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Random multiblock copolymer-homopolymer blends: Effect of sequence distribution and intramolecular repulsion

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Recently, Fredrickson, Milner, and Leibler [Macromolecules **25**, 6341 (1992)] introduced a mean-field analysis of linear random A-B multiblock copolymer melts, taking the sequence distribution explicitly into account. Here, we extend this approach to mixtures with homopolymers $P(C)$. Within the simple Flory-Huggins description, miscibility in random copolymer-homopolymer mixtures is often attributed to unfavorable A-B interactions described by a positive Flory-Huggins parameter χ_{AB} (intramolecular repulsion). The introduction of the sequence distribution sets an upper limit to this effect. For sufficiently large values of χ_{AB} the mixture phase separates again, very much like the pure copolymer melt. Likewise, miscibility improves in the direction of the alternating sequence distribution. Our analysis rationalizes frequently observed sequence distribution effects in random copolymer blends.

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INTRODUCTION

Phase behavior in polymer blends and block copolymer systems has been an important subject of polymer physics for several decades now [1,2]. Thermodynamically, these types of systems are dominated by two factors: a vanishingly small entropy of mixing and a tendency for a positive enthalpy of mixing [3]. Both facts are well understood and suggest that polymer-polymer miscibility is restricted to situations where specific interactions, i.e., hydrogen bonding, are present. Experimentally, however, many miscible polymer pairs violate this criterion. These have in common that at least one of the components is a random copolymer. This phenomenon was addressed in a series of papers [4–8] and attributed to the so called intramolecular repulsion effect. Within the familiar Flory-Huggins description the enthalpy of mixing is expressed in terms of the dimensionless exchange interaction parameter χ. In the case of a random copolymer $P(A_x\text{-co-}B_{1-x})$ and a homopolymer $P(C)$, three different parameters are required: χ_{AB}, χ_{AC}, and χ_{BC}. Assuming that before mixing the random copolymer sample contains a fixed, sequence distribution independent, number of A-B contacts, and this is essential, the mixture can be described in terms of one parameter χ_{eff} given by

$$\chi_{\text{eff}}=x\chi_{AC}+(1-x)\chi_{BC}-x(1-x)\chi_{AB} \; . \tag{1}$$

Miscibility requires this parameter to be smaller than $2/N$ if both polymers have equal chain length N. Since N is in general large, this statement implies that χ_{eff} should be less than or equal to zero. As the equation shows, this can be accomplished even if all parameters are positive provided χ_{AB} is sufficiently large; hence the phrase intramolecular repulsion. This model has been applied to numerous systems and has been shown to describe the phase behavior in these systems at least semiquantitatively [9,10]. It requires treating the χ parameters as independent adjustable parameters, which is somewhat questionable since it is not unreasonable to expect that some kind of relation exists between them [6,11].

It was also recognized early on that the sequence distribution of the random copolymer cannot be ignored. A striking experimental example involves the huge difference in phase behavior between on the one hand a blend of an alternating copolymer of styrene (S) and methyl methacrylate (MMA) with poly(methyl methacrylate) (PMMA) and on the other a blend of a 50%-50% random copolymer of S and MMA with PMMA [12]. Similar observations hold for systems involving either poly(vinyl chloride) (PVC) (an alternating copolymer of CH_2 and CHCl) or chlorinated polyethylene (a random copolymer of the same units) [13]. The early analysis of these effects has been based on a modification of the simple Flory-Huggins treatment considered above [14–16]. It starts from the observation that in a copolymer $P(A\text{-co-}B)$ A (and B) units can occur in four different triplets: A-A-A, A-A-B, B-A-A, B-A-B. Additional interaction parameters to describe this are introduced and reasonable agreement between theory and experiment is obtained.

