and have illustrated our method by using a poly[bis(*m*-chlorophenoxy)phosphazene] sample of known molecular weight distribution function. We have confirmed the bimodal distribution function of sample IIIe as determined by GPC analysis. Indirectly, we have also confirmed $b = 0.57$ for poly[bis(*m*-chlorophenoxy)phosphazene] in chloroform at 25 °C. A salient feature of our approach is the range of its applicability, since quasielastic light scattering can routinely measure diffusion coefficients from 10^{-6} to 10^{-9} cm^2/s. Thus, molecular weight distribution functions from 10^3 to 10^9 can be determined. Furthermore, only very small quantities of the solution are required to carry out the study and the measurement time is fairly short, in minutes under most circumstances.

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Small-Angle X-ray Scattering from Block Polymers. 3. Random Phase Approximation

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ABSTRACT: The random phase approximation (RPA) is used in the development of the theory for small-angle X-ray scattering from block copolymers which have not undergone microphase separation. Explicit expressions for the intensity of scattering as a function of scattering angle are presented for di-, tri-, and pentablock polymers and are shown to exhibit a reciprocity relation. Calculated scattering curves as a function of angle are presented for a variety of triblock structures, and it is suggested that the calculated maxima in some of the curves reflect the superposition of the RPA and a Debye function.

Information pertaining to the molecular structure of block polymers, both in dilute solution and the bulk state, is important in the development of a better understanding and an efficient use of such materials. In previous studies, we have calculated the expected small-angle X-ray scattering (SAXS) behavior of block polymers in dilute solutions and in the structured bulk state.[1,2] In these works, we adopted and extended the classic concepts and works of Debye. Recently, deGennes has proposed the use of the random phase approximation (RPA) in attempting to explain the X-ray scattering behavior of mono- and dihalogenated alkanes as presented by Brady and Coworkers.[3-6] At the suggestion of deGennes and our own interest in developing alternate models to predict the SAXS of block polymers, we have explored the use of RPA in calculating the SAXS from block polymers in the bulk state. It is believed that this model should be applicable to block polymers where microphase separation is not expected due to either small differences in cohesive energy density or the size of the comonomeric blocks is so small that geometric restrictions alone ensure random mixing.

Theory

We assume that the block polymer molecules are monodisperse in structure, composition, and molecular weight. As shown elsewhere, the expected SAXS intensity for a dilute solution would be given as

$$I(\mathbf{q}) = k_{\mathrm{B}}T\sum\sum\alpha_i\chi_{ij}{}^0(\mathbf{q})\alpha_j \qquad (1)$$

where α_i is the scattering amplitude for the ith monomer, $\mathbf{q}$ is the scattering wave vector, and $\chi_{ij}{}^0(\mathbf{q})$ is a response function and is proportional to the pair correlation function $P_{ij}{}^0(\mathbf{r})$ for two species on the chain.[1] For an ideal coil, $\chi_{ij}{}^0(\mathbf{r})$ is given by

$$\chi_{ij}{}^0(\mathbf{r}) = \frac{\rho}{Nk_{\mathrm{B}}T}P_{ij}{}^0(\mathbf{r}) \qquad (2a)$$

$$\chi_{ij}{}^0(\mathbf{r}) = \frac{\rho}{Nk_{\mathrm{B}}T}\,\frac{3}{(2\pi|i-j|\sigma^2)^2}\exp\left(-\frac{3r^2}{2|i-j|\sigma^2}\right) \qquad (2b)$$

When interactions between the species are taken into account by the use of the RPA (a brief discussion behind the use and physics of the RPA is presented in the Appendix), then instead of eq 1, one obtains[3]

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$$I(\mathbf{q}) = k_BT\sum\sum\alpha_i\chi_{ij}(\mathbf{q})\alpha_j \qquad (3)$$

and $\chi_{ij}(\mathbf{q})$ is given by

$$\chi_{ij}(\mathbf{q}) = \chi_{ij}{}^0(\mathbf{q}) - \frac{\sum_h\chi_{ih}(\mathbf{q})\sum_l\chi_{lj}(\mathbf{q})}{\sum_i\sum_j\chi_{ij}(\mathbf{q})} \qquad (4)$$

The first term in eq 4 represents the direct correlation function between species i and j on the same chain while the second term represents the effect of repulsion between the chains. As noted in the introduction, we expect this model to be applicable to block polymers wherein the differences in the cohesive energy density and size are small and in particular should not be applicable to systems which have undergone microphase separation.

