

# The Effect of Interactions in Polymer Blends Studied by Monte Carlo Simulations

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Interactions play a decisive role in polymer-polymer miscibility. However, direct elucidation of interactions from thermodynamic mixing properties is experimentally cumbersome because of high viscosity and the glass transition temperature ( $T_g$ ) effects in polymer systems, and because there are theoretical problems attributable to its mean-field approximation. Therefore we are interested in Monte Carlo (MC) simulations which overcome some of these restrictions and are an alternative to the experimental and theoretical approaches. Results of such simulations are available for only a few model systems. We present the results of three applications of the MC method to polymer blend systems.

## Introduction

The preparation and processing of new polymer blends and the control of their morphology requires a detailed knowledge of the thermodynamics of polymer mixtures. It is well known that favorable interactions are a prerequisite for miscibility in heteropolymer blends because of the very small entropy of mixing in high-molecular-weight polymer mixtures. The heat of mixing ( $\Delta H_m$ ) of a polymer system then becomes a direct measure of favorable interactions. There are, however, experimental obstacles that prevent direct measurement of  $\Delta H_m$ . For example, the high viscosity of polymer systems retards attainment of equilibrium; also there can be a  $T_g$  intervention which affects the mixing-demixing transition. Although

it is possible to overcome these difficulties<sup>1)</sup> in measuring  $\Delta H_m$  by using low-molecular-weight analogue systems or Hess' law calculations for experimental enthalpies of solution for the blend and both pure components, few results are available.

A similar but somewhat more favorable situation exists in the theoretical treatment of the thermodynamics of polymer blends. Equations derived from mean-field (MF) theories, which are extensions of the classical Flory-Huggins (FH) theory, can be fitted to experimental data to find the phenomenological interaction parameter  $\chi$ . This parameter represents an average over all interactions and, to a large extent, absorbs other effects such as those associated with the equation of state, composition, and chain length. The problem is that MF theories assume random mixing and do not account for correlations in chains, that is, chain connectivity. Deviations from random mixing are greatest for the most favorable interactions.

Because of the experimental and theoretical difficulties, we have studied MC simulations as

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an alternative to these approaches. This method, using the power of a fast computer, does not require the assumption of random mixing and can be formulated to include correlations within and among the chains. We present below three examples of studies of the thermodynamics of polymer blends using MC simulation techniques. The first example concerns the estimation of the relation between the phenomenological  $\chi$  parameter and microscopic interactions. The second example is the evaluation of the mixing-demixing problem in a copolymer/homopolymer blend; and in the third example we examine the effect of interactions and blend composition on the size of polymer coils in the system.

The mixing-demixing problem in copolymer containing systems has been the subject of numerous studies, and over the past few years much progress has resulted from the conceptualization of an intramacromolecular "repulsion" or "dilution" effect<sup>2,3</sup>. Early conclusions about unambiguous poor mixing of polymers have been reconsidered in light of this effect, and miscibility curves have been calculated to show the proportions needed for preparing miscible blends. Thus, in certain blends miscibility occurs as a result of repulsion between comonomers of a copolymer and the consequent favorable mixing with the other polymer which dilutes the unfavorable contacts in the system. Miscibility may be observed even in systems in which all binary interaction parameters are unfavorable to mixing. The method has been successfully applied to blends of random copolymers, randomly modified polymers<sup>4,5</sup>, and systems in which homologous series of homopolymers are treated as copolymers<sup>3,6</sup>. The method provides a way to derive segmental interaction parameters between different monomers of the mixture from miscibility data. This concept has provided a very useful way to represent the data, and new parameters have appeared. It provides a basis for interpreting real data similar to the successful group contribution schemes that predict thermodynamic behavior of low-molecular-weight mixtures. To

obtain more extensive insight in to the problems involved, we have used an approach different from the original mean-field copolymer theory, namely, MC computer simulation. We have studied this problem on a model  $A_x B_{1-x}/C$  blend, using MC simulations to obtain insights independent of mean-field approximation. Most important, by this method we can observe the interaction coefficient of the blend not only at the miscibility boundaries studied by mean-field copolymer theory<sup>2,3</sup> but also within miscibility and immiscibility regimes.

