Entropy Driven Molecular Motion of Semiconducting Polymers in Solution

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We investigate the entropy driven large-scale dynamics of semiconducting conjugated polymers in solution. Neutron spin echo spectroscopy reveals a finite dynamical stiffness that reduces with increasing temperature and molecular weight. The Zimm mode analysis confirms the existence of beads with a finite length that corresponds to a reduced number of segmental modes in semi-flexible chains. More flexible chains show thermochromic blue-shift in the absorption spectra.

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The mechanical, optical, and electrical properties of semiconducting polymers are determined by their molecular interactions. Delocalized π-electron system in such polymers determines their optoelectronic properties and is related to the increased chain stiffness. Although there is a wealth of studies on the effect of chain conformation on optoelectronic properties of conjugated polymers [1–5], the impact of chain dynamics is still poorly understood. In a step toward better understanding of the chain conformation, chain dynamics and optical response in conjugated polymers, we want to exploit the high temporal and spatial resolution of neutron spin echo spectroscopy (NSE). The point of interest is to determine a unique set of physical parameters that can quantify the impact of the chain stiffness on the large scale polymer dynamics.

In general, with increasing temperature, the energy barriers associated with conformational changes of the polymer backbone are reduced. Twisting can lead to the breakdown of π-electron conjugation, which causes the thermochromic blue-shift in the absorption spectra [6–11]. A recent small angle neutron scattering (SANS) study on poly(3-alkylthiophene) (P3AT) semiconducting polymers reported a direct relationship between the conjugated polymer conformation and solvatochromic/thermochromic phenomena [10, 12].

The same thermal fluctuations that cause the conformational changes determine the degree of overlap of the π-orbitals [13]. Quasi-elastic neutron spectroscopy investigations highlighted that the reduced conductivity of semiconducting polymers is associated with the local relaxation of the alkyl side chains [14]. However, the effects of entropic forces and solvent-mediated interactions on the large-scale chain dynamics are still unexplored.

Depending on the solvent quality and temperature, long flexible polymers in dilute solution can assume a swollen coil, a Gaussian chain, or collapse to a globule conformation. On the contrary, semi-flexible polymers can exhibit random coil to rod-like conformation. Their inherent rigidity reduces the segmental mobility and can lead to a partially frozen or glassy state. De Gennes suggested that these effects the mode spectrum of single chains [18]. NSE spectroscopy demonstrated the existence of such single chain glassy (SCG) states in semi-flexible polymers [16, 17]. However, the occurrence of SCG states has not been verified in semiconducting conjugated polymers. In addition, chemical defects [2] in semiconducting polymers cause dynamic disorder [14, 19] that can lead to structural and dynamical heterogeneity. As such, it can be an ideal model system to investigate in comparison to glassy materials [20–22].

In this letter, we report a comprehensive study of the temperature-dependent single chain conformation and dynamics of amorphous regioregular poly(3-hexylthiophene) (P3HT) in deuterated 1,2-dichlorobenzene (DCB) solvent using SANS and NSE. P3HT was chosen as a well-studied representative of conjugated polymers that has proven to be an archetypical material for electronic and optoelectronic applications [23]. We carried out experiments on two P3HT samples of different molecular weights, which had close to 100% regioregularity (Table I). Experiments were conducted at elevated temperatures and a low concentration (φ = 0.75%) to reduce inter-chain aggregation [24].

We determined the unperturbed chain dimensions in SANS experiments. Fig. 1 displays the Kratky plot [25] for two different molecular weights and temperatures in DCB. The plateau at intermediate momentum transfer, $Q$, is a signature of a Gaussian coil and indicates a scaling relationship, $I \sim Q^{-1/2} = Q^{-2}$, with the Flory exponent, $\nu = 0.5$ (Θ solvent) [25]. A fit with the Debye function, $2/u^2 [u - 1 + \exp(-u)]$, with $u = Q^2 R_g^2$, shows an increasing radius of gyration $R_g$, with increasing molecular weight and a slight variation with temperature (Table I). The persistence length, $\ell_p \sim 5$ nm, as derived from our SANS data, is in agreement with literature values [10, 26]. It shows only a minor change with both molecular weight and temperature. Slight deviations of the fit at high $Q$’s are due to the incoherent background that increases the noise level, but do not change our findings.

