Chain conformation of polymer melts with associating groups

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Abstract

Molecular association has profound influences on the viscoelastic properties of polymers with associating side groups. The conventional wisdom is that interchain association dominates in the melt state, and the dynamics of the associative polymer network therefore might be understood by extending the classical molecular approaches such as the Rouse and reptation models for linear chains. Using small-angle neutron scattering and molecular dynamics simulation, here we show that while interchain association is important, intrachain association can not be neglected in determining the static structures of associating polymers in the melt state. Analyses of the radius of gyration, static structure factor, and intrachain mean-square distance of polymers with associating side groups have revealed a substantial deviation from the random walk structure at even moderate association strength and degree of functionality. This finding emphasizes the important role of intrachain loops in associative polymer networks.

1. Introduction

A wide variety of polymers existing in nature or used in industrial applications are characterized by weak, reversible molecular associations such as hydrogen bonding, $\pi-\pi$ interaction, metal coordination, and hydrophobic effects. Some examples include ionomers, block copolymers in selective solvent, and hydrogen bonding polymers. Despite the ubiquity of this type of polymeric material, the influence of molecular association on the dimensions of polymer molecules has not been well understood. Because of the profound influence of molecular association on viscoelastic properties, a significant amount of theoretical and experimental effort has been directed towards understanding the conditions for thermoreversible gelation and corresponding phase diagrams. As such, these studies generally speak very little about how the shape and size of polymers are affected by molecular associations. In dilute and semidilute solutions, the importance of intrachain association is well recognized [1–7]. On the other hand, interchain association is generally expected to dominate in the melt state [8]. As a result, theories concerning the structure and dynamics of associating polymer melts typically do not consider the effects of the intrachain association on chain conformation. For example, the sticky Rouse approach formulated by Baxandall [9] explicitly assumes that the configuration probability distribution function is simply the product of the distribution functions of segments between stickers, each of which is a Gaussian distribution of linear-chain type. Similarly, the theory of Forsman [10] about the effect of molecular association on chain dimensions lacks the consideration of intrachain loops. On the experimental side, our understanding is still impeded by the lack of experimental data on well-defined model systems.

To illustrate how the polymer chain conformation could be affected by molecular associations, in this work we focus on a classical associating polymer system, 4-phenyl-1,2,4-triazolidine-3,5-dione (PTAD) modified polybutadienes (PB), which has been extensively studied by Stadler and his collaborators [11–19]. By selecting monodisperse protonated and deuterated polybutadienes of matching molecular weights, we are able to prepare a model system for applying small-angle neutron scattering (SANS) to study the melt structure of associating...
polymers. In contrast to ionomer solutions, such hydrogen-bonding polymers are free from the complications associated with the 'polyelectrolyte effect' [20–22], and therefore more suitable for comparison with the theoretical arguments proposed in the literature, in which no long-range electrostatic interactions are considered [5, 23, 24]. Moreover, previous studies [25, 26] have indicated that the molecular association in PB-PTAD is predominantly pairwise, and higher-order aggregations are absent. It is generally considered that the linear viscoelastic data from this particular system, i.e., PB-PTAD, provides the most crucial experimental support for the sticky (hindered) reptation model pioneered by Leibler, Rubinstein, and Colby [27]. Therefore, this study has direct theoretical relevance as to how one should treat the dynamics of associating polymers. To complement our SANS study, we have also performed coarse-grained molecular dynamics simulations of associating polymer chains. We demonstrate that while the statistical analysis previously presented is qualitatively correct, i.e., interchain association dominates in the melt state, the effect of intrachain association on polymer melt structure generally should not be neglected.

2. Materials and methods

Fully protonated (h-PB) and deuterated polybutadienes (d-PB) of narrow molecular weight distribution were obtained from Polymer Source (h-PB: $M_m = 84$ kg mol$^{-1}$, $M_n/M_w = 1.07$; d-PB: $M_w = 89$ kg mol$^{-1}$, $M_n/M_w = 1.08$). 4-phenyl-1,2,4-triazolidine-3,5-dione (PTAD) was purchased from Sigma-Aldrich and used as received. The modification reaction was conducted according to the well-documented procedures in the literature [13, 28]. We prepared samples with different degrees of functionalization $f = 1\%$, $2\%$, and $5\%$ for both h-PB and d-PB. For the SANS experiments, protonated and deuterated samples with matching molecular weight and degree of functionality were mixed at 50:50 weight ratio in chloroform. The solvent was subsequently slowly evaporated to produce bubble-free polymer melts for the neutron scattering study. Small-angle neutron scattering (SANS) measurements were performed on the NG7 SANS diffractometer at NCNR NIST. The wavelength of the incident neutrons was 8 Å with wavelength spreads $\Delta \lambda/\lambda$ of 15%. The scattering wave vector $Q$ ranges from 0.001 to 0.3 Å$^{-1}$.