### Thermodynamics and MC Simulation

According to FH theory, the free energy of mixing ( $\Delta G_m$ ) per unit volume of a binary polymer system is given by the familiar form:

$$\frac{\Delta G_m}{kT} = \frac{\phi_A}{n_A} \ln \phi_A + \frac{\phi_B}{n_B} \ln \phi_B + \chi \phi_A \phi_B \quad (1)$$

where  $\phi_i$  is the volume fraction of a component and  $n_i$  is its degree of polymerization, and  $\chi$  is the interaction parameter. The simplest interpretation of the interaction parameter is through an interchange energy  $\Delta \epsilon_{AB} = \epsilon_{AB} - (\epsilon_{AA} + \epsilon_{BB})/2$ , since  $\chi = \Delta \epsilon_{AB}(Z - 2)/kT$ , where  $\epsilon_{ij}$  is the relevant segmented interaction energy and  $Z$  is the coordination number. Furthermore, we define the reduced interaction energies as  $e_{ij} = \epsilon_{ij}/kT$ . The critical condition for demixing occurs when  $\chi$  reaches the value

$$\chi_c = \frac{2}{n}, \text{ for the simple case } n_A = n_B = n \quad (2)$$

For the random copolymer/homopolymer blend  $A_x B_{1-x}/C$ , the effective  $\chi$  parameter in the corresponding expression for the free energy of mixing<sup>2</sup>) is

$$\chi_{\text{blend}} = x\chi_{AC} + (1-x)\chi_{BC} - x(1-x)\chi_{AB} \quad (3)$$

This expression shows that miscibility ( $\chi \leq \chi_c$ ) is possible even in systems in which all the segmental interaction parameters are positive. By using Eq. (3) and the corresponding  $\chi_c$ , we can evaluate the segmental interaction parameters  $\chi_{ij}$  from experimental miscibility boundaries

as a function of composition  $x$ . The number of boundaries must be equivalent or greater than the number of independent  $\chi_{ij}$  in system.

MC simulation provides insight into these systems in two ways. First, simulation is an independent method that is free of mean-field approximations, so it enables us to account both for connectivity of monomers within the chains and for concentration fluctuations due to nonrandom mixing. Second, this method is a useful supplement to the standard copolymer theory because it enables us to investigate  $\chi_{\text{blend}}$  over the complete polymer composition range. This flexibility allows us to see whether  $\chi_{\text{blend}}$  behaves according to the quadratic mixing rule in equation (3) over the total composition range  $0 < x < 1$ . In other words, we can determine whether the segmental interaction parameters  $\chi_{ij}$  obtained from miscibility boundaries at two copolymer compositions accurately represent  $\chi_{ij}$  over this range.

The MC methodology used here has been described in an earlier contribution<sup>7)</sup>. We used a cubic lattice of  $L \times L \times L$  sites with  $L = 22$  in examples I and III. For copolymer/homopolymer blends in this study, a planar square lattice with  $L = 22$  was used. Use of the two-dimensional system does not affect our findings qualitatively. (Note that the original FH theory does not differentiate between systems of different dimensionalities.) In examples I and II, the blend composition was always 1:1. Composition was varied in example III. Chains with 20 segments (monomers) were used throughout.

The simulation of copolymer chains used here is similar to that used previously<sup>8)</sup> to assess miscibility behavior in copolymer blends with single interactions. At first, a linear statistical  $A_x B_{1-x}$  copolymer with 20-segment chains was generated in a step-by-step procedure according to ideal statistical copolymerization kinetics. The probabilities for the addition of an A or a B segment in each step were  $p_A$  for A segments and  $p_B = 1 - p_A$  for B segments. These probabilities were held constant during

“copolymerization.” This procedure produced an assembly of  $A_x B_{1-x}$  chains in which the average of  $x$  was close to  $p_A$ . The computation allowed for the generation of a monodisperse system.

