Variation of the chain dimensions with the concentration and quality of the monomer and polymer solvent

Peter Cifra* and Tomáš Bleha
Polymer Institute, Slovak Academy of Sciences, 842 36 Bratislava, Slovakia
(Received 7 February 1992; revised 13 April 1993)

Monte Carlo simulations on the cubic lattice were used to investigate how the functions describing the concentration-dependent size of macromolecular solutes are affected when the usual, low-molecular-weight ('monomeric') solvent is replaced by a chain-like 'polymeric' solvent. The simulations confirm the expected trend of coil shrinkage with the increase of solute volume fraction ϕ. Remarkably, however, only a minor difference was found between the monomeric and polymeric solvents in the concentration dependence of the expansion coefficient α. The double logarithmic plot of the function α^2 *versus* ϕ^γ in the range of semidilute solutions gives a value of exponent $\gamma \approx -0.24$ for both types of solvents, which is in good accord with the arguments of the mean-field and scaling theories. In contrast to the concentration dependence of α, the chain-like character of the solvent has a considerable effect on the variation of the expansion coefficient α with the solvent quality given, for example, by the χ parameter.

(Keywords: Monte-Carlo simulations; chain dimensions; semidilute solution; miscible polymer blends; scaling theory)

INTRODUCTION

Recent investigations of the concentration dependence of polymer chain dimensions in solution have focused on the integral description of the chain behaviour over the whole span of concentration, c, from the dilute to the semidilute and concentrated regimes. For thermodynamically good solvents, the following picture seems to be generally accepted. The flexible coil with the maximum degree of swelling at infinitely dilute solution is gradually compressed with the increase of polymer concentration in solution. In the limiting case when the volume fraction of the polymer ϕ approaches unity, the mean dimensions of chains converge to their unperturbed value characteristic of the theta state. Consequently, the mean dimensions in the theta solvent should be independent of concentration.

Such a description of the concentration behaviour was originally based on data obtained mainly in dilute solutions, where the expressions were derived[1] in the closed form or as a power series for the expansion coefficient $\alpha^2 = \langle r^2 \rangle / \langle r_0^2 \rangle$ as a function of concentration. Here $\langle r^2 \rangle$ and $\langle r_0^2 \rangle$ are mean-square end-to-end distances of chains in the solvent and in the theta state, respectively. The related concept of the concentration-dependent effective hydrodynamic volume of the soft impenetrable coils proved to be extremely useful in the rationalization of the numerous equilibrium and transport properties of dilute solutions of flexible macromolecules[2,3].

The mean-field and scaling theories have been developed to describe the behaviour of the chain molecules in the semidilute and concentrated regimes. The scaling theory predicts universal relations for the chain dimensions as a function of c. For example, in semidilute solutions the reduction of chain dimension should be proportional to $\phi^{-(2\nu-1)/(3\nu-1)}$, ν being the Flory excluded-volume exponent, equal to 0.6 in good solvents[4]. Similarly, some mean-field theories[5] provide the value of the expansion coefficient α as a function of the chain length, concentration and solvent quality throughout the concentration scale. The predictions of the mean-field theory[5] are similar to, but differ slightly in detail from, the results of the scaling theory. The general conclusions of both theories are fully supported by the experimental measurements of the radius of gyration R_g of macromolecules in good solvents by small-angle neutron scattering[6,7].

The question of a macromolecular size in concentrated solution also represents an attractive opportunity for the application of Monte Carlo (MC) simulations on a lattice. The results of simulations carried out so far[8-10] provide additional evidence for the change of coil size with concentration under various conditions. Computations to imitate situations that would be difficult or impossible to measure in laboratory experiments are particularly valuable; these include simulations of the chain dimensions in non-solvents[8] or of macromolecules confined in pores[11]. Simulations are also useful in cases where no suitable theory of a phenomenon is available. This category includes the question of how concentration functions found for low-molecular-weight solvents are affected by the use of solvents with a chain-like ('polymeric') character. A prominent example of such a

---

* To whom correspondence should be addressed

0032-3861/93/234924-06

system is the binary polymer mixture with a high concentration of one component ('polymeric solvent').

The related problem of chain dimensions in polymer blends has recently been addressed by MC simulations[12–16]. Simulations of a single chain of polymer A embedded in a matrix of polymer B predicted[15,16] changes in the dimensions of the A-type chain as a function of the segment interaction energy. Similarly, in multiple chain systems of a polymer A dispersed in the matrix of a major component B, a marked expansion (up to 26%) of the minor chain component was observed[13] for the case of favourable interactions between the components of the mixture. In contrast, a study[14] that assumed unfavourable interactions between the mixture components reported a noticeable contraction in the dimensions of the minor chain component. These predictions of simulations are supported by observation[17] of the positive and negative changes of the chain size relative to the theta dimensions by small-angle neutron scattering in several compatible and incompatible binary polymer mixtures.