We have also performed coarse-grained molecular dynamics simulations of polymer chains at the melt density, with degree-of-polymerization, $N = 35$. And every chain has $N_c$ associating beads (stickers), which have attractive interactions among each other (red beads in figure 1). Because of the high molecular weight of the experimental system, a direct mapping between simulation and experiment is not possible in the current case. Additionally, the association in PB-PTAD is mostly pairwise, whereas the current simulation model allows higher-order aggregates. Our simulation is designed to explore only the qualitative structural features of associating polymer melts. The simulations were carried out using the LAMMPS [29] software package with GPU acceleration [30] at the Oak Ridge Leadership Computing Facility. The initial equilibrated configuration of the polymer melt, composed of Lennard-Jones bead having a diameter $\sigma$, was obtained from a previous simulation [31]. There are $m_c = 1417$ chains inside a cubic box with volume $L^3 = 38,793\sigma^3$ and number density, $\rho = 0.85\sigma^{-3}$. Based on this initial configuration, several systems were created by assigning beads to a polymer chain with varying number of associating beads per chain, $N_g$ (figure 1). The attractive interaction in polymer bonds is described by the finite extensible nonlinear elastic (FENE) bonds were $R_m = 1.5\sigma$ and $k_r = 30.0k_BT$,

$$U_{\text{FENE}}(r) = -\frac{1}{2}k_rR_m^2\ln\left(1 - \frac{r^2}{R_m^2}\right),$$

while the repulsive portion of the bonds, as well as the non-bonded interactions between blue-to-red and blue-to-blue beads are described by the WCA potential with $\varepsilon_{\text{WCA}} = k_BT$, 

![Figure 1. (a) Snapshot of the simulation box, with dimension $L$, and showing the associating beads (red) and the non-associating beads (blue). (b) Arrangements or positions of the associating bead within a polymer chain for different values of $N_g$.](image-url)
To illustrate the interaction between associating beads (computing the radius of gyrations for polymers with and without associating groups. The scattering intensities Jones potential with well depth, associating polymers from the MD simulation. 

3. Results and discussion

The interaction between associating beads (red-to-red beads) is described by the truncated and shifted Lennard-Jones potential with well depth, $\epsilon$$_{\text{LJ}}$, ranging from 1 to 5$k_B T$ and $r_{\text{cut}} = 2.5\sigma$,

$$U_{\text{WCA}}(r) = \begin{cases} 4\epsilon_{\text{WCA}} \left( \frac{\sigma}{r} \right)^{12} - \frac{\sigma}{r} \right)^{6} + \epsilon_{\text{WCA}} & \text{for } r < 2^{0.5}\sigma \\ 0 & \text{for } r \geq 2^{0.5}\sigma. \end{cases}$$

$$U_{\text{LJ}}(r) = \begin{cases} 4\epsilon_{\text{LJ}} \left[ \left( \frac{\sigma}{r} \right)^{12} - \frac{\sigma}{r_{\text{cut}}} \right] - \frac{\sigma}{r_{\text{cut}}} \right)^{6} + \left( \frac{\sigma}{r_{\text{cut}}} \right)^{12} & \text{for } r < r_{\text{cut}} \\ 0 & \text{for } r \geq r_{\text{cut}}. \end{cases}$$

The simulations were carried out in the canonical ensemble (NVT) with $T = 1/k_B$. The temperature was maintained by coupling the system to a Langevin thermostat with friction coefficient, $\zeta$, set to $m/7\tau$ where $\tau$ is the reduced time unit. The velocity-Verlet algorithm with a time step of 0.01$\tau$ was used for time integration. Each system was equilibrated for $10^5\tau$, after which a production run proceeded for another $6 \times 10^6\tau$. A number of thermodynamic quantities as well as the chain conformations were monitored to ensure the systems were well equilibrated before the production run. It is worth noting that the equilibration time $10^5\tau$ is significantly longer than the characteristic sticker lifetime. Snapshots of the simulation box were taken every 50$\tau$ resulting in 1200 data points used for data analysis per system. In this report, we will focus on only the static structure of the associating polymers from the MD simulation.

The scattering intensities $I(q)$ of both parent and modified PB are shown as function of $q$ in figure 2(a). The angular dependence of scattering intensity $I(q)$ of the parent polymer and the 1% and 2% functionalized PBs can be reasonably modeled by the celebrated Debye function for a Gaussian chain: $I(q) = I_0(e^{-q^2R_g^2} + q^2R_g^2 - 1)/(q^2R_g^2) + B$, where $R_g^2$ is the mean-square radius of gyration, $I_0$ is the forward scattering intensity and $B$ is the background. On the other hand, $I(q)$ of the 5% modified sample cannot be completely described by the Debye function. This failure can be more clearly seen through the Kratky plot analysis presented in the next section. The radius of gyration extracted from the Debye fits of $I(q)$ are shown as function of the degree of functionality $f/n$ the inset of figure 2. Overall, the introduction of PTAD groups to the PB backbone leads to a slight swelling of the polymer coil. This result is consistent with the general trend revealed by the previous SANS study of sulfonated polystyrene ionomers [32]. However, it should be noted that the dependence of $R_g$ on $f$ is monotonic up to $f = 8.5$ mol% in [32], whereas a maximum is found around $f = 1.0$ mol% in our system.

