is related to the limiting characteristic ratio of the linear chain. Exceptions do occur, with the initial slope of g vs. $1/n$ for polymethylene being a noteworthy example.

Acknowledgment. The author thanks Professor Stockmayer for providing a preprint of ref 5. This work was supported by National Science Foundation Grant PCM 78-22916.

References and Notes

(1) Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301.
(2) Mattice, W. L. *Macromolecules* **1975**, *8*, 644.
(3) Mattice, W. L. *Macromolecules* **1976**, *9*, 48.
(4) Mattice, W. L. *Macromolecules* **1977**, *10*, 1171.
(5) Mansfield, M. L.; Stockmayer, W. H. *Macromolecules* **1980**, *13*, 1713.
(6) Kratky, O.; Porod, G. *Recl. Trav. Chim. Pays-Bas* **1949**, *68*, 1106.
(7) Mattice, W. L.; Carpenter, D. K. *Macromolecules* **1976**, *9*, 53.
(8) Mattice, W. L. *Macromolecules* **1977**, *10*, 511.
(9) Mattice, W. L. *Macromolecules* **1978**, *11*, 15.
(10) Mattice, W. L. *Macromolecules* **1980**, *13*, 506.
(11) Brant, D. A.; Flory, P. J. *J. Am. Chem. Soc.* **1965**, *87*, 2788.
(12) Benoit, H.; Doty, P. *J. Phys. Chem.* **1953**, *57*, 958.
(13) Abe, A.; Jernigan, R. L.; Flory, P. J. *J. Am. Chem. Soc.* **1966**, *88*, 631.
(14) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Interscience: New York, 1969.
(15) Mattice, W. L. *J. Am. Chem. Soc.* **1977**, *99*, 2325.

Improved Blob Hypothesis in Single-Chain Statistics

A. Ziya Akcasu,* M. Benmouna, and S. Alkhafaji

Department of Nuclear Engineering, The University of Michigan, Ann Arbor, Michigan 48109. *Received June 18, 1980*

ABSTRACT: An improved version of the blob hypothesis is proposed in which the local swelling is modeled by a formula similar to Flory's for the end-to-end distance. The improved version leads to smoother transitions from Θ- to good-solvent behavior of polymer solution properties such as α_s, α_H, and $S(q)$ but preserves all the qualitative aspects of the original blob hypothesis.

The calculation of both static and dynamic properties of a single chain in solution as a function of temperature requires knowledge of the equilibrium distribution $\psi_0(\mathbf{R}_{ij})$ of the vector distance between the ith and jth monomers in the presence of excluded-volume effects.[1] This function is usually modeled[2] in two steps: first, it is assumed to be Gaussian so that its characteristic function is taken to be

$$\psi_0(q) = \exp\left(-\frac{q^2}{6}\langle|R_{ij}|^2\rangle\right) \tag{1}$$

The second step involves a simplifying assumption for the second moment $\langle|R_{ij}|^2\rangle$. Peterlin[2] assumed it to be of the form

$$\langle|\mathbf{R}_{ij}|^2\rangle = l^2|i-j|^{1+\epsilon} \tag{2}$$

where l is the statistical length and ϵ is a monotonically increasing function of z, the excluded-volume parameter, determined from $\epsilon = (1/2)\partial \ln \alpha_R^2/\partial \ln z$, where α_R is the swelling factor for the end-to-end distance; i.e., $\langle R^2\rangle = l^2N^{1+\epsilon}$. This model implies that portions of the chain with the same chemical length $n = |i-j|$ swell uniformly with the same exponent.

