Macromolecules 1988, *21*, 1449–1464

gram through the Center for Materials Research at Stanford University. We are grateful to Dr. Roger J. Lewis who initiated the DNA program in our laboratory and provided invaluable advice and encouragement during this study.

References and Notes

(1) Rouse, P. E., Jr. *J. Chem. Phys.* **1955**, *21*, 1272.
(2) Zimm, B. H. *J. Chem. Phys.* **1956**, *24*, 269.
(3) Pecora, R. *J. Chem. Phys.* **1965**, *43*, 1562; **1968**, *49*, 1032.
(4) Saito, N.; Ito, S. J. *J. Phys. Soc. Jpn.* **1968**, *25*, 1446.
(5) de Gennes, P.-G. *Physics* **1967**, *3*, 37. Dubois-Violette, E.; de Gennes, P.-G. *Physics* **1967**, *3*, 181.
(6) Borochov, N.; Eisenberg, H.; Kam, Z. *Biopolymers* **1981**, *20*, 231.
(7) Borochov, N.; Eisenberg, H.; Kam, Z. *Biopolymers* **1981**, *20*, 2671.
(8) Yamakawa, H. *Annu. Rev. Phys. Chem.* **1984**, *35*, 23.
(9) Eden, D.; Elias, J. G. In *Measurements of Suspended Particles by Quasi-Elastic Light Scattering*, Dahneke, B. E., Ed.; Wiley: New York, 1983; p 401.
(10) Porschke, D. *Annu. Rev. Phys. Chem.* **1985**, *36*, 159.
(11) Stockmayer, W. H.; Baur, M. E. *J. Am. Chem. Soc.* **1964**, *86*, 3485.
(12) Lewis, R. J.; Pecora, R.; Eden, D. *Macromolecules* **1986**, *19*, 134.
(13) Nash, P. J.; King, T. A. *Polymer* **1985**, *26*, 1003.
(14) Koppel, D. E. *J. Chem. Phys.* **1972**, *57*, 4814.
(15) Akcasu, A. Z.; Benmouna, M.; Han, C. C. *Polymer* **1980**, *21*, 866.
(16) Wilcoxon, J.; Schurr, J. M. *Biopolymers* **1983**, *22*, 849.
(17) Maeda, T.; Fujime, S. *Macromolecules* **1984**, *17*, 1157, 2381.
(18) Lin, S. C.; Schurr, J. M. *Biopolymers* **1978**, *17*, 425.
(19) Thomas, J. C.; Allison, S. A.; Schurr, J. M.; Holder, R. D. *Biopolymers* **1980**, *19*, 1451.
(20) Soda, K.; Wada, A. *Biophys. Chem.* **1984**, *20*, 185.
(21) Schurr, J. M.; Schmitz, K. S. *Annu. Rev. Phys. Chem.* **1986**, *37*, 271.
(22) Provencher, S. W.; Hendrix, J.; De Maeyer, L.; Paulussen, N. *J. Chem. Phys.* **1978**, *69*, 4237.
(23) Provencher, S. W. *Makromol. Chem.* **1979**, *180*, 201.
(24) Provencher, S. W. *CONTIN User's Manual*, Technical Report EMBL-DA02; European Molecular Biology Laboratory: Heidelberg, 1980.
(25) Provencher, S. W. *Comput. Phys. Commun.* **1982**, *27*, 213, 229.
(26) *Particle Size Distribution: Assessment and Characterization*; Provder, T., Ed; American Chemical Society: Washington, DC, 1987.
(27) Lewis, R. J.; Huang, J. H.; Pecora, R. *Macromolecules* **1985**, *18*, 944.
(28) Langowski, J.; Giesen, U.; Lehmann, C. *Biophys. Chem.* **1986**, *25*, 191.
(29) Lewis, R. J.; Huang, J. H.; Pecora, R. *Macromolecules* **1985**, *18*, 1530.
(30) Marko, M. A.; Chipperfield, R.; Birnboim, H. C. *Anal. Biochem.* **1982**, *121*, 382.
(31) Maier, K. R. Ph.D. Thesis, Stanford University, Stanford, CA, 1986.
(32) Provencher, S. W. *Biophys. J.* **1976**, *16*, 27.
(33) Provencher, S. W. *J. Chem. Phys.* **1976**, *64*, 2772.
(34) Aragón, S. R. *Macromolecules* **1987**, *20*, 370.
(35) Aragón, S. R.; Pecora, R. *Macromolecules* **1985**, *18*, 1868.
(36) Bott, S. E. Ph.D. Thesis, Stanford University, Stanford, CA, 1984.
(37) Maniatis, T.; Fritsch, E. F.; Sambrook, J. *Molecular Cloning, A Laboratory Manual*; Cold Spring Harbor Laboratory: Cold Spring Harbor, NY, 1982.
(38) Perico, A.; Piaggio, P.; Cuniberti, C. *J. Chem. Phys.* **1975**, *62*, 2690.
(39) Lewis, R. J. Ph.D. Thesis, Stanford University, Stanford, CA, 1985.
(40) Kovacic, R. T.; van Holde, K. E. *Biochemistry* **1977**, *16*, 1490.
(41) Han, C. C.; Akcasu, Z. A. *Macromolecules* **1981**, *14*, 1080.
(42) Lewis, R. J.; Pecora, R. *Macromolecules* **1986**, *19*, 2074.
(43) Allison, S. A. *Macromolecules* **1986**, *19*, 118.
(44) Lewis, R. J.; Allison, S. A.; Eden, D.; Pecora, R., submitted for publication in *J. Chem. Phys.*
(45) Schaefer, D. W.; Han, C. C. In *Dynamic Light Scattering: Applications of Photon Correlation Spectroscopy*; Pecora, R., Ed.; Plenum: New York, 1985.
(46) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row: New York, 1971.
(47) Adam, M.; Delsanti, M. *Macromolecules* **1977**, *10*, 1229.
(48) Lewis, R. J.; Pecora, R.; Eden, D. *Macromolecules* **1987**, *20*, 2579.
(49) Pusey, P. N.; Tough, R. J. A. In *Dynamic Light Scattering: Applications of Photon Correlation Spectroscopy*; Pecora, R., Ed.; Plenum: New York, 1985.
(50) Voordouw, G.; Kam, Z.; Borochov, N.; Eisenberg, H. *Biophys. Chem.* **1978**, *8*, 171.
(51) Newman, J.; Swinney, H. L.; Berkowitz, S. A.; Day, L. A. *Biochemistry* **1974**, *13*, 4832.
(52) Berkowitz, S. A.; Day, L. A. *Biochemistry* **1974**, *13*, 4825.
(53) Batchelor, G. K. *J. Fluid Mech.* **1976**, *74*, 1.
(54) Yamakawa, H. *J. Chem. Phys.* **1962**, *36*, 2995.
(55) Imai, S. *J. Chem. Phys.* **1969**, *50*, 2116.
(56) Pyun, C. W.; Fixman, M. *J. Chem. Phys.* **1964**, *41*, 957.
(57) Altenberger, A. R.; Deutch, J. M. *J. Chem. Phys.* **1973**, *59*, 894.
(58) Akcasu, A. Z.; Benmouna, M. *Macromolecules* **1978**, *11*, 1193.
(59) Akcasu, A. Z. *Polymer* **1981**, *22*, 1169.

Scattering Theory and Properties of Block Copolymers with Various Architectures in the Homogeneous Bulk State

H. Benoit

Institut Charles Sadron (CRM-EAHP), 6 rue Boussingault, 67083 Cedex, France

G. Hadziioannou*

IBM Research, Almaden Research Center, 650 Harry Road,
San Jose, California 95120-6099.

Received July 13, 1987;
Revised Manuscript Received October 13, 1987

ABSTRACT: We have developed a general theory to predict the scattering profiles in the homogeneous state and the phase separation behavior of multiblock copolymers having various architectures such as "linear", "comb", and "star". We found that the scattering intensity versus angle in the homogeneous state has a universal slope at small angles independent of the architecture of the block copolymers. The position of the maximum intensity is almost independent of the number N of sequences, and its amplitude rapidly reaches a plateau value, indicating that the microphase separation for $N \geq 20$ is independent of N. Detailed calculations concerning the molecular dimensions and conformations and the thermodynamic behavior of the three types of the multiblock copolymer architectures have been performed based on fundamental variables such as the radius of gyration of each block, the composition, the degree of polymerization, the number of sequences, and the polymolecularity in molecular weight and composition.

Introduction

Block copolymers at the homogeneous state have been the subject of extensive theoretical studies,[1-12] but usually the authors have restricted their interest to copolymers made only of a few blocks.

In this paper we would like to generalize these known

0024-9297/88/2221-1449$01.50/0

results to copolymers made of many blocks, identical or not. These types of copolymers correspond to polymers prepared by polycondensation or polyaddition of two different types of monomer units and are of considerable industrial interest. Polymers made of hard and soft segments belong to this category, and scattering studies of this type of materials in the amorphous state could bring useful information allowing a better understanding of their structures and properties.

In the first part we shall summarize what is known about general properties of copolymers that are independent of their architecture. In the second part we shall discuss the properties that are specific of copolymers made of many blocks, emphasizing the case where the number of monomer units can be considered as infinity.

General Laws of the Scattering and Properties of Copolymers in Homogeneous Bulk State

Scattering Equations of Copolymers. Assuming that the scattering due to compressibility is negligible, the intensity scattered by copolymer chains is given by

$$(a-b)^2 I^{-1}(q) = \frac{\sum \nu_i n_i^2 P_i(q)}{\sum \nu_i n_{ia}^2 P_{ia}(q) \sum \nu_i n_{ib}^2 P_{ib}(q) - [\sum \nu_i n_{ia} n_{ib} P_{iab}(q)]^2} - \frac{2\chi}{\sum \nu_i n_i} \tag{1}$$

This formula is written for a system containing copolymers made of two kinds of monomers, which shall be called a and b, respectively. They are ν_i molecules of species i having n_i monomers from which n_{ia} and n_{ib} are of types a and b, respectively ($n_i = n_{ia} + n_{ib}$). These monomers are not taken here in the classical sense of polymer chemistry. They are subunits having the same volume and characterized by a scattering length (or index of refraction of electron density) a and b, respectively. The quantity χ is the interaction parameter, following Flory[13] between two units of different nature. The quantities $P_i(q)$, $P_{ia}(q)$, $P_{ib}(q)$, and $P_{iab}(q)$ are the structure factors of the molecule of type i. $P_i(q)$ corresponds to the whole polymer and is defined as

$$P_i(q) = \frac{1}{n_i^2} \sum_{j=1}^{n_i} \sum_{k=1}^{n_i} \langle \exp(-i\vec{q}\vec{r}_{jk}) \rangle \tag{2}$$

where $\vec{r}_{jk}$ is the distance between the monomeric units j and k and $\vec{q}$ is the scattering vector, its module being $4\pi/\lambda \sin(\theta/2)$, with λ the wavelength of the incident beam and θ the scattering angle.

The quantities $P_{ia}(q)$ and $P_{ib}(q)$ are of the same form as $P_i(q)$, the summation being limited to the a or to the b type of monomer. $P_{iab}(q)$ is a cross term for which j is an a segment and k a b segment

$$P_{iab}(q) = \frac{1}{n_{ia} n_{ib}} \sum_{j=1}^{n_{ia}} \sum_{k=1}^{n_{ib}} \langle \exp(-i\vec{q}\vec{r}_{j_a k_b}) \rangle \tag{3}$$

All the $P(q)$'s are such that $P(0) = 1$ and the relation

$$n_i^2 P_i(q) = n_{ia}^2 P_{ia}(q) + n_{ib}^2 P_{ib}(q) + 2 n_{ia} n_{ib} P_{iab}(q) \tag{4}$$

is always obeyed. Equation 1 can be used even if some of the molecules of the system are homopolymers.

In the case of a monomolecular copolymer, we shall introduce, in order to simplify eq 1, the composition of the copolymer $u = n_a/(n_a + n_b) = n_a/n$, $v = (n_b/n)$, $(u + v = 1)$, and a reduced scattered intensity which will be defined as the intensity scattered per monomeric unit divided by the square of the contrast factor, $(a - b)^2$

$$i(q) = \frac{I(q)}{n\nu} \frac{1}{(a-b)^2} \tag{5}$$

With these notations eq 1 reduces to

$$\frac{1}{i(q)} = \frac{P(q)}{nu^2v^2(P_a(q)P_b(q) - P_{ab}^2(q))} - 2\chi \tag{6}$$

or

$$i(q) = \frac{nu^2v^2[P_a(q)P_b(q) - P_{ab}^2(q)]}{P(q) - 2\chi nu^2v^2[P_a(q)P_b(q) - P_{ab}^2(q)]} \tag{7}$$

Scattering by a Monomolecular Block Copolymer. 1. Behavior at Small Angles. All $P(q)$'s are equal to unity for $q = 0$, $i(0) = 0$. This can be explained qualitatively by saying that in such a system there are no concentration fluctuations in a large volume since its composition is always the composition of the copolymer. If we expand $i(q)$ as function of q we obtain

$$i(q) = nu^2v^2(q^2/3)(2R_{ab}^2 - R_a^2 - R_b^2) \tag{8}$$

where R_a^2 and R_b^2 are the radii of the gyration of parts a and b of the copolymer and R_{ab}^2 is cross term obtained by writing

$$P_{ab}(q) = 1 - (q^2/3)R_{ab}^2 \tag{9}$$

It has been established[14] that the quantity in parentheses on the right-hand side of eq 8 has a very simple geometrical meaning. If we call G_a the center of mass of part a of the copolymer and G_b the same quantity for segment b, we have

$$G_aG_b^2 = L^2 = 2R_{ab}^2 - R_a^2 - R_b^2 \tag{10}$$

From eq 8 and 10 we obtain

$$i(q) = nu^2v^2(q^2/3)L^2 \tag{11}$$

The initial slope of the absolute intensity plotted as a function of q^2 gives the average of the squares of the distance between the centers of mass of the a and the b segments. This shows clearly that for a copolymer with randomly distributed monomer G_a and G_b coincide and the scattered intensity will be very weak and practically nonexistant.

