Effects of Solvent Size on Microscopic Structures and Properties in Polymer Solutions

Yunqi Li, Tongfei Shi, Lijia An

State Key Laboratory of Polymer Physics and Chemistry, Changchun
Institute of Applied Chemistry, Chinese Academy of Sciences,
Changchun, 130022, China

Introduction

Although intensive attention has been paid to polymer solutions with added medium-sized solvent for scientific research and technological applications due to the addition leading to many interesting phenomena, such as vitrifaction, crystallization, and gelation, fundamental problems regarding the effects of the medium-sized solvent on physical properties and phase behaviors of polymer solutions still remain unsolved.

To better understand the effects of solvent molecular size on the physical properties and phase behaviors of polymer solutions, several issues must be addressed: First, does the solvent size affect the scaling behavior? Second, how does the solvent molecular size affect the critical overlap concentration? Third, how does the solvent molecular size affect the microscopic structure of polymer solution? Finally, in what range the solvent can be defined as the middle-size solvent?

In this work, a lattice Monte Carlo simulation on homopolymer solutions with solvents of different sizes was carried out to address these problems. The simulation model is first concisely introduced, then the effects of solvent molecular sizes on the conformation of polymer chains and the critical overlap concentration in polymer solutions is discussed, followed by a quasi-quantitative definition of the medium-sized solvent. Interesting physical properties and possible microscopic structures in the medium-sized solvent solutions are also presented.

Simulation Model

Monte Carlo simulation is performed in a lattice model based on the eight-site bond fluctuation model where polymer chains are generated in a cubic lattice with periodic boundary conditions in all directions. Here the length of polymer chain N is fixed to 50. The lattice size is 128×128×128. Since the solvent molecule here is not a normal structureless solvent molecule typically assumed in various theories, a dimensionless parameter ξ ($\xi = N^{1/2}/N_S$) proposed by de Gennes,[17] which is also called size ratio, is introduced to generalize the problem about the effect of solvent molecular size, where N_s is the length of solvent. All interactions are null except that the nearest neighboring interaction pairs between the monomers in polymer chains and the monomers in solvent molecules have an attractive potential of $-0.5k_BT$, which makes good solvent for polymers.

In order to give convincing results, five parallel simulations with random initial configurations and different random sequences are carried out. All of the simulation results are collected from the ensemble average of these five parallel samples under thermodynamic equilibrium after 1×10^7 MCS running on each sample. The simulation steps for a sample to reach thermodynamic equilibrium are not larger than 2×10^6 MCS in all cases.

Results and discussion

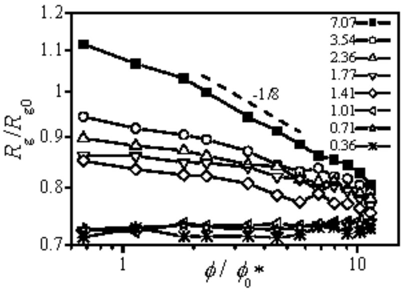

Figure 1. The log-log plots of the root-mean-square radius of gyration of the polymer chains versus polymer concentration ϕ at different size ratios (ξ). The dash line represents the scaling exponent at the semi-dilute region for normal solvent.

Figure 1 shows the plots of R_g/R_{g0} versus ϕ/ϕ_0^* at different ξ values. Here R_{g0}, which is equal to $(N/6)^{1/2}$, is the ideal root-mean-square radius of gyration of the polymer chains, and ϕ_0^*, which is equal to $N^{-4/5}$, is the ideal critical overlap concentration. When $\xi = 7.07$, at least two ϕ/ϕ_0^* regions are observed. (1) when $\phi/\phi_0^* \leq 2$, R_g/R_{g0} is larger than 1 for a normal solvent, indicating that the polymer chains are swollen. These results are similar to those reported by Wang et al.; and (2) when $\phi/\phi_0^* > 2$, the scaling behavior agrees well with the prediction of the scaling theory, namely $R_g \sim \phi^{-1/8}$. In general, when $\xi > 1$, R_g decreases with increasing ϕ or decreasing ξ and becomes less sensitive to ϕ changes at small ξ This qualitative trend of ξ dependence of R_g is in good agreement with the reported results from similar systems. The reason for this trend is believed to be due to the larger-sized solvent induced solvent quality decrease. However, when $\xi \leq 1$, R_g becomes nearly independent of the concentration, which is reasonable because the solvent molecule is so large that the system can be regarded as a bulk mixture. When ξ approaches 1, the dramatic change in the scaling behavior may originate from the loss of configuration entropy, or the depletion potential from the competition between the translation entropy of the medium-sized solvent and the conformation entropy of polymer.