In this contribution based on MC simulations, we compare the concentration variation of coil expansion in a polymeric solvent to that in a system with an analogous 'monomeric' solvent. The comparison should identify the effect of segment connectivity in solvent molecules on the concentration functions of the size of a macromolecular solute. The results show that the connectivity effect plays a minor role, the effect of solvent power being dominant in the concentration functions. On the contrary, the variation of the expansion coefficient α with intermolecular interactions is a sensitive function of the chain-like character of the solvent.

EXPERIMENTAL

Simulations were done on a simple cubic lattice with box length $L=22$, following the procedure used previously[12,13]. Simulations started from the system with 484 chains, each of length $N_L=20$ segments, which occupied 90.9% of the lattice points, the rest being void. The multichain system was equilibrated by 6×10^7 reptation trial moves under athermal conditions, i.e. assuming only the intra- and intermolecular excluded volume based on site occupancy. From this point, the procedure was differentiated for the systems with monomer (M) and polymer (P) solvents.

In simulations with the P solvent, the assembly of 484 chains was divided randomly into components A (solute) and B (solvent) in a ratio representing the preset composition of the mixture. The chain lengths of solute (N_L) and of solvent (N_S) were assumed to be identical. Various states of the system were simulated by variations of the volume fraction ϕ of the polymer solute (voids are not included in ϕ) and of the reduced intersegmental nearest-neighbour interaction energy $\varepsilon=\varepsilon'/kT$. A zero value of ε corresponds to an athermal system, whereas good solvents, featuring attraction between segments of solute and solvents, are characterized by negative values of ε. The number of reptation trial moves needed to ensure proper statistics was kept within the range $(1–2.2)\times10^8$ attempts, and the moves were distributed over the whole volume of the mixture.

In the system with M solvent, after division of the chains into types A and B, chains of type B were eliminated from the lattice and were replaced by monomers located in the vacant lattice points. Again, the quality of solvent was controlled by the reduced nearest-neighbour interaction energy ε_c between the chain segments and the surrounding sites occupied by M solvent. The energy of ε_c was converted to ε by multiplying by a factor 0.909, to take into account the presence of voids in the lattice and to ensure proper comparison with the P solvent.

The assumed high density of the lattice occupation prevented the extension of simulations to the longer chains. In lattice computations there is always a trade-off between the occupational density and the mode of chain movement on one hand and the chain length on the other. Sometimes the longer chains are simulated by using, rather than physical movement on the lattice, a 'non-physical' mode of bond breaking and subsequent formation; however, this procedure results in a polydispersity of equilibrated chains. The reduction of occupational density in the system with P solvent would certainly enable the treatment of longer chains. However, as will be commented on later, such an approach may affect the resulting concentration functions of the coil dimensions.

The mean-square end-to-end distance of the solute chains $\langle r^2\rangle$ and the average number of intermolecular contacts per chain N_{AB} were evaluated. The value of 28.90, obtained previously[13] for the athermal mixture, was used for the reference unperturbed dimensions $\langle r_0^2\rangle$ in expressing the expansion coefficient α of the solute chains.

RESULTS AND DISCUSSION

Variation of expansion coefficient with concentration

The effect of concentration on the expansion coefficient α will be analysed first. The variation of α with the volume fraction ϕ of solute is plotted in *Figure 1* for good solvents of the M and P type with interaction energy $\varepsilon=-0.5$. Both curves are very similar; the expansion coefficient decreases with increasing concentration of the solute. The choice of less favourable interaction energy $\varepsilon=-0.2$,

