Macroscopic Structural Compositions of π-Conjugated Polymers: Combined Insights from Solid-State NMR and Molecular Dynamics Simulations


ABSTRACT: Molecular dynamics simulations are combined with solid-state NMR measurements to gain insight into the macroscopic structural composition of the π-conjugated polymer poly(2,5-bis(3-tetradecyl-thiophen-2-yl)thieno[3,2-b]thiophene) (PBTTT). The structural and dynamical properties, as established by the NMR analyses, were used to test the local structure of three constituent mesophases with (i) crystalline backbones and side chains, (ii) lamellar backbones and disordered side chains, or (iii) amorphous backbones and side chains. The relative compositions of these mesophases were then determined from the deconvolution of the 1H and 13C solid-state NMR spectra and dynamic order parameters. Surprisingly, on the basis of molecular dynamics simulations, the powder composition consisted of only 28% of the completely crystalline mesophase, while 23% was lamellar with disordered side chains and 49% amorphous. The protocol presented in this work is a general approach and can be used for elucidating the relative compositions of mesophases in π-conjugated polymers.

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Structural motifs of organic materials,25−28 in addition to being sensitive to conformational effects and chain dynamics.20,26 Here, we show that it is possible to resolve the macroscopic structural composition of a π-conjugated polymer (PBTTT-C16) by combining solid-state NMR analyses with molecular dynamics simulations, in a manner that is analogous to what has been achieved recently using inelastic neutron scattering for doped P3HT.21

The local ordering of polymer backbones in the sample can be quantitatively determined by analyses of solid-state onedimensional (1D) single-pulse 1H magic-angle-spinning (MAS) NMR spectra. For example, the spectrum in Figure 2a shows resolved resonances around 6−7 ppm from two types of aromatic protons on the π-conjugated backbone (shown in green and blue in Figure 1d, top). This signal indeed consists of two distinct contributions (cyan and blue curves in Figure 2a), with maxima at 6.9 and 6.1 ppm and relative integrated signal intensities of 0.49 and 0.51, respectively. In solution, these aromatic protons give rise to isotropic 1H chemical shifts of 7.15 and 7.30 ppm (Figure S1). The fact that the aromatic 1H
signal at 6.1 ppm is displaced by ~1.2 ppm shows that these protons are strongly influenced by nuclear shielding effects associated with π–π stacking of the aromatic polymer backbones. In contrast, the aromatic 1H signal at 6.9 ppm is not displaced by only 0.2 ppm, demonstrating that this signal is not exposed to significant π–π shielding effects. These observations are consistent with the two 1H signals at 6.9 and 6.1 ppm being assigned to disordered and ordered backbone moieties, respectively, where each 1H signal is a sum of signals from the thiophene (TT) and thienothiophene (TH) groups. Hence, we conclude that the fractions of ordered (π-stacked) and disordered backbones are 0.49 and 0.51, respectively.

Apart from the backbone conformations, the composition of the PBTTT-C_{16} sample can be elucidated from the conformational statistics of the C_{16} side chains. In solid-state NMR, these statistics can be assessed through the π–π stacking of the aromatic polymer backbones. In contrast, the aromatic 1H signal at 6.9 ppm is not displaced by only 0.2 ppm, demonstrating that this signal is not exposed to significant π–π shielding effects. These observations are consistent with the two 1H signals at 6.9 and 6.1 ppm being assigned to disordered and ordered backbone moieties, respectively, where each 1H signal is a sum of signals from the thiophene (TT) and thienothiophene (TH) groups. Hence, we conclude that the fractions of ordered (π-stacked) and disordered backbones are 0.49 and 0.51, respectively.

Figure 2. (a) Solid-state 1H MAS NMR spectrum of PBTTT-C_{16} recorded at room temperature under MAS conditions of 29.7 kHz. Optimized fits of the two aromatic contributions at 6.1 and 6.9 ppm are depicted in blue and cyan, respectively. (b) Single-pulse solid-state 13C MAS NMR spectrum (black) recorded at 298 K with a MAS frequency of 12.5 kHz. The optimized fits of the dominant methane 13C signals at 33.15 and 30.80 ppm are shown in green and blue, respectively, to yield the combined spectral fit (red).

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Figure 1. Model mesophases of PBTTT-C_{16}: (a) crystalline, (b) lamellar, and (c) amorphous. (d) Chemical structure of PBTTT-C_{16} and atom labeling used in this study. \( \mathbf{a} \) is a unit vector that defines the orientation of the CH\_2 group, and the angles \( \theta_l \) and \( \theta_t \) identify the local environment of a CH\_2 moiety to account for the \( \gamma \)-gauche effect.