These nearest neighbor effects, although obviously present, are only one side of the problem. Another aspect concerns the assumption of a fixed, sequence distribution independent, number of A-B, A-C, and B-C interactions in the random copolymer-homopolymer mixture of given composition. This problem has only been addressed recently, and so far only for the pure $P(A\text{-co-}B)$ copolymer melt. Initially, the theoretical models describing the quenched disorder were based on the spin-glass theory [17–20]. Very recently, Fredrickson, Milner, and Leibler [21] introduced an alternative description, which can be generalized more easily to mixtures with homopolymers $P(C)$. The starting point is a system of random block copolymers consisting of segments A and B, each of which contains M monomers. Although M can in principle have any integer value including 1, interesting phase behavior occurs for values of the segmental interaction parameter that in practice are more likely to correspond to a number of ten or more monomers. The sequence distribution of the copolymer is described in terms of two parameters: the average copolymer composition f and the sequence distribution parameter λ. The latter is defined by

$$\lambda = p_{AA} + p_{BB} - 1 , \tag{2}$$

where p_{AA} and p_{BB} are the conditional probabilities that during the reaction A reacts with A; respectively, B reacts with B. From this it is obvious that λ varies between -1, corresponding to an alternating copolymer, via 0, corresponding to a purely random copolymer, to 1, corresponding to two homopolymers $P(A)$ and $P(B)$. For $\lambda < -0.268$, microphase ordering is found for sufficiently large values of χ_{AB}. For larger values of λ, macrophase separation occurs related to sequences of increasing length of A and B units in different copolymers. The presence of additional homopolymers $P(C)$ will modify this behavior and that is the subject of the present paper.

RESULTS AND DISCUSSION

Consider a mixture of linear random multiblock copolymers consisting of segments A and B and homopolymers $P(C)$. All segments are assumed to consist of M monomers of the same size. The number of segments per chain is also taken to be the same for all polymer molecules involved and is denoted by Q. Both types of molecules therefore consist of an equal number of monomers $N = MQ$. The specific composition of a random copolymer varies from molecule to molecule and is determined by the fraction f of segments of type A combined with the chemical correlation λ between successive segments. Of course, f and λ are not entirely independent.

The interaction between the different *monomers* is expressed in terms of the familiar Flory-Huggins parameters mentioned before. The total number of molecules is denoted by n, of which nc are random copolymers and $n(1-c)$ are homopolymers. The system is assumed to be incompressible, whence c also equals the volume fraction of random copolymers in the mixture.

To derive an expression for the Landau free energy functional the procedure developed by Fredrickson, Milner, and Leibler [21] is followed. Because of this, only a brief outline will be given here. A configuration of the system is denoted by $\{R_i(s)\}$, where $R_i(s)$ represents the position of monomer s of molecule i. For $i \in [1, cn]$ the molecule is a random copolymer and for $i \in [cn+1, n]$ a homopolymer. For a specific configuration the deviation from the average concentrations, expressed in volume fractions, is given by

$$\psi_A(x) = \varphi_A(x) - \langle \varphi_A \rangle = \varphi_A(x) - cf , \tag{3}$$

$$\psi_B(x) = \varphi_B(x) - \langle \varphi_B \rangle = \varphi_B(x) - c(1-f) , \tag{4}$$

$$\psi_C(x) = -[\psi_A(x) + \psi_B(x)] , \tag{5}$$

where $\varphi_A(x)$ denotes the volume fraction of monomers belonging to segments of type A at position x, $\langle \varphi_A \rangle$ its space averaged value. Equation (5) follows directly from the assumed incompressibility.

The above functions depend on the specific configuration and the chosen disorder of the random copolymers. The two order parameters of our model, $m_A(x)$ and $m_B(x)$, are obtained by averaging over the disorder and all possible configurations

$$m_A(x) = \| \psi_A \{ R_i(s), \text{disorder} \}(x) \| , \tag{6}$$

$$m_B(x) = \| \psi_B \{ R_i(s), \text{disorder}(x) \| . \tag{7}$$

The Hamiltonian of the system consists of two contributions. The first part represents the nonbonded interaction and is given by

$$V\{R_i(s)\} = -\int dx \{ \chi_{AC}[\psi_A(x)]^2 + \chi_{BC}[\psi_B(x)]^2 - \Delta\chi \psi_A(x) \psi_B(x) \} , \tag{8}$$

with

$$\Delta\chi = \chi_{AB} - \chi_{AC} - \chi_{BC} . \tag{9}$$

The second part takes the chain connectivity into account and is given by

$$H_0\{R_i(s)\} = \frac{3}{2b^2} \sum_{i=1}^{n} \sum_{s=1}^{N-1} [R_i(s+1) - R_i(s)]^2 , \tag{10}$$

where b is the monomer length.