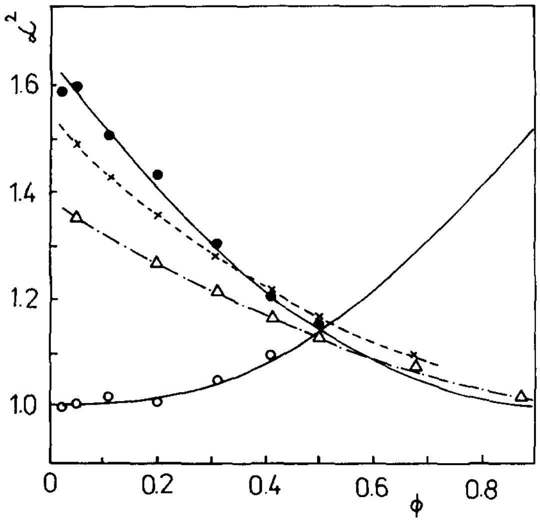

Figure 1 Variation of the expansion coefficient α with the volume fraction of the solute polymer ϕ for M solvents with $\varepsilon=-0.5$ (×), $\varepsilon=-0.2$ (△) and for the P solvent with $\varepsilon=-0.5$ (●); ○, chain dimensions of the molecules of the P solvent. Since in a polymer blend $N_S=N_L$, a symmetrical extension of curves relative to the 1:1 composition is shown

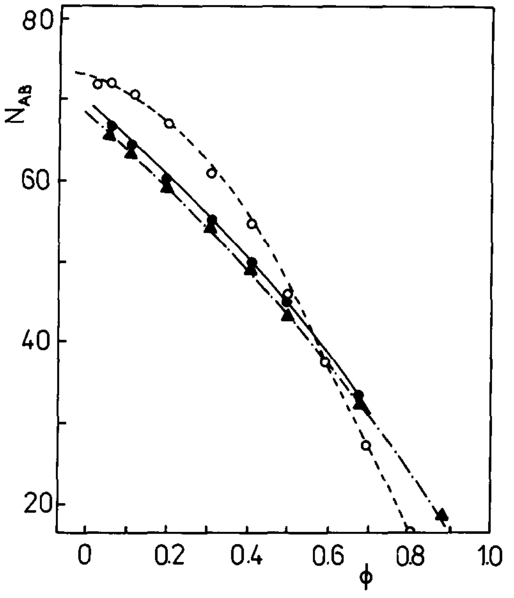

Figure 2 Plot of the number of intermolecular contacts of segments per chain N_{AB} *versus* the solute volume fraction ϕ. M solvents: ●, $\varepsilon=-0.5$; ▲, $\varepsilon=-0.2$. P solvent: ○, $\varepsilon=-0.5$

approximating a moderately good solvent, results, as expected, in the reduction of the coil expansion, the overall shape of the curve being unaffected. To complete the picture, *Figure 1* also shows the variation of the solvent chain dimensions, i.e. of component B in the polymer mixture[13]. Solvent molecules expand from their originally unperturbed dimensions with the gradually diminishing concentration of solvent in the mixture. Owing to the identical chain lengths of the solvent and solute, both curves for the P system in *Figure 1* are symmetrical and cross at the point of 1:1 composition of the mixture.

The number of intersegmental contacts per solute chain N_{AB}, an indicator of solvation of the solute, is plotted in *Figure 2* for the same systems as in *Figure 1*. We see that at concentrations $\phi<0.5$ and for the identical attraction energy $\varepsilon=-0.5$, the solute macromolecules are better solvated by the P solvent than by the M solvent. This rather surprising observation is also reflected in *Figure 1* by the higher expansion coefficient α in the P solvent relative to the M solvent in about the same range of ϕ. Apparently, the solute–solvent attraction is high enough to secure the maximum attainable saturation of the solvation points. The solvation in the P solvent may be enhanced by the partial alignment of solute and solvent chains (similar to complexation) due to the solvent chain connectivity. It appears that the effect of solvation is dominant at concentrations $\phi<0.5$. At higher solute concentrations, interactions with the solvent are less abundant and the effect of entanglements sets in. For the M solvent, a stronger expansion is allowed than for the P solvent which, by forming entanglements with solute, screens out the excluded volume in solute chains. These two effects probably lead to inversion of the behaviour of the P and M solvents in the crossover region at about $\phi=0.5$. It should be noted that the concentration of the first coil overlap in these systems of relatively short chains is $\phi^*=0.23$ and entanglements set in for higher concentrations. The crossover points, where the coil expansion and the solvation become larger for the M solvent, are located at slightly different values of ϕ in *Figures 1* and *2*, presumably because the chain swelling is governed by intrachain self-avoiding repulsion as well as by intermolecular interactions. It is instructive to realize that the curves for P and M solvents in *Figures 1* and *2* should meet for $\phi=1$ (but not for $\phi=0$).