The resulting single-pulse 13C MAS spectrum of the alkyl region in Figure 2 exhibits two peaks at 33.15 and 30.80 ppm associated with the C_{16} side chains, which are assigned to \( tt \) and either of the less ordered \( tg \) or \( gg \) conformers, respectively. The resulting integrated intensities enable the relative conformer fractions to be determined, with the \( tt \) conformations accounting for 56% of the overall signal intensity, while 44% arises from the \( tg \) and \( gg \) conformations.

These conformations, however, do not directly represent the fractions of crystalline and amorphous domains in the sample, as has often been assumed, for example, for semicrystalline polyhydrocarbons.33–35 While the crystallites of PBTTT indeed have C_{16} side chains predominantly in the \( tt \) state, the disordered mesophases have C_{16} side chains that include both \( tt \) and \( tg \) and \( gg \) conformers, which contribute to both 13C resonances in the spectrum. Thus, to determine the structural composition, we assume that three mesophases are present in the material: crystalline (c), lamellar (l), and amorphous (a), as shown in Figure 1a–c, where lamellar refers more specifically to π-stacked backbones and disordered side chains. Because every mesophase has its own fraction of \( tt \), \( tg \), and \( gg \) conformers, \( f_{tt} \), \( f_{tg} \), and \( f_{gg} \) the NMR signal from a powdered sample is the sum of these fractions weighted by the mesophase number fractions, \( n_c \), \( n_l \), and \( n_a \):

\[
f_{tt} n_c + f_{tg} n_l + f_{gg} n_a = f_{\text{NMR}}^{13C}
\]

(1)

\[
n_c + n_l + n_a = 1
\]

(2)

Similar relations hold for the \( tg \) and \( gg \) conformations. The second equation is the normalization condition for the mesophase number fractions. Unfortunately, the fractions \( f_{tt} \), \( f_{tg} \), and \( f_{gg} \) cannot be accessed directly, because it has so far not been possible to prepare a π-conjugated polymer sample containing a specific mesophase only. However, this is straightforward to do using computer simulations. The three mesophases were each modeled using molecular dynamics simulations of 128 PBTTT-C_{16} polymer chains, as detailed in the Supporting Information. Representative snapshots are shown in Figure 1a–c. The classification of conformations into \( tt \), \( tg \), and \( gg \) states was achieved via discrete partitioning of two dihedral angles, \( \theta_1 \) and \( \theta_4 \) (Figure 1d), attached to the

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moiety of interest. Further details concerning the partitioning of $tt$, $tg$, and $gg$ states are given in the Supporting Information.

The fractions of the $tt$ and $tg+gg$ conformations in the PBTPTT material, as determined from molecular dynamics, are listed in Table 1. As expected, the C$_{16}$ side chains are predominantly in the $tt$ state for the crystalline mesophase. Interestingly, the partitioning of $tt$ and $tg+gg$ states is similar for the C$_{16}$ side chains in the lamellar and amorphous mesophases. Thus, we assume in the following $f^0_{tt} \approx f^0_t$. Substituting the values of simulated fractions into eq 1, we obtain $n_t = 0.28$ and $n_c + n_a = 0.72$. To distinguish between amorphous and lamellar mesophases, we utilize the fact that the intermolecular separations between backbones in crystalline and lamellar domains are expected to be similar (see the Supporting Information for details) and contribute to one peak in the solid-state $^{13}$C MAS NMR spectrum only (see Figure 2b). Hence, $n_t + n_c = 0.49$; therefore, $n_c = 0.21$ and $n_a = 0.51$. This is a remarkable result: our calculations suggest that only 28% of the system is in a true crystalline state, in which both the C$_{16}$ side chain and PBTTT backbones are ordered. The remaining part of the sample is either in the lamellar (21%) or amorphous (51%) mesophases. Had we assumed that we have only two mesophases (amorphous and crystalline), the C$_{16}$ side chain statistics would have predicted that the fraction of the crystalline phase is 28% ($n_t = 0$), which is inconsistent with the value of 49% from $^1$H MAS NMR for the PBTPTT backbone. Thus, it is essential to account for the lamellar mesophase presence in a $\pi$-conjugated polymer in order to interpret properly the solid-state NMR results.