2. Intermediate Range. If we assume that $1/R < q < 1/\ell$, ℓ being Kuhn's statistical element, we look at what has been called the intermediate range. In this region of q the cross term $P_{ab}(q)$ can be neglected, especially if the sequences are long enough, and we obtain from eq 6

$$\frac{1}{i(q)} = \frac{u^2P_a(q) + v^2P_b(q)}{nu^2v^2P_a(q)P_b(q)} - 2\chi \tag{12}$$

This result has to be compared with the intensity scattered by a mixture of two homopolymers of degree of polymerization n_a and n_b and of structue factor $P_a(q)$ and $P_b(q)$. Applying the formula[5] of de Gennes, we obtain eq 13 by using the same notation:

$$\frac{1}{i(q)} = \frac{1}{n}\left(\frac{1}{u^2P_a(q)} + \frac{1}{v^2P_b(q)}\right) - 2\chi \tag{13}$$

The two formulas (eq 12 and 13) are the same, which means that a copolymer at large q behaves like a mixture of its sequences.

A close examination of eq 12 shows that the scattering intensity is going to zero with a power law characteristic of the statistics of the polymer. If the chains are Gaussian, $i(q) \sim q^{-2}$.

We show that for a monomolecular block copolymer the scattering intensity at $q = 0$ starts from zero and then at large q tends to zero with a characteristic power law. These results qualitatively indicate that $i(q)$ versus q or q^2 has to go through a maximum. A classical example of this fact is the two-block copolymer A-B with $u = v = 0.5$, which has a maximum at $qR \sim 2$ (ref 6).

3. Influence of the Interaction Parameter. All the results which have been obtained until now are independent of the value of χ, as long as χ is sufficiently small to keep $i(q) > 0$.

In order to study the influence of χ let us assume that we know, for a given copolymer, the value of $i(q)$ (for $\chi = 0$, $i(q)$ is $i_0(q)$). According to the preceding discussion, $i_0(q)$ has a maximum; its value is m for $q = q^*$, where $m = i_0(q^*)$. This allows us to rewrite eq 6 and 7 as

$$\frac{1}{i(q)} = \frac{1}{i_0(q)} - 2\chi \tag{14}$$

or

$$i(q) = \frac{i_0(q)}{1 - 2\chi i_0(q)} \tag{14'}$$

One sees first that the position of the maximum is independent of χ ($\mathrm{d}i(q)/\mathrm{d}q = 0$ if $\mathrm{d}i_0(q)/\mathrm{d}q = 0$). Its magnitude, however, depends strongly on χ

$$i(q^*) = \frac{m}{1 - 2\chi m} \tag{15}$$

and goes hyperbolically to infinity when $\chi = \chi_c = 1/2m$. This means that one reaches the spinodal.[6] The system becomes totally unstable and a phase transition occurs. Since the phase transition occurs at $q = q^*$ and not at $q = 0$, it is a special transition where this system goes from an isotropic liquid to a mesomorphic state. From the above, obviously, it is sufficient to know $i_0(q)$ to be able to discuss with the help of eq 14 or 14′ the effect of χ.

4. Influence of the Solvent. If we introduce a solvent, the physical problems become much more difficult, because we deal with a three-component system and we have to take into account the concentration fluctuations in solution and not only the fluctuation of component a relative to component b. An elegant method to suppress, or more exactly to make invisible, these fluctuations consists in choosing a solvent having a coherent scattering length s equal to that of the polymer mixture $s = au + bv$. (This can be achieved readily in neutron scattering by choosing as solvent a mixture of hydrogenous and deuteriated liquids.) This procedure makes, following eq 30 of ref 10, $I(0) = 0$ at any concentration. If, at low concentration, we define $i(q)$ as in the bulk, we obtain

$$i(q) = nu^2v^2[P_a(q) + P_b(q) - 2P_{ab}(q)] \tag{16}$$

which has to be compared with eq 7 in the case where $\chi = 0$

$$i(q) = nu^2v^2\frac{P_a(q)P_b(q) - P_{ab}^2(q)}{P(q)} \tag{17}$$

Both equations are very similar. We can even show that they are identical in the case of a symmetrical copolymer for which $P_a(q) = P_b(q)$ and $u = v = {}^1/_2$. This means that in this case the peak has the same shape in bulk with $\chi = 0$ and in dilute solution. In fact there are changes of shape as a function of the concentration and the quality of the solvent with respect to the different sequences, but we are not sure that these effects are experimentally observable.

In the general case the only thing which can be said is that at the limiting cases, bulk with $\chi = 0$ and dilute solution, the initial slope and the asymptotical behavior are identical. This lets us assume that there is no essential difference between the symmetric and the general case.

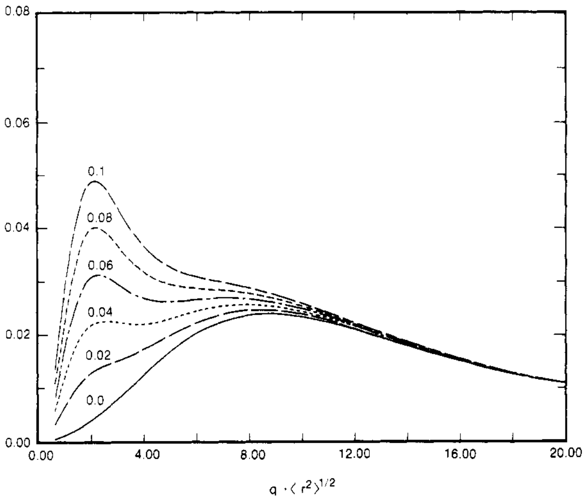


Figure 1. Scattering profiles from a mixtue of two symmetrical two-block copolymers (AB, A_1B_1; $u = u_1 = 0.5$) having radii of gyration in a ratio of 4.47. The scattering curves have been drawn for different concentrations, $\zeta = \nu(n_a + n_b)/[\nu(n_a + n_b) + \nu_1(n_{a1} + n_{b1})]$.

It is known (see above) that when χ is in the vicinity of χ_c ($\chi_c - \chi$, small and positive) one obtains a very large peak in the bulk. Its height diminishes when one adds solvent, and it can be shown[15] that this decrease can be described if we replace χ by $\chi\phi$, calling ϕ the volume fraction occupied by the polymer.

Scattering Intensity of a Polymolecular Block Copolymer. Since eq 1 is valid for any polymolecular polymer, it can be used for any block copolymer containing only a and b units. In order to discuss the effect of polymolecularity qualitatively we shall consider two cases, polymolecularity in molecular weights with fixed composition and polymolecularity in composition as well as in molecular weight. In this discussion we shall always assume that $\chi = 0$ since it has been shown that knowing $i_0(q)$ one obtains very easily $i(q)$ (see eq 14 and 14′, which are general).

1. With Fixed Composition. Starting from eq 1 we obtain $i_0(q)$ as

$$i_0(q) = \frac{\sum \nu_i n_i^2 P_{ia}(q) \sum \nu_i n_i^2 P_{ib}(q) - (\sum \nu_i n_i^2 P_{iab}(q))^2}{\sum \nu_i n_i \sum \nu_i n_i^2 P_i(q)} \tag{18}$$

The scattered intensity is zero for $q = 0$, which is easy to understand. At large q if we assume the $P_{ab}(q)$ to be negligible, we find again that the intensity is the same as for a mixture of a and b homopolymers.

In order to see more clearly what the shape of the curve is, the case of the two identical block copolymers, $u = v = {}^1/_2$, $P_{ia}(q) = P_{ib}(q)$, will be considered. In this case the intensity can be written as

$$i_0(q) = \frac{1}{8}\,\frac{\sum \nu_i n_i^2 (P_{ia}(q) - P_i(q))}{\sum \nu_i n_i} \tag{19}$$

We see that the scattering is just the sum of the scattering by the different species present in the solution. Each of them will show a peak for $qR_i \approx 2$. If their radii of gyration are very different one can obtain more than one peak for $i_0(q)$. As an example, Figure 1 shows the value of $i_0(q)$ for a mixture of two polymers having a ratio of their radii of gyration equal to 4.47 for different compositions of the system. We see clearly the existence of two peaks.

2. In Composition as Well as Molecular Weight. In this general case it is difficult to study the complete curve since its shape depends very much on the architecture of each of the copolymers in the mixture. The discussion will be limited to the value of $i(0)$ summarizing recent results.[16] We define the following averages:

$$\langle u \rangle = \frac{\sum \nu_i n_i^2 u_i}{\sum \nu_i n_i^2} \qquad \langle u^2 \rangle = \frac{\sum \nu_i n_i^2 u_i^2}{\nu_i n_i^2} \tag{20}$$

and the quantity $\langle \Delta u^2 \rangle = \langle u^2 \rangle - \langle u \rangle^2$. With these notations eq 1 becomes

$$i_0(0) = N_w \langle \Delta u^2 \rangle \tag{21}$$

calling N_w the quantity $\sum \nu_i n_i^2 / \sum \nu_i n_i$, the weight average degree of polymerization.

As soon as the system is heterogeneous in composition $i_0(0)$ increases and can become important if $\langle \Delta u^2 \rangle$ is large. It has been shown,[7] in the case of a diblock copolymer where the average length of each block is the same and obeys a Zimm–Schulz[17,18] length distribution, that the maximum of $i_0(q)$ disappears as soon as for each block $N_w/N_n = 2$; above this value the curve decreases monotonically when q increases.

Scattering Intensity of a Mixture of a Homopolymer and a Block Copolymer. Qualitatively it seems that if one adds to a copolymer a homopolymer of larger molecular weight one should have at low q the scattering of the dilute solution of the homopolymer, therefore, a sharp decrease of the scattered intensity when q increases. At large q, the scattering of the homopolymer should be negligible, and one should obtain the peak characteristic of the block copolymer.

In fact, this is an oversimplification, and, in order to study this problem quantitatively, we shall discuss the following example. A mixture is made of (a) a volume fraction φ of a homopolymer (type a or b) with degree of polymerization n_0 and (b) a diblock symmetrical copolymer with volume fraction $1 - \varphi$ and degree of polymerization n:

$$i_0(q) = \frac{1}{8}\,\frac{(1-\varphi)n(P_a(q) - P_{ab}(q)) + 2\varphi n_0 P_0(q)(P_a(q)/P(q))}{1 + (\varphi n_0/(1-\varphi)n)(P_0(q)/P(q))} \tag{22}$$

where $P_0(q)$ is the structure factor of the homopolymer and $P(q)$ is the total structure factor of the copolymer following eq 4. If $q = 0$, then

$$i_0(0) = \frac{1}{8}\,\frac{2\varphi n_0}{1 + \varphi n_0/(1-\varphi)n} \tag{23}$$

This intensity has to be larger than the intensity at the peak for the copolymer alone, which is of the order of $^1/_8(n/2)$. We have to choose, therefore, in order to satisfy the inequality

$$\frac{4\varphi(n_0/n)}{1 + (\varphi/(1-\varphi))(n_0/n)} > 1 \tag{24}$$

On the other side, $(\varphi n_0)/(1-\varphi)n)$ has to be of the order of unity in order for the copolymer effect to be seen. This gives φ a rather narrow bracket in the vicinity of $\varphi \sim (n/n_0)$. As an example, parts a and b of Figure 2 give $i_0(q)$ for the case $n_0 = 20n$ and different values of φ. One sees, as predicted qualitatively, a curve presenting a minimum and a maximum (the best one for $\varphi = 0.8n/n_0$). In other cases one has either a maximum or a continuously decreasing curve. The same behavior as above has been observed by a mixture of two block copolymers of the same molecular weight but different composition.[27] These two examples show that it is possible, from a theoretical point of view, to prepare mixtures of copolymers and homopolymers with almost any desired scattering shape.

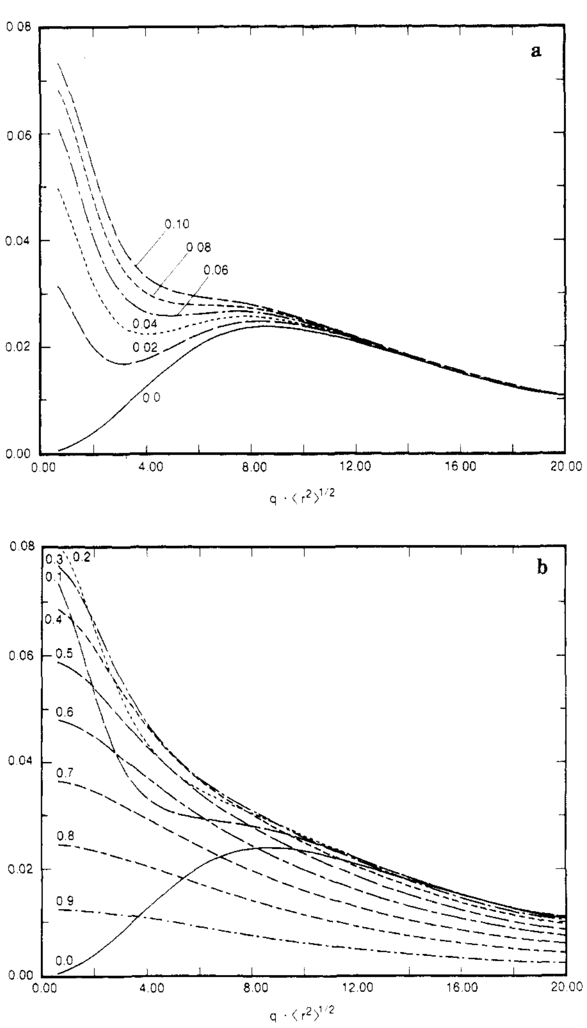


Figure 2. Scattering profiles from a mixture of a two-block copolymer AB ($u = 0.5$) with a homopolymer, having radii of gyration in a ratio of 4.47. The scattering curves have been drawn for different concentrations φ: (a) $\varphi = 0.0$–0.1; (b) $\varphi = 0.1$–0.9.