Interestingly, a similar trend is also observed in our MD simulation. Figure 2(b) shows the average $R_g^2$ as a function of the number of stickers of per chain $N_S$ for chains with different association strengths. In all cases, a non-monotonic behavior is found for the dependence of $\langle R_g^2 \rangle$ on $N_S$. In particular, a collapse of the polymer coil can be clearly seen from figure 2(b) when a large number of stickers with relatively strong association strength

![Figure 2](image-url)
are present. Such a trend was not anticipated in the previous theoretical investigation \cite{10}, where intrachain loop formation was not considered. On the other hand, we consider the peculiar dependence of $R_g$ on $f$, revealed by SANS measurements as well as simulation, is indicative of the existence of substantial amount of intrachain association.

To further confirm this interpretation, we proceed to analyze the angular $(q)$ dependence of scattering intensity in the form of Kratky plot (figure 3). The product $I(q)q^2$, determined from SANS measurements, is plotted as a function of $q$ for all the samples. As a comparison, the single chain structure factor $S(q)$ computed from the MD simulation is also presented in the Kratky form (i.e., $S(q)q^2$ versus $q$). In both cases, a peak emerges at the intermediate $q$ range as the fraction of sticker increase—a feature that is indicative of either branching (interchain association) \cite{33–35} or loop formation (intrachain association) \cite{36,37}. However, it is important to recognize that the fraction of interchain bonding decreases as the number of stickers per chain increases. On the other hand, the peak becomes more pronounced as $N_S$ increases. This observation suggests that intrachain loop formation should be the main driving force for the qualitative change of $I(q)$.

To quantify how the fraction of intrachain association ($p_{\text{intra}}$) changes with the number of stickers per chain and the sticker interaction strength, we proceed to analyze the contacts between sticky beads (figure 4). $p_{\text{intra}}$ is defined as the probability of a given sticker to be involved in an intrachain association. Figure 4 shows $p_{\text{intra}}$ increases with increasing interaction strength $\epsilon_{\text{LJ}}$ and $N_S$, consistent with simple statistical analysis \cite{8}. For example, the overlapping volume fraction $\phi_o$ for strands between stickers is expected to scale with $N_S$ as: $\phi_o \sim N_S^{1/2}$, and increasing $N_S$ decreases the probability for a sticker to find another sticker from a different chain and thus favors intrachain association. For $\epsilon_{\text{LJ}} = 5.0$ and $N_S = 8$, intrachain association constitutes nearly 1/4 of all the sticker contacts. It becomes apparent from figure 4 that intrachain association should play an important role in determining the static structure of these chains.

Yet another useful way to reveal the influence of intrachain bonding on the configuration of the associating polymers is to analyze the intrachain mean-square distance $\langle (R_i - R_j)^2 \rangle$ between two beads $i$ and $j$ within the same chain. For a chain without associating beads ($N_S = 0$), $\langle (R_i - R_j)^2 \rangle$ should follow the expected scaling $\langle (R_i - R_j)^2 \rangle \sim |i - j|$ at large separations. At short distance, $\langle (R_i - R_j)^2 \rangle$ grows faster than linearly, due to the
excluded volume effect. The above described behavior produces a monotonically increasing curve that would eventually plateau, when \( \langle (R_i - R_j)^2 \rangle / |i - j| \) is plotted as a function of \( |i - j| \) (e.g., black curve in figure 5, corresponding to \( N_S = 0 \)) [38]. However, the presence of molecular association significantly distorts the distribution of mean-square intrachain distance (figure 5). Notice that the ratio \( \langle (R_i - R_j)^2 \rangle / |i - j| \) is substantially reduced at large \( N_S \)—this is a direct consequence of the formation of intrachain loops.

All the above analyses of SANS measurements and molecular simulations, when taken together, clearly illustrate the importance of intrachain association in determining the structure of associating polymer melts. We note that in practice the degree of functionalization \( f \) for many associating polymer melts is on the order of \( \sim 10 \) mol\% with association strength in the range \( 1 - 10 k_B T \). This falls exactly into the parameter space explored by our current investigation. Only in the limit of \( f \approx 1 \), i.e., large separation between stickers, the effect of intrachain association on the static structure can probably be neglected. However, as noted, such a theoretical limit is not fulfilled in many systems of practical interests.