The "temperature blob" model by Daoud[3] modifies this aspect of Peterlin's model as

$$\langle|\mathbf{R}_n|^2\rangle = nl^2 \qquad \text{for } n \le N_\tau \tag{3a}$$

and

$$\langle|\mathbf{R}_n|^2\rangle = (n/N_\tau)^{2\nu-1}nl^2 \qquad \text{for } n \ge N_\tau \tag{3b}$$

which implies Θ-solvent behavior within the so-called "temperature blob", referring to a section of the chain for which $n \le N_\tau$, and good-solvent behavior among the blobs. The crossover occurs at $n = N_\tau$, which depends on the temperature as

$$N_\tau \sim \tau^{-2} \tag{4}$$

where τ denotes the reduced temperature $(T-\Theta)/T$. The main feature of the blob hypothesis is that the exponent of the local swelling takes on only two discrete values, namely, $\nu = 0.5$ within the blob and $\nu = 0.6$ (or any other value) among the blobs. In contrast to the previous model, where ϵ is a continuous function of temperature, the exponent ν is independent of temperature but the size of the blobs decreases with temperature. As demonstrated in earlier work,[1-4] the blob model of $\psi_0(\mathbf{R}_{ij})$ explains the qualitative features of static and dynamic quantities, such as the static form factor $S(q)$ as a function of q, the radius of gyration R_G, the first cumulant $\Omega(q)$ of the dynamic structure factor, the hydrodynamic radius R_H, and the intrinsic viscosity[5] $[\eta]$. However, the step change in the statistics of portions of the chain below and above N_τ leads to numerical inaccuracies of about 15% or less, as pointed out in ref 1, when N_τ becomes comparable to the chain length. For example, the model predicts no swelling near the Θ temperature, where $N_\tau > N$, which is not consistent with first-order perturbation theory.

In this article, we propose an improvement of these aspects of the blob model by abandoning the concept of two discrete exponents for short and long portions of the chain. We first introduce

$$\langle|\mathbf{R}_{ij}|^2\rangle = l^2|i-j|\alpha^2(i,j) \tag{5a}$$

where $\alpha(i,j)$ is the local swelling factor of the chain. It is, of course, well-known[6] that $\alpha(i,j)$ not only is a function of the chemical length $n = |i-j|$ but also depends on i, i.e., the location of the subchain relative to the ends. We first assume, as done in the previous two models,[2,3] that $\alpha(i,j) \approx \alpha(n)$. In Peterlin's model $\alpha(n) = n^\epsilon$, and in Daoud's model $\alpha(n) = 1$ for $n \le N_\tau$ and $\alpha(n) = (n/N_\tau)^{2\nu-1}$ when $n \ge N_\tau$. The main idea in our model is that $\alpha(n)$ is approximated, for all n, by a formula similar in form to Flory's formula[7]

$$\alpha^5(n) - \alpha^3(n) = \gamma_R z(n) \tag{5b}$$

0024-9297/81/2214-0147$01.00/0

for the end-to-end distance. Here z is the excluded-volume parameter for a section of the chain, i.e.

$$z(n) = \left(\frac{3}{2\pi}\right)^{3/2}\left(\frac{v}{l^3}\right)n^{1/2} \tag{6}$$

In order to maintain contact with the blob hypothesis we rewrite (5b) as

$$\alpha^5(n) - \alpha^3(n) = (n/N_\tau)^{1/2} \tag{7}$$

by introducing N_τ as

$$N_\tau = \frac{1}{{\gamma_R}^2}\left(\frac{2\pi}{3}\right)^3\left(\frac{l^3}{v(\tau)}\right)^2 \tag{8}$$

The temperature dependence of N_τ is inherent in the binary cluster integral $v(\tau)$, which is usually approximated as $v(\tau) = v_\infty\tau$, so that (8) can be written as

$$N_\tau = \alpha/\tau^2 \tag{9}$$

with

$$\alpha = \frac{1}{{\gamma_R}^2}\left(\frac{2\pi}{3}\right)^3\left(\frac{l^3}{v_\infty}\right)^2 \tag{10}$$

More accurate models for $v(\tau)$ vs. τ may be considered in the present model, especially for high temperatures. The value of γ_R in (10) may be taken as $\gamma_R = 1.45$,[6] although other values are also reported. The proportionality constant α may be treated as an adjustable parameter, unless an independent estimate of (v_∞/l^3) is available.[1]