Phase Separation Behavior of Block Copolymers. With eq 14 or 14′, it is possible to describe the phase separation behavior of the block copolymers when χ increases from zero to the critical value, $\chi_c = 1/2m$, where the scattered intensity becomes infinite and the system reaches the spinodal and phase separates. In a monomolecular block copolymer where there is a maximum $q^* \neq 0$ (Figure 4a), the phase separation leads to a mesomorphic state with two phases present, one liquid and one mesomorphic. However in a polymolecular block copolymer when χ increases, the scattered intensity for some cases becomes infinite first at $q = 0$, which means that we have a classical liquid–liquid phase separation. The above arguments predict the formation of the two phases, but a more rigorous analysis is required to determine their exact composition. The phase separation of a polymolecular block copolymer could be compared to a kind of fractionation in the bulk since it leads to two liquid phases. A combination of the above two cases could be present in one single system. Figure 3a represents a typical example where it is possible that $I_0(0) = I(q^*) = m$, which will lead to three phases in equilibrium: two liquid and one mesophase. And a last, more general (but not least) case is represented by Figure 3b, where $I(q^*) = I(q^{**}) = m$, with which we should obtain four phases in equilibrium: two liquids and two mesophases. These conclusions are speculative, but it should be possible to see them verified experimentally. Already observations in the mesomorphic

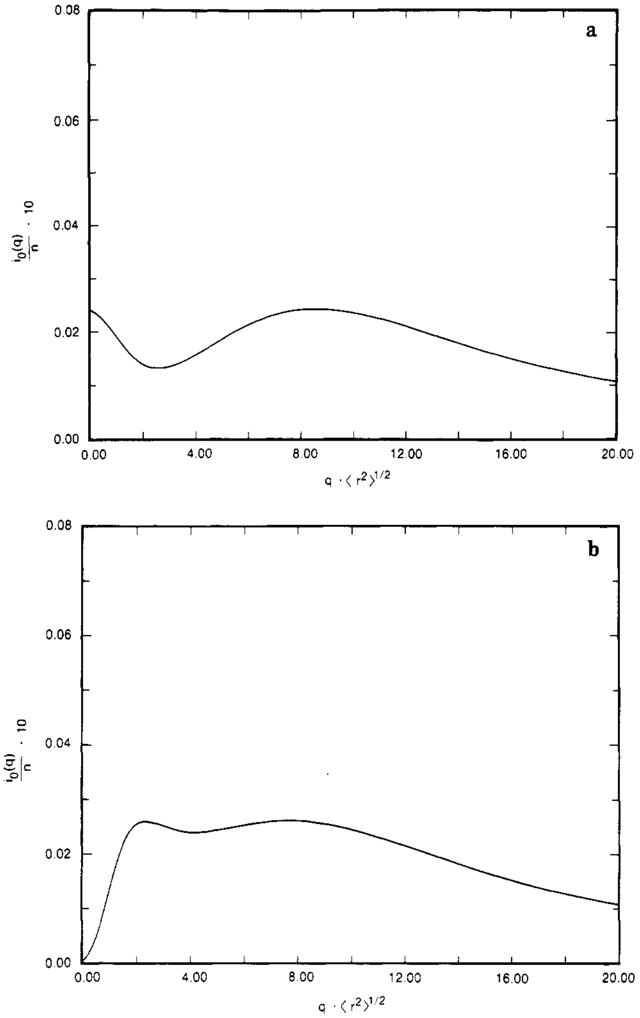


Figure 3. Schematic representation of scattering profile: (a) from a mixture of a two-block copolymer and homopolymer with $\zeta = 0.049$ where $I(0) = I(q^*) = m$; (b) from a mixture of two two-block copolymers having $u = u_1 = 0.5$ and $r > r_1$ with $\zeta = 0.047$ where $I(q^*) = I(q_1^{**}) = m$.

state proved the existence of the two mesophases in one case and the liquid and mesophase in another.[19]

Laws of Scattering and Properties of Block Copolymers Having a Large Number of Sequences

General Scattering Laws. As was mentioned in the Introduction, we will discuss the scattering behavior and the properties of multiblock copolymers made of two types of monomeric units, A and B. We consider three different architectures: (a) a copolymer made of N identical A and B sequences alternately attached to one another in a so-called "linear" structure, $-(\mathrm{A{-}B})_N-$; (b) a copolymer where the backbone is made out of the B sequences and the A sequences are laterally equally spaced, the so-called "comb" structure, $-(\mathrm{B}(-\mathrm{A}))_N-$; (c) and a block copolymer with each branch made out of an A–B block copolymer the "star" structure, $(\mathrm{B{-}A})_N-$.

Each sequence A and B is made of n_a and n_b monomer units, respectively. The quantities $u = n_\mathrm{a}/(n_\mathrm{a} + n_\mathrm{b})$ and $v = n_\mathrm{b}/(n_\mathrm{a} + n_\mathrm{b})$ characterize the composition of the building sequence A–B, a measure of the relative length of the blocks and the total composition of the block copolymer. In order to calculate the scattering intensity, $I(q)$, from the above architectures, the first step is to evaluate $P_\mathrm{A}(q)$, $P_\mathrm{B}(q)$, $P_\mathrm{AB}(q)$, and $P(q)$ as a function of the structure of the blocks and the number N. The above exercise has been done at least partially by different authors,[2,4,8-12] but we have made the calculation in a more systematic way: the details of the calculation are given in Appendix I; here we will give only the results. In the calculation we assumed that there are no correlations between the orientations of the blocks, and in the first step we assumed nothing about the statistics of the blocks. For the "linear" $-(\mathrm{A{-}B})_N-$ block copolymer we obtained

$$N^2P_\mathrm{A}(q) = NP_\mathrm{a}(q) + 2A_\mathrm{a}^2(q)x_\mathrm{b}\left[\frac{N}{1-x} - \frac{1-x^N}{(1-x)^2}\right] \tag{25}$$

$$N^2P_\mathrm{B}(q) = NP_\mathrm{b}(q) + 2A_\mathrm{b}^2(q)x_\mathrm{a}\left[\frac{N}{1-x} - \frac{1-x^N}{(1-x)^2}\right] \tag{26}$$

$$N^2P_\mathrm{AB}(q) = A_\mathrm{a}(q)A_\mathrm{b}(q)\left[\frac{1-x^N}{1-x} + \frac{2}{1-x}\left(N - \frac{1-x^N}{1-x}\right)\right] \tag{27}$$

For the "comb" $-(\mathrm{B}(-\mathrm{A}))_N-$ block copolymer we obtained

$$N^2P_\mathrm{A}(q) = NP_\mathrm{a}(q) + 2A_\mathrm{a}^2(q)x_\mathrm{b}\left[\frac{N}{1-x_\mathrm{b}} - \frac{1-x_\mathrm{b}^N}{(1-x_\mathrm{b})^2}\right] \tag{28}$$

$$N^2P_\mathrm{B}(q) = NP_\mathrm{b}(q) + 2A_\mathrm{b}^2(q)\left[\frac{N}{1-x_\mathrm{b}} - \frac{1-x_\mathrm{b}^N}{(1-x_\mathrm{b})^2}\right] \tag{29}$$

$$N^2P_\mathrm{AB}(q) = A_\mathrm{a}(q)A_\mathrm{b}(q)\left[\frac{1-x_\mathrm{b}^N}{1-x_\mathrm{b}} + \frac{2}{1-x_\mathrm{b}}\left(N - \frac{1-x_\mathrm{b}^N}{1-x_\mathrm{b}}\right)\right] \tag{30}$$

For the "star" $(\mathrm{B{-}A})_N-$ block copolymer we arrived at

$$N^2P_\mathrm{A}(q) = NP_\mathrm{a}(q) + N(N-1)A_\mathrm{a}^2(q) \tag{31}$$

$$N^2P_\mathrm{B}(q) = NP_\mathrm{b}(q) + N(N-1)A_\mathrm{b}^2(q)e^{-2q^2r_\mathrm{a}^2} \tag{32}$$

$$N^2P_\mathrm{AB}(q) = NA_\mathrm{a}(q)A_\mathrm{b}(q) + N(N-1)A_\mathrm{a}(q)A_\mathrm{b}(q)e^{-q^2r_\mathrm{a}^2} \tag{33}$$

In eq 25–33 $P_\mathrm{a}(q)$ and $P_\mathrm{b}(q)$ are the structure factor of each block, and their definition is similar to the one given in the eq 2, where i is either a or b and the sign $\langle\ \rangle$ indicates that the quantity in the bracket has to be averaged over all conformations and orientations. The quantities $A_\mathrm{a}(q)$ and $A_\mathrm{b}(q)$ are defined as

$$A_\mathrm{a}(q) = \frac{1}{n_\mathrm{a}}\sum_{j=1}^{n_\mathrm{a}} \langle \exp(-i\vec{q}\vec{r}_{1i})\rangle \tag{34}$$

$$A_\mathrm{b}(q) = \frac{1}{n_\mathrm{b}}\sum_{j=1}^{n_\mathrm{b}} \langle \exp(-i\vec{q}\vec{r}_{1i})\rangle \tag{35}$$

The vector $\vec{r}_{1i}$ joins one end of the block to an arbitrary point. Moreover

$$x_\mathrm{a} = \langle \exp(-i\vec{q}\vec{r}_{1n_\mathrm{a}})\rangle \tag{36}$$

$$x_b = \langle \exp(-i\vec{q}\vec{r}_{1n_\mathrm{b}})\rangle \tag{37}$$

$$x = x_\mathrm{a}x_\mathrm{b} \tag{38}$$

$\vec{r}_{1n_\mathrm{a}}$ is the vector joining the ends of a block. These general formulas, eq 25–38, are valid for any structure of the blocks A and B.

In order to calculate the scattering intensity from a multiblock copolymer with a specific architecture, one has to specify more precisely the model to arrive at explicit results. We shall envisage two models, the Gaussian one where we assume the segments A and B to be both

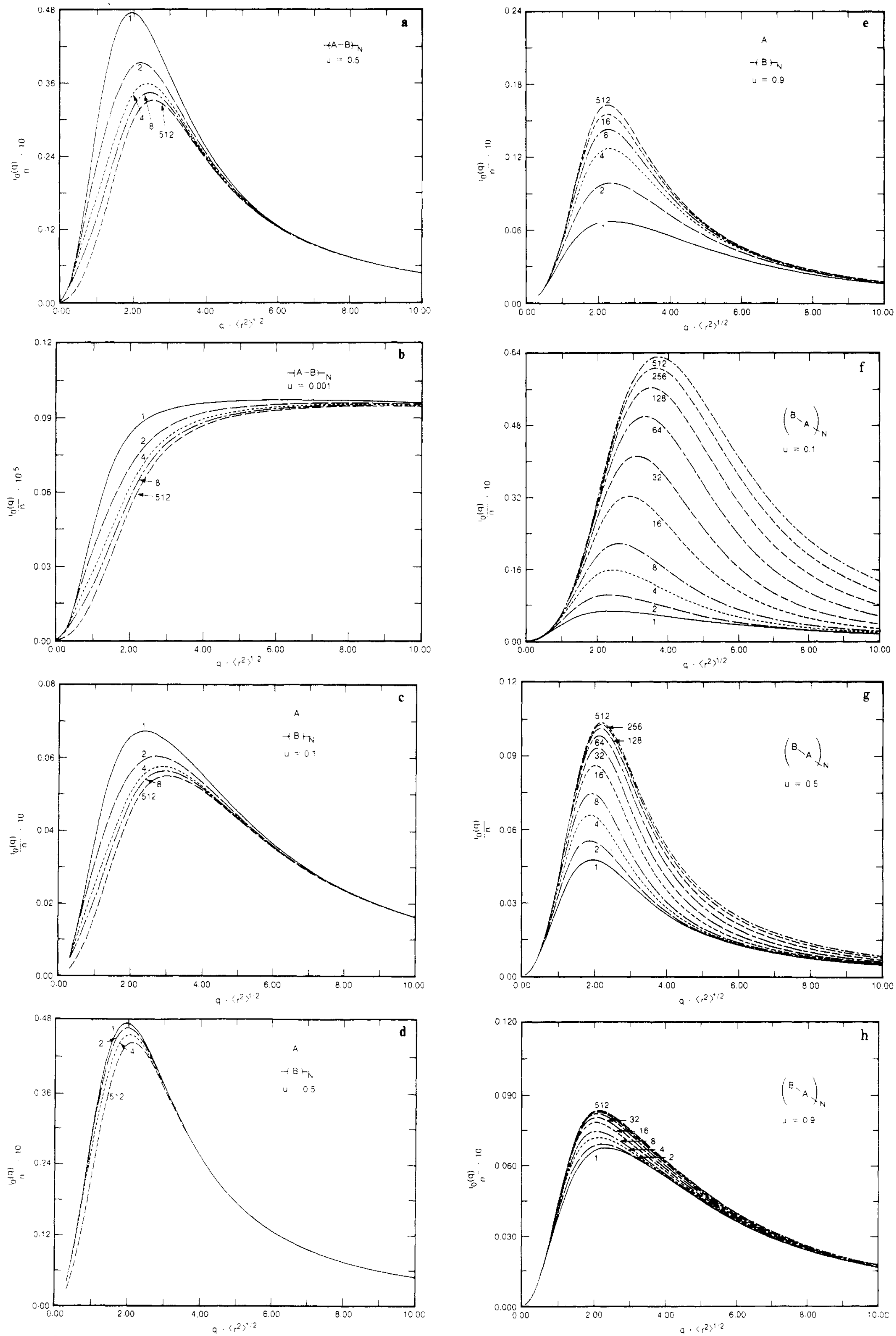


Figure 4. Scattering profiles of multiblock copolymers as a function of N with both blocks Gaussian: linear, $u = 0.5$ (a), $u = 0.001$ (b); comb, $u = 0.1$ (c), $u = 0.5$ (d), $u = 0.9$ (e); star, $u = 0.1$ (f), $u = 0.5$ (g), $u = 0.9$ (h).