In terms of these contributions the partition functions is given by

$$Z = \int d\{R_i(s)\} \delta(1-\varphi) \times \exp[-V\{R_i(s)\} - H_0\{R_i(s)\}] , \tag{11}$$

with $\varphi = \varphi_A + \varphi_B + \varphi_C$. In order to express the free energy as a functional of the order parameters the partition function is rewritten in the following way:

$$Z = \int d\{R_i(s)\} \int D[m_A] \int D[m_B] \delta(1-\varphi) \delta(\psi_A - m_A) \times \delta(\psi_B - m_B) \times \exp[-H_0 - V(m_A, m_B)] . \tag{12}$$

Using the Fourier representation of the δ function it follows that

$$Z = \int D[m_A] \int D[m_B] \exp(-V\{m_A, m_B\}) \int D[J_\varphi] \int D[J_A] \int D[J_B] \exp\left[i \int dx (J_\varphi + J_A m_A + J_B m_B) \right] \times \left\langle \exp\left[-i \int dx (J_\varphi \varphi + J_A \psi_A + J_B \psi_B \right] \right\rangle_0 , \tag{13}$$

where $\langle\ \rangle_0$ denotes an ensemble average with respect to the Edwards Hamiltonian (10). Next define

$$G[J_\varphi,J_A,J_B]=\ln\left\langle \exp\left[-i\int dx(J_\varphi\varphi+J_A\psi_A+J_B\psi_B)\right]\right\rangle_0 \tag{14}$$

then

$$G[J_\varphi,J_A,J_B]=\sum_{i=1}^{cn}\ln\left\langle \exp\left[-i\int dx(J_\varphi\varphi^i+J_A\psi_A^i+J_B\psi_B^i)\right]\right\rangle_0 + \sum_{i=cn+1}^{n}\ln\langle\exp(-iJ_\varphi\varphi^i)\rangle_0+ifc\int dxJ_A+i(1-f)c\int dxJ_B\ , \tag{15}$$

where

$$\varphi^i(x)=\sum_s\delta(x-R_i(s))\ ,$$
$$\psi_A^i(x)=\sum_s(\tfrac{1}{2}\sigma_{il}+f)\delta(x-R_i(s))\ , \tag{16}$$
$$\psi_B^i(x)=\sum_s(-\tfrac{1}{2}\sigma_{il}+1-f)\delta(x-R_i(s))\ .$$

Here $\sigma_{il}=\theta_{il}-(2f-1)$, with l denoting the segment number of molecule i. θ_{il} equals 1 for segments of type A and -1 for segments of type B.

Since in the thermodynamic limit all possible sequence distributions occur with the correct frequencies described by the probability distribution (f,λ), the summation over the random copolymers can be replaced by the average multiplied by the number of molecules. In this way the replica trick is avoided. Next, the integrals over the fields J_φ, J_A, and J_B are replaced by the maximum of the integrand. The result is the Landau free energy which, expanded up to second order in the order parameters, in terms of wave vectors reads

$$F[m_A(\mathbf{k}),m_B(\mathbf{k})]=\frac{1}{2V}\sum_k(m_A^*(\mathbf{k}),m_B^*(\mathbf{k}))\times M(k^2)\begin{bmatrix}m_A(\mathbf{k})\\ m_B(\mathbf{k})\end{bmatrix}\ , \tag{17}$$

where $M(k^2)$ is a 2×2 matrix given by

$$M(k^2)=\begin{bmatrix}A(k^2) & B(k^2)\\ B(k^2) & C(k^2)\end{bmatrix}\ , \tag{18}$$

with

$$A(k^2)=\frac{(1-f)^2}{cG(k^2R_M^2)}+\frac{1}{c(1-c)Ng(k^2R_N^2)}-2\chi_{AC}\ , \tag{19}$$

$$B(k^2)=\frac{-f(1-f)}{cG(k^2R_M^2)}+\frac{1}{c(1-c)Ng(k^2R_N^2)}+\Delta\chi\ , \tag{20}$$

$$C(k^2)=\frac{f^2}{cG(k^2R_M^2)}+\frac{1}{c(1-c)Ng(k^2R_N^2)}-2\chi_{BC}\ . \tag{21}$$

The functions appearing in these expressions are all related to the Debye function $g(x)$,

$$g(x)=\frac{2}{x^2}(e^{-x}-1+x)\ , \tag{22}$$

$$G(x)=f(1-f)M\left[g(x)+\frac{2\lambda h(x)}{1-\lambda e^{-x}}\right]\ , \tag{23}$$

$$h(x)=\frac{(e^{-x}-1)^2}{x^2}\ . \tag{24}$$

Furthermore, $R_M^2=Mb^2/6$ and $R_N^2=Nb^2/6$, the familiar radii of gyration expressions.

