X_{12} becomes negative and its absolute value

Table III. Chain Characteristics in Function of Negative and Positive Values of the Interaction Energy Parameter X_{12} for $r = 6000$, $r_b = 10$, $\nu_m = 0.200$, and $\nu_t = 0.100$. Other Parameters Listed in the Text.

$\frac{X_{12}}{\text{J cm}^{-3}}$	$\frac{N_{ce}}{2}$	$\frac{b_c}{b}$
-164.0	0	0
-160.0	30.4	0.0510
-115.0	58.2	0.0998
-95.0	75.4	0.1318
-75.0	95.2	0.1724
-55.0	116.7	0.2243
-50.0	122.1	0.2396
-45.0	127.5	0.2561
-40.0	132.6	0.2738
-35.0	137.6	0.2931
-30.0	142.1	0.3140
-25.0	146.2	0.3370
-20.0	149.6	0.3624
-15.0	152.0	0.3907
-10.0	153.2	0.4225
-5.0	152.8	0.4590
-2.0	151.4	0.4827
-1.0	150.8	0.4912
0.0	150.0	0.5000
0.1	149.9	0.5009
0.2	149.8	0.5018
0.3	149.7	0.5027
0.5	149.6	0.5045
1.0	149.1	0.5090
2.0	148.1	0.5184
5.0	144.2	0.5481
10.0	134.4	0.6042
15.0	119.6	0.6693
20.0	99.4	0.7420
25.0	75.6	0.8159
30.0	52.3	0.8800
40.0	0	1

increases, we clearly have conversions of the kind



which result in a decrease of b_c accompanied by an increase of N_{ce} . Beyond the maximum, when X_{12} becomes more negative, N_{ce} and b_c decrease simultaneously (compare the behavior for positive X_{12} values, e.g., in Table I). It should be clear that the location of the N_{ce} maximum depends on the characteristic parameters of a given chain.

We see in Table III how a sufficiently negative value of X_{12} converts the chain into a fully extended one. The absolute value of X_{12} necessary to achieve this is much higher than the absolute value of positive X_{12} necessary to produce a completely compact chain. Limits of this kind depend also on the chain characteristics.

So far we have studied bundles that contain 10 segments each. In a solid polymeric material such as semicrystalline polyethylene one traversal of the crystal lamella involves 100–200 segments.^(21,22) Compact bundles in solution are expected to be smaller, and this is the reason for the value $r_b = 10$ hitherto used. It is also interesting, however, to consider the case when a crystalline stem upon dissolution becomes a compact bundle in its entirety. Other conditions being equal, an increase of r_b is equivalent to increasing X_{12} . In Fig. 2 we see the curve of b_c/b in function of X_{12} .

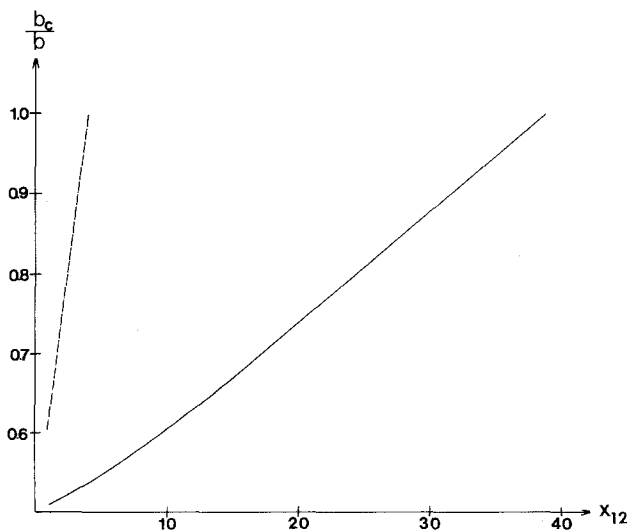


Fig. 2. Dependence of the ratio b_c/b on the interchange energy parameter X_{12} . The number of segments $r = 6000$; $\nu_m = 0.200$; $\nu_t = 0.100$. Continuous line: $r_b = 10$; dotted line: $r_b = 100$. Other parameters are listed in the text.

corresponding to the data in Table III. In the same figure we also show the curve for $r_b = 100$, while all remaining parameters are the same; the limiting value of $b_c = b$ is reached 10 times faster.

In the preceding paper⁽¹⁾ and also in Section 3 of the present one we have already mentioned the interrelationship between the energetic situation in solution (X_{12}), the volume pervaded by a chain (the radius of gyration R_g), and the degree of compactness (b_c/b). Values of X_{12} calculated for a number of liquid mixtures by Abe and Flory⁽²³⁾ show the following trend: for a given pair of components an increase of temperature T produces a *decrease* of the interaction energy parameter X_{12} . The phenomenon seems to be fairly general, and independent of the kind of materials involved. All our computations, including those reported above, show that a lower X_{12} produces a lower degree of compactness. Consider now a polymer in a not-too-good solvent. Our model now predicts that a temperature increase shall make the solvent better (at the same time more favorable according to the definition given above); the b_c/b ratio will decrease; in consequence, the pervaded volume and R_g will become larger.

