Predicting the plateau modulus from molecular parameters of conjugated polymers

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Abstract:
The relationship between Kuhn length $l_k$, Kuhn monomer volume $v_0$, and plateau modulus $G_0N$, initially proposed by Graessley and Edwards for flexible polymers, and extended by Everaers, has a large gap in experimental data between the flexible and stiff regimes. This gap prevents the prediction of mechanical properties from chain structure for any polymer in this region. Given the chain architecture, including a semiflexible backbone and side chains, conjugated polymers are an ideal class of material to study this cross-over region. Using small angle neutron scattering, oscillatory shear rheology, and the freely rotating chain model, we have shown that twelve polymers with aromatic backbones populate a large part of this gap. We also have shown that a few of these polymers exhibit nematic ordering, which lowers $G_0N$. When fully isotropic, these polymers follow a relationship between $l_k$, $v_0$, and $G_0N$, with a simple crossover proposed in terms of the number of Kuhn segments in an entanglement strand $N_e$. 
Synopsis:

Bridging the previously unpopulated gap between flexible and stiff entangled polymers using semiflexible conjugated polymers.
1. Introduction

Advances in technology and consumer electronics have progressed quickly from large stationary computers to portable and wearable technology, requiring flexible and stretchable bio-integrated electronics. As human tissues and organs have low modulus, implanting electronic devices based on high modulus materials like silicon can have negative effects on the body, such as tissue scarring, device rejection due to inflammatory responses, and changes in cell division and growth in tissues around the device.\(^{1-4}\)

Conjugated polymers and gels range in mechanical modulus (Young’s modulus, E) from 16 GPa to less than 100 kPa\(^{4-6}\), and are much closer in stiffness to biological tissues than inorganic materials such as silicon (E of 130 GPa).\(^7\) As such, devices based on conjugated polymers could be ideal for implantable bioelectronics.\(^{8-10}\)

While semicrystalline conjugated polymers are often applied as the active layer of electronic devices, they are often too brittle and stiff for bio applications.\(^4\) Instead, entangled amorphous conjugated polymers are an interesting class of material for use in soft and stretchable electronics; nevertheless, predicting the modulus for this class of materials remains a challenge.

Mechanical moduli of amorphous polymers above their glass transition temperature \((T_g)\) are governed by entanglements, which are temporary physical crosslinks in the polymer that create a plateau modulus \((G_0)_N\) at time scales before the chains can unentangle and the modulus can further decrease. If \((G_0)_N\), Rouse time of an entanglement strand \(\tau_e\), and molecular mass distribution of the material are known, one can use various polymer models to predict the time and temperature dependence of the mechanical modulus.\(^{11}\) Relationships have been proposed for the prediction of mechanical properties from chain architecture\(^{12}\) that, if verified for semiflexible conjugated polymers, could enable more efficient design of modulus-specific conjugated polymers for various applications, such as bioelectronics.
In 1981 Graessley and Edwards proposed a dimensionless relationship between the mechanical properties ($G^0_N$) and the chain dimensions of the polymer (Kuhn length, $l_k$ and Kuhn monomer volume, $v_0$)\textsuperscript{13} that we recast as:

$$\frac{G^0_N v_0}{k_B T} = \left( \frac{l_k}{v_0} \right)^a$$  \hspace{1cm} (1)

where $k_B$ is the Boltzmann constant. $G^0_N$ is inversely related to the entanglement molecular mass $M_e$ as\textsuperscript{14}:

$$G^0_N = \frac{\rho k_B T N_A}{M_e}$$  \hspace{1cm} (2)

where $\rho$ is the mass density and $N_A$ is Avogadro’s number. The Kuhn length, $l_k$, is the length over which the chain backbone is no longer correlated in direction, and a scale of local backbone rigidity. The Kuhn monomer volume, $v_0$, is how much space a Kuhn monomer occupies, described by\textsuperscript{15-17}:

$$v_0 = \frac{m_0 l_k}{\rho N_A l_0}$$  \hspace{1cm} (3)

where $m_0$ and $l_0$ are the molar mass and length of the repeat unit, respectively.