Each lattice site contained either an A, B, or C segment or a void. An overall void fraction of 0.0909 allowed for chain motion to equilibrate in this incompressible system. During the computation, periodic boundary conditions were imposed on the lattice. In order to minimize finite-size effects, we chose the dimension of the lattice so that it always exceeded the equilibrium dimension of a single chain. The initial configuration for the simulation of the mixture was a completely ordered arrangement of parallel chains in an alternating order of blend components. For the simulation of the copolymer, we filled the lattice with copolymer chains alone, but used the same void fraction, and then imposed interactional constraints on the system. Whenever  $i$  and  $j$  segments occupied adjacent sites, a single interaction energy  $\epsilon_{ij}$  was counted in the total energy of the system;  $ij \equiv A, B, \text{ or } C$ . The total energy of each configuration was

$$E = \epsilon_{AB}N_{AB} + \epsilon_{AC}N_{AC} + \epsilon_{BC}N_{BC} \quad (4)$$

with  $N_{ij}$  being the total nearest-neighbor heterocontacts in the system. The interaction energy between a segment and a void is defined as zero. We allowed for  $4 \times 10^6$  reptation moves to equilibrate the two-dimensional system and up to  $2 \times 10^8$  for the three-dimensional systems for each state. Reptation is a well-established algorithm for equilibrating systems at high densities. For each move, both an intrachain and an interchain excluded volume effect were operative on the basis of site occupancy. Note also that when the copolymer chain reptates, we must evaluate the changes in energy along the whole chain rather than only at the chain ends, as is the usual practice for a homopolymer chain undergoing a reptation move. New configurations were accepted or rejected in thermodynamic averaging, according to the well-known rules of Metropolis, which samples the states

with correct thermodynamic distribution proportional to  $\exp(-E/kT)$ : After each attempted move successfully passed the steric restrictions, the move was accepted only if

$$\exp \frac{-\Delta E}{kT} \geq \xi \quad (5)$$

where  $\Delta E$  is the change in total energy before and after the attempted move and  $\xi$  is a random number between zero and unity. The averages were then calculated as arithmetic averages over acceptable configurations. Each time a configuration was rejected, the previous configuration was counted again in the average. Equilibration of each state was preceded by an initial intermixing period during which all interaction energies were held equal to zero. As a major thermodynamic variable, we calculated the equilibrium number of three types of heterocontacts in the blend:  $N_{AB}$ ,  $N_{AC}$ , and  $N_{BC}$ . This calculation also yielded a net interaction parameter  $\chi_{\text{blend}}$ . In example III we also evaluated the mean-square end-to-end distance  $\langle R^2 \rangle$  of the polymer coils.

## Results and Discussion

### Example I. A homopolymer blend

Figure 1 depicts the average number of A-B heterocontacts per chain plotted as a function

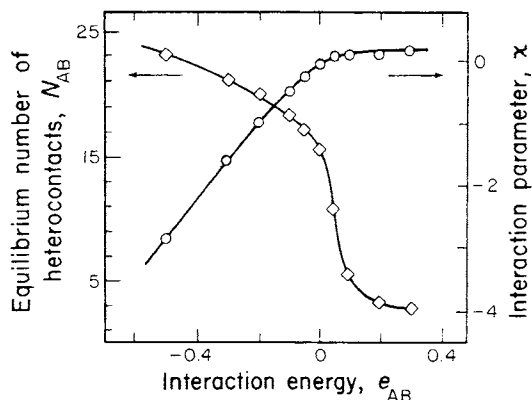


Fig. 1 Dependence of the number of A-B contacts in the system per chain and of the  $\chi$  parameter on the nearest-neighbor interaction energy  $e_{AB}$ . Reprinted, with permission, from ref. 7.