Table 1. Simulated and Measured Fractions of $tt$ and $tg+gg$ Conformers and $tt$-Resolved Dynamic Order Parameters in the Crystalline, Lamellar, and Amorphous Mesophases

<table>
<thead>
<tr>
<th></th>
<th>crystalline</th>
<th>lamellar</th>
<th>amorphous</th>
<th>sample (NMR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f^0_t$</td>
<td>0.95</td>
<td>0.41</td>
<td>0.39</td>
<td>0.56</td>
</tr>
<tr>
<td>$f^0_{tg}$</td>
<td>0.05</td>
<td>0.59</td>
<td>0.61</td>
<td>0.44</td>
</tr>
<tr>
<td>$S^0$</td>
<td>0.83</td>
<td>0.46</td>
<td>0.49</td>
<td>0.71</td>
</tr>
</tbody>
</table>

Apart from the statistics for the C$_{16}$ side chain and PBTPTT backbone conformations, solid-state NMR can also provide access to the dynamic order parameters, or equivalently the relative number of microstates visited by a specific bond vector during an NMR measurement. Here, we have employed the 2D $^{13}$C($^{1}$H) rotor-encoded rotational-echo double resonance (REREDOR) and rotor-encoded polarization transfer heteronuclear dipolar-order (REPT-HDOR) experiments to evaluate the one-bond $^1$H–$^{13}$C order parameters. While the dipolar coupling constant ($D_{CH}$) of a rigid $-CH_2-$ group is 21.0 kHz, any rotational motion faster than the NMR time scale ($>\mu$s) partially averages the $^1$H–$^{13}$C dipole–dipole coupling (DDC) and hence decreases $D_{CH}$. This enables determination of a dynamic order parameter $S_{NMR}$ by dividing the experimentally measured value $D_{CH}$ by the theoretical value for a fully rigid $-CH_2-$ group, $S_{NMR} = D_{exp}/D_{rigid}$. Values of $S_{NMR}$ range from 0 to 1, where values closer to unity correspond to greater local rigidity. The resulting rotor-encoded $^1$H–$^{13}$C dipole–dipole sideband patterns are shown in Figure 3a,c. The $^1$H–$^{13}$C DDCs were obtained by a spectral fitting procedure that accounts for the strong DDC contribution of the directly bonded $-CH_2-$ ($n = 1–3$) moieties and an additional weak background contribution due to couplings with remote protons.

The results provide insight into site-selective rotational dynamics of the main-chain and alkylic side chains in PBTPTT-C$_{16}$: For the ordered PBTPTT backbone, corresponding to the crystalline and lamellar PBTPTT regions, the analysis leads to mean DDCs of 19.6 kHz and 18.7 kHz for the $-CH-$ groups of the thienothiophene and thiophene rings, respectively. Both DDCs are close to 21.0 kHz with $S_{NMR}$ being around ~0.9, corresponding to a fairly rigid $-CH-$ moiety. Hence, the well-ordered $\pi–\pi$-stacking arrangement in PBTPTT-C$_{16}$ only allows the aromatic backbone to experience minor dynamic reorientations on the approximately microsecond NMR time scale most likely associated with small out-of-plane fluctuations. Insufficient signal intensity prevented a detailed analysis of the

Figure 3. (a1–a7) Experimental $tt$/tg + gg-resolved 1D $^{13}$C($^{1}$H) REREDOR dipolar sideband patterns (black) and corresponding fits (color) for all spectrally distinct $^{13}$C moieties of the C$_{16}$ side chain. Here, $tg$ is used to denote $tg+gg$. (b) $^{13}$C chemical shifts in the $^{13}$C($^{1}$H) CP/MAS NMR spectrum. (c1, c2) Experimental $^{13}$C($^{1}$H) REPT-HDOR dipole–dipole sideband patterns (black) and corresponding fits (color) for proton-bearing $^{13}$C moieties of the thiophene (TH) and thienothiophene (TT) groups of the PBTPTT polymer backbone. Numbering and coloring correspond to the scheme given in Figure 1d.

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dipolar coupling constants at $^{13}$C spectral positions corresponding to the $-\text{CH}-$ moieties of disordered $\pi-\pi$ stacks (see Figure S2).