NSE spectroscopy measures the normalized dynamic structure factor $S(Q, t)/S(Q)$ as a function of Fourier time, $t$ at a given momentum transfer, $Q$ (cf. SI [42] for details). At the intermediate length scale the center
of mass diffusion and segmental relaxation of a polymer melt is well described by the Rouse model. The molecular motion originates from the balance between entropic and frictional forces caused by the surrounding heat bath and is best described by its spectrum of relaxation modes [27]. For polymers in solution, the hydrodynamic interactions become important, and the dynamic structure factor can be formulated within the framework of the Zimm model [28]:

\[
S_{\text{Zimm}}(Q,t) = \exp \left[ -Q^2 D_Z t \right] S_{\text{chain}}(Q) \times \\
\exp \left\{ -\frac{2 R_{ee}^2 Q^2}{3 \nu} \sum_p \frac{1}{p^{2
u+1}} \cos \left( \frac{p \pi m}{N} \right) \cos \left( \frac{p \pi n}{N} \right) \left( 1 - \exp \left( -\frac{t p^2 \nu}{\tau_Z} \right) \right) \right\} 
\]

\[
S_{\text{chain}}(Q) = \frac{1}{N} \sum_{n,m} \exp \left\{ -\frac{1}{6} \left| n - m \right|^{2
u} Q^2 \ell^2 \right\} 
\]

with

\[
Q = \frac{10^2}{\tau} \text{cm}^{-1} \quad \text{and} \quad \ell = \frac{1}{\sqrt{6}} \text{nm}
\]

The parameter \( P \) represents the number of modes necessary to describe the experimental \( S(Q,t) \)/\( S(Q) \) at different temperatures and molecular weights simultaneously for all \( Q \)'s. We would like to emphasize that this theoretical description of the experimental NSE data involves no free parameters, except \( P \).

However, limiting the analysis to a finite number of modes neglects a substantial part of the mode spectrum and seems to be unjustified. On the other hand, the increased stiffness caused by the delocalized \( \pi \)-electron system introduces a finite correlation length (dynamic Kuhn segment), which can be taken into account by adding a fourth-order term, \( p^2 + \alpha p^4 \), to the entropic spring constant \( (k = 3k_B T/\ell^2 \propto p^{-2}) \), with the dynamic stiffness parameter \( \alpha \) [16, 31]. The modified Zimm scattering model (Eq. (1)) is obtained by replacing the mode dependence \( p^{2
u} \) by \( p^{2\nu + \alpha p^4 - \nu} \), and \( 1/(p^{2\nu+1}) \) by \( 1/(p^{2\nu+1 + \alpha p^4}) \). Unlike limiting the number of modes, we now exploit the fact that by increasing the momentum transfer \( Q \), the dynamic structure factor becomes more sensitive to higher modes. In addition, for a given \( Q \), the calculated \( S(Q,t) \)/\( S(Q) \) becomes independent of \( p \), beyond a certain threshold \( (p > \nu_{\text{min}}) \). This uses the fact that \( 2\pi/Q \) probes a certain finite length, which limits the number of modes required to theoretically describe the experimental data. As a consequence, the stiffness parameter \( \alpha \) is unaffected by the maximum \( Q \).

Figure 2 illustrates \( S(Q,t)/S(Q) \) obtained by NSE experiments over a \( Q \)-range from 0.062 to 0.124 Å\(^{-1}\), for P3HT samples of two different molecular weights, at 313 and 353 K. The incoherent and coherent contributions were determined by polarization analysis in the diffraction mode of the spectrometer. The elastic incoherent scattering from the background, including the solvent, the scattering that results from empty cell, sample environment and instrument, were subtracted accordingly (cf. Figs. S3 (a) and (b), SI [42]). The much faster decay of our experimental data indicates a substantial contribution of another relaxation mechanism.

In the next step, we considered P3HT in solution as a rigid wormlike chain as proposed by McCulloch et al. [10], which requires to add the rotational diffusion \( \nu \). The comparison with the experimental data (cf. Figs. S3 (c) and (d), SI [42]) shows that this is still not sufficient. Hence, we improve the model by considering a polymer coil with mobile segments, that requires to include the segmental relaxation \( (p > 1) \). We obtained an accurate description of the full mode spectrum associated with the segmental relaxation by adding only a finite number of modes, \( p = 1, 2 \ldots, P \) (cf. Figs. S4 (a) and (b), SI [42]). The number of modes needed is surprisingly low, with \( P = 15 \) to 27.