Table I
Radii of Gyrations for the Three Architectures in the Monomolecular Case for the Gaussian (F–F) and Semiflexible (R–F or F–R) Model[a]

A–B	linear $-(\mathrm{A{-}B})_N-$	comb $-(\mathrm{B}(-\mathrm{A}))_N-$	star $(\mathrm{B{-}A})_N-$
F–F	$R_A{}^2 = N(r_a{}^2 + r_b{}^2) - r_b{}^2/N$	$R_A{}^2 = (3 - 2/N)r_a{}^2 + (N - 1/N)r_b{}^2$	$R_A{}^2 = (3 - 2/N)r_a{}^2$
	$R_B{}^2 = N(r_a{}^2 + r_b{}^2) - r_a{}^2/N$	$R_B{}^2 = Nr_b{}^2$	$R_B{}^2 = 6(1 - 1/N)r_a{}^2 + (3 - 2/N)r_b{}^2$
	$R_{AB}{}^2 = (r_a{}^2 + r_b{}^2)(N + 1/2N)$	$R_{AB}{}^2 = (^3/_2)\, r_a{}^2 + (N + 1/2N)r_b{}^2$	$R_{AB}{}^2 = 3(^3/_2 - 1/N)r_a{}^2 + {}^3/_2 r_b{}^2$
R–F	$R_A{}^2 = (\mathcal{R}^2/12N)(2(N - 1)N + 1) + (r_b{}^2/N)(N^2 - 1)$	$R_A{}^2 = (\mathcal{R}^2/12)(4 - 3/N) + (N - 1/N)r_b{}^2$	$R_A{}^2 = (\mathcal{R}^2/12)(4 - 3/N)$
	$R_B{}^2 = (\mathcal{R}^2/6)(N - 1/N) + Nr_b{}^2$	$R_B{}^2 = Nr_b{}^2$	$R_B{}^2 = (3 - 2/N)r_b{}^2 + (1 - 1/N)\mathcal{R}^2$
	$R_{AB}{}^2 = (\mathcal{R}^2/12)(2N + 1/N - 1) + (N + 1/2N)r_b{}^2$	$R_{AB}{}^2 = \mathcal{R}^2/6 + (N + 1/2N)r_b{}^2$	$R_{AB}{}^2 = (^3/_2)r_b{}^2 + (^2/_3 - N/2)\mathcal{R}^2$
F–R			$R_A{}^2 = (3 - 2/N)r_a{}^2$
			$R_B{}^2 = (\mathcal{R}^2/12)(4 - 3/N) + 6(1 - 1/N)r_a{}^2$
			$R_{AB}{}^2 = 3(^3/_2 - 1/N)r_a{}^2 + \mathcal{R}^2/6$

[a] F = flexible; R = ridig. $\mathcal{R}$ is the radius of gyration of the rigid block, and the other symbols are as defined in the text.

Gaussian, and the semiflexible one, where one of the blocks is rodlike[20] and the other Gaussian. For the Gaussian model, we shall distinguish two cases. For one case, where the blocks are monodisperse, we have the following functional dependence for $P_a(q)$, $P_b(q)$, $A_a(q)$, $A_b(q)$, x, x_a, and x_b:

$$P_a(q) = \frac{2}{q^4 r_a{}^4}(q^2 r_a{}^2 - 1 + e^{-q^2 r_a{}^2}) \tag{39}$$

$$P_b(q) = \frac{2}{q^4 r_b{}^4}(q^2 r_b{}^2 - 1 + e^{-q^2 r_b{}^2}) \tag{40}$$

$$A_a(q) = \frac{1 - e^{-q^2 r_a{}^2}}{q^2 r_a{}^2} \tag{41}$$

$$A_b(q) = \frac{1 - e^{-q^2 r_b{}^2}}{q^2 r_b{}^2} \tag{42}$$

$$x = e^{-q^2(r_a{}^2 + r_b{}^2)} \tag{43}$$

$$x_a = e^{-q^2 r_a{}^2} \tag{44}$$

$$x_b = e^{-q^2 r_b{}^2} \tag{45}$$

where r_a and r_b are the radii of gyration of the blocks A and B.

In the case where the blocks are polymolecular,[21,22] assuming a Zimm–Shultz[17,18] distribution (see Appendix II), we have

$$P_a(q) = \frac{2}{q^4 r_a{}^4}(q^2 r_a{}^2 - 1 + (1 + \epsilon q^2 r_a{}^2)^{-1/\epsilon}) \tag{46}$$

$$P_b(q) = \frac{2}{q^4 r_b{}^4}(q^2 r_b{}^2 - 1 + (1 + n q^2 r_b{}^2)^{-1/\eta}) \tag{47}$$

$$A_a(q) = \frac{1}{q^2 r_a{}^2}(1 - (1 + \epsilon q^2 r_a{}^2)^{-1/\epsilon}) \tag{48}$$

$$A_b(q) = \frac{1}{q^2 r_b{}^2}(1 - (1 + \eta q^2 r_b{}^2)^{-1/\eta}) \tag{49}$$

$$x = x_a x_b \tag{50}$$

$$x_a = (1 + \epsilon q^2 r_a{}^2)^{1/\epsilon} \tag{51}$$

$$x_b = (1 + \eta q^2 r_b{}^2)^{1/\eta} \tag{52}$$

$$\left(\frac{M_w}{M_n}\right)_A = 1 + \epsilon \tag{53}$$

$$\left(\frac{M_w}{M_n}\right)_B = 1 + \eta \tag{54}$$

where ϵ and η are the classical heterogeneity parameters.

For the semiflexible model where half of the blocks are rigid, the possibility of using the random phase approximation[1,3,5,6] is questionable because of the orientation correlation of neighboring rods; however, with our approach we are able to calculate the scattering intensity. This has to be done cautiously because the dependence of the mutual orientation of the rods is not taken into account. We believe that if the rodlike segments are short and imbedded in a sufficient amount of soft segments the error is not large and the formulas below can be used. For instance if the block A is a rigid rod with length $\mathcal{R}_a$ and the B block is Gaussian, we have

$$P_a(q) = \frac{2}{q\mathcal{R}_a}\int_0^{q\mathcal{R}_a} \frac{\sin \chi}{\chi}\, d\chi - \left(\frac{\sin (q\mathcal{R}_a/2)}{q\mathcal{R}_a/2}\right)^2 \tag{55}$$

$$A_a(q) = \frac{1}{q\mathcal{R}_a}\int_0^{q\mathcal{R}_a} \frac{\sin \chi}{\chi}\, d\chi \tag{56}$$

$$x_a = \frac{\sin q\mathcal{R}_a}{q\mathcal{R}_z} \tag{57}$$

For the B block, since it is Gaussian, the same formulas apply: eq 40, 42, and 45 for the monomolecular case and 47, 49, and 52 for the polymolecular case. The definitions of n_a, n_b, u, and v in the semiflexible model are not absolutely straightforward. These quantities do not appear in the form factors $P_A(q)$, $P_B(q)$, and $P_{AB}(q)$, but they appear in $P(q)$ as well as in the front factor (see eq 58). We could define n_a as the number of monomers of the Gaussian chain which occupy the same volume as the rod. In fact, we assumed in these theoretical calculations that $n_a = \mathcal{R}_a/\ell$, calling ℓ the length of the statistical element of the Gaussian chain and $u = r_a{}^2/(r_a{}^2 + r_b{}^2)$ or $u = n_a/(n_a + n_b)$.

Scattering by Monomolecular Multiblock Copolymers. 1. Behavior of Small Angles. We have seen in the first part and from eq 11 that $i(q)$ could be expressed at small q for the multiblock copolymers as

$$i(q) = nNu^2v^2\frac{q^2}{3}\bar{L}^2 \tag{58}$$

where $\bar{L}^2$ is the distance between the centers of mass G_A and G_B. In what follows, we are going to see how this quantity, $\bar{L}^2$, which is the initial slope of $i(q)$ versus q^2, depends on N. In Table I we present the results of the radii of gyrations, $R_A{}^2$, $R_B{}^2$, and $R_{AB}{}^2$, of the block copolymers having the three architectures and for the Gaussian and semiflexible models. From the values $R_A{}^2$, $R_B{}^2$, and $R_{AB}{}^2$ (Table I) and eq 10 we find, for the Gaussian model and all three architectures, that $\bar{L}^2$ has the value

$$\bar{L}^2 = \frac{2}{N}(r_a^2 + r_b^2) \tag{59}$$

where $r_a^2 + r_b^2$ is the radius of gyration of the sequence A–B. Inserting eq 59 into eq 58 shows that the scattered intensity is independent of N

$$i(q) = \tfrac{2}{3} n u^2 v^2 q^2 (r_a^2 + r_b^2) \tag{60}$$

Therefore, the initial slope should not depend on N. In fact, this is not observed (Figure 4a) and has to be related to the anomalous behavior of $P_A(q)$, $P_B(q)$, $P_{AB}(q)$, and $P(q)$ for $q = 0$. These quantities can be written for small angles as $1 - (N/3)q^2(r_a^2 + r_a^2)$ and have an infinite initial slope. The correct value is given by the use of the asymptotic limit of eq 64 for $N \to \infty$

$$i(q) = \tfrac{1}{6} n u^2 v^2 q^2 (r_a^2 + r_b^2) \tag{61}$$

which differs from eq 60 by the numerical factor 4.

2. Influence of the Number of Repeat Units N. The intensity scattered by the system depends on the number N. In order to see what this means physically, we shall assume that we have a constant number of monomers in the scattering volume or that the density of the system does not depend on the degree of polycondensation. Writing again eq 1, assuming that the number of segments is constant (Nvn = const), one obtains the scattered intensity per monomeric unit:

$$i_0(q) = nu^2v^2 \frac{N[P_A(q)P_B(q) - P_{AB}^2(q)]}{u^2P_A(q) + v^2P_B(q) + 2uvP_{AB}(q)} \tag{62}$$

There, if we keep the molar mass of the monomer constant, we plot the quantity

$$Y(q) = \frac{i_0(q)}{n} \tag{63}$$

as a function of $q\langle r^2\rangle^{1/2}$, calling $\langle r^2\rangle^{1/2}$ the square root of the radius of gyration of the building sequence A–B, and we see how the scattered intensity depends on N. In parts a, d, and g of Figure 4 we present the results for the three architectures: linear, comb, and star, assuming $u = v = 0.5$[28] and a Gaussian model. Very rapidly the intensity ($Y(q)$) becomes independent of N reaching an asymptotic value. We see that the peak, well known for $N = 1$, stays around $q\langle r^2\rangle^{1/2} \simeq 2$. Its shape is slightly modified and very rapidly reaches a constant form after a few decades of N. It is possible to obtain the equations giving the scattering intensity at the limiting case $N \to \infty$. The results for the linear block copolymer are

$$i_0(q) = nu^2v^2\left[\frac{2}{\lambda uv} - \frac{2}{\lambda^2u^2v^2}\,\frac{(1 - e^{-\lambda u})(1 - e^{-\lambda v})}{1 - e^{-\lambda}}\right] \tag{64}$$

where $\lambda = (q^2\ell^2)((n_a + n_b)/6)$. From Figure 4a and the above relation (eq 64), we conclude that as soon as N is large the scattered intensity does not depend any more on N. In Figure 5a we plotted the scattering intensity for $N \to \infty$ as a function $q\langle r^2\rangle^{1/2}$ for different values of u ($0 < u < 0.5$), this is sufficient since eq 64 is symmetric in u and $v = (1 - u)$. In the comblike copolymer we have also calculated $i_0(q)$ for $N \to \infty$

$$i_0(q) = nuv\left[\frac{2}{\lambda}\left(1 - \frac{1 - e^{-\lambda u}}{\lambda u}\right) + \frac{2u}{\lambda}\left(\frac{1 - e^{-\lambda u}}{\lambda u}\right)^2\left(\frac{e^{-\lambda u}}{1 - e^{-\lambda v}} - \frac{1}{\lambda u}\right)\right] \tag{65}$$

and present its variation as a function of $q\langle r^2\rangle^{1/2}$ for different values of u ($0 < u < 1$) (Figure 5b) since, in the case of comblike architecture, we do not have symmetry. For $u = 0.5$ Figure 4d shows that the difference between the curves $N = 1$ and $N = \infty$ is much smaller than in the case of the linear copolymer. The height of the maximum decreases only slightly with N, and its position is going toward larger q. We derived also the equation in the limiting case $N \to \infty$ for a starlike structure:

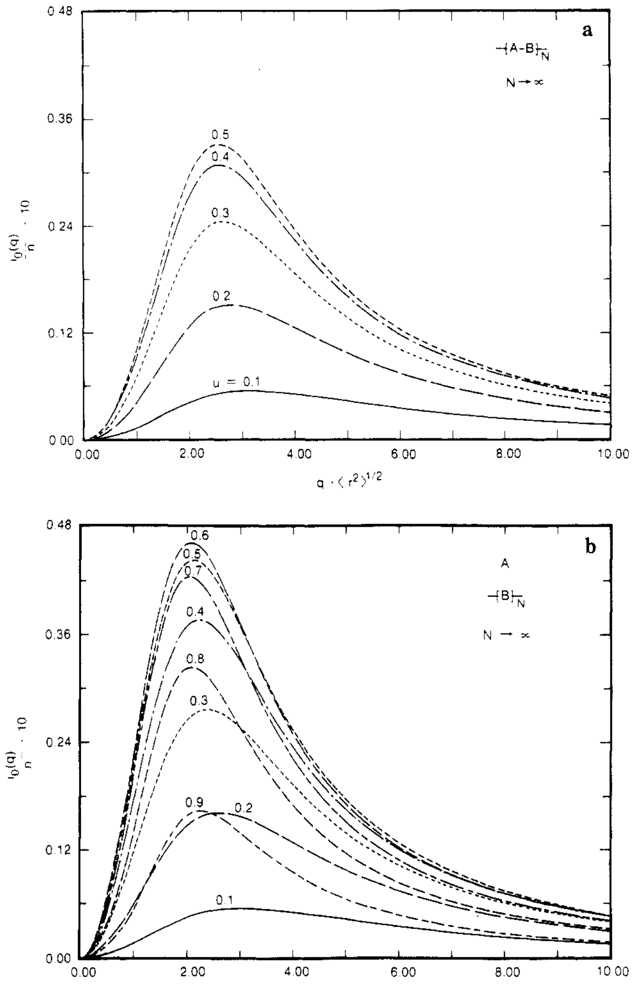


Figure 5. Scattering profiles of multiblock copolymers in the limiting case $N \to \infty$ as a function of u: (a) linear and (b) comb block copolymer.

$$i_0(q) = nu^2v^2\frac{A_a^2(q)P_b(q) + A_b^2(q)P_a(q)e^{-2\lambda u} - 2A_a^2(q)A_b^2(q)e^{-\lambda u}}{\lambda^{-2}(1 - e^{-\lambda})^2} \tag{66}$$

This is not very meaningful since the radius of the chain does not become infinite, and this does not allow enough room for the segments. For the semiflexible model when $N \to \infty$ and for $u = v = 0.5$, the results are almost similar to the ones depicted in parts a, d, and g of Figure 4. The only small difference is at the high q region where the q dependence of the $P_A(q)$ rigid block is different from that of the $P_B(q)$ flexible block.

3. Influence of the Composition u. One sees clearly in Figure 4b (linear Gaussian case) that when u decreases the maximum becomes less pronounced. This is due to the fact that when n_a decreases the structure factor $P_A(q)$ goes very slowly to zero when q increases. At very low values of n_a ($u = 0.001$) the scattering intensity reaches a limiting value at high q range, Figure 4b. Another way of looking into the composition influence on the scattering intensity is in Figure 5a, where we have plotted for $N \to \infty$

the limiting scattering intensity given by eq 64 for different values of u ($0 < u < 0.5$) as a function of $\lambda^{1/2} = q\langle r^2\rangle^{1/2}$. Regardless of the value of u one observes the same general behavior. It is only for very small values of u that the maximum moves to larger values of λ and becomes less and less pronounced. It is easy to see what happens if u is going to zero (let us say it is of the order $1/n$). In the range of λ where $e^{-\lambda}$ vanishes and $e^{-\lambda u}$ is equal to 1 eq 64 can be written as

$$i_0(q) = nu^2 \tag{67}$$

In order to see the physical meaning of this equation we go back to $I(q)$, the total intensity scattered by the ν chains, obtained with $u = 1/n$:

$$I(q) = \nu\frac{N}{n} = M \tag{68}$$

calling M the total number of blocks u in the system. This has been observed by de Gennes[1,5] for diblock copolymers and is generalized to multiblock copolymers, showing that in this case the scattering can be evaluated as if these segments are a perfect gas of independent particles. The limiting intensity (Figure 4b) at large q is proportional to the molecular weight of the block copolymer (e.g., 67 and 68). The same behavior is observed for the two other cases, comb and star Gaussian, when $u \rightarrow 0.001$. In the comblike architecture for $u < 0.5$ (Figure 4c), the maximum of the intensity decreases. For $u > 0.5$ (Figure 4e), the intensity increases when $N \rightarrow \infty$. For large u, this height increase is much less and the position of the peak is practically invariant. There is a large difference between the cases where $u \ll 1$ and $v \ll 1$; they correspond to two different architectures. For $u \ll 1$, the side chains are very small and there is similarity with the linear copolymer; for $v \ll 1$, the backbone is short and the molecule is similar to a star copolymer. We observe always an increase of the maximum in the starlike architecture when $N \rightarrow \infty$ but a faster increase for $u < 0.5$ (Figure 4f) rather than for $u > 0.5$ (Figure 4h). The above observations of the maximum intensity have implications on the phase behavior and miscibility of the multiblock copolymers, as we will see below. Another model we shall discuss is the semiflexible one in which one of the blocks is rigid. All the main features observed in the preceding cases are unchanged with some minor differences at the high q range due to the fact that the functions of $P_A(q)$ (rigid blocks A) and $P_B(q)$ (flexible blocks B) do not obey the same power law. One interesting result is that for $u = 0.99$ in the linear-like and $u = 0.9$ in the starlike architectures one obtains, as soon as N is larger than 2, a succession of oscillations due to the sin x/x factor (Figure 6a). This is very interesting because it shows that even in an isotropic liquid one can obtain a scattering intensity behavior much more sophisticated than expected, which could be easily interpreted by a crystallographer as a system partially crystallized.

Scattering by Polymolecular Multiblock Copolymers. Since the scattering intensity of a multiblock copolymer is essentially the same as the diagram of a diblock copolymer, all that has been said about mixtures of copolymers of the same composition and mixtures of a homopolymer with a copolymer remains valid. The only point which has to be added is that in this last case in order to have a minimum for $i_0(q)$ the homopolymer of degree of polymerization M has to satisfy the inequality $M \gg n$ and not $M \gg nN$.

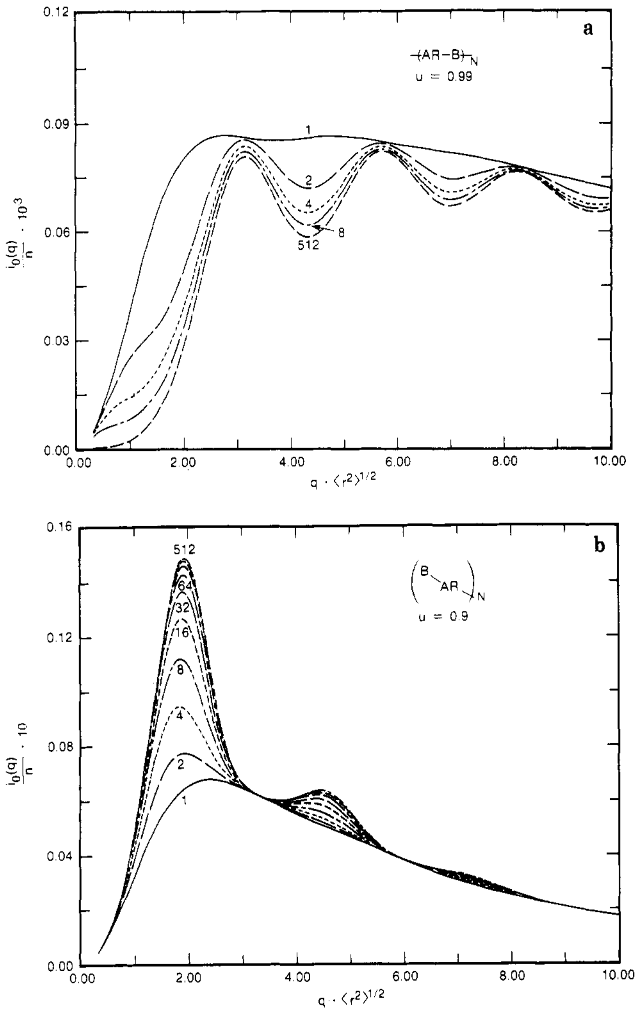


Figure 6. Scattering profiles of multiblock copolymers as a function of N with A-blocks rigid and B-blocks Gaussian: (a) linear, with $u = 0.99$; (b) comb, with $u = 0.9$.

It has been established that $i_0(q)$ does not depend on N (at least when $N > 10$). The only point which remains to be treated is the polymolecularity of the length of the segments a and b; this leads as a limiting case to the scattering by a statistical copolymer.[12] We show in the introduction of this section that it is possible to calculate the scattering intensity from a polymolecular system assuming a Zimm–Schultz[17,18] distribution, in the case of two block copolymers. Equations 46–54 give the results from our calculations (see Appendix II) in the case of Gaussian polymolecular A and B blocks. We define the polymolecularity of the blocks A and B by eq 53 and 54 or similarly by

$$\frac{n_{w_a}}{n_{n_a}} = 1 + \epsilon \tag{69}$$

$$\frac{n_{w_b}}{n_{n_b}} = 1 + \eta \tag{70}$$

n_w and n_n are the weight average and the number average molecular weight of each sequence, and ϵ and η are therefore the classical heterogeneity parameters. In the following the symbols n_a and n_b will be used for the number average degree of polymerization of the sequences as well as

$$u = \frac{n_{n_a}}{n_{n_a} + n_{n_b}} \tag{71}$$

$$v = \frac{n_{n_b}}{n_{n_a} + n_{n_b}} \tag{72}$$

and $n = n_{n_a} + n_{n_b}$. To take into account the polymolecularity the only thing to do is to replace the quantities $e^{-\lambda u}$ and $e^{-\lambda v}$ by the relations

$$(1 + \lambda u \epsilon)^{-1/\epsilon} \qquad (73)$$

$$(1 + \lambda v \eta)^{-1/\eta} \qquad (74)$$

which are equal to $e^{-\lambda u}$ and $e^{-\lambda v}$ for $\eta = \epsilon = 0$. The above substitution applies to all equations given in this paper under the strict condition that the chains are Gaussian. For instance the limiting linear case for $N \rightarrow \infty$, eq 64, becomes

$$i_0(q) = nuv\frac{2}{\lambda}\left[1 - \frac{1}{\lambda uv}\,\frac{(1 - (1 + \epsilon\lambda u)^{-1/\epsilon})(1 - (1 + \eta\lambda v)^{-1/\eta})}{1 - (1 + \epsilon\lambda u)^{-1/\epsilon}(1 + \eta\lambda v)^{-1/\eta}}\right] \qquad (75)$$

The above equation can be expanded as a function of λ, giving for the first terms

$$i_0(q) = nu^2v^2\left[(\epsilon + \eta) + \frac{\lambda}{6}\,(1 - \epsilon^2 u - \eta^2 v - 3(\eta + \epsilon)^2 uv) + \ldots\right] \qquad (76)$$

The first term of eq 76 is independent of the shape of the distribution. The result obtained here is therefore quite general and can be obtained from the general eq 62 and the consequent substitution eq 46–54 for the polymolecular Gaussian case of blocks and eq 25–33 for the three architectural structures. One can show then that if N is not infinite

$$i_0(0) = nu^2v^2\frac{\epsilon + \eta + \epsilon\eta/N}{1 + (u^2\epsilon + v^2\eta)/N} \qquad (77)$$

which reduces to eq 76 for large values of N. If one assumes $\epsilon = \eta$ and $u = v = 0.5$, one obtain

$$i_0(0) = \frac{n}{8}\epsilon \qquad (78)$$

Regardless of the values of u, v, ϵ, and η, the intensity $i_0(0)$, which is zero for a monodisperse system, increases when ϵ and η increase. The initial slope s depends on the shape of the molecular weight distribution curve. More general formulas could have been established introducing for each sequence not only n_n and n_w but also n_z, but this makes the equations cumbersome and is useless unless one has to explain experimental results. The initial slope is proportional to the quantity given by

$$s = 1 - \epsilon^2 u - \eta^2 v - 3(\eta + \epsilon)^2 uv \qquad (79)$$

For $\epsilon = \eta = 0$ one recovers a known result, the slope is positive, and when the polymolecularity increases its sign changes.[7] This can be considered as a measure of the limit between systems giving mesomorphic phases and the classical liquid–liquid phase separation. The equation of this limit is therefore

$$\epsilon^2 u + \eta^2 v + 3(\epsilon + \eta)^2 uv = 1 \qquad (80)$$

Assuming $v = v = {}^1/_2$ and $\epsilon = \eta$ it gives $\epsilon = \eta = 0.5$. This means that for $\epsilon = \eta < 0.5$ one has a peak and for $\epsilon = \eta > 0.5$ the peak disappears. The above result is slightly different from the result obtained by Leibler and Benoit[7] for the diblock copolymer since in their case ($u = v$, $\eta = \epsilon$) the limit was reached for $\epsilon = \eta = 1$. It appears that the polymolecularity affects more the multiblock copolymers than the diblock ones. As an example, in parts a and b of Figure 7 we give the results for a diblock copolymer and a multiblock one, respectively, with $u = v = 0.5$ and $\epsilon = \eta = 0.5$ in one case and $\epsilon = \eta = 1$ in another. The initial slope is zero for the multiblock copolymer, when $M_w/M_n = 1.5$ (eq 80) and not 2 as in the diblock case.