of interaction energy  $e_{AB}$ . From these results, we can find the relation between the phenomenological interaction parameter  $\chi$  and the microscopic interaction energy  $e_{AB}$ . We can represent the interaction free energy of mixing,  $\Delta G_{\text{int}}$ , in two ways. The first comes from the MF expression of FH theory, which assumes that the number of heterocontacts is proportional to the product of the volume fractions of A and B,  $\phi_A$  and  $\phi_B$ . In this representation, the interaction is varied through  $\chi$  and the number of contacts is fixed. The second comes from MC results, where the total number of contacts  $N_{AB}$  depends on the microscopic interaction energy  $e_{AB}$ , which is constant. Equating these two expressions yields

$$\frac{\Delta G_{\text{int}}}{kT} = \chi \phi_A \phi_B = \frac{e_{AB} N_{AB}}{N} \quad (6)$$

where  $N$  is the total number of sites in the mixture, including voids. The resulting dependence of  $\chi$  on  $e_{AB}$  is also shown in Fig. 1. The dependence is seen to be linear in the miscibility regime, as expected from the classical relation  $\chi \propto \Delta \epsilon_{AB}$ . From these calculations, we obtain the relation between the phenomenological  $\chi$  parameter and the true molecular constants  $\epsilon_{AB}$ . In the product  $e_{AB} N_{AB}$ , the free energy change is included in  $N_{AB}$ . Note that the entropy of mixing is included in the evaluation of  $\chi_{\text{blend}}$  through the MC sampling algorithm. If it were not so, then even an infinitesimal repulsive interaction would lead to a complete demixing. However, nonzero  $N_{AB}$  is always obtained. Using Eq. (6), we find the value of  $\chi_c$  corresponding to the mixing-demixing transition centered at  $e_{AB} = 0.05$  to be 0.11, a value that agrees with the value of  $\chi_c = 2/n = 0.1$  predicted from FH theory.

### Example II. Evaluation of interactions in a copolymer/homopolymer blend

The primary results of our study of the  $A_x B_{1-x}/C$  systems are again the equilibrium numbers of the three types of contacts in the mixture. We prefer, however, to show our

results in terms of the well-established thermodynamic variable  $\chi_{blend}$ . To do so, we must make two assumptions: (1) The mean-field interaction free energy per unit volume (or per site in this study)  $\chi_{blend}\phi_{AB}\phi_C$  is set equal to the equivalent expression formed by the terms  $e_{ij}N_{ij}/N$  (as we assumed for the A/B system just discussed). (2) According to the “molecular soup” scheme of copolymer-copolymer theory<sup>2,3</sup>, the interactions both in the blend and in the pure copolymer melt become the thermodynamic reference states for the mixing properties. We obtain the expression

$$\begin{aligned} &\chi_{blend}\phi_{AB}\phi_C \\ &= \frac{1}{N} \{ e_{AB}N_{AB} + e_{AC}N_{AC} + e_{BC}N_{BC} \\ &\quad - \phi_{AB}e_{AB}(N_{AB})_{\infty,x} \} \end{aligned} \quad (7)$$

where the first three terms on the right-hand side characterize the blend, and  $(N_{AB})_{\infty,x}$  is the equilibrium number of heterocontacts in the pure copolymer melt at a copolymer composition  $x$ . One can see that this expression corresponds to the “molecular soup” scheme, except that the individual terms are not mean-field estimates but parameters arising from the MC calculation. (Note that this expression is a special case of the general relation given in Ref. 8, Eq. 6.)

Results of a simulation in terms of  $\chi_{blend}$  versus copolymer composition  $x$  for a constant 1:1 blend composition are shown in Figs. 2 and 3. Figure 2 illustrates the results when both intermacromolecular interactions are equal, that is, when  $e_{AC} = e_{BC} = 0.05$ . This value corresponds to the demixing transition in blends of the homopolymers A/C and B/C. We see, however, that the corresponding  $\chi$  found here (0.075) is somewhat lower than that (0.11) found in example I for a three-dimensional homopolymer binary blend. The two curves, which connect the axes representing binary homopolymer blends, represent the effects of different A-B repulsive interactions within the copolymer in the copolymer/homopolymer