If the double sum of the right hand side of eq 3 is written in the format of a matrix[1]

$$I(\mathbf{q}) = \left|\begin{array}{lll} \alpha_a{}^2\sum_1^m\sum_1^m & +\alpha_a\alpha_b\sum_1^m\sum_{m+1}^{m+n} & +\ldots \\ \alpha_a\alpha_b\sum_{m+n+1}^{2m+1}\sum_1^m & +\ldots & \\ \vdots & +\ldots & \\ \sum_{5m+5n+1}^{6m+5n}\sum_1^m & +\ldots & \\ \vdots & +\ldots & \end{array}\right| \qquad (5)$$

where the first block contains m segments of type a, the second n segments of type b, etc., and eq 4

$$\chi_{ij} = \chi_{ij}{}^0 - \frac{\sum_{h=1}^N\sum_{l=1}^N\chi_{ih}{}^0\chi_{lj}}{\sum_i\sum_j\chi_{ij}{}^0} \qquad (6)$$

is applied to each double sum within the brackets, then it is found that all sums are of the type

$$\sum_x^Y\sum_1^N\chi_{xj} = \sum_1^N\sum_x^Y\chi_{ix} \equiv 0 \qquad (7)$$

As a result of this condition, it is found that the equation for scattering for any block polymer will be given as

$$I(\mathbf{q}) = (\alpha_a - \alpha_b)^2\sum{}'\sum{}'\chi_{ij} \qquad (8)$$

and further, two or more mathematically equivalent expressions may be obtained depending on the number of blocks in the polymer chain.

As simple examples, the diblock case yields either

$$I(\mathbf{q}) = (\alpha_a - \alpha_b)^2\sum_1^m\sum_1^m\chi_{ij} \qquad (9a)$$

or

$$I(\mathbf{q}) = (\alpha_a - \alpha_b)^2\sum_{m+1}^N\sum_{m+1}^N\chi_{ij} \qquad (9b)$$

and the triblock case yields either

$$I(\mathbf{q}) = (\alpha_a - \alpha_b)^2\sum_{m+1}^{m+n}\sum_{m+1}^{m+n}\chi_{ij} \qquad (10a)$$

or

$$I(\mathbf{q}) = (\alpha_a - \alpha_b)^2\sum_1^m\sum_1^m\chi_{ij} + 2\sum_1^m\sum_{m+n+1}^N\chi_{ij} + \sum_{m+n+1}^N\sum_{m+n+1}^N\chi_{ij} \qquad (10b)$$

which is similar to the reciprocity relation discussed in many textbooks on scattering.

As our last example, we give the expression for a pentablock molecule, which may be written as either

$$I(\mathbf{q}) = (\alpha_a - \alpha_b)^2\left[\sum_{m+1}^{m+n}\sum_{m+1}^{m+n} + \ldots + 2\sum_{m+1}^{m+n}\sum_{2m+n+1}^{2m+n} + \sum_{2m+n+1}^{2m+n}\sum_{2m+n+1}^{2m+n}\right] \qquad (11a)$$

or

$$I(\mathbf{q}) = (\alpha_a - \alpha_b)^2\sum_1^m\sum_1^m + 2\sum_1^m\sum_{m+n+1}^{2m+n} + 2\sum_1^m\sum_{2m+2n+1}^{3m+2n} + 2\sum_{m+n+1}^{2m+n}\sum_{2m+2n+1}^{3m+2n} + \sum_{m+n+1}^{2m+n}\sum_{m+n+1}^{2m+n} + \sum_{2m+2n+1}^{3m+2n}\sum_{2m+2n+1}^{3m+2n} \qquad (11b)$$

or other combinations.