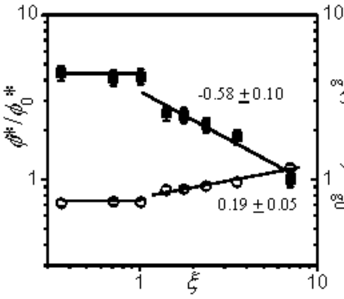

Figure 2. The log-log plot of the size ratio dependence of the overlap concentrations (solid squares) and radius of gyration of polymer chains in infinitely dilute solutions (empty circles)

The exact relationship between R_g and ξ can be obtained from de Gennes' scaling theory by balancing the elastic free energy with excluded volume in the Flory arguments, as

$$R_g(\phi \to 0) \sim N^{3/5} N_S^{-1/5}$$

where $R_g(\phi \longrightarrow 0)$ is the root-mean-square radius of gyration of the polymer chains in infinitely dilute solution. Since N is a constant, $R_g(\phi \to 0)$ is proportional to $\xi^{1/5}$. Our simulation results (See Figure 2) show that the power exponent is 0.19±0.05 when $\xi > 1$, which agrees very well with this scaling law (exponent of 1/5).

The critical overlap concentration ϕ^*, which is a key parameter for the polymer solution and closely associated with $R_g(\phi \longrightarrow 0)$, is calculated by

$$\phi^* = 3N\nu \big/ 4\pi R_g^3(\phi \to 0) \tag{1}$$

From this equation, a scaling relation of $\phi^* \sim \xi^{-3/5}$ can be obtained. However, our results indicate that this scaling exponent of 3/5 satisfied only when $\xi > 1$, and ϕ^* jumps to about $4.5\phi_0^*$ when $\xi \leq 1$, as shown in Figure 2. The jump is concomitant with the dramatic change in the scaling of R_g, and also driven by entropy loss. This solvent molecular size dependence of the ϕ^* agrees with the experimental results reported by Sun et al. for poly(vinyl chloride) (PVC, Mw 11.3×10^4) tetrahydrofuran solutions, where the ϕ^* was ten fold of that in normal solvent after dioctyl phthalate (DOP, Mw 391) was added. Note that we neglect the difference in chemical sequence, the size ratio ($\mathrm{Mw}_{,\mathrm{PVC}}^{1/2}/\mathrm{Mw}_{,\mathrm{DOP}}$) is about 0.86, and our result is in the same order as this experimental results.

To further elucidate the origin of the effect of solvent molecular size and to discuss the microscopic structure in polymer solutions, the interactions between polymer and polymer, as well as polymer and solvent must be clarified. The reduced polymer-solvent interaction pairs C_{PS}, the reduced intra-chain polymer-polymer interaction pairs $C_{PP,intra}$, and the reduced inter-chain polymer-polymer interaction pairs $C_{PP,inter}$ are introduced to explore the microscopic structures of polymers in solutions, and are defined as

$$C_{\mathrm{PS}} = \left\langle \frac{N_{\mathrm{PS}}}{N_{\mathrm{PP,intra}} + N_{\mathrm{PP,inter}} + N_{\mathrm{PS}}} \right\rangle \tag{1}$$