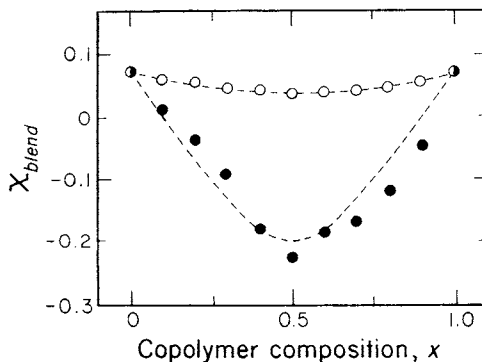


Fig. 2 Variation of  $\chi_{blend}$  with copolymer composition  $x$  (for constant  $e_{AC} = e_{BC} = 0.05$  and a 1:1 blend composition) for two repulsions:  $\circ$ ,  $e_{AB} = 0.2$ ;  $\bullet$ ,  $e_{AB} = 1.2$ .

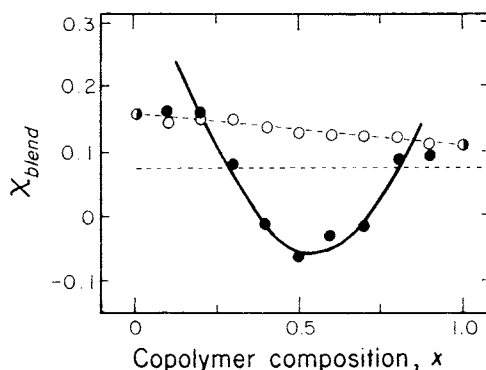


Fig. 3 Variation of  $\chi_{blend}$  with copolymer composition  $x$  (for constant  $e_{AC} = 0.1$ ,  $e_{BC} = 0.2$ , and a 1:1 blend composition) for two repulsions:  $\circ$ ,  $e_{AB} = 0.2$ ;  $\bullet$ ,  $e_{AB} = 1.2$ . The solid curve represents the fitting of Eq. (3) from the data within the miscibility window.

blend. For  $e_{AB} = 0.2$  (open circles), we found a smaller effect of additional mixing due to A-B repulsion, which manifests itself by reducing  $\chi_{blend}$ . For the stronger repulsion  $e_{AB} = 1.2$  (filled circles), we found a large decrease in  $\chi_{blend}$ . Both curves can be well characterized by the quadratic equation (3) predicted from copolymer theory.

In contrast Fig. 3 shows deviations from the MF picture. Here  $e_{AC}$  and  $e_{BC}$  were chosen to

be greater than the demixing transition in the A/C and B/C systems ( $e_{AC} = 0.1$  and  $e_{BC} = 0.2$ ), so that the introduction of a sufficiently large A-B repulsion would lead to a real miscibility window. For a relatively small repulsion ( $e_{AB} = 0.2$ , open circles), we do not see the effect of enhanced miscibility and the system stays immiscible over the whole range of compositions. A stronger repulsion ( $e_{AB} = 1.2$ , filled circles) within the copolymer leads to a miscibility window. However, there is an important distinction. We can recognize two behaviors for this case. Within the miscibility window, we find that the system obeys Eq. (3), but outside the window  $\chi_{\text{blend}}$  values level off because  $\chi$  cannot substantially exceed  $\chi_c$ , a finding also seen in the simple A/B blend. Figure 3 reveals that the segmental parameter  $\chi_{AC}$ , if evaluated according to Eq. (3) outside the miscibility window, does not correspond to a real A-C interaction in an A/C binary homopolymer blend ( $\chi_{\text{blend}} = \chi_{AC}$  for  $x = 1$ ). The same conclusion is valid for  $\chi_{BC}$  and the B/C system. In fact,  $\chi_{BC}$  must be smaller than that estimated by Eq. (3). Again, the real repulsive term must be smaller in order to satisfy Eq. (3). This result is analogous to the peculiar experimental results showing some excessively large  $\chi_{ij}$  values. For example, for the styrene acrylonitrile system,  $\chi_{S,AN} = 0.98$ , and for styrene-maleic anhydride system,  $\chi_{S,MA} = 1.85$  have been reported<sup>9</sup>). However, this behavior is not a failure of the copolymer theory represented by Eq. (3). Our MC results for  $\chi_{\text{blend}}$  over the total composition range  $x$  only shows that an approach based on Eq. (3) treats the system as though it were miscible or at the phase boundary. Thus, the  $\chi_{ij}$  parameters extracted from phase boundaries depict the situation for randomly mixed, and miscible situations. Thus it is correct to use these segmental interaction parameters for characterizing the miscibility boundaries in copolymer mixtures (at the miscibility boundary, the mixing is still nearly random) and also to transfer the  $\chi_{ij}$  obtained from one copolymer system to predict or analyze the miscibility boundaries