The system is stable with respect to small fluctuations provided both eigenvalues of $M(k^2)$ are positive. The limit of stability, i.e., the spinodal, corresponds to the value of the parameters involved for which one of the eigenvalues becomes zero. If this occurs at a nonzero value $\mathbf{k}^*$ of $\mathbf{k}$ it corresponds to microphase separation otherwise, if $\mathbf{k}^*=0$, to macrophase separation.

In this paper spinodals will be presented for the special case $f=c=\frac{1}{2}$ in the limit $N\rightarrow\infty$. The phase boundaries will be presented in a $(M\chi_{AB},\lambda)$ plane where M is the number of monomers per segment. The first classes of systems to be considered correspond to (i) $\chi_{AC}=\chi_{BC}=0$ and (ii) $\chi_{BC}=0$, $\chi_{AC}>0$. These are the most characteristic ones for a demonstration of the combined effect of intramolecular repulsion and sequence distribution. The resulting spinodal curves are presented in Fig. 1.

For the first mentioned case the simple Flory-Huggins description given by Eq. (1) predicts miscibility for $\chi_{AB}\geq0$ and macrophase separation for $\chi_{AB}<0$. Because of the infinite chain limit, the macrophase separated phases consist of the pure polymers. This conclusion is still valid for the present treatment. However, for sufficiently positive values of $M\chi_{AB}$, the system will phase separate again; this time in the form of macrophase separation for $\lambda>-0.267$ and microphase separation for $\lambda<-0.267$. This last observation resembles closely the results for random multiblock copolymer melts. The figure demonstrates that for λ approaching -1, the phase boundary approaches $M\chi_{AB}=15$. This value is twice the value found in Ref. [22] for pure linear multiblock copolymers in the limit of a large number of blocks, which is a consequence of the presence of homopolymer $P(C)$, uniformly distributed in both phases. Table I contains the composition of the fluctuations with wavelength k^* along the phase boundaries expressed in terms of the order parameters m_A and m_B. Also presented is m_C, which follows from incompressibility.

In the same figure the phase boundaries for the asym-

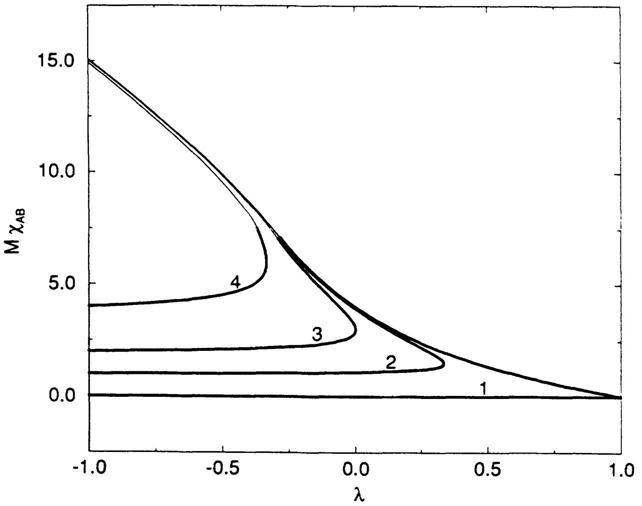

FIG. 1. Spinodals for $\chi_{BC}=0$ and $\chi_{AC}=0(1)$, 0.5(2), 1(3), and 2(4). Thick line: macrophase separation; thin line: microphase separation.

metric case of $\chi_{BC}=0$ and $\chi_{AC}=0.5$, 1.0, and 2.0 are also presented. In all three cases a closed miscibility gap is found. For values of λ approaching 1 the system is, as expected, always phase separated. The lower branch of the phase boundary corresponds to macrophase separation into two phases, one predominantly containing the random copolymer and the other with a high concentration of homopolymer. The upper branch contains a microphase separated and a macrophase separated part. The former consists of domains rich in A segments and domains rich in B segments. Homopolymer $P(C)$ is present in both types of domains, although somewhat enhanced in the B rich domains. The compositions of the fluctuations with wave vector k^* are for the case of $\chi_{AC}=1$ also presented in Table I. The point where the macrophase separated part meets with the lower branch is characterized by a uniform distribution of B segments throughout both phases. This follows from the numerical calculations but can also be demonstrated directly in the following way.