A mean $D_{\text{CH}}$ value of 14.9 kHz was determined for the central methylene groups of the C$_{16}$ side chains in the $tt$ conformation (see Figure 3a1). While this part of the alkyl chain is fairly rigid with $S_{\text{NMR}} \sim 0.71$, the $S_{\text{NMR}}$ values are lower (0.65, 0.49, and 0.39) for the last three methylene and methyl groups of the C$_{16}$ side chains in the $tt$ conformation (see Figure 3a2–a4). It is surprising that both structural and dynamic ordering prevail up to the terminal $-\text{CH}_3$ group for side chains composed of as many as 16 structural units. For all $^{13}$C moieties of the C$_{16}$ side chains in gauche conformations, the $D_{\text{CH}}$ values are considerably smaller than their counterparts in $tt$ conformations. For example, $D_{\text{CH}}$ values of the central methylene groups decrease by more than a factor of 2, yielding an $S_{\text{NMR}}$ value as low as 0.34 (see Figure 3a5–a7).

Similar values of 0.32 and <0.4 are obtained for the terminal methylene and methyl moieties. Hence, the decrease in structural order of the C$_{16}$ side chains with gauche conformations is manifested by a considerable increase in segmental rotational mobility. Similar to the statistics of $tt$ and $tg + gg$ states, dynamic order parameters can be used to determine (or refine) the macroscopic structural composition of the sample. To do this, we have evaluated the dynamic order parameter, $S_{\text{MD}}$, as the long-time limit of an autocorrelation function (ACF)$^{37,38}$

$$S_{\text{MD}}^2 = \lim_{t \to \infty} \langle P_2(\vec{u}(t)) \cdot \vec{u}(t) \rangle$$

(3)

Here, $\vec{u}(t)$ is the unit vector along the $-\text{CH}_2-$ moiety in the alkyl chain as illustrated in Figure 1d, and $P_2$ is the second Legendre polynomial; the average $\langle ... \rangle$ is performed over initial times $t_0$ and the ensemble of equivalent $-\text{CH}_2-$ groups (64 backbones and 512 C$_{16}$ side chains). $S_{\text{MD}}$ for backbone $-\text{CH}_2-$ groups were determined to be 0.96, 0.93, and 0.83 in the crystalline, lamellar, and amorphous mesophases, respectively. The first two values (experimental data for amorphous backbones are not available) compare well to the measured values of 0.9, confirming that the PBT TT backbones are rather immobile, at least on a microsecond time scale. For the C$_{16}$ side chains, the $\gamma$-gauche effect can be used to differentiate between the $tt$- and $tg + gg$-conformers. In the MD simulations, we do this by following the dynamics of $\theta_1$ and $\theta_2$ dihedral angles, which are shown in Figure 1d, and assign every $-\text{CH}_2-$ group to one of the states $tt$ or $tg + gg$. $S_{\text{MD}}$ is then evaluated for every state and $-\text{CH}_2-$ group. As anticipated, interdigitated crystalline C$_{16}$ side chains in the $tt$ state have higher $S_{\text{MD}}$ values in the range 0.74–0.88 than the corresponding disordered C$_{16}$ side chains of lamellar and amorphous mesophases ($S_{\text{MD}}^2 = 0.33–0.60$), in qualitative agreement with previous works.$^{14,15}$ Note that the fraction of $tg + gg$ conformers is too small (about 5%) to evaluate their $S_{\text{MD}}$ in the crystalline mesophase (see the Supporting Information for details).

We can now use the calculated $S_{\text{MD}}$ to refine the sample’s composition. To do this, we complement eq 1 with an equation for the dynamic order parameter $S_{\text{NMR}}$ for the $tt$ states only:

$$S_{\text{MD},tt}^2 n_t + S_{\text{MD},tg}^2 n_t + S_{\text{MD},gg}^2 n_g = S_{\text{NMR}}^2$$

(4)

Solving eqs 1, 2, and 4 (see the Supporting Information) yields $n_t = 0.28$, $n_t = 0.23$, and $n_g = 0.49$. Remarkably, these equations contain information about the C$_{16}$ side chains only, yet they give values consistent with the PBT TT backbone solid-state NMR data, namely, $n_t = 0.51$ and $n_t + n_g = 0.49$. The composition of a crystalline PBT TT-C$_{16}$ powdered sample can therefore be deduced from either the static or dynamic properties of alkyl side chains and backbones.

For the present case of PBT TT-C$_{16}$, the ordered fraction of PBT TT backbones accounts for 51% of the powdered sample with $S_{\text{NMR,MD}}$ of 0.90. As measured from the entire sample, the alkyl side chains have fractions of 0.54 ($tt$) and 0.46 ($tg + gg$) with $S_{\text{NMR}}$ of 0.71 ($tt$) and 0.34 ($tg + gg$) for the inner carbons. Complementing these measurements with MD simulations of crystalline, lamellar, and amorphous mesophases, we are able to elucidate the structural composition of the entire powdered PBT TT-C$_{16}$ sample. In particular, the MD simulations reveal that the crystalline and lamellar mesophases account for 28% and 23%, respectively, while 49% of the sample is amorphous. Our study clearly shows that the interpretation of experimental data requires a model that accounts for the local molecular packing, as well as mesoscopic structural composition of a material. The strategy presented in this work is expected to be general and useful for quantitative analyses of the structural compositions of similar $\pi$-conjugated polymer materials.