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The solid lines in Figs. 2 (a) and (b) compare the re-
TABLE I: Sample labels, molecular weight $M_n$, polydispersity $M_w/M_n$, radius of gyration $R_g$, the chain end-to-end distance $R_{ee}$, Zimm diffusion $D_z$, Zimm time $\tau_z$, the Zimm modes $p_{\text{min}}$, the stiffness parameter $\alpha$ and the size of the bead $R_{\text{rigid}}$.

| P3HT | $M_n$ (kg/mol) | $M_w/M_n$ | $T$ (K) | $R_g$ (Å) | $R_{ee}$ (nm) | $D_z \times 10^{-2}$ (nm$^2$/ns$^{-1}$) | $\tau_z$ (ns) | $p_{\text{min}}$ | $\alpha$ | $R_{\text{rigid}}$ (nm) |
|------|---------------|------------|---------|-----------|-------------|----------------------|-----------|---------------|-------|-----------------|
| 63k  | 63.1          | 1.51       | 313     | 15±1      | 37±2        | 2.36                  | 4125      | 60            | 0.030±0.007 | 4.77±0.09       |
| 63k  | 63.1          | 1.51       | 353     | 17±1      | 41±3        | 3.43                  | 3195      | 75            | 0.022±0.003 | 4.72±0.05       |
| 90k  | 89.7          | 1.54       | 313     | 19±1      | 48±2        | 1.67                  | 8884      | 100           | 0.013±0.006 | 4.77±0.07       |
| 90k  | 89.7          | 1.54       | 353     | 21±1      | 50±3        | 2.70                  | 5998      | 120           | 0.008±0.001 | 4.60±0.13       |

FIG. 2: The normalized dynamic structure factor $S(Q, t)/S(Q)$ of P3HT in DCB for two molecular weights ((a) 90 and (b) 63 kg/mol) at temperatures, 313 (red symbols ) and 353 K (cyan symbols). Symbols represent $Q = 0.062$ (□), 0.087 (○) and 0.124 Å$^{-1}$ (△). Solid lines represent the best fit summing over a large number of modes $p_{\text{min}}$, and a finite dynamical stiffness $\alpha$.

As a result of our analysis with the experimental dynamic structure factor, we can accurately describe our experimental data by simultaneously fitting all the $Q$s. We obtain the stiffness parameter $\alpha$ that decreases with increasing molecular weight and/or temperature, cf. Table I.

Based on this result, we can now estimate the minimum number of modes, $p_{\text{min}}$, that are required to theoretically describe the experimental $S(Q, t)$ within the $Q$-range of our NSE experiments by solving $S(Q, t, \alpha, N = p_{\text{min}}) = S(Q, t, \alpha, N = \infty)$ [33]. We find considerably greater values of $p_{\text{min}}$ than in the case of simple assumption of a finite number of modes $P$, without taking into account the finite stiffness $\alpha$ (cf. Table I). The absence of higher order modes elucidates the fact that the chain dynamics is partially frozen. Therefore, this is the first experimental evidence of the existence of single chain glass (SCG) state in a conjugated polymer.

If we compare the quality of the fits based on the stiffness parameter (Fig. 2) with those calculated assuming a low number of modes (Fig. S4 in SI [42]), we observe a similarly good description irrespective of their physical origins. The description of the relaxation of a chain by its mode spectrum assumes a certain number of statistically independent segments, connected by entropic springs. Numerous experiments justified the assumption of an infinite number of modes in case of flexible polymers like poly(ethylene-alt-propylene) or poly(ethylene glycol) (with $\alpha = 0$) [34, 35]. In the present case, the increased stiffness caused by the delocalized $\pi$-electron system introduces a finite correlation length, which decreases the number of statistically independent beads. Thus, the calculation of $S(Q, t)/S(Q)$ using a reduced number of modes is formally equivalent to the calculation using a stiffness parameter. However, the highest $Q$ is limited in experiments. Hence, limiting the number of modes does not represent the full mode spectrum.

This explanation can be rationalized by a simple estimation. For semi-flexible polymer the number of modes, $p_{\text{min}}$ in Eq. (1), limits the displacement, $\cos(p_{\text{min}} \pi m/N)$, over $m = N/p_{\text{min}}$ segments. Therefore, we can estimate the size of the bead $R_{\text{rigid}}$, in our bead spring approach. For distances less than $R_{\text{rigid}}$, the segments are correlated. It is given by: $R_{\text{rigid}} = \ell (N/p_{\text{min}})^\nu = R_{ee} N^{-\nu} (N/p_{\text{min}})^\nu = R_{ee} p_{\text{min}}^{-\nu}$ [16]. From Table I it is evident that the effects of temperature and molecular weight are negligible, and we obtain $\langle R_{\text{rigid}} \rangle = 4.7±0.1$ nm.