In order to obtain explicit equations for the scattering intensity for these examples, one needs the response functions for random coils which are

$$\chi_{ij}{}^0(\mathbf{q}) = \frac{\rho}{NkT}\exp[-b|i - j|] \qquad (12)$$

$$\sum_{h=1}^N\chi_{ih}{}^0(\mathbf{q}) = \frac{\rho}{NkT}\,\frac{1 + e^{-b} - (e^{-bi} + e^{-b(N+1-i)})}{1 - e^{-b}} \qquad (13)$$

$$\sum_i^N\sum_h^N\chi_{ih}{}^0(\mathbf{q}) = \frac{\rho}{NkT}N\frac{1 + e^{-b}}{1 - e^{-b}} - \frac{2e^{-b}(1 - e^{-Nb})}{(1 - e^{-b})^2} \qquad (14)$$

where $b = q^2a^2/6$.

Using eq 12, 13, 14 in eq 10, one arrives at the following equation for the triblock polymer for the case where the scattering is due primarily to the A species.

$$I_3(\mathbf{q}) = 2\frac{(\alpha_a - \alpha_b)^2\rho}{N}(1 - e^{-b})^{-2}\left[m(1 - e^{-2b}) - 2e^{-b}(1 - e^{-bm}) + e^{-b(n+1)}(1 - e^{-bm})^2 - \frac{2[m(1 - e^{-2b}) - e^{-b}(1 + e^{-b(m+n)} - e^{-bm} - e^{-bN})]^2}{[N(1 - e^{-2b}) - 2e^{-b}(1 - e^{-Nb})]}\right] \qquad (15)$$

The first term, i.e.,

$$\langle m(1 - e^{-2b}) - 2e^{-b}(1 - e^{-bm})\rangle(1 - e^{-b})^{-2}$$

corresponds to the scattering by the A species, the second term, i.e.,

$$e^{-b(n+1)}(1 - e^{-bm})^2(1 - e^{-b})^{-2}$$

is a correlation effect between the A species on the same chain, and the third term is a correlation hole due to the repulsion between chains.

When $m = 1$ and $n = N - 2$, eq 15 reduces to

$$I_3(\mathbf{q}) = \frac{2\rho(\alpha_a - \alpha_b)^2}{N}\left[1 + e^{-b(N-1)} - \frac{2(1 - e^{-bN})^2}{N(1 - e^{-2b}) - 2e^{-b}(1 - e^{-bN})}\right] \qquad (16)$$

which is equivalent to deGennes' case B, eq III 8 (3).

A similar procedure can be used for the pentablock copolymer.

It should be clear from eq 3–10 that as the number, size, type, and positioning of coblocks increase, the necessary mathematical manipulations to yield analytic expressions for the scattering becomes both tedious and cumbersome. As a result, a computer program was written to evaluate

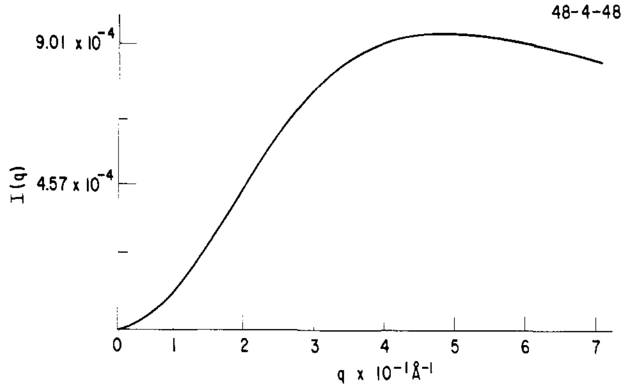

Figure 1. Calculated X-ray scattering intensity as a function of the wave vector (q) using the parameters in Table I where m = 48, n = 4, and N = 100.