In order to compare the MC results with the predictions of polymer solution theories developed for the intermediate range of concentrations, the data from *Figure 1* are replotted in *Figure 3* in a double logarithmic representation. The function $\log\alpha$ *versus* $\log\phi$, smooth and almost horizontal in the dilute solution, changes abruptly in the semidilute region and decreases linearly up to the limiting state of $\phi=1$. As mentioned already, the scaling theory predicts[4] the reduction of chain swelling by the relation $\alpha^2=\phi^\gamma$, where in good solvents $\gamma=-0.25$. Similar values of the exponent γ were reported from experimental measurements of the radius of gyration R_g by small-angle neutron scattering[6,7]. In the model of soft impenetrable spheres[2] which can contract or expand but never overlap, the exponent γ attains[5] the value $-2/3$, the steepest possible slope.

The linear portion of the MC curves in *Figure 3* for good solvents with $\varepsilon=-0.5$ gives the exponent $\gamma=-0.24$, regardless of whether the P or M solvent is assumed. In the moderately good solvent with $\varepsilon=-0.2$, the exponent $\gamma=-0.19$. All these values from the MC simulations conform very well with the scaling theory as well as with the mean-field theory[5] of the concentration effect. The theory[5] predicts the function $\log\alpha$ *versus* $\log\phi$ to be of similar shape to that shown in *Figure 3*; moreover, the theory is able to account for the chain length dependence of the solute polymer. For a given quality of solvent, the increase in chain length should manifest itself in *Figure 3* by the enhancement of the coefficient α and by the shift of the linear part of the curves to the left; consequently, the volume fraction where the unit value

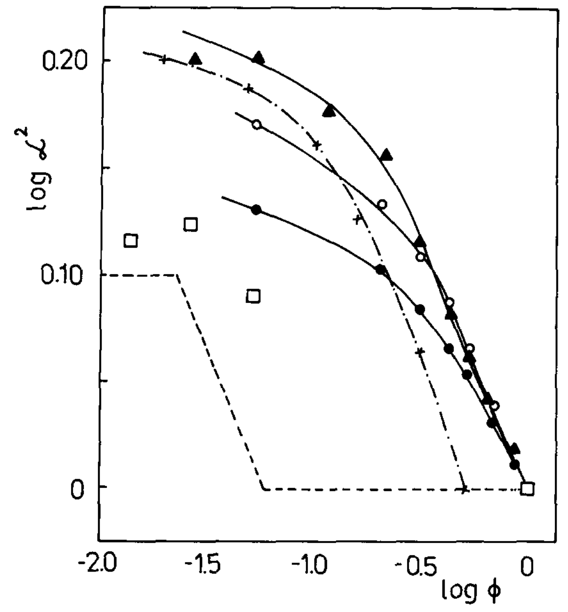

Figure 3 Double logarithmic plot of the square of the expansion coefficient *versus* the solute volume fraction ϕ for the polymer solute $\varepsilon=-0.5$ (▲) and for the two M solvents $\varepsilon=-0.5$ (○) and $\varepsilon=-0.2$ (●). –·–·, Smoothed experimental data for polyisoprene in hexadecane[18]; □, experimental data[19] for a PI blend; ---, scaling theory prediction for a bimodal chemically homogeneous blend[19,23]

of the expansion coefficient is reached, usually denoted as ϕ^{**}, is less than one.

Most experimental studies of the concentration dependence of the chain size were conducted by measuring the radius of gyration, viscosity, diffusion coefficient, etc. The concentration dependence of $\langle r^2 \rangle$ has so far been measured only by the method of dielectric spectroscopy refined by Adachi *et al.*[18,19]. Their results[18] for *cis*-polyisoprene (PI), with $M_w \approx 10^5$ in hexadecane, are replotted in *Figure 3*. Hexadecane corresponds partially to the notion of a chain-like solvent of moderately good quality; the χ parameter of this system[18] is 0.24. Owing to the much longer length of PI chains than MC chains, the linear part of the experimental curve in *Figure 3* is shifted to a lower value of ϕ, and the reference coil swelling with $\alpha = 1$ is reached at $\phi^{**} = 0.50$, in accordance with the deductions of the mean-field theory[5]. The slope of the experimental curve gives $\gamma = -0.31$, a value higher than the maximum predicted by the scaling theory. This observation was interpreted by the authors[18] by means of another variant of the mean-field theory[20] which further divides the semidilute region into two zones differing in power-law functional dependence on concentration. The slope γ in the second (more concentrated) zone can be higher than the limit $\gamma = -0.25$ predicted by the scaling theory.

Subsequently, using the same technique, the chain expansion was measured[19] for PI with $M_w = 1550$. The results (*Figure 3*) show that the low-molecular-weight component acts as a marginally good solvent and therefore the high-molecular-weight component is in an expanded conformation. Three experimental points for this bimodal blend, located in the crossover concentration region, indicate that the concentration dependence of α is much weaker than in the case of hexadecane solvent.