It should be noted that, independently of the observed length scale, we obtained two significant parameters, namely, finite global stiffness, $\alpha$ and a finite size of the bead, $R_{\text{rigid}}$. The parameter $\alpha$ describes the damping of the mode relaxation. In the Rouse or Zimm approach, normal coordinates are introduced to solve the Langevin equation by simple exponential functions. The orthogonality of these normal coordinates follows from the uncorrelated random forces. This assumption corresponds to the freely jointed chain model that neglects correlations between bond vectors. In a good approximation, those
some of the essential facts. (i) The bead size, $R_d$, dynamics and thermochromic properties, lets sum up temperature, cf. Fig. S5, SI [42]. These results agree P3HT in DCB are independent of the molecular weight, $M_w$, and temperature. (ii) The renormalized stiffness $\bar{\alpha}$ is independent of molecular weight and temperature. To understand the temperature dependence of the stiffness, we now want to explore its relationship to chain end-to-end distance, $\alpha(353K)/\alpha(313K) = (R_{ee}(353K)/R_{ee}(313K))^{-\nu} \approx 0.7$. The thermal expansion of P3HT, accounts only for a ratio of 0.9, which alone is not sufficient to explain the reduction of the stiffness [41]. This highlights the fact that the static chain end-to-end distance is not associated with the conjugation length or the thermochromic blue-shift, and more attention needs to be paid to the large-scale chain dynamics.

To summarize, we studied the large-scale dynamics of P3HT in DCB by neutron spin echo spectroscopy. We used a coarse-grained approach based on the Zimm model to understand our experimental data. We introduced two parameters, namely the bead size $R_{\text{rigid}}$, and the stiffness $\alpha$, that represent the mode spectrum. The effect of global stiffness is exhibited clearly on the chain dynamics, either by the limited number of modes $p_{\text{min}}$ or by the introduction of $\alpha$ as a damping term. We derived a renormalized stiffness $\bar{\alpha}$ from the generic scaling of the stiffness $\alpha \propto R_{ee}^{-\nu}$, and the molecular weight. We observe that chains with higher flexibility show a thermochromic blue-shift in the absorption spectra. The first observation of the existence of single chain glass modes in P3HT could open a new pathway to understand semiconducting polymers by models developed for colloidal glasses.

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finite correlations in a real polymer can be neglected if greater distances along the chain contour are considered. This leads to the introduction of $R_{\text{rigid}}$ and similarly to $\alpha$.

In order to investigate the scaling behavior between the chain end-to-end distance and the dynamical chain stiffness $\alpha$, we systematically varied $R_{ee}$. The results are illustrated in Fig. 3. In addition to our results, we have included the stiffness parameter $\alpha_{PNB}$ of polynorbornene (PNB) of different molecular weights in a good solvent [16]. For a better comparison, we rescaled $\alpha_{PNB}$ by a factor $\sim 7$. Irrespective of the polymer, molecular weight and temperature, we observe a generic power-law scaling, $\alpha \propto R_{ee}^{-\nu}$. As a consequence, the molecular weight dependence of $\alpha$ is attributed to the increase in Gaussian coil dimension, $R_{ee}$ by a factor $\sim 1.26$.

To identify correlations between the large-scale chain dynamics and thermochromic properties, lets sum up some of the essential facts. (i) The bead size, $R_{\text{rigid}}$, is independent of molecular weight and temperature. (ii) The renormalized stiffness $\bar{\alpha} = \alpha/R_{ee}^{-\nu}$, decreases with increasing temperature. (iii) The absorption spectra of P3HT in DCB are independent of the molecular weight, but show a thermochromic blue-shift with increasing temperature, cf. Fig. S5, SI [42]. These results agree with those found earlier for regioregular P3HT and seem to be common for semiconducting polymers [36–40].

The constant bead size excludes a correlation with the observed changes in the absorption spectra. The reduced renormalized stiffness $\bar{\alpha}$. The associated breakdown of the $\pi$-electron conjugation can lead to the thermochromic blue-shift in the absorption spectra.

FIG. 3: Generalized scaling behavior, $\alpha \propto R_{ee}^{-\nu}$, of the polymer stiffness $\alpha$ as a function of the chain dimension $R_{ee}$ of P3HT (two molecular weights and two temperatures) and polynorbornene (PNB) samples (three molecular weights, [16]). Here, $\alpha$ is vertically scaled by a factor $c$. 

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