of another system including the same  $ij$  interactions. However, a problem would appear if we were to apply the  $\chi_{ij}$  obtained from copolymer blend experiments to the binary homopolymer  $ij$  blend.

To summarize, segmental interaction parameters  $\chi_{ij}$  obtained from miscibility windows or generally from the phase boundaries characterize only this region. One cannot extrapolate blend behavior beyond this region to obtain individual  $\chi_{ij}$  that could apply to binary  $ij$  polymer blends. We find the real  $\chi_{ij}$ 's operative for individual  $ij$  blends are actually lower than the values extracted from the copolymer scheme. Segmental interaction parameters obtained from the copolymer scheme should therefore be considered as parameters characterizing the critical behavior of the copolymer blend. They represent only the interactions involved and are not transferable to a corresponding binary homopolymer blend.

### Example III. The effect of interactions and composition on polymer coil size in a polymer blend

It is already well established that polymer coils in a condensed homopolymer phase have an ideal unperturbed behavior (which resembles the  $\theta$ -state in solution). However, this ideality is not necessarily so in polymer blends, where interactions and composition may introduce perturbations in coil behavior. More recently, as experimental and theoretical techniques have been used to investigate single chains in condensed polymer systems, this discrepancy has become more apparent.

The first report was made by Kirste *et al.*,<sup>10</sup> who concluded that coil sizes are nearly ideal; although in some cases they found a very small expansion. We reported the results of an MC simulation of the expansion of coils in miscible blends with a 1:1 (symmetrical) composition in two-dimensional<sup>11</sup>) and three-dimensional systems<sup>7</sup>). In two dimensions, the expansion was large for favorable interactions. For the more realistic three-dimensional system, how-

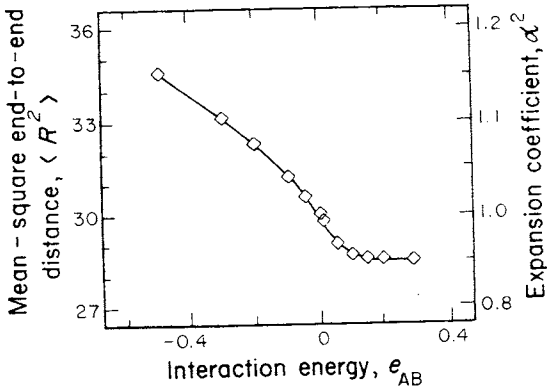


Fig. 4 Expansion coefficient  $\alpha^2$  and mean-square end-to-end distance  $\langle R^2 \rangle$  in interaction energy  $e_{AB}$ . Reprinted, with permission, from ref. 7.

ever, we found nearly ideal behavior with relatively small expansion (only a few percent greater than the unperturbed coil size). Figure 4 illustrates this relatively small expansion of a 1:1 blend for various interactions.

Recently Ediger *et al.*<sup>12)</sup> indicated that the coil size of one polymer dispersed in a matrix of the other is a very sensitive indicator of the interactions between the polymers. In accordance with that finding, Binder *et al.*<sup>13)</sup> observed a collapse of chains dispersed in another matrix polymer, an observation indicating unfavorable interactions between components. This observation leads to the corollary prediction that, for asymmetric composition and favorable interactions, one should observe an expansion of the dispersed minority chains. Example III deals with an MC simulation of the latter situation.