4. Summary

By combining SANS measurements and molecular simulations, we show that the melt structure of associating polymers is strongly influenced by the presence of a non-negligible fraction of intrachain loops. The effect of intrachain association is reflected by the change of radius of gyration, \( q \) dependence of scattering intensity, and the distribution of intrachain mean-square distance. Therefore, to fully understand the structure and dynamics of associating polymers, the presence of loops should be taken into consideration. While this work is confined to the study of static structures, we note that intrachain association should also affect the dynamics in an important way. This aspect is currently not included in dynamic models of associating polymers.

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Figure 5. Influence of number of stickers (\( N_S \)) on the intrachain mean-square distance, determined from the MD simulation.
References

[1] Cates M and Witten T 1986 Macromolecules 19 732–9
[2] Baljon A R C 1993 Macromolecules 26 4339–45
[3] Urakami N and Takasu M 1996 J. Phys. Soc. Jpn. 65 2694–9
[4] Kumar S K and Panagiotopoulos A Z 1999 Phys. Rev. Lett. 82 5060–3
[5] Dobrynin A V 2004 Macromolecules 37 3881–93
[6] Loverde S M, Ermoshkin A V, La Cruz D and Olivera M 2005 J. Polym. Sci. Part B: Polym. Phys. 43 796–804
[7] Sing C E and Alexander-Katz A 2011 Macromolecules 44 6962–71
[8] Rubinstein M and Semenov A N 2001 Macromolecules 34 1058–68
[9] Barxandall L G 1989 Macromolecules 22 1982–8
[10] Forsman W C 1982 Macromolecules 15 1032–40
[11] Stadler R and de Lucca Freitas L 1986 Colloid Polym. Sci. 264 773–8
[12] de Lucca Freitas L, Burgert J and Stadler R 1987 Polym. Bull. 17 431–8
[13] de Lucca Freitas L and Stadler R 1987 Macromolecules 20 2478–85
[14] de Lucca Freitas L and Stadler R 1988 Colloid Polym. Sci. 266 1095–101
[15] Seidel U, Stadler R and Fuller G G 1994 Macromolecules 27 2066–72
[16] Muller M, Fischer E, Kremer F, Seidel U and Stadler R 1995 Colloid Polym. Sci. 273 38–46
[17] Muller M, Stadler R, Kremer F and Williams G 1995 Macromolecules 28 6942–9
[18] Bica C I, Burchard W and Stadler R 1996 Macromol. Chem. Phys. 197 3407–26
[19] Bica C I, Burchard W and Stadler R 1997 Eur. Polym. J. 33 1759–66
[20] Lantman C W, MacKnight W J, Higgins J S, Peiffer D G, Sinha S K and Lundberg R D 1988 Macromolecules 21 1339–43
[21] Lantman C W, MacKnight W J, Sinha S K, Peiffer D G, Lundberg R D and Wignall G D 1988 Macromolecules 21 1344–9
[22] Hara M 1992 Polyelectrolytes: Science and Technology (New York: CRC Press)
[23] Semenov A N and Rubinstein M 1998 Macromolecules 31 1373–85
[24] Rubinstein M and Semenov A N 1998 Macromolecules 31 1386–97
[25] Hilger C, Draeger M and Stadler R 1992 Macromolecules 25 2498–501
[26] Hilger C and Stadler R 1992 Macromolecules 25 6670–80
[27] Leibler L, Rubinstein M and Colby R H 1991 Macromolecules 24 4701–7
[28] Butler G B 1980 Ind. Eng. Chem. Prod. Res. Dev. 19 512–28
[29] Plimpton S 1995 J. Comput. Phys. 117 1–19
[30] Brown W M, Wang P, Plimpton S J and Tharrington A N 2011 Comput. Phys. Commun. 182 898–911
[31] Carrillo J M Y and Sumpter B G 2014 J. Chem. Phys. 141 074904
[32] Earnest T R, Higgins J S, Handlin D L and MacKnight W J 1981 Macromolecules 14 192–6
[33] Burchard W 1983 Static and Dynamic Light Scattering from Branched Polymers and Biopolymers (Berlin, Heidelberg: Springer)
[34] Hammouda B 1993 J. Chem. Phys. 99 9182–7
[35] Hammouda B 1993 SANS from Homogeneous Polymer Mixtures: A Unified Overview (Berlin, Heidelberg: Springer) pp 87–133
[36] Casassa E F 1965 J. Polym. Sci. Part A: Polym. Chem. 3 605–14
[37] Tsubouchi R, Ida D, Yoshizaki T and Yamakawa H 2014 Macromolecules 47 1449–54
[38] Auhl R, Everaers R, Grest G S, Kremer K and Plimpton S J 2003 J. Chem. Phys. 119 12718–28