TABLE I. Composition of fluctuations with wave vector k^*.

System	λ	m_A:m_B:m_C Lower branch	Upper branch
$\chi_{AC}=\chi_{BC}=0$	$[-1,1]$	1:1:−2	1:−1:0
$\chi_{AC}=1$, $\chi_{BC}=0$	−1	1:1:−2	1:−0.93:−0.07
	−0.6	1:0.86:−1.86	1:−0.88:−0.12
	−0.4	1:0.75:−1.75	1:−0.82:−0.18
	−0.2	1:0.56:−1.56	1:−0.56:−0.44
	≃0	1:0:−1	1:0:−1

At the "tip" of the spinodal line the system always becomes unstable with respect to macrophase separation, so we will concentrate on this. The spinodal line corresponding to this situation is determined by the condition that one eigenvalue of the following matrix [i.e., Eq. (18) for $k=0$ and $N=\infty$] is zero and one is positive:

$$\begin{bmatrix} \dfrac{(1-f)^2}{c\Lambda}-2\chi_{AC} & \dfrac{-f(1-f)}{c\Lambda}+\Delta\chi \\ \dfrac{-f(1-f)}{c\Lambda}+\Delta\chi & \dfrac{f^2}{c\Lambda}-2\chi_{BC} \end{bmatrix}, \tag{25}$$

where Λ is given by

$$\Lambda=\frac{(1-f)(1-\lambda)}{cfM(1+\lambda)} . \tag{26}$$

If λ_i and λ_2 denote the eigenvalues, the spinodal corresponding to macrophase separation is determined by

$$\lambda_1\lambda_2=0 \text{ and } \lambda_1+\lambda_2>0 . \tag{27}$$

This leads to the following two expressions:

$$\left[\frac{(1-f)^2}{c\Lambda}-2\chi_{AC}\right]\left[\frac{f^2}{c\Lambda}-2\chi_{BC}\right] = \left[\frac{-f(1-f)}{c\Lambda}+\Delta\chi\right]^2, \tag{28}$$

$$\left[\frac{(1-f)^2}{c\Lambda}-2\chi_{AC}\right]+\left[\frac{f^2}{c\Lambda}-2\chi_{BC}\right]>0 . \tag{29}$$

Since in the "tip" of the spinodal the quadratic equation (28) for χ_{AB} will only have one root, two possibilities arise, either

$$\frac{(1-f)^2}{c\Lambda}=2\chi_{AC} \text{ and } \frac{f(1-f)}{c\Lambda}=\Delta\chi \tag{30}$$

or

$$\frac{f^2}{c\Lambda}=2\chi_{BC} \text{ and } \frac{f(1-f)}{c\Lambda}=\Delta\chi . \tag{31}$$

The first (last) possibility corresponds to B (A) being homogeneously distributed throughout both phases. Which of these two possibilities occurs follows from Eq. (29). The first possibility requires

$$(1-f)^2\chi_{BC}<f^2\chi_{AC} \tag{32}$$

whereas the second possibility requires exactly the opposite. Since the examples considered correspond to $\chi_{BC}=0$ and $\chi_{AC}>0$, inequality (32) is satisfied.

Although the upper branches of the phase boundaries are rather similar to that of pure random multiblock copolymers, there are also interesting differences. For some values of λ macrophase separation occurs for two different values of χ_{AB}, which for the case of $\chi_{AC}=2$ even occurs for values of λ for which the pure random multiblock copolymer only shows microphase separation.