Figures 5 and 6 show the effects of interactions and blend composition on coil size. Both favorable interactions between blend components and a composition asymmetry have to be present to observe significant differences in the sizes of the coils. Figure 5 shows that at compositional symmetry ( $x_B = 0.5$ ) both A and B chains are equal in size and exhibit a small expansion because of favorable interactions. As the system becomes more asymmetric, the

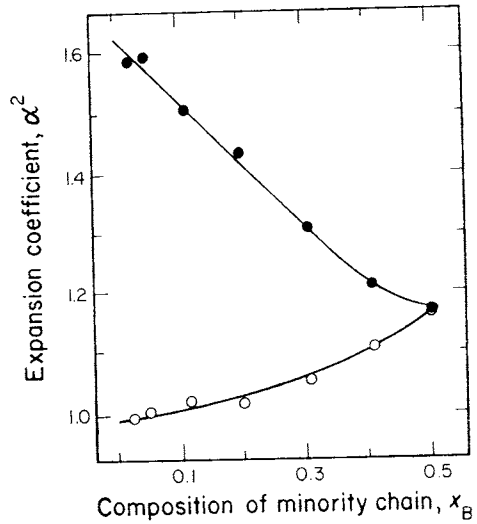


Fig. 5 Variation of expansion coefficient  $\alpha^2$  of the minority B chains ( $\bullet$ ) and the majority A chains ( $\circ$ ) with blend composition  $x_B$  in the mixture, for a constant A-B attraction,  $e_{AB} = -0.5$ . Reprinted, with permission, from ref. 11.

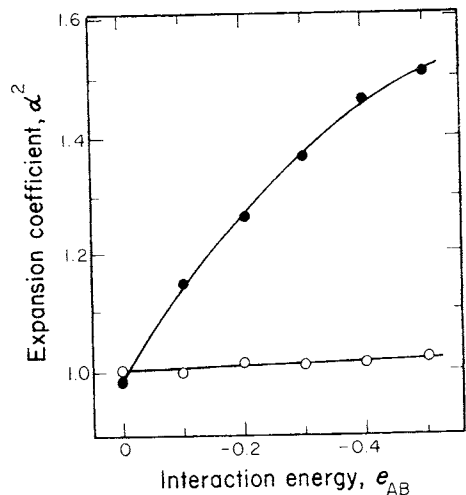


Fig. 6 Variation of chain expansion with reduced interaction energy  $e_{AB}$  for a constant asymmetric chain composition,  $x_B = 0.1136$ ;  $\bullet$ , minority B chains;  $\circ$ , majority A chains. Reprinted, with permission, from ref. 11.

majority chains experience more and more of their own environment and approach the unperturbed dimension ( $\alpha^2 = 1$ ). The minority chains, however, are dispersed in the other polymer and expand as a result of the many favorable interactions with the matrix. Figure 6 shows that when the composition is asymmetric, the minority chains react strongly (*i.e.*, they expand) to even small changes in interaction energy, whereas the majority chains retain their unperturbed dimensions and do not respond to the changing interaction energy.

These results show that the coil expansion under asymmetric composition conditions is significantly greater than a few percent and thus is definitely accessible by experiment and must play a role in the various phenomena touched on below. Figure 6 supports previous observations indicating a high sensitivity of the coil dimensions of dispersed B chains to polymer B-polymer A interactions.

The implications of the variation of coil size with changes in interaction energy and composition are numerous. For example, at polymer-polymer interfaces, at surfaces, and in confined systems such as pores, the different coil sizes will lead to different behaviors of the interface layer when the interface thickness is of the same order of magnitude as the dimensions of the coils. In fact, the larger coils will be expelled from the interface to the bulk region, whereas the smaller coils will remain in the interface layer. However, this effect of different coil sizes is complicated at interfaces by other surface effects that act concomitantly.

#### Acknowledgement

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#### References

- 1) F.E. Karasz and W.J. MacKnight, *Pure Appl. Chem.* **52**, 409 (1980).
- 2) G. ten Brinke, F.E. Karasz and W.J. MacKnight, *Macromolecules* **16**, 1827

(1983).