$$C_{\mathrm{PP,inter}} = \left\langle \frac{N_{\mathrm{PP,inter}}}{N_{\mathrm{PP,intra}} + N_{\mathrm{PP,inter}} + N_{\mathrm{PS}}} \right\rangle \tag{2}$$

$$C_{\mathrm{PP,intra}} = \left\langle \frac{N_{\mathrm{PP,intra}}}{N_{\mathrm{PP,intra}} + N_{\mathrm{PP,inter}} + N_{\mathrm{PS}}} \right\rangle \tag{3}$$

where N_{PS}, $N_{\mathrm{PP,intra}}$, and $N_{\mathrm{PP,inter}}$ averaged out for each polymer chain, are the numbers of the polymer-solvent interaction pairs, the intra-chain polymer-polymer interaction pairs, and the inter-chain polymer-polymer interaction pairs, respectively. The < > denotes the ensemble average of five parallel samples at each ϕ and ξ. Large $C_{\mathrm{PP,intra}}$, $C_{\mathrm{PP,inter}}$, and C_{PS} can be understood as polymer chains that are shrunk, aggregated or interpenetrated, and swollen by solvent molecules, respectively. In contrast, small $C_{\mathrm{PP,intra}}$, $C_{\mathrm{PP,inter}}$, and C_{PS} can be interpreted as polymer chains that are stretched, segregated, and separated from solvent molecules, respectively.

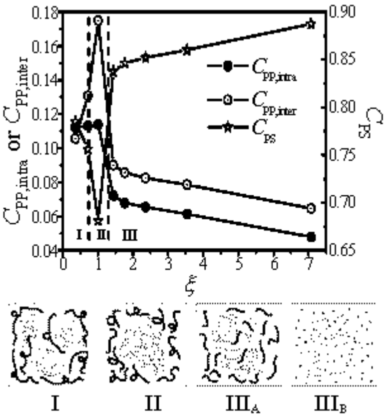

Figure 3. The dependence of the reduced intra-chain polymer-polymer interaction pairs, the reduced inter-chain polymer-polymer interaction pairs and reduced polymer-solvent interaction pairs on size ratios with polymer concentration fixed at 0.15. The vertical dash lines label the boundaries between regions I, II and III. The schematic diagrams illustrate different microscopic structures in polymer solutions, where the thin and the bold lines represent polymer chains and solvent molecules, respectively.

Figure 3 shows the plots of $C_{\mathrm{PP,intra}}$, $C_{\mathrm{PP,inter}}$, and C_{PS} versus ξ at a fixed polymer concentration of 0.15. For each given polymer concentration, the dependencies of these three parameters on ξ are similar. It can be seen that when $\xi > 1$, both $C_{\mathrm{PP,intra}}$ and $C_{\mathrm{PP,inter}}$ increase as ξ decreases, indicating that the polymer chains shrink and tend to aggregate when the solvent molecular size becomes larger. C_{PS} decreases as ξ decreases, suggesting that the polymer chains tend to separate from the solvent molecules. When $\xi \approx 1$, $C_{\mathrm{PP,intra}}$ reaches a maximum and remains almost constant in the region of $\xi < 1$, which is in agreement with the dependency of R_g on ξ, implying that the polymer solution is bulk-like. $C_{\mathrm{PP,inter}}$ also reaches a maximum at $\xi \approx 1$, indicating the polymer chains are greatly aggregated or interpenetrated. However, C_{PS} exhibits a minimum at $\xi \approx 1$, implying that the polymer chains and the solvent molecules are largely separated. When $\xi < 1$, as ξ decreases, $C_{\mathrm{PP,inter}}$ decreases, suggesting that polymer chains are segregating. In contrast, C_{PS} increases, indicating that when the solvent molecular size is very large, the solvent molecules tend to dissolve individual polymer coils rather than polymer monomers.

In order to present a clear description of the effects of ξ on microscopic structures of the polymer solutions, four schematic illustrations are included in Figure 3.