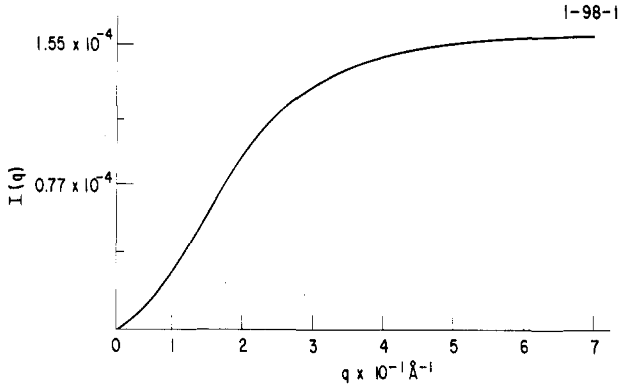

Figure 2. Calculated X-ray scattering intensity as a function of q where m = 1, n = 98, and N = 100.

Table I
Molecular Parameters

$a = 1.54$ Å $\alpha_a = 1.1$
$\lambda = 1.54$ Å $\alpha_b = 1$

the scattering as a structure for any given copolymer structure.[10] The program was checked by comparison with deGennes' results as well as with calculations for a given structure and scattering angle using a solid state hand calculator. Table I shows the molecular parameters used in the calculations.

Results

In order to make contact with the work of deGennes, we have calculated SAXS curves where instead of placing the dissimilar species at one or both ends of the chain they were placed near the center of the chain. These results are presented in Figure 1 and can be compared with deGennes' results shown in Figure 2 and with the results shown in Figure 3, where the species have been put on the end of the chain. The broad pronounced maximum in Figure 1 was unexpected, but close examination of Figure 3 also reveals a slight maximum. If one evaluates the position of these maxima in terms of a Bragg condition, then the range of correlation or the size of the correlated regions is of the order of 30 Å. In order to investigate this effect and its relation to molecular structure, we evaluated the scattering curves for other materials as shown in Figures 4 and 5. In Figure 4 we observe a significant change in the initial slope and a clearly defined maximum at $q \simeq 0.32$ Å.$^{-1}$ Similarly in Figure 5, the initial slope and the position of the maximum have changed.

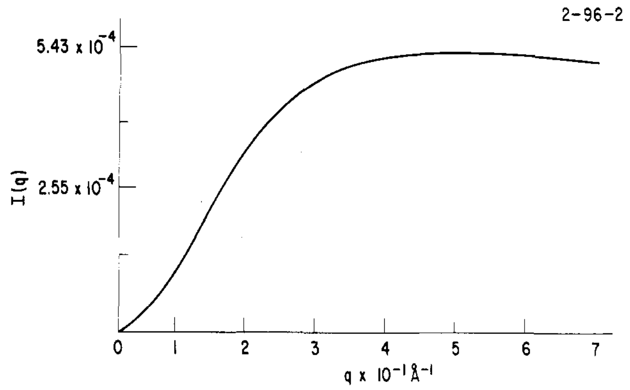

Figure 3. Calculated X-ray scattering intensity as a function of q where m = 2, n = 96 and N = 100.

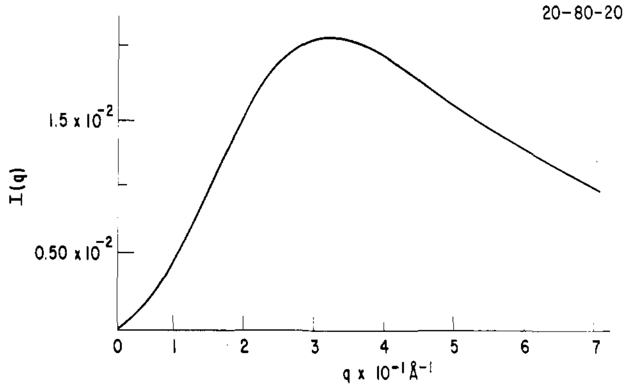

Figure 4. Calculated X-ray scattering intensity as a function of q where m = 20, n = 80, and N = 100.