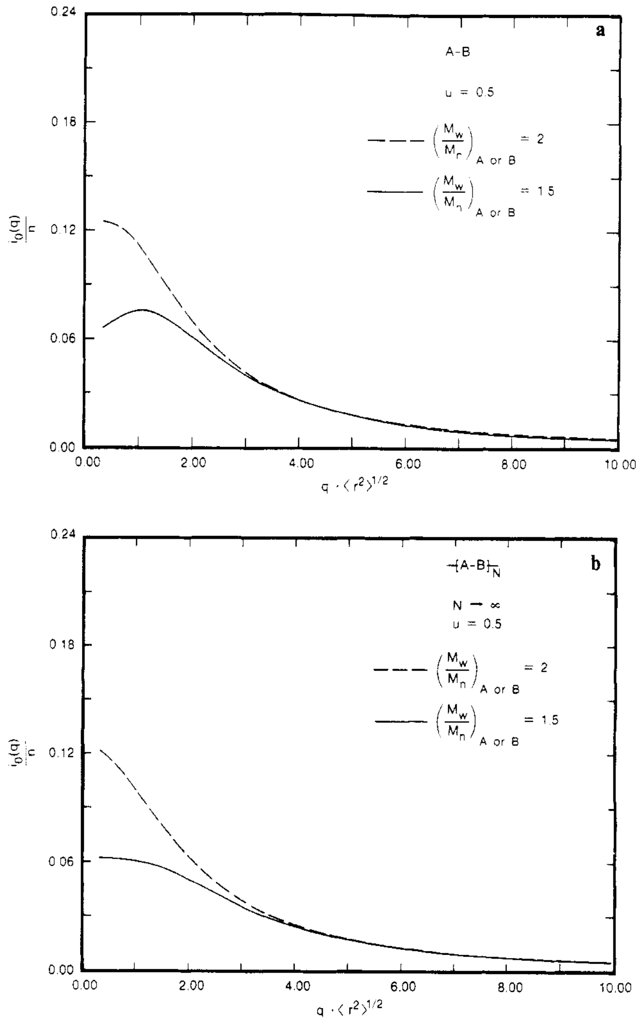


Figure 7. Scattering profiles of (a) a diblock copolymer with $u = 0.5$ and (b) a multiblock linear block copolymer: $N \rightarrow \infty$, $u = 0.5$, $M_w/M_n = 2$, $M_w/M_n = 1.5$.

Table II
Radii of Gyration of the Linear and Comb Multiblock Copolymers in the Polymolecular Case

Linear

$R_A^2 = N(1 + 2\epsilon/N)r_a^2 + [(N - 1/N)/(1 + \epsilon/N)]r_b^2$

$R_B^2 = N(1 + 2\eta/N)r_a^2 + [(N - 1/N)/(1 + \eta/N)]r_b^2$

$R_{AB}^2 = (N(1 + {}^3/_2(\epsilon/N)) + 1/2N)r_a^2 + (N(1 + {}^3/_2(\eta/N)) + 1/2N)r_b^2$

$\bar{L}^2 = (N + 1/N)(r_a^2 + r_b^2) - (N - 1/N)(r_a^2/(1 + \eta/N) + r_b^2/(1 + \epsilon/N)) + \epsilon r_a^2 + \eta r_b^2$

Comb

$R_A^2 = [(1 + \epsilon)(3 - 2/N - 2\epsilon/N)/(1 + \epsilon/N)]r_a^2 + [(N - 1/N)/(1 + \epsilon/N)]r_b^2$

$R_B^2 = N(1 + 2\eta/N)r_b^2$

$R_{AB}^2 = {}^3/_2(1 + \epsilon)r_a^2 + (N + 1/2N + {}^3/_2\eta)r_b^2$

$\epsilon = (M_w/M_n)_A - 1; \quad \eta = (M_w/M_n)_B - 1$

In parts a–f of Figure 8 we present the influence of polymolecularity on the calculated intensity for the linear, comb, and star (four-arm) architectures in the Gaussian model. We observe that the slope becomes zero for M_w/M_n values between 1.5 and 2.0. In Table II we present the values for R_A^2, R_B^2, and R_{AB}^2 in the case of linear and comb architectures for the Gaussian polymolecular model. Here,

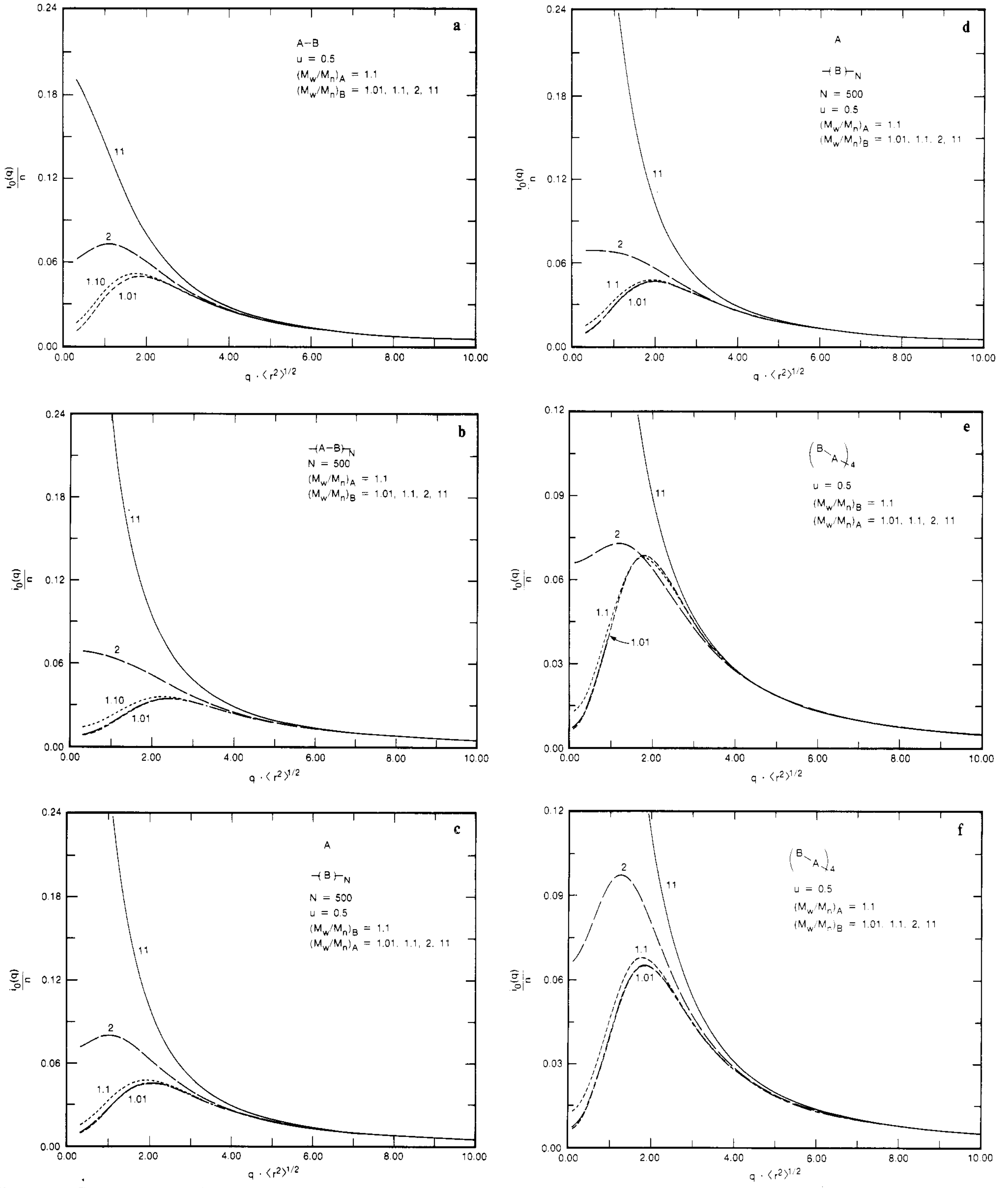


Figure 8. Scattering profiles as a function of polymolecularity: (a) diblock copolymer, $u = 0.5$; (b) linear block copolymer, $N \rightarrow \infty$, $u = 0.5$; (c) comb, A-blocks polymolecular, B-blocks monomolecular, $u = 0.5$; (d) comb, A-blocks monomolecular, B-blocks polymolecular, $u = 0.5$; (e) star (4 arms), A-blocks polymolecular, B-blocks polymolecular, u = 0.5; (f) star (4 arms), B-block monomolecular, A-block polymolecular, $u = 0.5$.

we do not find a unified $\bar{L}^2$ for the two models since its value is greatly dependent on the polydispersities of the two blocks. It is known that the polymolecularity does not affect the results in the intermediate domain ($1/R < q < 1/\ell$) significantly. This can be checked by the general formula or its asymptotic form:

$$i_0(q) = \frac{2nuv}{\lambda}\left(1 - \frac{1}{\lambda uv} + \frac{1}{\lambda N}\right) \tag{81}$$

If one plots $i_0(q)^{-1}$ as function of q^2 using the classical Zimm diagramm, one obtains in the intermediate q range an asymptotic straight line:

$$i_0(q)^{-1} = \frac{q^2\ell^2}{12nuv} + \frac{1}{2nu^2v^2} - \frac{1}{2nNuv} \tag{82}$$

Its slope, $\ell^2/12uv$, gives the statistical length of the chain. Its intercept $1/2nu^2v^2 + 1/2nNuv$ depends on n and N.

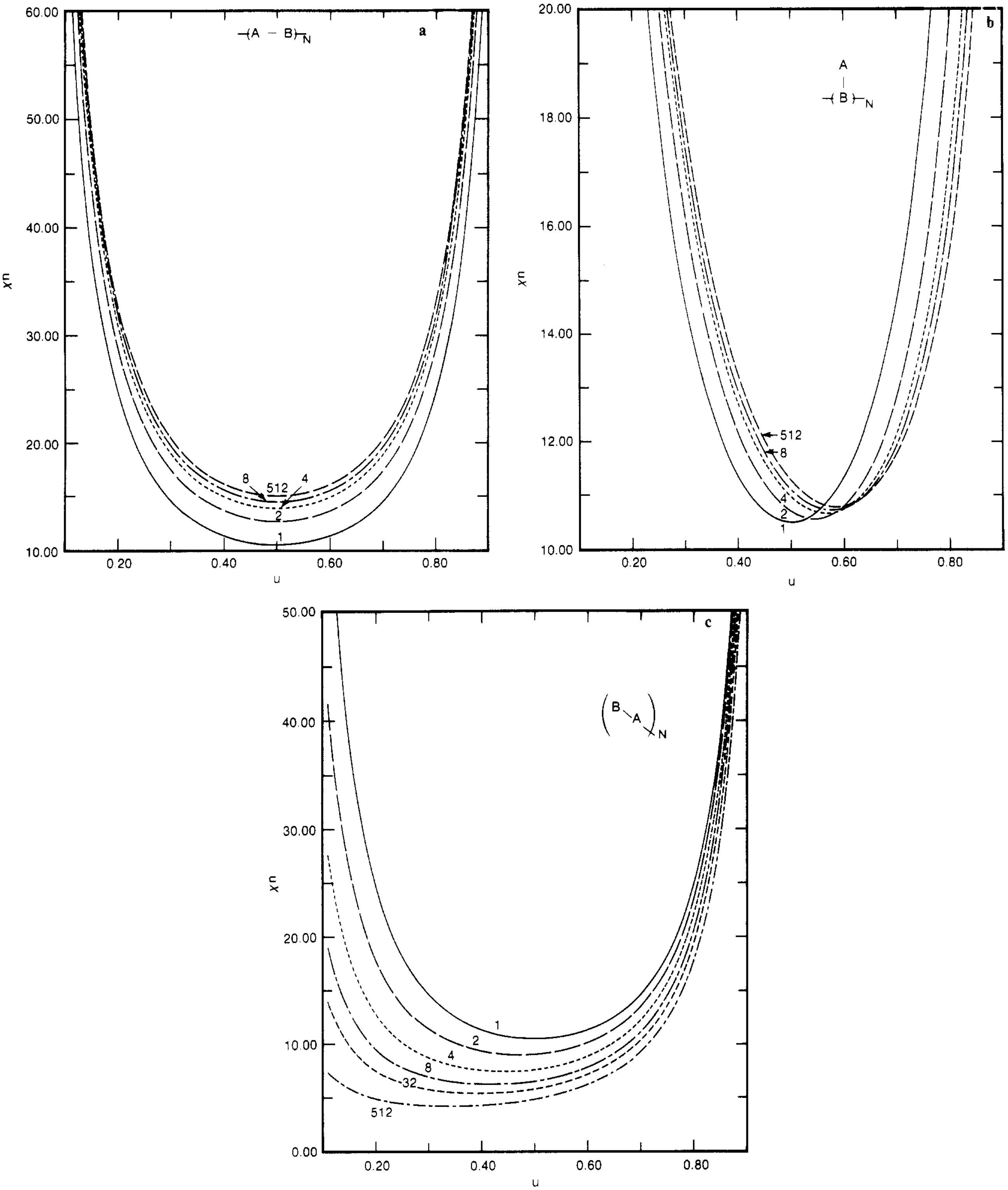


Figure 9. Phase diagram as a function of N for (a) linear, (b) comb, and (c) star multiblock copolymers.

If N is very large, the second term disappears and one obtains n, the number average of the molecular weight of the sequence A + B. If n is known this gives the possibility of measuring N, the degree of condensation of the copolymer. The above results are valid as well for comblike and starlike multiblock copolymers.