Dependences of the chain dimensions on ϕ similar to those in *Figures 1–3* were observed in other MC simulations in good solvents[8,9]. Studies of solvents corresponding to the unfavourable (positive) values of the energy ε confirmed[8,9] that at first the chain dimensions in the theta state are independent of ϕ, and second that in non-solvents below the theta state, where chains assume the contracted conformation, a gradual expansion of the coils to the unperturbed dimensions takes place with an increase of ϕ.

The results on the variation of the chain dimensions for the P solvent are inversely related to the appropriate choice of the concentration of voids in a lattice (see Experimental section). The introduction of voids changes the binary melt into an effectively ternary system, polymer A + polymer B + voids. In principle, the variation of the chain dimension with the volume fraction of voids in a ternary system should be similar to the concentration functions based on volume fractions (ϕ) of polymer components only, of the type shown in *Figure 3*. Therefore, the selection of the concentration of voids is not necessarily trivial, and may affect some computed properties. An analysis of this questionable point in bulk polymer system simulations is so far completely absent from the literature.

To minimize the possible influence of void concentration on the results in this and the related study[13], we have assumed a very low concentration (<10%) of voids in simulations. Simulations in such dense systems are notoriously difficult, and to facilitate the computations we have worked with the *effective* concentration of voids instead of with an explicit differentiation of the lattice sites occupied by the solvent monomers and by voids. As a next step, more time-consuming simulations, with the explicit identification of site occupation by the monomers or by voids, should be considered. However, such treatment will be complicated by the phenomenon of 'preferential solvation' of chains by the solvent monomers relative to voids.

In the very dense system assumed in our simulations, the chain dimensions computed for $\phi = 1$ closely approach the unperturbed dimensions $\langle r^2 \rangle_0$. The higher fraction of voids (40–60%) usually assumed in the simulation practice makes the treatment of polymer systems much more convenient. However, in that case, the chain dimensions $\langle r^2 \rangle_{\mathrm{ref}}$ computed for $\phi = 1$ represent some reference value only, which could be expanded relative to $\langle r^2 \rangle_0$ because of the variation of coil size with the amount of voids in a lattice. The choice of a moderate concentration of voids in a lattice may be acceptable in studies of certain properties of bulk polymer systems, but it is prudent not to use such a procedure in the evaluation of the concentration functions of the chain dimensions.

The MC results in *Figures 1–3* are in overall agreement with concentration dependences available from the theory, MC simulations and measurements pertinent to the low-molecular-weight solvents. The inconspicuous influence of the polymer-like solvent on the concentration functions seen in *Figures 1–3* is rather surprising. Evidently, the difference between the segments separated in the M solvent or interconnected in the P solvent plays only a minor role in the systems studied, where rather strong solute–solvent interaction was assumed. This may be connected with the fact that the lattice calculations do not take into account interactions of the solvent–solvent type, the free volume of the solvents and the other subtle differences between the M and P solvents. Unfortunately, apart from polymer blends[17,19], no other experimental data for the concentration-dependent size of macromolecular solutes determined in polymer-like solvents seem to be available.

Variation of α with solvent quality

We next describe how the chain-like character of the solvent influences the dependence of coil swelling on solvent power. *Figure 4* shows the number of intersegmental contacts N_{AB} as a function of the reduced energy ε in the region of good solvents. In the M solvent, the number of contacts (the degree of solvation) is affected only a little by the changing solvent power from the athermal to very good solvents, whereas in the P solvent a sharply increasing function is observed. The relative insensitivity of N_{AB} to ε also explains the proximity of curves in *Figure 2* for the two M solvents.

The differences in solvation behaviour between the M and P solvents are transferred into analogous functions of the expansion coefficients (*Figure 5*). The solvent power affects the coil expansion much more in the P solvent than in the M solvent. *Figure 5* clearly shows that in the P solvent the solute chains exhibit unperturbed dimensions ($\alpha = 1$) in an athermal system at $\phi = 0.114$, whereas in the M solvent under the same conditions the coils are moderately expanded with $\alpha \approx 1.1$. Because of the steeper dependence of the coil expansion, the P solvent matches the expansion coefficient in M solvents at $\varepsilon = 0.3$, and above this value of ε the coil swelling in the P solvent predominates.