The case $\chi_{AC}=0.5$ demonstrates the sensitivity of the phase behavior with respect to the sequence distribution effect in situations that resemble ordinary random copolymer blends. For instance, the analysis on the basis of the simple Flory-Huggins model of phase behavior in blends of PMMA and a random copolymer of styrene and acrylonitrile (SAN) results in the following values for the χ parameters involved: $\chi_{\text{S-AN}}=0.83$, $\chi_{\text{MMA-AN}}=0.46$, and $\chi_{\text{MMA-S}}=0.03$ [23]. These values are in the

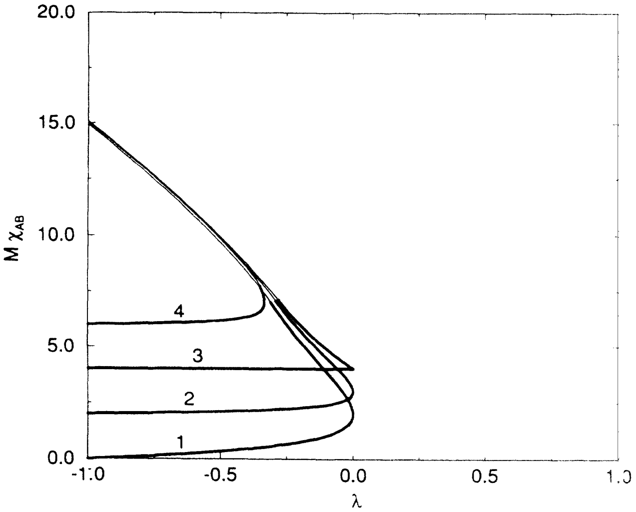

FIG. 2. Spinodals for $\chi_{BC}=1$ and $\chi_{AC}=-1$ (1), 0(2), 1(3), and 2(4). Thick line: macrophase separation; thin line: microphase separation.

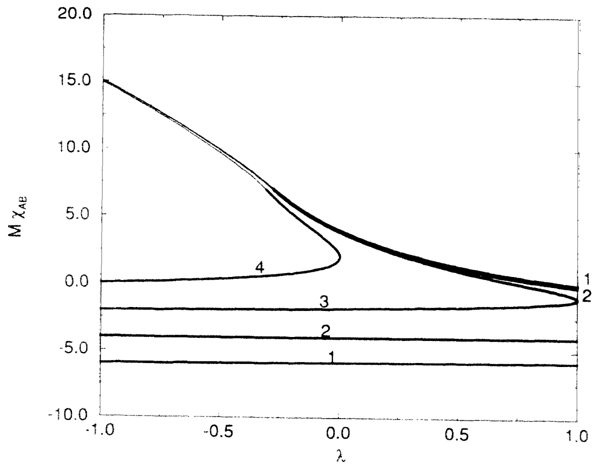

FIG. 3. Spinodals for $\chi_{BC}=-1$ and $\chi_{AC}=-2$(1), -1(2), 0(3), and 1(4). Thick line: macrophase separation; thin line: microphase separation.

same range of values as those corresponding to curve (2) for $\lambda > 0$. Although the analysis presented is not directly applicable to PMMA-SAN, because the segments of the theoretical model comprise several monomers, it clearly demonstrates the role of the sequence distribution. Miscibility improves towards the alternating sequence distribution, a well known phenomenon also for ordinary random copolymer blends.

For completeneness two other parameter sets have been considered as well. The first corresponds to $\chi_{BC}=1$ with χ_{AC} taking the values $-1,0,1,2$. The second one corresponds to $\chi_{BC}=-1$ with χ_{AC} taking the values -2, -1, 0, 1. The resulting spinodals are presented in Figs. 2 and 3. Although different in detail, the overall features are similar to the above considered class of systems.

CONCLUSIONS

The simple mean-field description of phase behavior in random copolymer-homopolymer blends has been improved by introducing the sequence distribution of the random copolymer. Whatever the sequence distribution is, taking it explicitly into account sets an upper limit to the copolymer repulsion effect. For sufficiently large values of the intramolecular Flory-Huggins parameter, the system will always phase separate either in the form of microphase or macrophase separation. Miscibility greatly improves in the direction of the alternating sequence distribution, as could already be expected on the basis of the results of Fredrickson, Milner, and Leibler.

ACKNOWLEDGMENTS

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[1] See, e.g., *Polymer Blends*, edited by D. R. Paul (Academic, New York, 1978), Vol. 1.

[2] See, e.g., *Developments in Block Copolymers*, edited by I. Goodman (Applied Sciences, New York, 1982), Vol. 1; *Developments in Block Copolymers*, edited by I. Goodman (Applied Sciences, New York, 1985), Vol. 2.

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