- 3) R.D. Paul and J.W. Barlow, *Polymer* **25**, 487 (1984).
- 4) S.H. Goh and S.Y. Lee, *Eur. Polym. J.* **24**, 923 (1988).
- 5) H. Ueda and F.E. Karasz, *Macromolecules* **18**, 2719 (1985).
- 6) T.S. Ellis, *Macromolecules* **22**, 742 (1985).
- 7) P. Cifra, F.E. Karasz and W.J. MacKnight, *J. Polym. Sci. Polym. Phys.* **26**, 2379 (1988).
- 8) P. Cifra, F.E. Karasz and W.J. MacKnight, *Macromolecules* **22**, 3649 (1989).
- 9) Y. Aoki, *Macromolecules* **21**, 1277 (1988).
- 10) J. Jelenic, R.G. Kirste, R.C. Oberthur and S. Schmitt-Strecker, *Makromol. Chem.* **185**, 129 (1984).
- 11) P. Cifra, F.E. Karasz and W.J. MacKnight, *Macromolecules* **21**, 446 (1988).
- 12) M.D. Ediger, R.P. Domingue, K.A. Peterson and M.D. Fayer, *Macromolecules* **18**, 1182 (1985).
- 13) A. Sariban and K. Binder, *Macromolecules* **21**, 711 (1988).

#### 要 旨

ポリマーの相互溶解性に対して分子間相互作用は決定的な役割を担うが、相互作用の本性を溶解に関する熱力学的性質から明らかにしようとする試みには、高分子固有の高い粘性とガラス転移および解析において導入される分子場近似のもたらず困難が付きまとう。そこで我々はこれらの制約を受けることなく理論と実験のいずれの代わりともなる第三の方法としてモンテカルロ法に関心を払うようになった。ここではポリマーブレンドへのMC法の応用3例の結果を述べる。

#### F. E. Karasz 教授紹介

平成2年第26回熱測定討論会を九州大学で開催するにあたり、実行委員である庶務幹事の阿竹徹先生から外人学者の講演も企画するようにとのお話がありました。特定テーマ“有機化合物および高分子の熱測定と熱分析”に関連した外人学者として、Univ. of Massachusetts, Polymer Science & EngineeringのFrank E. Karasz教授にお願いしたところ、快諾を得ました。特別講演の内容は、当時の本誌編集委員長の松尾隆祐先生の依頼により論文となりました。ここに、簡単に





講演中の Karasz 教授,  
九州大学工学部本館にて  
1990年11月23日

Karasz 教授の紹介を致す次第です。

教授は1954年 Univ. of London, Imperial College を卒業し, Ph. D. を1957年 Univ. of Washington から, また D. Sc. を1972年 Univ. of London から授与されました。1961~67年 General Electric Research Laboratory に勤務し, 高分子の熱力学, 輸送現象に関する研究を展開され, 1967年以降現在の大学に移り, 71年に

教授に, また86年には Distinguished Univ. Professor の称号を受けています。また, 本年 National Academy of Engineering に選任され, 非常に名誉にしていました。名前が示すように非常にフランクで, また親しみ易い人柄の方です。

熱測定グループの方には, GE 時代の断熱カロリメータによる高分子の熱容量測定で有名でしょう。大阪工業大学の影本彰弘先生は, 1968年から約1年の滞在印象記を本誌の前身である *Newsletter* 2, 51 (1971) に投稿されています。1979年私の滞在時にも GE から持参したカロリメータは実験室にありましたが, 自分が測定しなければデータは出ないと, 愛着をもっているようでした。

彼の最近の研究範囲は, 導電性高分子, 非線形光学効果, 動的光散乱による拡散の研究から高分子ブレンドの相溶性まで非常に多岐にわたり, 1990年度までに285の報文を報告しています。本論文は, 最後のテーマに関連するもので, 最近のアメリカの一つの研究動向を反映しています。特別講演を依頼した時も, 直接的な熱測定でないことを幾分気にしていましたが, 本年の熱測定討論会のミニシンポジウムのテーマの一つが“計算機シミュレーションと熱測定”であることを考えると適切であったと云えるでしょう。 (高見沢徹一郎)