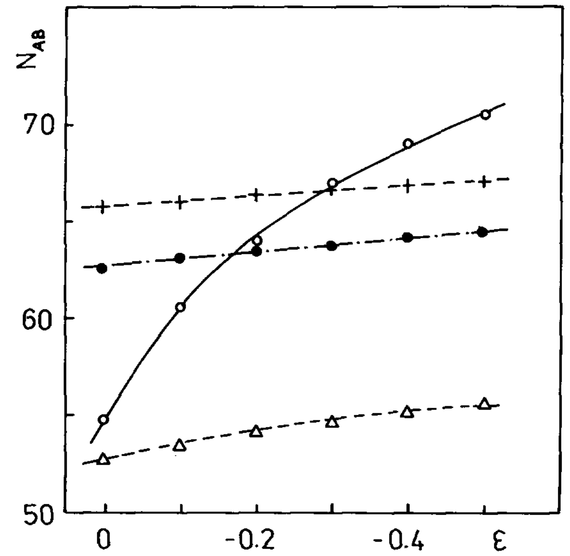

Figure 4 Variation of the number of intermolecular contacts per chain N_{AB} with reduced intersegmental energy ε for the P solvent with solute volume fraction $\phi=0.114$ (○) and for the M solvents with $\phi=0.027$ (+), 0.114 (●) and 0.301 (△)

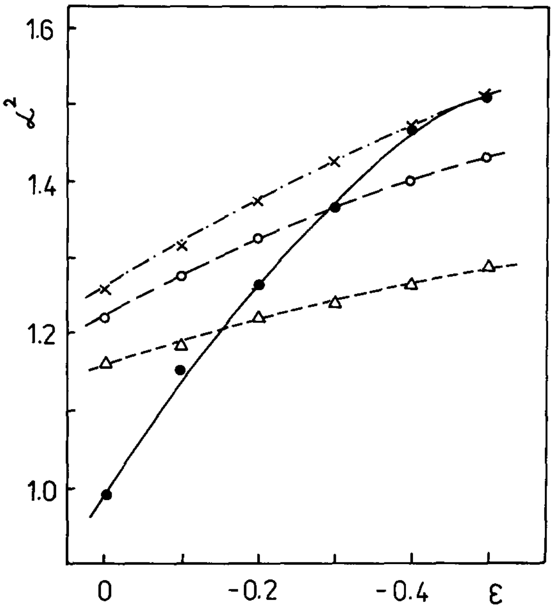

Figure 5 Variation of the square of the expansion coefficient with intersegmental energy ε for the P solvent with $\phi=0.114$ (●) and for the M solvents with $\phi=0.027$ (×), 0.114 (○) and 0.301 (△)

It should be pointed out that only the region of attractive intersegmental energy was sampled in *Figures 4* and *5*. With the transition to positive values of ε, a reduction of coil size to theta dimensions, and even below, takes place. This behaviour was observed for the positive ε in MC simulations of polymer blends[14], where the gradual contraction of the minor chain component was observed up to 85% of the theta dimensions in the limiting point of phase demixing.

It would be expedient to know the analytical functions in order to calculate the effects of both concentration and solvent quality on the expansion coefficient. However, despite progress in the theoretical approach, no such expressions seem to be available for the wide range of concentrations and solvent quality. In dilute solutions, this type of relation[1–3] gives the solvent quality by the product A_2M, where A_2 is the second virial coefficient and M is molecular weight. For the wide concentration range a relation was proposed[21]:

$$\alpha^2=0.932(0.5-\chi)^{0.25}\phi^{-0.25} \tag{1}$$

but its validity is restricted to good solvents only.

The double logarithmic plot of our results for the M solvents in a fashion complying with equation (1) does not bring the expected linear dependences (*Figure 6*). The χ parameter was estimated in this procedure using a simple relation $\chi=\varepsilon(z-2)$, where z is the coordination number of a lattice ($z=6$ for a simple cubic lattice). Previous treatment[13] of the data for the expansion of the minority chain component in a polymer mixture by equation (1) yielded a straight line with a slope of 0.27 (*Figure 6*). However, in the P solvent, a variant of equation (1) is more appropriate, where the term $(0.5-\chi)$ is replaced by $[(1/2N_L)-\chi]$. Using this modification of equation (1), a non-linear curve is obtained for the P solvent with $N_L=20$ (*Figure 6*). The power-law function $\phi^{-0.25}$ in equation (1) is approximately satisfied by our data, as shown by the analysis of *Figure 3*. Thus, the failure of equation (1) to fit the MC data may originate from the improper form of the interaction term. It is difficult to assess the degree to which the approximate conversion of ε to the χ parameter contributes to this failure. In the lattice calculations of polymer blends[12], the linear proportionality between these two quantities was observed in the miscibility region.