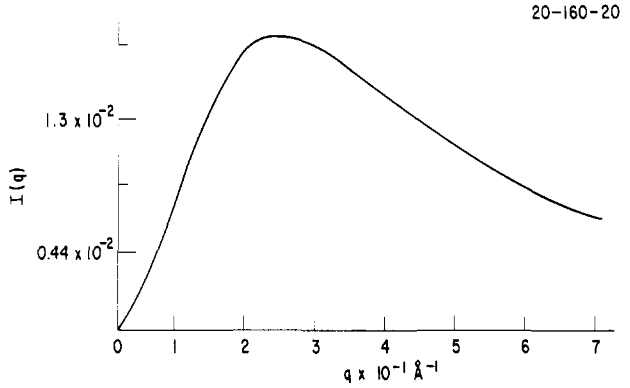

Figure 5. Calculated X-ray scattering intensity as a function of q where m = 20, n = 160, and N = 200.

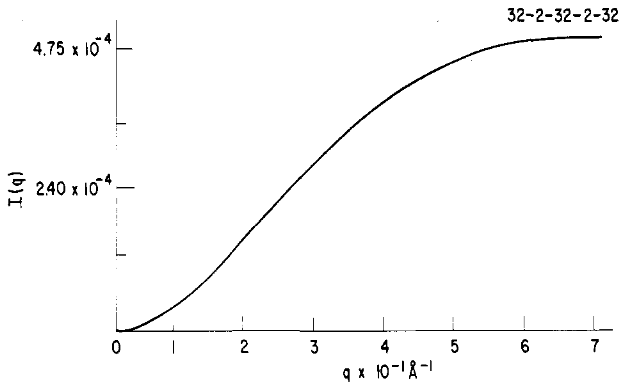

Figure 6. Calculated X-ray scattering intensity as a function of q where m = 32, n = 2, and N = 100.

In order to determine what happens to the scattering curve when species are redistributed within a given chain, we started with the structure shown in Figure 1. The quadruplet in the center of the chain was subdivided into

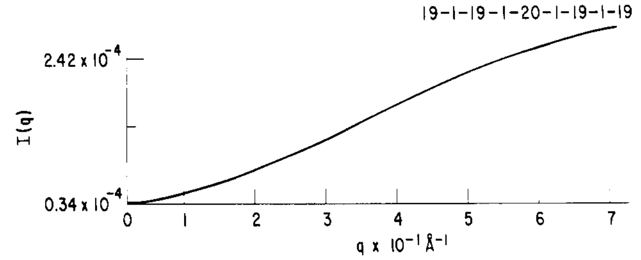

Figure 7. Calculated X-ray scattering intensity as a function of q where $m = 19$, $n = 1$ and $N = 100$.

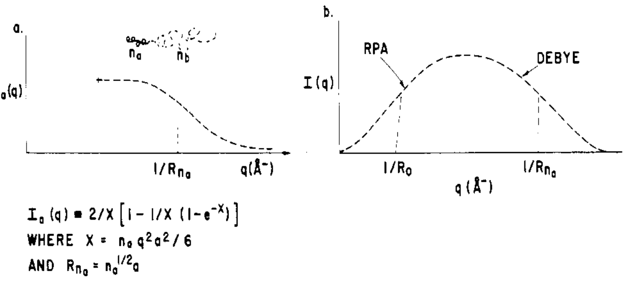

Figure 8. (a) A typical scattering curve for the structure shown in the upper right hand corner (an A_mB_n copolymer) using the Debye function for the A_m block. (b) A hypothetical scattering curve which is obtained by combining the curve shown in Figures 2 and 8a.

two doublets and then into four singlets. The scattering curves, calculated for these new structures, are shown in Figures 6 and 7. A comparison of these curves with that shown in Figure 1 reveals that the maximum is lost and that there is a very significant decrease in the initial slope.

Discussion

The calculated SAXS curves presented in Figures 1–7 clearly indicate that the shape of the SAXS curves is sensitive to the molecular structure of the block polymer and suggest that if the interactions in such materials can be treated by the RPA then information about their micromorphology can be derived from scattering studies.