Phase Separation Behavior of Multiblock Copolymers. All the results presented in the preceding section were obtained assuming that the interaction parameter χ between unlike monomers was equal to zero. More precisely, what we have plotted on our scattering figures is the quantity $Y(q)$ defined by eq 62 and 63. If we now take χ into account, the intensity $i(q)$ will be given by eq 14, or using eq 63 we have

$$\frac{1}{i(q)} = \frac{1}{nY(q)} - 2\chi \tag{83}$$

By definition $i(q)$ is positive. This implies that

$$2\chi nY(q) \leq 1 \tag{84}$$

For all monodisperse systems which have been considered in this paper the quantity $Y(q)$ present a maximum m for a value of $q\langle r^2\rangle^{1/2}$, which shall be called $(q\langle r^2\rangle^{1/2})^*$. The

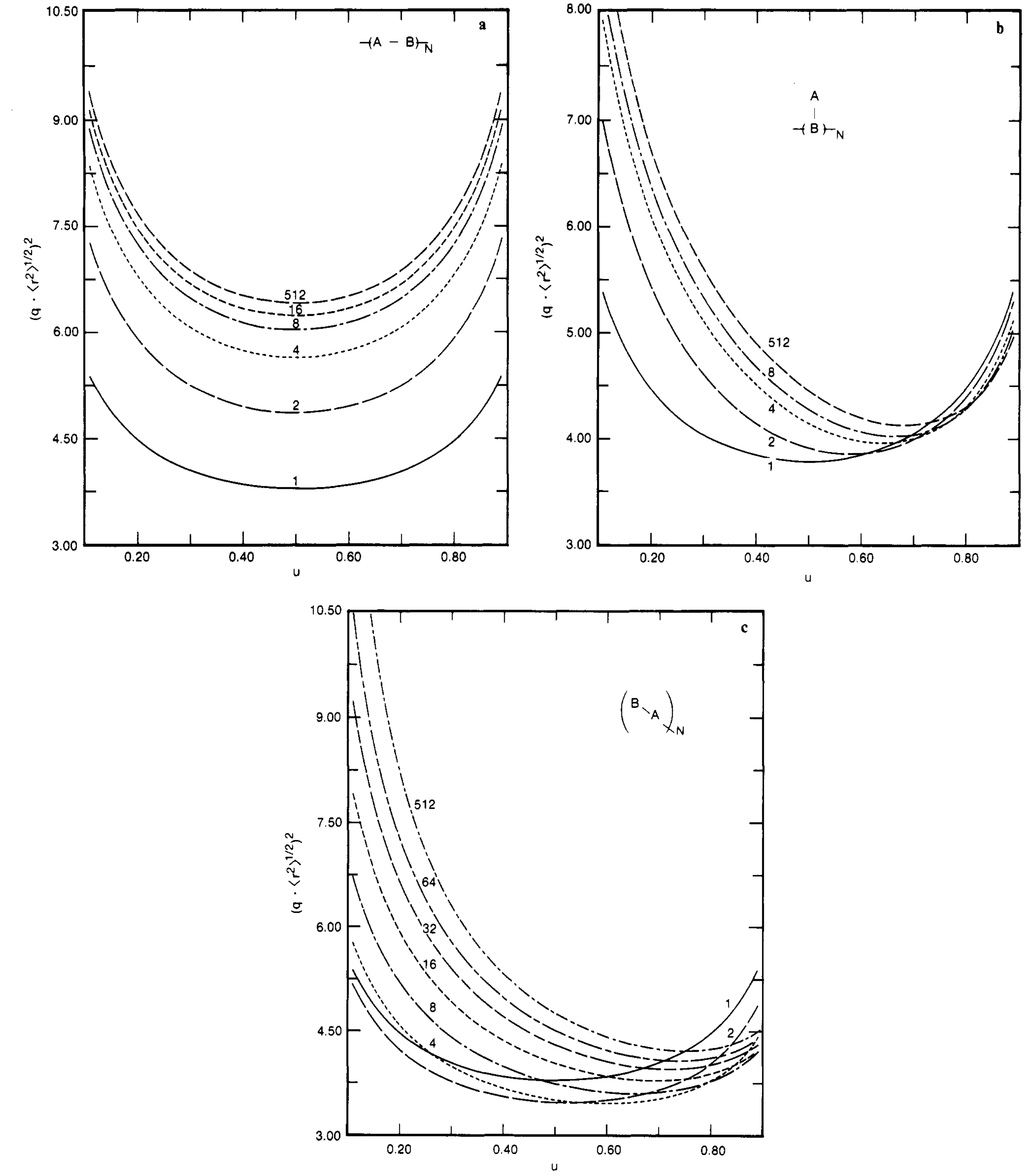


Figure 10. Plots of $(q^* \langle r^2 \rangle^{1/2})^2$ versus composition u as a function of N for (a) linear, (b) comb, and (c) star multiblock copolymers.

condition of existence of the system in the amorphous liquid is therefore

$$2\chi n \leq 1/m \qquad (85)$$

If the above condition is not fulfilled, the system cannot exist as an amorphous liquid and has to be mesomorphic with a characteristic distance of the order of $r^* = (q\langle r^2 \rangle^{1/2})^* q^{-1}$. (See Figure 10a–c for $(q\langle r^2 \rangle^{1/2})^*$ as a function of u.) In fact, this is only a rough assumption because this "mean-field" approach is not valid next to the spinodal.

In all the different architectures studied the quantity $Y(q)$ was reaching a value independent of N as soon as N was above approximately 20. This shows that the stability condition is independent of N and that the parameter governing the system is χn and not χN. This had to be expected. It could explain the interest of the multiblock copolymers. For these systems one can achieve compatibility between the blocks and keep the advantages of a large degree of polymerization.

1. Phase Diagram of Monomolecular Copolymers. It is possible, as pointed out by Leibler,[6] to determine the spinodal from eq 83 and from there the phase diagram for multiblock copolymers. In parts a–c of Figure 9 we present the phase diagrams for the three architectures, linear, comb, and star, and for the Gaussian model. The phase diagrams for the semiflexible model have also been calculated, but they are not presented here mainly because they have the same features as the Gaussian model. We observe in the linear case (Figure 9a) that when N increases the system becomes more miscible, but this effect is rather small. In the case of the binodal a similar result can be obtained by using the equations established by S. Krause,[23] which show also that when N is large the binodal becomes independent of N. The phase diagram in this case is always symmetric around the minimum, which is at $u = 0.5$. In the comblike case (Figure 9b), we also observe an increase of the miscibility when $N \rightarrow \infty$, but the minimum of the phase diagram moves from $u = 0.5$ for $N = 1$ to higher values of u when $N \rightarrow \infty$. This phase diagram for starlike block copolymers (Figure 9c) has been reported earlier.[11] Contrary to the previous examples, here, when the number of arms increases, the system becomes less compatible and more so for $u < 0.5$. This behavior lets us speculate that, in the case of network synthesis where the cross-linking material is different from the chains and small in quantity, $u < 0.1$ could lead to phase separation of the junctions at the different states of the reaction, thus producing an inhomogeneous system regarding the cross-links.[24] It has been shown by Leibler[6] that the minimum of the phase diagram corresponds to the point where the spinodal and the binodal are tangent and that it is therefore a critical point. We see that the critical point for the comb (Figure 9b) is found at $u = 0.58$, and the corresponding $\chi n = 10.8$, which is slightly higher than the value for the diblock A–B ($\chi n = 10.5$). It is also interesting to point out that the critical point in the comblike structure moves from $u = 0.58$ for $N = 2$ to higher values of u for $N \rightarrow \infty$, and also the value of χn tends to become higher.

2. Phase Diagram of Polymolecular Copolymers. As long as the polymolecularity is limited, it changes mainly the intensity at very low q values and does not affect the maximum. When it increases the maximum is shifted toward small q meaning, that the characteristic distance r_t^* increases (which is difficult to understand for the diblock copolymer). For large polymolecularity the maximum is obtained for $q = 0$. Equation 77, established for the linear copolymers, is valid for any structure; combined with eq 83 it yields

$$\frac{1}{2\eta\chi_c} = (\epsilon + \eta) = \left[\frac{n_{w_a}}{n_{n_a}} + \frac{n_{w_b}}{n_{n_b}} - 2\right] \tag{86}$$

We see also that χ_c does not depend on N. This result is not in contradiction with what has been said in the first part. One can say that $\langle \Delta n^2 \rangle$ is proportional to $1/N$, which eliminates N. In conclusion, a polymolecular copolymer can always be made self-compatible, which means that it has only one phase in the bulk if the average length of the sequences is short enough.

Scattering from Other Structures. Another model which can be used is a succession of objects bonded together by a free rotating linear chain. These objects are made of A and B segments but are such that their centers of mass G_A and G_B do not coincide $(G_AG_B)^2 \neq 0$. Such an object would also give in the bulk a scattering similar to what has been described. One can guess that this type of scattering should also exist in networks where there is a contrast between the junctions points and the chains. If one could consider the networks as an infinite chain, this would be rigorous, but the existence of loops makes a correct calculation very difficult. In fact, early experiences of Duplessix and Picot[25] having cross-links labeled with deuteriated molecules did show this type of scattering and suggest strongly that the explanation we are presenting here is valid.

Conclusion

In this paper, we have presented the generalization of what is known on two or three block copolymers to systems made of a large number of blocks. The main result is that this number N of sequences does not affect drastically the thermodynamical properties of the system and its scattering behavior. It shows also that the transition from isotropic liquid to mesomorphic state should occur at approximately the same temperature regardless of the number of sequences.

Acknowledgment. H. Benoit gratefully acknowledges the support of IBM France and IBM Almaden Research Center for the summer visits of 1985 and 1986 and Dr. C. Picot and Prof. S. Krause for their comments and discussions during the editing of the manuscript. G. Hadziioannou is thankful for criticism and help from G. ten Brinke.

Appendix I. Structure Factor Calculations for Multiblock Copolymers

Since the problem of the calculation of the structure factor of copolymers has already been discussed many times, we shall limit this Appendix to a summary of the method which we have used.

$P_A(q)$ and $P_B(q)$ for the Linear Multiblock Copolymers. Each molecule is made of N A–B sequences in which the A blocks are made of n_a monomeric units and the B blocks of n_b. The structure factor of $P_A(q)$ is

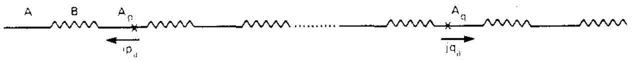
$$P_A(q) = \frac{1}{N^2 {n_a}^2} \sum_{ip_a=1}^{n_a} \sum_{jq_a=1}^{n_a} \sum_{p_a=1}^{N} \sum_{q_a=1}^{N} \langle \exp(-i\vec{q}(\vec{r}_{ip_a} - \vec{r}_{ip_a})) \rangle \tag{A1}$$

In the expression above $\vec{r}_{ip_a} - \vec{r}_{jq_a}$ is the vector joining the ith monomer of the A block p to the jth monomer of the A block q. The sign $\langle\ \rangle$ indicates that the average is taken over all conformations and orientations.

We now separate the terms for which $p = q$ and $p \neq q$. In the case $p = q$ one obtains the structure factor ${n_a}^2 P_a(q)$ of one block. When p and q are different one has the same result for $p > q$ and $p < q$ as long as $|p - q|$ is the same. Therefore we have

$$P_A(q) = \frac{P_a(q)}{N} + \frac{2}{N^2 {n_a}^2} \sum_{p_a<q_a}^{N} \sum^{N} \sum_{ip_a=1}^{n_a} \sum_{jq_a=1}^{n_a} \langle \exp(-i\vec{q}(\vec{r}_{iq_a} - \vec{r}_{jp_a})) \rangle \tag{A2}$$

In order to evaluate the exponential term one has to know the number of monomer units ψ between ip_a and jq_a. For this purpose one refers to the following diagram—counting i from the right to the left and j from the left to the right.



One sees immediately that the number ψ is

$$\begin{aligned} \psi &= i + n_a(q - p - 1) + n_b(p - q) + j \\ &= i + j + n(q - p - 1) + n_b \end{aligned} \tag{A3}$$

with $n = n_a + n_b$. If the chain has ψ segments, one can write in the case of Gaussian statistics

$$\langle \exp(-i\vec{q}(\vec{r}_{jq_a} - \vec{r}_{ip_a})) \rangle = \exp\left(-\frac{q^2 \ell^2 \psi}{6}\right) \tag{A4}$$

where q is the module of the scattering vector and ℓ the length of the statistical element. Writing

$$y = \exp\left(-\frac{q^2\ell^2}{6}\right)$$

we obtain for $P_A(q)$

$$P_A(q) = \frac{P_a(q)}{N} + \frac{2}{N^2 n^2_a}\sum_i^{n_a}\sum_j^{n_a}\sum_{p<q}^{N}\sum^{N} y^{\psi} \qquad \text{(A5)}$$

The summation on i and j is straightforward

$$\sum_{i=0}^{n_a} y^i = \frac{1 - y^{n_a}}{1 - y} = \frac{1 - e^{-\lambda n_a}}{\lambda} \quad \lambda = \frac{q^2\ell^2}{6}$$

This gives for $P_A(q)$

$$P_A(q) = \frac{P_a(q)}{N} + \frac{2}{N^2}\left(\frac{1 - e^{-\lambda n_a}}{\lambda n_a}\right)^2 y^{n_b}\sum_{p<q}^{N}\sum^{N} y^{n(q-p-1)} \qquad \text{(A6)}$$

After making the summation first with respect to p and then with respect to q, we replace $(1 - e^{-\lambda n_a})/\lambda n_a$ by $A_a(q)$, $e^{-\lambda n_b}$ by x_b, and $e^{-\lambda(n_a+n_b)}$ by x. We then have

$$N^2 P_A(q) = N P_a(q) + 2A_a^2(q) x_b\left[\frac{N}{1 - x} - \frac{1 - x^N}{(1 - x)^2}\right] \qquad \text{(A7)}$$

The expression for $P_B(q)$ is obtained by exchanging the index a by b.