Scaling relations for the bimodal blends

The universal analytical relation linking the expansion coefficient, the concentration and the solvent quality is still a challenge in the theory of polymer solutions. Since such relations are absent for the M solvent, their formulations for the P solvent will undoubtedly be an

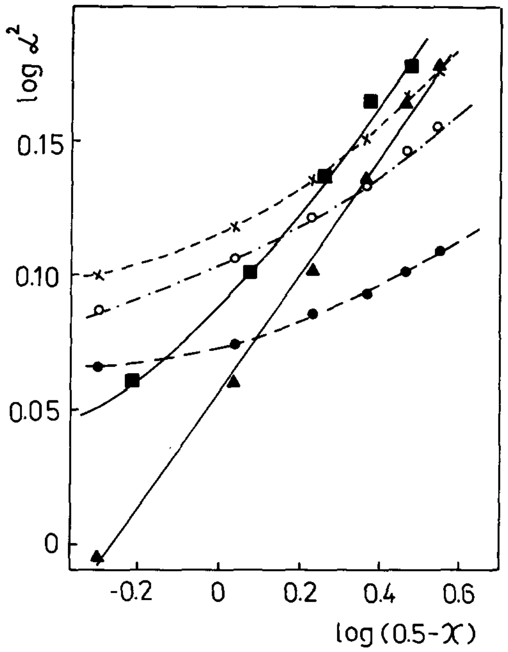

Figure 6 Plot of the MC results according to equation (1) for the M solvents with $\phi=0.027$ (×), 0.114 (○) and 0.301 (●). The full lines correspond to the P solvent at $\phi=0.114$: ▲, using equation (1); ■, using a modified version of equation (1), see text

even more difficult task. As a first step in this direction, the scaling relations for some systems with a P solvent were presented[22–24]. In the ternary system of the semidilute solution of a guest polymer in a mixture of a host polymer and a good solvent, power-law relations were established[22] for the radius of gyration as a function of the chain lengths of host and guest polymers, their concentration and the χ parameter of the system.

A binary system more directly related to our simulations, consisting of a polymer solute dissolved in a melt of shorter, chemically identical chains with variable chain length N_S, was recently treated by the scaling theory[23,24]. For this athermal system, the authors[23,24] analysed the excluded volume of the guest solute chains of length N_L. Chains longer than some threshold length, $N_L^* = N_S^2$, are partially swollen due to the intrachain excluded volume repulsion, and their end-to-end distance scales as:

$$r \cong a N_L^{3/5} N_S^{-1/5} \tag{2}$$

where a is a segment size and all numerical coefficients are omitted. In solute chains shorter than the threshold length N_L^*, the screening of monomer–monomer interactions leads to partial deswelling, and solute chains behave as ideal with the unperturbed dimensions $r_0 \cong a N_L^{1/2}$. By introducing the asymmetry factor $x = N_L/N_S$, a simple proportionality can be deduced from the last two scaling relations:

$$\alpha^2 = r^2/r_0^2 \cong x^{2/5} \tag{3}$$

In contrast, starting from the classical mean-field expressions for dilute solutions, a relation was derived[19] for the expansion coefficient in dilute athermal bimodal blends which in our notation reads:

$$\alpha^2 \cong x^{2/5} N_L^{-1/5} \tag{4}$$

The overlapping concentration (critical threshold), where the semidilute regime sets in, is in the scaling notation given by the expression $\phi^* = N_L^{-4/5} N_S^{3/5}$. In the semidilute regime, the scaling theory predicts the following proportionality[19,23] for the expansion coefficient of the high-molecular-weight component of the blend:

$$\alpha^2 \cong (N_S \phi)^{-1/4} \tag{5}$$

It can be seen from relation (5) that in the semidilute regime the solute chain expansion should be independent of the solute chain length. The scaling predictions of the concentration variation of chain expansion are shown schematically in *Figure 3* by the dotted line, including the concentration regime where the solute chains of the blend assume the unperturbed dimensions.