However, it is important to note that the amplitude at a particular angle of scattering is sensitive not only to the structure but to the electron density difference between the comonomeric species. As a result, SAXS studies of block polymers made from the glassy–glassy blocks may need to be made at temperatures exceeding the glass transition of the lower block but less than that of the upper one, in order to amplify small differences in electron density.

The last point to be discussed is the calculated maxima in SAXS curves. While such peaks might seem to be indicative of an ordering in the material, one can, by following the work of deGennes, interpret them in the following way. The argument which is illustrated in Figure 8 assumes that one has a block of similar species connected to a second block of dissimilar species. If one assumes that the scattering of the first block is given by the Debye function $(1/X^2)(1 - x + e^{-x})$, as shown in Figure 8a, and then combines this with a RPA of the type shown in Figure 2, one obtains the type of scattering curve shown in Figure 8b. Therefore, the position of the maximum and the shape of the curves are a reflection of the superposition of these two effects. To test this hypothesis, a series of SAXS curves were calculated for an $A_mB_nA_m$ block polymer, wherein the total number of species was held constant and the values of m and n were varied. The results of our calculations as shown in Figures 9a and 9b indicate three major effects:

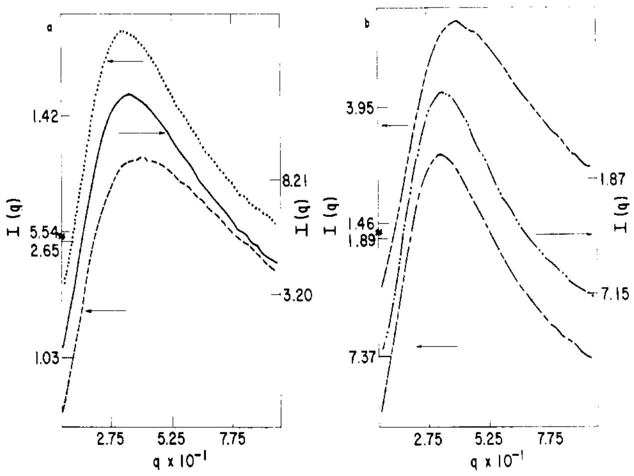

Figure 9. A series of scattering curves which were calculated for a triblock polymer $A_mB_nA_m$ with N constant for various values of M and n: (a) [···] 15-70-15, [—] 10-80-10, [- - -] 5-90-5; (b) [– – –] 20-60-20, [–··–] 33-34-33, [– - - –] 45-10-45.

(1) The position and magnitude of the maximum is related to molecular structure.

(2) The shape of the curves is not in general symmetric with respect to q.

(3) The position of the maximum decreases to small q values as n is increased and m is decreased, and then this trend is reversed. If one increases the number of blocks from 3 to 5 or 7 for constant values of m and n, the shapes of the curves are almost identical, which suggests that this technique is capable of probing the submacromolecular structure of block polymer molecules. On the basis of these calculations, it seems clear that maxima in SAXS curves does not necessarily imply an "ordering" but can simply be a reflection of the various contributions to the total scattering, i.e., the RPA and the Debye function.

Professors Benoit and Fischer have informed us that they have obtained neutron scattering data which support our work.[7] However, it is our belief that a systematic investigation of well-characterized block polymers must be performed before such an interpretation will be acceptable to those familiar with the field. On the other hand, the implications of this work suggest that micromolecular morphology and cocommitantly the properties of appropriately terminated polymers and thermoplastics can be influenced by both end groups and the incorporation of dissimilar mer units within a molecule. The degree to which such effects may be of importance, to current technological problems, lies beyond the current endeavor but may, in the end, be of primary consequence.

Conclusions

The results contained herein have been obtained by applying the RPA to the theory of SAXS from block polymers. The expected SAXS has been calculated for several different structures and are found to be sensitive to the structure. The theory is expected to be applicable to materials where microphase separation has not occurred.

It is suggested that SAXS studies as a function of temperature may allow one to bring out details which cannot be obtained under room-temperature conditions.