It is clear that the original blob hypothesis is equivalent to approximating the solution of (7) by $\alpha(n) = 1$ when $n \leq N_\tau$ and by $\alpha(n) = (n/N_\tau)^{1/10}$ when $n \geq N_\tau$, which is consistent with (3b) with $\nu = {}^3/_5$. Therefore the proposed model preserves the main idea of the blob hypothesis that the swelling of the chain sections is not uniform. On the other hand, it abandons the idea that there are only two discrete exponents at any temperature for short and long chain sections. In this sense, the proposed model is closer to Peterlin's model. However, it is not equivalent to assuming $\langle|\mathbf{R}_n|^2\rangle = l^2n^{2\nu}$ and allowing ν to be a function of n and N_τ because it also involves renormalization of the statistical length l by $lN_\tau^{(1-2\nu)/2}$ (cf. eq 3), thereby satisfying the scaling laws correctly.

In order to illustrate the improvement made possible by the present modified blob model, we compare the swelling factors for the radius of gyration and hydrodynamic radius using the original blob hypothesis (3) and its improved version (7) in modeling $\alpha(n)$.

Radius of Gyration

The swelling factor α_s for the radius of gyration is

$${\alpha_s}^2 = \frac{6}{N^2}\sum_{n=1}^{N}\left(1 - \frac{n}{N}\right)n\alpha^2(n) \tag{11}$$

where $\alpha(n)$ is to be obtained from (7). In the definition of the swelling factor one tacitly assumes that the statistical length l is independent of temperature. When large temperature differences are involved one may have to multiply (11) and the expressions derived from it by $[l(T)/l(\Theta)]^2$. Replacing the summation in (11) with integration and after some change of variables one obtains

$${\alpha_s}^2(Z) = \frac{12}{Z^4}\int_0^Z dy\, y^3\left(1 - \frac{y^2}{Z^2}\right)\alpha^2(y) \tag{12}$$

with $\alpha^5(y) - \alpha^3(y) = y$ and $Z^2 = N/N_\tau$. This integration can be performed exactly by changing the variable y to $\alpha(y)$. The result is

$${\alpha_s}^2(Z) = \left(\frac{27}{35}\right){\alpha_R}^2 + \left(\frac{81}{770Z}\right){\alpha_R}^7 - \left(\frac{2}{77Z^2}\right){\alpha_R}^{12} + \left(\frac{3}{13\times 770Z^3}\right){\alpha_R}^{17} + \left(\frac{17}{13\times 770Z^4}\right){\alpha_R}^{22} + \frac{1}{770Z^4} - \left(\frac{4}{13\times 770Z^5}\right){\alpha_R}^{27} + \left(\frac{1}{4\times 13\times 770Z^6}\right)({\alpha_R}^{32} - 1) \tag{13}$$

where α_R is the swelling factor for the end-to-end distance of the entire chain, given by ${\alpha_R}^5 - {\alpha_R}^3 = Z$. In the infinite-chain limit where $Z \to \infty$ and $\alpha_R \to Z^{1/5}$, (13) yields the asymptotic behavior of α_s as

$$\alpha_s \to 0.923Z^{1/5} \tag{14}$$

The maximum swelling as a function of temperature for a fixed molecular weight would occur, in the modified blob model, when $Z = [N\tau^2/\alpha]$ attains its maximum at $\tau = 1$ or at $T \to \infty$. However, we still choose $N_\tau = \alpha/\tau^2 \cong 1$ as the smallest value of the temperature blob to determine the maximum temperature T_M, as explained in ref 1, above which the solvent reaches the good-solvent limit.