**ASSOCIATED CONTENT**

* Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.7b01443.

Details of molecular dynamics simulations, solid-state NMR experimental details, and the solution-state NMR spectrum (PDF)

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**Notes**

The authors declare no competing financial interest.

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REFERENCES

(1) McCullough, R. D. The Chemistry of Conducting Polyelectro- 
 (1) McCullough, R. D. The Chemistry of Conducting Polyelectro- 
(2) McCullough, I.; Heeney, M.; Chabinyc, M. L.; DeLongchamp, D.; 
(3) Boudreau, P.-L.; T.; Najari, A.; Leclerc, M. Processable Low- 
(4) McCulloch, I.; Ashraf, R. S.; Binieck, L.; Bronstein, H.; Combe, C.; 
(6) McCulloch, I.; Heeney, M.; Bailey, C.; Genevics, K.; 
(7) DeLongchamp, D. M.; Kline, R. J.; Toney, M. F.; Kline, R. J.; McCulloch, I.; 
(8) DeLongchamp, D. M.; Kline, R. J.; Jung, Y.; Germack, D. S.; Lin, 
(9) McCulloch, I.; Heeney, M.; McCulloch, I.; Northrup, J. E. High 
(10) DeLongchamp, D. M.; Kline, R. J.; Jung, Y.; Germack, D. S.; Lin, 
(11) DeLongchamp, D. M.; Kline, R. J.; Jung, Y.; Germack, D. S.; Lin, 
(12) Cho, E.; Risso, C.; Kim, D.; Gysel, R.; Cates Miller, N.; Breiby, 
(13) Alberga, D.; Perrier, A.; Ciofini, I.; Felice Mangiatordi, G.; 
(14) Alberga, D.; Mangiatordi, G. F.; Torsi, L.; Lattanzi, G. Effects of 
(15) Toney, M. F.; Zieauddin Kufian, M.; Mohd Noor, I. S.; Kariem Arof, A. Effect of 
(16) Hansen, M. R.; Graf, R.; Spiess, H. W. Solid-State NMR in 
(17) Casal, H. L.; Mantsch, H. H. Positional Dependence of Solvent 
(18) Lee, M. J.; Gupta, D.; Zhao, N.; Heeney, M.; McCulloch, I.; 
(20) Noriega, R.; Rinay, J.; Vandewal, K.; Koch, F. P. V.; Stingelin, N.; Smith, P.; Toney, M. F.; Salleo, A. A General Relationship between 
(21) Rahman, M. H. A.; Uddin Khandaker, M.; Raza Khan, Z.; 
(22) Snyder, C. R.; Nieudewaald, R. C.; DeLongchamp, D. M.; 
(24) Shen, X.; Hu, W.; Russell, T. P. Measuring the Degree of 
(25) May, F.; Marcon, V.; Hansen, M. R.; Grozema, F.; Andrienko, D. Relationship between Supramolecular Assembly and Charge- 
(26) Hansen, M. R.; Graf, R.; Spiew, H. W. Interplay of Structure and 
(27) Tonelli, A. E.; Schilling, F. C. Carbon-13 NMR Chemical Shifts 
(28) Hansen, M. R.; Graf, R.; Spiess, H. W. Solid-State NMR in 
(29) Toney, M. F.; Zieauddin Kufian, M.; Mohd Noor, I. S.; Kariem Arof, A. Effect of 
(30) Hansen, M. R.; Graf, R.; Spiess, H. W. Conformational Effects and Configura- 
(31) Born, R.; Spiess, H. W. Conformational Effects and Configura- 
(32) Born, R.; Spiess, H. W. Conformational Effects and Configura- 
(33) Born, R.; Spiess, H. W. Conformational Effects and Configura- 
(34) Born, R.; Spiess, H. W. Conformational Effects and Configura- 
(35) Snyder, R. G.; Poore, M. W. Conformational Structure of Polyethylene Chains from the Infrared Spectrum of the Partially 
(36) Snyder, R. G.; Poore, M. W. Conformational Structure of Polyethylene Chains from the Infrared Spectrum of the Partially 

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