The maxima in the calculated SAXS curves in some block polymer systems are suggested to be a result of the superposition of two effects: (1) the normal RPA and (2) the typical Debye function for polymeric species.

Appendix

For block polymers in the bulk state, repulsive interactions between species on different chains may modify the structure of the material without giving rise to the formation of domains. If we use the variable, *ρh*, which describes the density fluctuations of a given wave vector, then we can view the position of the local fluctuations as a set of collective coordinates. It is under such circumstances that the RPA was introduced and is a mathematical tool similar to a variety of others developed for the expressed purpose of reducing intractable mathematical equations such that simple approximate solutions can be obtained. On the other hand, its use imposes certain constraints upon the system's response and in particular assumes only weak interaction.

The physics behind the RPA may be best illustrated by the following simple examples.

Since we assume that $\chi_{ij}^{0}(\mathbf{r})$ is proportional to the pair correlation function $P_{ij}^{0}(\mathbf{r})$ for two monomers in the absence of an external potential, then it can be expected that the presence of one perturbation at the *k*'th position will influence the *i*'th position (where *k* and *i* may be either on the same chain or on different chains). If one now considers these perturbations as a set of plane waves, χ_j, interacting with a set of lattice sites, then the major effect in terms of scattering should occur when a critical condition exists between the plane waves and the lattice. This is then similar to the Debye–Sears photon–phonon problem. However, due to the fact that some of the lattice sites are interconnected by molecular chemical bonds and others by van de Waals forces, the overall response will be biased. In particular, cross-linked materials, where the cross-linking sites are the scatterers, will represent one extreme where due to chemical connectivity any adjustments must be accommodated by changes in the chain's configuration. Very short diterminated chains represent the other extreme because such effects will be couched in intramolecular considerations due to geometric packing. We refer those who are more interested in the RPA to ref 8 and 9.

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Molecular Thermodynamics of Polymer Compatibility: Effect of Contact Agility

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ABSTRACT: While the influence of interaction energy on polymer–polymer compatibility has long been recognized, little explicit attention has been given to the influence of "structural effects", i.e., of component contact agility, *c*/*q*. Calculated phase equilibria are shown for some polymer–polymer and some polymer–polymer–solvent systems using a perturbed-hard-chain theory. This theory predicts an LCST-type phase diagram for a polymer–polymer binary mixture when the contact agilities for polymers are different even though all energy parameters are identical. For ternary systems containing two polymers and a common solvent, solvent contact agility affects the compatibility differently in the UCST and the LCST region. When solvent contact agility is within a good solvent limit, so that the polymer–solvent binary is completely miscible, the lower contact-agility solvent is more efficient in the LCST region; however, the opposite holds in the UCST region.

It has long been recognized that the configurational entropy of mixing for a polymer–polymer mixture is much smaller than that for a mixture of ordinary liquids. A small, positive enthalpy of mixing is sufficient for phase separation; therefore, mutually soluble polymer pairs are the exception, rather than the rule. Several authors have discussed the thermodynamics of polymer–polymer mixtures,[1–4] using classical Flory–Huggins theory wherein the parameter χ_{12} plays a central role.

As shown by Flory and others,[3,5–9] the main defect of the classical theory follows from its failure to take into account the free-volume effect or, in Flory's words, "equation-of-state contributions to the free energy of mixing". These free-volume effects are responsible for partial miscibility at *high* temperatures, leading to a *lower* critical solution temperature (LCST).

As shown by Flory and others,[3,10] free-volume effects in mixtures can be quantitatively described through an equation of state of the van der Waals type, coupled with Prigogine's assumption that at liquid-like densities external rotational and vibrational degrees of freedom can be considered as equivalent translational degrees of freedom.[10]

McMaster[11] and Patterson and Robard[12] have applied the Flory–Prigogine theory to the thermodynamics of polymer compatibility. According to Patterson, for a mixture containing polymer 1 and polymer 2, the Flory–Huggins parameter χ_{12} can be approximated by the sum of two terms

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