The small-Z limit, either directly from (13) or more easily from (12) with $\alpha^2(y) \approx 1 + y$, yields

$${\alpha_s}^2 \to 1 + 0.686Z \tag{15}$$

The numerical coefficients in (14) and (15) are $({}^{75}/_{88})^{1/2}$ and ${}^{24}/_{35}$, respectively. These two asymptotic results satisfy ${\alpha_s}^5 - {\alpha_s}^3 = \gamma_s Z$ with $\gamma_s = 0.671$ for large Z and $\gamma_s = 0.686$ for small Z. In fact the results calculated with (13) are reproduced very accurately (better than 2%) by ${\alpha_s}^5 - {\alpha_s}^3 = 0.671Z$ for all values of Z. Flory's formula[7] ${\alpha_s}^5 - {\alpha_s}^3 = 1.276z$ with Stockmayer's modification that ensures the correct first-order perturbation theory[6] is obtained by adjusting the value of the free parameter in N_τ (cf. eq 9) such that $Z = (1.276/0.686)z = 1.86z$. However, one may also choose the adjustable parameter in N_τ as $Z = (1.67/0.671)z$ such that (14) reproduces the asymptotic behavior ${\alpha_s}^5 \to 1.67z$ of Fujita–Norisuye–Fixman,[8,9] with some deviation from first-order perturbation theory near the Θ temperature. Since z itself is not calculable from first principles, in ref 1 we determined the numerical value of the adjustable parameter experimentally by representing the data by $\alpha_s = 0.923(N/N_\tau)^{1/10}$ in the asymptotic region. Once the value of the adjustable parameter is fixed, one can proceed to calculate other dynamic and static parameters such as the hydrodynamic radius and the static structure factor in terms of $Z = (N/N_\tau)$ without any free parameter.

It is interesting to note in passing that (14) predicts

$$\alpha_R/\alpha_s = 1.083 \tag{16}$$

in the large-z limit. Using ${\alpha_R}^5 \to 1.45z$ and ${\alpha_s}^5 \to 1.67z$ reported in the literature,[6] we find $\alpha_R/\alpha_s = 0.972$, which is only about 10% less than 1.083. We also find from (15) that, in the small-z limit

$$\alpha_R/\alpha_s \to 1 + 0.314Z \tag{17}$$

which is to be compared with the perturbation result[6] $\alpha_R/\alpha_s \to 1 + 0.0285z$. Using $Z = 1.86z$ determined above, we find that (17) overestimates the z dependence of α_R/α_s for small values of z. This discrepancy is not much of a concern because it is based on ${\alpha_R}^5 - {\alpha_R}^3 = Z$ in which the coefficient of Z may be allowed to be different from unity to improve the agreement. One should keep in mind, however, that the modified (as well as the original) blob model is noncommittal as far as α_R is concerned, but it

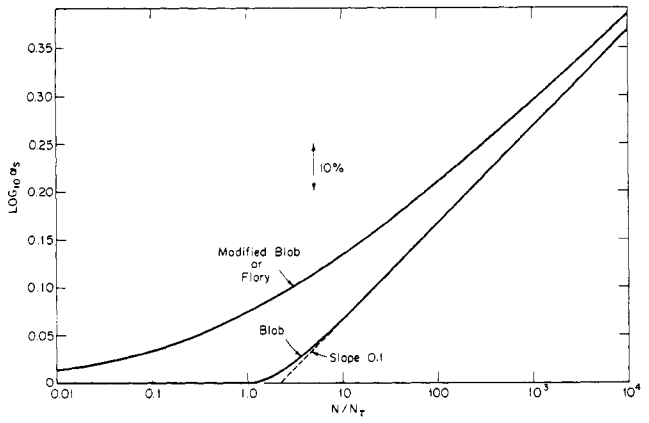

Figure 1. Comparison of the original and modified blob hypotheses in the case of the expansion factor α_s for radius of gyration as a function of N/N_τ.