The preceding discussion calls for further comments. First, for freely jointed chains we have⁽⁴⁾ the root-mean-square end-to-end length $(\bar{R}_e^2)^{1/2} = r^{1/2}l$ and $R_g^2 = \bar{R}_e^2/6$, where l is the length of a segment (average, if segments are unequal in size). Since our chains are not freely jointed, neither relation applies here. Second, a completely compact chain (with $b_c/b = 1$) will have the characteristic ratio $\rho = (\bar{R}_e^2)^{1/2}/(r^{1/2}l)$ fairly high, due to the relative stiffness of the chain. A completely extended chain ($b_c/b = 0$) will also have a still higher characteristic ratio, due to strong attractions between the polymer chain and the solvent. A minimum of ρ is expected somewhere in between, probably relatively close to the $b_c/b = 1$, since every break in the compact structure (an extended bundle) can contribute significantly to decreasing \bar{R}_e^2 . Below this minimum of ρ we have the typical behavior such that a decrease in X_{12} (a more favorable solvent) produces an increase of \bar{R}_e^2 and of related quantities such as the characteristic ratio. We note, at the same time, the existence of a contrary effect: an increase in flexibility which accompanies an improvement in solvent quality acts in the opposite direction upon \bar{R}_e^2 .

In a series of papers Utracki and his colleagues⁽²⁴⁻²⁷⁾ have studied Newtonian viscosities of polymer solutions, polymer melts, and also of nonpolymeric liquid phases, organic as well as inorganic ones. The key objective was establishing a corresponding states principle for viscosity η in function of temperature T and concentration c . Some of the $\eta(T)$ as well as some $\eta(c)$ curves have shown changes of slope. Utracki points out⁽²⁴⁾ that changes of chain conformations with concentration can be the reason for discontinuity points. He also⁽²⁴⁾ notes earlier evidence^(25,26) concerning

possible structural transitions caused by temperature changes, in single component liquids as well as in solutions. While more studies of this specific problem would be worthwhile, the phenomena observed by Utracki can well be connected with those studied in this and in the preceding paper. In Section 1 of Part I⁽¹⁾ we have discussed a rapid change between two widely different conformations as a rather degenerate but possible case, as compared to more gradual changes. In Fig. 1 of the present paper we see that in some cases the conformational changes with concentration are slow, and in a different case they might be quite fast. This provides a neat connection to the finding of Utracki⁽²⁴⁾ that some viscosity curves vs. a concentration-dependent parameter defined by him are straight lines, while other such curves exhibit inflection points.

Necessarily, chain conformation changes reflected by viscosities have to be also reflected in other properties. An interesting case in point is the study of viscosity of stereoisomers of poly (1,4-dichloro-2,3-epoxybutane) in dimethylformamide, dimethylacetamide, cyclohexanone, and benzene by Forsman and Poddar.⁽²⁸⁾ They have found abrupt changes in slope in the viscosity vs. concentration curves, similar to those observed by Utracki for other systems. At the same time, Poddar and Forsman⁽²⁹⁾ have studied dilute solutions of the same polymer in a number of solvents by the methods of light scattering, osmometry, and gel permeation chromatography. They have found evidence that an ordered structure in solution is disrupted by strong polymer + solvent interactions. Just as we have done in the preceding paper,⁽¹⁾ Poddar and Forsman assume a parentage relationship between chain conformations in the solid state and in solution: since the solid polymer is helical, they believe that the ordered structure in solution has the helical block conformation. Further, in a third paper from the same series, Poddar and Forsman⁽³⁰⁾ say that the more ordered structure involves higher stiffness—one more parallel to our approach.

In a series of papers Mark and collaborators⁽³¹⁻³⁴⁾ have studied effects of flexibility of polyoxides $[(\text{CH}_2)_y - \text{O}]_r$ upon their properties. To compare different compounds (y was the main variable of interest), all materials were studied in their unperturbed states (subscript 0). Since our main interest is in the effect of solvent upon properties of one polymeric material, the study of Mark and his group and ours are complementary. The main conclusions of Mark⁽³⁴⁾ are (i) the characteristic ratio ρ_0 vs. y curve passes through a minimum; (ii) the curve of the combinatorial partition function Q^c vs. y passes through a maximum, and the maximum appears close to the minimum of the ρ_0 vs. y curve; (iii) the curve of the melting point T_m vs. y has a minimum at a location close to the two extrema just mentioned. We thus find that Mark's conclusions agree well with and indeed complement

ours. His conclusion (i) fits well with our picture of changes of ρ with X_{12} discussed above. As for Mark's conclusion (ii), our Q^c as given in Eq. (9) in Part I⁽¹⁾ consists of the appropriate Boltzmann factor multiplied by the combinatorial Ising-like factor Ω , the latter defined by Eq. (10) in Part I. Our Table III shows that N_{ce} vs. X_{12} passes through a maximum, and necessarily so does Ω . Therefore, while our independent variable is X_{12} and not Mark's y , there is also an approximate coincidence of a ρ minimum with a Q^c maximum. As for the third Mark's conclusion, we have $T_m = H_m/S_m$, where H_m and S_m are, respectively, the enthalpy and the entropy of melting (or of fusion). Mark⁽³⁴⁾ notes that low melting temperatures are for polymers generally thought to be produced by high S_m values. If this is the case, a polymer chain going from a liquid phase (melt or solution) into a solid would tend to change its entropy more if its Q^c was larger, while a smaller Q^c would be associated with smaller S_m . Thus, from our approach we would also expect a not too far location of a maximum of Q^c from a minimum of T_m , while again the independent variable is different from that studied by Mark and collaborators.

There are various ways of looking at a polymeric chain. For instance, the rotational isomeric state approach⁽³⁵⁾ deals with the chemical structures of individual segments and provides large amounts of pertinent information. The model developed in this and in the preceding paper provides relatively less description, but it is concerned with somewhat different facets of the chain. There exist still more ways of dealing with macromolecular chain configurations (and properties). For instance, a very interesting problem has been considered by Forsman:⁽³⁶⁾ effects of segment-segment association on chain dimensions.

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