In region III ($\xi > 1$), R_g decreases and $C_{\mathrm{PP,intra}}$ increases with the decrease of ξ, implying the shrinkage of polymer coils. The slight increase of $C_{\mathrm{PP,inter}}$ with decreasing ξ suggests that polymer chains are slightly aggregated and solvent molecules are excluded from the polymer coils at the same time. C_{PS} slightly decreases as ξ decreases due to partial exclusion of the solvent molecules from the interior of the polymer coils, but the polymer chains are still swollen ($\mathrm{III_B}$) or partially swollen ($\mathrm{III_A}$).

In region II ($\xi \approx 1$), R_g is very small and $C_{\mathrm{PP,intra}}$ is very large, implying that a great portion of the conformation entropy of the polymer chains is lost and the polymer chains are shrunk coils. C_{PS} has a minimum, corresponding to the minimum of the mixing enthalpy, because most of the solvent molecules are excluded from the domains formed through polymer aggregation. $C_{\mathrm{PP,inter}}$ exhibits a maximum, suggesting large scale aggregation, which may lead the solution to undergo micro-phase separation instead of macroscopic phase separation (No inflexion points for free energy vs. concentration suggest that there is no macro-phase separation in the system), i.e. some rather than all of the polymer chains are heavily aggregated. This aggregation, induced by solvent of medium size, can lead to a high local monomer density of the polymer and the self-assembly of polymer chains. Our results support the speculation by Zhou et al. that this kind of self-assembly of polymers is driven by entropy, which is in contradistinction to the result about aggregation of polymer chains driven by enthalpy. In our original aim to describe medium-sized solvents, we propose that the term medium-sized solvent is defined as a solvent whose linear length approaches the ideal root-mean-square end-to-end distance of the polymer chain ($N_S \approx N^{1/2}$), i.e. $\xi \approx 1$, instead of the traditional expression of $1 << N_S << N$.

Comparing the results in region II with those in region I ($\xi <<$ 1), both R_g and $C_{\mathrm{PP,intra}}$ remain almost the same, indicating that the polymer chains adopt similar conformations. However, $C_{\mathrm{PP,inter}}$ decreases significantly while C_{PS} becomes much larger than that in region II, suggesting that the polymer coils shrink and segregate, and must be enwrapped by the large solvent molecules. Furthermore, according to the transition from region II to region I, it can be seen that the packing fraction of the polymer coils decreases significantly, which qualitatively agrees with the results reported by Bolhuis *et al.*, where the colloid packing fraction tends to zero for increasing polymer length (decreasing ξ in this work) in non-interacting polymers and colloids mixture, with a presupposition to consider the polymer chains as penetrable colloids and the solvent molecules as polymer chains.

Conclusion

Increasing the solvent molecular size leads to shrinkage of the polymer chains and increase of the critical overlap concentrations. The root-mean-square radius of gyration of polymer chains (R_g) is less sensitive to the variation of polymer concentration in solutions of larger solvent molecules. In addition, the dependency of R_g on polymer concentration under normal solvent conditions and solvent molecular size is in good agreement with scaling laws. When the solvent molecular size approaches the ideal end-to-end distance of the polymer chain, an extra aggregation of polymer chains occurs, and the solvent becomes the so-called medium-sized solvent. When the size of solvent molecules is smaller than the medium size, the polymer chains are swollen or partially swollen. However, when the size of solvent molecules is larger than the medium size, the polymer coils shrink and segregate, enwrapped by the large solvent molecules.

References

[1] Zhou, D.; Li, L.; Li, Y.; Zhang, J.; Xue, G. *Macromolecules* **2003**, 36, 4609.
[2] de Gennes, P.G.; Scaling Concepts in Polymer Physics (Ithaca, Ny: Cornell Univ. Press, 1979).
[3] Sun, Q.; Zhou, D.; Wang, X.; Xue, G. *Macromolecules* **2002**, 35, 7089.
[4] Wang, Y.; Teraoka, I. *Macromolecules* **33**, 3478 (2000)

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