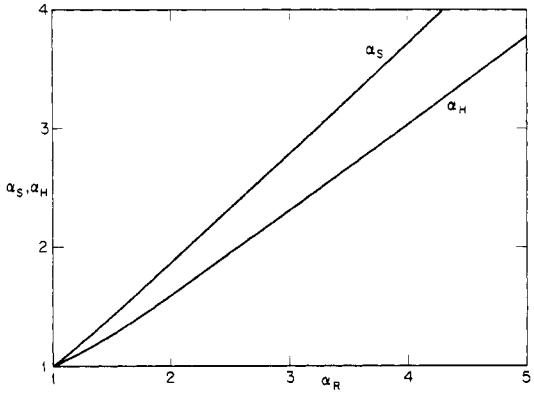

Figure 2. Variation of α_s and α_H with α_R.

attempts to explain the global features of the dynamic and static quantities such as α_s, α_H, and $S(q)$ through a single model for $\psi_0(\mathbf{R}_{ij})$.

Figure 1 compares the variation of α_s with N/N_τ as calculated in both blob models. In Figure 2 we plot the variation of α_s with α_R.

Hydrodynamic Radius

The swelling factor for the hydrodynamic radius is given by

$$\alpha_H^{-1}(Z) = \frac{3}{4N^{1/2}}\sum_{n=1}^{N}\left(1-\frac{n}{N}\right)\frac{1}{\alpha(n)n^{1/2}} \tag{18}$$

when the diffusion coefficient is calculated in Kirkwood's approximation.[6] In integral form (18) reads

$$\alpha_H^{-1}(Z) = \frac{3}{2Z}\int_0^Z dy\left(1-\frac{y^2}{Z^2}\right)\frac{1}{\alpha(y)} \tag{19}$$

where $\alpha(y)$ is given by $\alpha^5(y) - \alpha^3(y) = y$. The integration can be performed exactly and the result is

$$\alpha_H^{-1}(Z) = (3/8)(5\alpha_R^2 - 1)/\alpha_R^3 - 3\alpha_R^4/4Z + \alpha_R^9/4Z^2 - (\alpha_R^{14} - 1)/28Z^3 + 9\alpha_R^2/16Z - 9\alpha_R^7/40Z^2 + 3(\alpha_R^2 - 1)/80Z^3 \tag{20}$$

In the large-Z limit (20) yields

$$\alpha_H \to 0.747Z^{1/5} \tag{21}$$

where $^{56}/_{75} \cong 0.747$ is used. The small-Z limit is obtained as

$$\alpha_H \to 1 + {}^3/_{16}Z \tag{22}$$

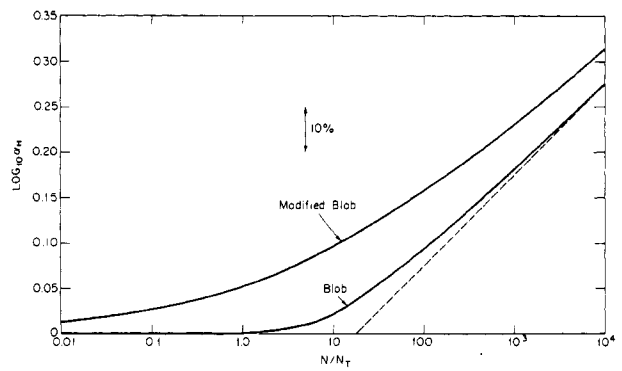

Figure 3. Comparison of the original and modified blob hypotheses in the case of the expansion factor α_H for hydrodynamic radius as a function of N/N_τ.

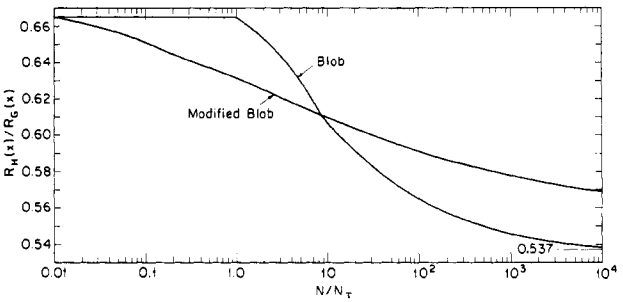

Figure 4. Comparison of the original and modified blob hypotheses for the ratio of the hydrodynamic radius to radius of gyration $R_H(x)/R_G(x)$ as a function of $x^{-1} = N/N_\tau$. Note that the asymptotic limit for large N/N_τ is 0.537 in both models.