$P_{AB}(q)$ for the Linear Multiblock Copolymers. With the same notation used previously, the expression for $P_{AB}(q)$ is

$$P_{AB}(q) = \frac{1}{N^2 n_a n_b}\sum_{ip_a}^{n_a}\sum_{jq_b}^{n_b}\sum_{p_a}^{N}\sum_{q_b}^{N}\langle\exp(-i\vec{q}(\vec{r}_{ip_a} - \vec{r}_{jq_b}))\rangle \qquad \text{(A8)}$$

Referring to a diagram similar to the one above one sees that the number ψ of segments between i and j is given by

$$\psi = i + j + n(p - q) \quad \text{if } q \geq p \qquad \text{(A9)}$$

or

$$\psi = i + j + n(p - q - 1) \quad \text{if } q < p$$

The summation of i and j leads to $A_a(q)$ and $A_b(q)$. To evaluate the sum over p and q, we make a square table with N lines corresponding to the N values of p and N columns:

q\p	1	2	3	4		p		N
1	1	y	y^2	y^3	•••	y^{p-1}	•••	y^{N-1}
2	1	1	y	y^2	•••	y^{p-2}	•••	y^{N-2}
3	y	1	1	y	•••	y^{p-3}	•••	y^{N-3}
4	y^2	y	1	1	•••	y^{p-4}	•••	y^{N-4}
⋮	⋮	⋮	⋮	⋮	⋱	⋮		⋮
p	y^{p-2}	y^{p-3}	y^{p-4}	y^{p-5}	•••	1	•••	y^{N-p}
⋮	⋮	⋮	⋮	⋮			⋱	⋮
N	y^{N-1}	y^{N-2}	y^{N-3}	y^{N-4}	•••••		1	1

The above table is not symmetrical and can be written as

$$T = (2N - 1) + (2N - 3)y + \{2N - (2p + 1)\}y^p + ... + y^{N-1} \qquad \text{(A10)}$$

or

$$T = (2N - 1)\sum_{p=0}^{N-1} y^p - 2y\sum_{p=1}^{N-1} p y^{p-1}$$

The first sum in the above formula is a geometric series $\sum_{p=0}^{N-1} y^p = S_1$, and the second is the first derivative of $S_1(S_2 = (\partial/\partial y)(S_1) = \sum_{p=1}^{N-1} p y^{p-1}$. After straightforward numerical calculations using the notations of eq A7 one obtains

$$N^2 P_{AB}(q) = A_a(q)A_b(q)\left[\frac{1 - x^N}{1 - x} + \frac{2}{1 - x}\left(N - \frac{1 - x^N}{1 - x}\right)\right] \qquad \text{(A11)}$$

$P_A(q)$, $P_B(q)$ and $P_{AB}(q)$ for the Comb Multiblock Copolymers. Let us consider the following model. All the B blocks are linearly linked together. The A blocks are regularly spaced on the B backbone. The evaluation of $P_A(q)$, $P_B(q)$, and $P_{AB}(q)$ does not need any new calculations. The quantity $P_B(q)$ is the structure factor of the backbone and could be written by using the Debye function for it (see eq 40 in text). However, it is more convenient to consider it as the asymptotic value of $P_B(q)$ for the linear block copolymer when the length of the block A is set equal to zero. Starting from eq A7 we have immediately

$$N^2 P_B(q) = N P_b(q) + 2A_b^2(q)\left[\frac{N}{1 - x_b} - \frac{1 - x_b^N}{(1 - x_b)^2}\right] \qquad \text{(A12)}$$

The reason we used this function instead of the Debye approximation is that we need precise information on the structure of the polymer at the scale of the radius of gyration (r_b) of the block B. Moreover if the blocks B are freely jointed segments at the grafting points this can be taken into account in this information.

For $P_A(q)$ one can use all that has been written for the linear block copolymer up to eq A3. At this stage ψ has to be written as

$$\psi = i + j + n_b(q - \mathrm{p}) \qquad \text{(A13)}$$

Equation A13 is equivalent to eq A3 when n_a goes to zero. Then $P_A(q)$ for the comb architecture is

$$N^2 P_A(q) = N P_a(q) + 2A_a^2(q) x_b\left[\frac{N}{1 - x_b} - \frac{1 - x_b^N}{(1 - x_b)^2}\right] \qquad \text{(A14)}$$

The same type of arguments is also valid for $P_{AB}(q)$, for which one gets

$$N^2 P_{AB}(q) = A_a(q)A_b(q)\left[\frac{1 - x_b^N}{1 - x_b} + \frac{2}{1 - x_b}\left(N - \frac{1 - x_b^N}{1 - x_b}\right)\right] \qquad \text{(A15)}$$

For the star multiblock copolymers the calculation is straightforward and has been reported earlier.[11,26]

Appendix II. Calculations of the Polymolecularity Effect

Assuming that all chains are Gaussian, one must, in order to evaluate $i_0(q)$, take into account the polymolecularity in the expressions of $N^2 n_a^2 P_A(q)$, $N^2 n_b^2 P_B(q)$, $N^2 n_a n_b P_{AB}(q)$, and $N^2(n_a + n_b)^2 P(q)$. For this purpose one has to multiply each of these quantities by its probability of occurrence and make an integration. Since it was shown that when N is large the value of $i_0(q)$ does not depend on N, we can replace this number by its average value. We shall therefore assume that polymolecularity comes uniquely from the length of the block or more precisely that we have a Zimm–Schultz[17,18] distribution for each sequence. We now introduce a reduced quantity $u = n/\langle n\rangle$, with $\langle n\rangle$ the number molecular weight of one sequence (a or b). This distribution can be written as

$$f(u)\,\mathrm{d}u = \frac{k^k}{\Gamma(k)}u^{k-1}\exp(-ku)\,\mathrm{d}u \qquad \text{(A16)}$$

where Γ is the function of the parameter k, which characterizes the width of the distribution $f(u)\mathrm{d}u$, the probability for a molecule to have a molecular weight between $n/\langle n\rangle$ and $(n + \mathrm{d}n)/\langle n\rangle$. From the above one verifies that

$$\int_0^\infty f(u)\,\mathrm{d}u = 1 \qquad \text{(A17)}$$

$$\int_0^\infty nf(u)\,\mathrm{d}u = \langle n\rangle \qquad \text{(A18)}$$

Moreover

$$n_\mathrm{w} = \frac{\langle n^2\rangle}{\langle n\rangle} = \langle n\rangle\frac{\int f(u)u^2\,\mathrm{d}u}{\int f(u)u\,\mathrm{d}u} = \langle n\rangle\frac{k+1}{k} \qquad \text{(A19)}$$

showing that the parameter

$$\epsilon = n_\mathrm{w}/n_\mathrm{n} - 1 \qquad \text{(A20)}$$

which characterizes the polymolecularity as being equal to $1/k$.

We shall need the average value of $e^{-\mu n}$, which is

$$\langle e^{-\mu n}\rangle = \int f(u)e^{-\mu\langle n\rangle u}\,\mathrm{d}u = (1 + \mu\langle n\rangle\epsilon)^{-1/\epsilon} \qquad \text{(A21)}$$

Let us now discuss the estimation of $\langle P_\mathrm{A}(q)\rangle$.

Following eq A17–A19

$$N^2{n_\mathrm{a}}^2P_\mathrm{A}(q) = \sum_{P=1}^{N}{n_\mathrm{a}}^2P_\mathrm{a}(q) + \sum_p\sum_q n_\mathrm{a}A_{\mathrm{a}_\mathrm{p}}(q)n_\mathrm{a}A_{\mathrm{a}_\mathrm{q}}(q){x_\mathrm{a}}^{p-q}{x_\mathrm{b}}^{p-q+1} \qquad \text{(A22)}$$

Since the last term involves a different segment one writes

$$\langle N^2{n_\mathrm{a}}^2P_\mathrm{A}(q)\rangle = N\langle{n_\mathrm{a}}^2P_\mathrm{a}(q)\rangle + \langle n_\mathrm{a}N_\mathrm{a}(q)\rangle^2\sum_p\sum_q{\bar{x}_\mathrm{a}}^{p-q}{\bar{x}_\mathrm{b}}^{p-q+1} \qquad \text{(A23)}$$

The evaluation of $\langle{n_\mathrm{a}}^2P_\mathrm{a}(q)\rangle$ has already been done

$$\langle{n_\mathrm{a}}^2P_\mathrm{a}(q)\rangle = \frac{2}{\mu^2}[\mu\langle n_\mathrm{a}\rangle - 1 + (1 + \mu\langle n_\mathrm{a}\rangle\epsilon_\mathrm{a})^{-1/\epsilon_\mathrm{a}}] \qquad \text{(A24)}$$

The same method gives

$$\langle n_\mathrm{a}A_\mathrm{a}(q)\rangle = \frac{1}{\mu}[1 - (1 + \mu\langle n_\mathrm{a}\rangle\epsilon_\mathrm{a})^{-1/\epsilon_\mathrm{a}}] \qquad \text{(A25)}$$

and

$$\bar{x}_\mathrm{a} = (1 + \mu\langle n_\mathrm{a}\rangle\epsilon_\mathrm{a})^{-1/\epsilon_\mathrm{a}} \qquad \text{(A26)}$$

$$\bar{x}_\mathrm{b} = (1 + \mu\langle n_\mathrm{b}\rangle\epsilon_\mathrm{b})^{-1/\epsilon_\mathrm{b}} \qquad \text{(A27)}$$

Here μ has been set equal to $q^2\ell^2/6$. One sees on this example that the rule which has been suggested is justified. It is sufficient to write everything as a function of $\langle n_\mathrm{a}\rangle$ or $\langle n_\mathrm{b}\rangle$ except the exponential, which has to be replaced by $(1 + \mu\langle n\rangle\epsilon)^{-1/\epsilon}$. (It is easy to show that for $\epsilon = 0$ one recovers $e^{-\mu\langle n\rangle}$.) Since the result is independent of N, it can as well be used for the formulas extrapolated to $N \rightarrow \infty$.

References and Notes

(1) de Gennes, P.-G. *J. Phys.* (*Les Ulis, Fr.*) **1970**, *31*, 235.
(2) Vitale, G. G.; LeGrand, D. G. *Macromolecules* **1976**, *9*, 749.
(3) Joanny, J. F.; Seances, C. R. *Acad. Sci., Ser. B* **1978**, *286B*, 89.
(4) LeGrand, A. D.; LeGrand, D. G. *Macromolecules* **1979**, *12*, 450.
(5) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*, Cornell University Press: Ithaca, NY, 1979; Chapter IX.
(6) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(7) Leibler, L.; Benoit, H. *Polymer* **1981**, *22*, 195.
(8) Wu, W.; Bauer, B. *Macromolecules* **1986**, *19*, 1613.
(9) Benmouna, L.; Benoit, H. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1227.
(10) Benoit, H.; Wu, W.; Benmouna, M.; Mozer, B.; Blauer, B.; Lapp, A. *Macromolecules* **1985**, *18*, 986.
(11) Olvera de la Cruz, M.; Sanchez, I. *Macromolecules* **1986**, *19*, 2501.
(12) Mori, K.; Tanaka, H.; Hashimoto, T. *Macromolecules* **1987**, *20*, 381.
(13) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1967; Chapter XII.
(14) Leng, M.; Benoit, H. *J. Polym. Sci.* **1962**, *57*, 263.
(15) Benoit, H., to be published.
(16) Benoit, H. In *Scattering, Deformation and Fracture in Polymers*; Wignall, G. D., Crist, B., Russell, T. P., Thomas, E. L., Eds.; Materials Research Society: Pittsburg, PA, 1987; Vol. 79, p 141.
(17) Schulz, G. V. *Z. Phys. Chem., Abt. B* **1939**, *43*, 25.
(18) Zimm, B. H. *J. Chem. Phys.* **1948**, *16*, 1099.
(19) Hadziioannou, G.; Skoulios, A. *Macromolecules* **1982**, *15*, 267.
(20) Luzzati, V.; Benoit, H. *Acta Crystallogr.* **1961**, *14*, 297.
(21) Ionescu, M. L. These de Docteur es-Sciences Physiques, Universite Louis Pasteur, Strasbourg, 1976.
(22) Ionescu, L.; Picot, Cl.; Duval, M.; Duplessix, R.; Benoit, H.; Cotton, J. P. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1019.
(23) Krause, S. *Macromolecules* **1970**, *3*, 84.
(24) Sony, V.; Stein, R. S., private communication.
(25) Duplessix, R. These de Docteur es-Sciences Physiques, Universite Louis Pasteur, Strasbourg, 1975.
(26) Benoit, H. *J. Polym. Sci.* **1953**, *11*, 561.
(27) Nojima, S.; Roe, R.-J. *Macromolecules* **1987**, *20*, 1866.
(28) In the symmetrical case $u = v = 0.5$ $P_\mathrm{A}(q) = P_\mathrm{B}(q)$; eq 62 is much simpler since one has the following relationship: $[P_\mathrm{A}(q)P_\mathrm{B}(q) - {P_\mathrm{AB}}^2(q)]/[u^2P_\mathrm{A}(q) + v^2P_\mathrm{B}(q) + 2uvP_\mathrm{AB}(q)] = [P_\mathrm{A}(q) - P_\mathrm{AB}(q)(P_\mathrm{A}(q) + P_\mathrm{AB}(q))/[{}^1/{}_2(P_\mathrm{A}(q) + P_\mathrm{AB}(q))] = 2(P_\mathrm{AB}(q) - P_\mathrm{AB}(q))$.