Expressing this relationship in terms of $v_0$ instead of the more commonly used packing length ($p$), as seen previously\textsuperscript{17}, leads to $G^0_N v_0/k_B T = 1/N_e$, where $N_e$ is the number of Kuhn monomers in an entanglement strand.\textsuperscript{18} Thus, measurements of $G^0_N$ as function of $p$ (or $v_0$) lie on a universal curve encompassing all polymers from the flexible regime to the stiff regime that was proposed by Everaers, and is known as the Everaers plot.\textsuperscript{12}

This relationship could be useful for designing new materials for modulus-specific applications, such as in organic bioelectronics. But, a large gap in experimental data between the flexible and stiff regimes exists, thereby limiting confidence in predictions within this crossover region. Conjugated polymers fall between flexible polymers and stiff polymers in the Everaers plot, and are thus a unique class of polymers that can be used to fill the gap. This verification would not only bring further insight to the inconsistencies between current scaling arguments as discussed by Hoy, Kroger, and Milner\textsuperscript{19, 20}, but also allow the use of the Everaers plot to develop modulus-specific polymers for various applications simply by knowing $l_k$. 
In this work, a systematic study of various entangled isotropic conjugated polymers with semiflexible chains were used to investigate the crossover regime between the flexible and stiff limits. A set of conjugated polymers designed to exhibit an isotropic phase over a wide range of temperatures and frequencies enables studies of entanglement when crystals or liquid crystallinity are not present (liquid crystalline phases such as the nematic phase, which is common in stiffer conjugated polymers, lowers the number of entanglements and therefore $G_{0N}^{0,21}$). Values for $l_k$ from small angle neutron scattering (SANS) verify that the simple freely rotating chain model can accurately predict $l_k$ for conjugated polymers with a wide range of backbone stiffnesses and flexible alkyl side chains. Using oscillatory shear rheology, we find that conjugated polymers appear to follow a universal relationship between chain properties ($l_k$ and $v_0$) and mechanical properties ($G_{0N}$), opening the door for future predictions of mechanical properties from the chemical structure.

2. Results and Discussion

![Chemical structures of conjugated polymers](image)

**Figure 1.** Chemical structures of conjugated polymers investigated in this study.

The chemical structures shown in Figure 1 were designed and synthesized to reduce crystallization through the addition of defects, by controlling regioregularity, adding steric hindrance, and breaking chain planarity through the addition of side chains, to span a wide range of backbone stiffnesses from flexible to semiflexible. PCT6BT, PFT6BT, and PPT6BT were designed to have increased steric hindrance and
therefore reduced crystallinity due to an addition of hexyl side chains on the thiophene units. This steric hindrance can prevent close interactions between the aromatic backbones, disrupt $\pi-\pi$ stacking in the material, and thereby suppress crystallization. The regio-random poly(3-alkylthiophenes) (RRa P3AT) have suppressed crystallinity due to a non-symmetric repeat unit adding randomly, and these defects often prevent crystallization. Keeping the backbone constant, such that $l_k$ is invariant, but the side chains differ, as is the case in the RRa P3AT and the poly(meta,meta,para-phenylene) (PmmpP) series in Figure 1, allows tuning of $v_0$ independent of $l_k$. This offers the ability to fine tune $v_0$ in hopes of populating a large area of the Everaers plot.

A series of experiments including differential scanning calorimetry (DSC) and oscillatory shear temperature ramp tests were conducted to investigate the phase behavior of these materials and ensure they are isotropic. DSC of the RRa P3AT’s shows an absence of any melting or crystallization peaks in heating and cooling runs, respectively; this lack of first order transitions in these materials suggests that they are amorphous. As rheology is more sensitive to microscopic changes in the material than DSC, it can more accurately investigate phase behavior. In a common temperature ramp test, any crystallinity would appear as a flat solid like plateau with a steep decrease in modulus upon melting. Rheology is also ideal for identifying the nematic to isotropic transition temperature ($T_{NI}$), as it is the only known cause for an increase in viscosity with temperature; this can be seen in SI 1 at 144 °C for PPT6BT. Frequency sweeps and constructing master-curves using time-temperature superposition (tTs) can also reveal phase transitions in the material as areas where tTs fails. The absence of any crystallization or $T_{NI}$ throughout the entire temperature range suggests isotropic behavior in PCT6BT and PFT6BT (see SI 2). In the case of PPT6BT (see SI 1), the $T_{NI}$ occurred at 144 °C. Therefore, all subsequent measurements of this polymer were performed approximately 40 °C above this temperature to ensure the material was fully isotropic. Thus, large temperature ranges where the polymers in Figure 1 were above the $T_g$ and also isotropic were identified. For PFTBT and PCDTBT, $T_{NI}$’s occur at 290 °C and 273 °C, respectively. As it is difficult to
measure 40 °C above these temperatures without the risk of degradation, these polymers still contain some nematic local alignment at the measurement temperature of 300 °C.\textsuperscript{21}