The simplified scaling analysis for a bimodal blend can be confronted qualitatively with our MC results. A major problem in such a comparison originates from the fact that in scaling arguments, because of the large disparity assumed between the chain length of both components (N_L and N_S), an athermal system represents a good solvent, whereas in our MC simulations the good solvent is modelled by the attractive intersegmental energy ε. In the dilute regime, the curves in *Figure 5* for the M and P solvents at $\phi = 0.114$ represent, in our calculations, two extreme limits of the asymmetry factor x: 20 and 1, respectively. In the athermal system ($\varepsilon = 0$), the data in *Figure 5* confirm the increase in the expansion coefficient with increasing x, assumed in equations (3) and (4); however, the exponent of this proportionality cannot be evaluated. Instead of a discontinuous jump from an ideal to a partially swollen state at some critical value of the asymmetry factor x^*, presumed[23,24] in the scaling arguments above, rather a gradual change of the coefficient α with increasing x can be expected. It should be stressed that the comparison of scaling and MC results should be restricted to the athermal system only; in the solvents with a rather high negative value of ε the coefficient α becomes inversely proportional to x (cf. *Figures 3* and *5*).

In the semidilute regime, the scaling relation (5) and MC data in *Figure 3* are in harmony with respect to the slope of the concentration variation of α, given by the exponent γ, even though the experimental data[19] for a PI blend (*Figure 3*) suggest a much lower value (in absolute terms) of the exponent γ. Both approaches concur that the slope (exponent γ) should be independent of the chain length of the solute. On the other hand, according to equation (5) the extent of coil swelling should be inversely proportional to the solvent chain length. Consequently, in an athermal system the expansion coefficient in the M solvent should be higher than in the P solvent. Accordingly, the curve for the P solvent in *Figure 3* should be shifted (with the same slope) to the left relative to that for the M solvent, α_P being lower than α_M and ϕ_P^{**} lower than ϕ_M^{**}. The actual location of curves from MC simulations shown in *Figure 3* differs from these scaling predictions since it corresponds to the situation where a rather high intersegmental attraction is assumed.

REFERENCES

1 Yamakawa, H. 'Modern Theory of Polymer Solutions', Harper and Row, New York, 1971

2 Rudin, A. and Wagner, R. A. *J. Appl. Polym. Sci.* 1976, **20**, 1483

3 Bleha, T., Mlýnek, J. and Berek, D. *Polymer* 1980, **21**, 798

4 Daoud, D. and Jannink, G. *J. Phys. (Paris)* 1976, **37**, 973

5 Lohse, D. J. *Macromolecules* 1981, **14**, 1658

6 Daoud, M., Cotton, J. P., Farnoux, B., Jannink, G., Sarma, G., Benoit, H., Duplessix, R., Picot, C. and de Gennes, P. G. *Macromolecules* 1975, **8**, 804

7 King, J. S., Boyer, W., Wignall, G. D. and Ullman, R. *Macromolecules* 1985, **18**, 709

8 Okamoto, H. *J. Chem. Phys.* 1979, **70**, 1690

9 Birshtein, T. M., Sariban, A. A. and Skvorcov, A. M. *Polymer* 1982, **23**, 1481

10 Bishop, M., Ceperley, D., Frisch, H. L. and Kalos, M. H. *J. Chem. Phys.* 1980, **72**, 3228

11 Bleha, T., Cifra, P. and Karasz, F. E. *Polymer* 1990, **31**, 1321

12 Cifra, P., Karasz, F. E. and MacKnight, W. J. *J. Polym. Sci., Polym. Phys. Edn* 1988, **26**, 2379

13 Cifra, P., Karasz, F. E. and MacKnight, W. J. *Macromolecules* 1992, **25**, 192

14 Sariban, A. and Binder, K. *Colloid Polym. Sci.* 1988, **266**, 389

15 Sariban, A. and Binder, K. *Makromol. Chem.* 1988, **189**, 2357

16 Olaj, O. F., Zifferer, G. and Lautschbauer, W. *Angew. Makromol. Chem.* 1991, **185/186**, 189

17 Peterson, K. A., Stein, A. D. and Fayer, M. D. *Macromolecules* 1990, **23**, 111

18 Adachi, K., Imanishi, Y., Shinkado, T. and Kotaka, T. *Macromolecules* 1989, **22**, 2391

19 Adachi, K., Nishi, I., Itoh, S. and Kotaka, T. *Macromolecules* 1990, **23**, 2550

20 Muthukumar, M. and Edwards, S. F. *J. Chem. Phys.* 1982, **76**, 2720

21 Muthukumar, M. *J. Chem. Phys.* 1986, **85**, 4722

22 Nose, T. *J. Phys. (Paris)* 1986, **47**, 517

23 Joanny, J. F., Grant, P., Pincus, P. and Turkevich, L. A. *J. Appl. Phys.* 1981, **52**, 5943

24 Brochard-Wyart, F. and Raphael, E. *Macromolecules* 1990, **23**, 2276