Figure 3 compares the variation of α_H with (N/N_τ) for modified and original blob models. The modified version shows a smoother transition from Θ- to good-solvent behavior, as in the case of α_s shown in Figure 1. The variation of α_H with α_R is shown in Figure 2 together with that of α_s. The ratio α_H/α_s in the large-Z limit is found to be

$$\alpha_H/\alpha_s = 0.81 \qquad \text{(large } Z\text{)} \tag{23}$$

Using $R_H(\Theta)/R_G(\Theta) = 0.664$ as calculated in the Kirkwood approximation and $R_H(Z)/R_G(Z) = 0.664(\alpha_H/\alpha_s)$, we obtain the limiting value of R_H/R_G in the large-Z limit as $R_H/R_G \to 0.537$.[1] The variation of R_H/R_G with N/N_τ is plotted in Figure 4 in both blob models. We have used (11) and (18) to calculate α_s and α_H in this figure because the closed expressions (13) and (20), based on replacing summations by integrations, yield numerical values accurate to 1.5% or better. In this figure such differences become noticeable due to the enlarged scale. For small N/N_τ the original blob model predicts a horizontal line, whereas the present modified version yields from (15) and (22)

$$\frac{R_H}{R_G} \to 0.664\left[1-\frac{87}{560}\left(\frac{N}{N_\tau}\right)^{1/2}\right] \tag{24}$$

as $N/N_\tau \to 0$.

Static Structure Factor

As a final example we compare the static structure factor calculated in the two versions of the blob model, using

$$S(q) = 1 + 2\sum_{n=1}^{N}\exp[-(q^2l^2/6)n\alpha^2(n)] \tag{25}$$

where we choose $N_\tau = 50$, which corresponds to an intermediate temperature between the Θ- and good-solvent limits (see Figure 5). The crossover in $S(q)$ as a function of q at $lq^* = (6/N_\tau)^{1/2}$ from $S(q) \sim q^{-1.66}$ for $q < q^*$ to $S(q)$

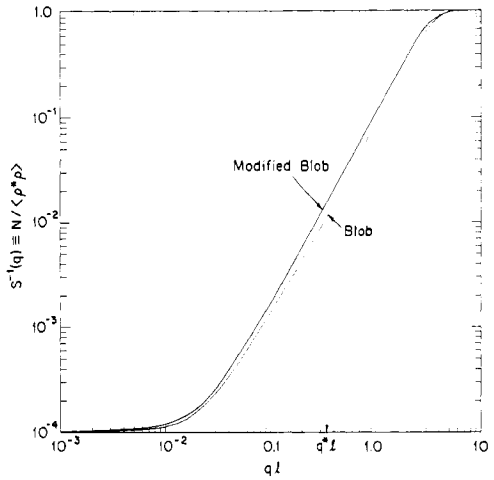

Figure 5. Comparison of the original and modified blob hypotheses in the case of the inverse static form factor $S^{-1}(q)$ as a function of q.

$\sim q^{-2}$ for $q > q^*$, which was reported by Farnoux et al.[10] using the original blob model, is even less apparent in the case of modified blob model.

Conclusion

The present modification of the blob hypothesis improves the numerical accuracy of the model in the region where $N/N_\tau \sim 1$, where discrepancies with experiment may be as large as 15%, as reported in ref 1. This improvement is obtained by abandoning the existence of only two discrete exponents in the swelling of sections of a chain, as postulated in the original blob model, but retaining the more fundamental idea that the smaller sections swell less than the longer ones. Therefore, all the qualitative predictions of the original blob concept remain valid. A recent work by Francois[11] also describes a procedure for improving the original blob model in the same direction as above.

The blob concept, in its modified or original form, provides a workable model for the equilibrium distribution $\psi_0(\mathbf{R}_{ij})$ for the vector distance between two monomers and enables one to calculate consistently several single-chain properties like the first cumulant $\Omega(q)$, α_H, α_s, and $S(q)$ as functions of q, molecular weight, and temperature, with one adjustable parameter. As such, its predictions can be tested by a variety of experiments over large ranges of experimental conditions, as we demonstrated in ref 1.

Acknowledgment. Fruitful discussions with Professor G. C. Summerfield are acknowledged. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support.

References and Notes

(1) Akcasu, Z.; Han, C. C. *Macromolecules* **1979**, *12*, 276.
(2) Peterlin, A. *J. Chem. Phys.* **1955**, *23*, 2462.
(3) Daoud, M. Thesis, Université de Paris VI, 1977.
(4) Benmouna, M.; Akcasu, Z. *Macromolecules* **1978**, *11*, 1187.
(5) Han, C. C. *Polymer* **1979**, *20*, 1083.
(6) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971.
(7) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, N.Y., 1953.
(8) Fujita, H.; Norisuye, T. *J. Chem. Phys.* **1970**, *52*, 1115.
(9) Fixman, M. *J. Chem. Phys.* **1962**, *36*, 3123.
(10) Farnoux, B.; Boué, F.; Cotton, J. P.; Daoud, M.; Jannink, G.; Nierlich, M.; de Gennes, P. G. *J. Phys. (Paris)* **1978**, *39*, 77.
(11) Francois, J.; Schwartz, T.; Weill, G. *Macromolecules* **1980**, *13*, 564.

Study of the Statistical Chemical Heterogeneity of Copolymers by Cross-Fractionation

Jaroslav Stejskal,* Pavel Kratochvíl, and Dagmar Straková

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia. *Received March 31, 1980*

ABSTRACT: The distribution functions of chemical composition describing the statistical heterogeneity of copolymers are discussed. The distribution functions for termination by disproportionation and combination are similar. Theoretical prediction is compared with the experimental result of cross-fractionation of an azeotropic copolymer of styrene and 2-methoxyethyl methacrylate. The experimental distribution function is much narrower than the predicted one, which suggests the limited efficiency of cross-fractionation.

Unlike the comparatively well-described[1-3] conversion chemical heterogeneity of statistical copolymers, the so-called statistical chemical heterogeneity of these copolymers has so far attracted less attention. This is justified in many respects because as a rule such a type of chemical heterogeneity is of a much smaller extent. Cases may be found, however, especially with low molecular weight copolymers, where statistical heterogeneity is not negligible[4] and may affect the experimental characterization of these copolymers, e.g., by light scattering. The importance of an analysis of statistical heterogeneity has lately increased owing to the development of novel and more sensitive methods of determination of the distribution of chemical composition (cross-fractionation,[5,6] adsorption high-speed liquid chromatography,[7,8] etc.).

The cross-fractionation of copolymers dealt with in this paper consists of a twofold fractionation in different solvent systems. Primary fractions obtained by fractionation in a system where chains richer in one type of monomeric unit are preferentially precipitated are refractionated in another solvent system in which, on the contrary, macromolecules with a higher content of the other type of monomeric unit are preferentially separated. This procedure seems to be one of the most efficient methods of copolymer fractionation by chemical composition. For this reason, cross-fractionation was used in the present study of comparatively small differences in chemical composition of copolymer molecules, given by the statistical nature of copolymer chain formation.

The theoretical analysis of the statistical heterogeneity is offered in a fundamental paper by Stockmayer[9] for the case of equal molecular weights of both types of monomeric units. The two-dimensional differential weight distribution of chemical composition has been derived and expressed

0024-9297/81/2214-0150$01.00/0