To verify that these polymers lie in the semiflexible gap of the Everaers plot, their Kuhn lengths were determined. The freely rotating chain model (FRC)\textsuperscript{18} has been used to predict $l_k$ from the chemical structure of conjugated molecules.\textsuperscript{28} While the FRC model has been used successfully to predict the $l_k$ of a few semiflexible polymers, it has not been verified for polymers with $l_k$’s larger than 11 nm.\textsuperscript{28} We verify the FRC using SANS from dilute solutions of $PmmpP10$ (56 kg/mol and 76 kg/mol), PPT6BT, PNDI(2OD)T2, RR P3HT, RRa P3HT, and RRa P3DDT. Data were acquired using the 10 m and 30 m SANS beam lines at the Center for Neutron Research (NCNR) at the National Institute of Standards and Technology (NIST) and were fit to a flexible cylinder model in SasView\textsuperscript{29} using Levenberg-Marquardt fitting with $10^5$ steps per fit, as shown in Figure 2a. As shown in Figure 2b, the FRC model accurately predicts $l_k$ for the polymers tested in the range $1.8 \leq l_k \leq 15$ nm (see Table 1).
Figure 2: Kuhn lengths obtained from small angle neutron scattering (SANS) and the freely rotating chain model. a) Typical SANS data for 7 conjugated or aromatic polymers in d5-chlorobenzene. Intensity is normalized to the scattering cross section and plotted vs. scattering vector $q$. These data are fit to the flexible cylinder model using contour length and dispersity ($D$) obtained from polystyrene-standard calibrated gel permeation chromatography (GPC) as upper bounds on parameters as well as a fixed scattering length density. Fits are shown as black lines. b) $l_k$'s predicted by the FRC model ($l_{k,FRC}$) are consistent with experimentally measured $l_k$'s from SANS ($l_{k,SANS}$) over a wide range of chain stiffnesses. Error bars are the best representation of one standard deviation in the experimental uncertainty.

Having obtained values for $l_k$, $v_0$ can be obtained using Equation 3 in combination with the mass density. The density was measured by melt-casting a bubble-free puck of known mass and measuring its height and diameter in a rheometer at various temperatures (Table 1). The Kuhn monomer volumes span a wide range of the flexible to semiflexible regime, allowing the conjugated polymers chosen for this study to populate the gap of the Everaers plot. To know whether these polymers follow the relationship between $l_k$, $v_0$, and $G_0^N$, however, a measurement of the plateau modulus is needed.

Oscillatory frequency sweeps were taken over a wide range of temperatures and shifted using $tTs$ to generate master-curves for each polymer in the isotropic liquid state (master-curves and shift factors can be seen in SI 3-9). $G_0^N$ can be approximated by taking the modulus value at the high frequency crossing of the storage modulus ($G'$) and loss modulus ($G''$) at the Rouse time of an entanglement strand, $\tau_e$. As these
polymers have high dispersity, fitting the master-curves to a tube model is needed for quantification. Herein we use the Branch-on-Branch (BoB) model developed by Das, et al.\textsuperscript{11} with molecular mass distribution as an input (mass average molecular mass, $M_w$, and dispersity, $D$, can be seen in Table 1), assuming that all chains are linear and that the tube diameter is larger than $l_k$ (meaning that the number of Kuhn monomers in an entanglement strand $N_e > 1$). These assumptions are met for the polymers presented in this study, allowing for fitting master-curves to BoB to obtain the entanglement molecular mass and $G_0N$. Two master-curves can be seen in Figure 3a and Figure 3b (others are in SI 3-5). As expected, the BoB fits are best at lower $l_k$; as the polymer gets stiffer BoB cannot be expected to accurately report $G_0N$ because the polymer entanglements are starting to be governed more by bending and strong reptation than Rouse motion (see SI 10).\textsuperscript{30} Nevertheless, these polymers approximately follow the experimental scaling relationship of 3.4 between $\tau_e$, the reptation time, $\tau_{rep}$, and the number of entanglements per chain as seen in Figure 3c.\textsuperscript{18} This shows that the usual relation between rubbery plateau width and number of entanglements per chain still applies for the twelve conjugated polymers of this study and their master curves can therefore be fitted using the BoB model. Approximations of $G_0N$ by taking the crossover modulus at $\tau_e$ (the high frequency end of the plateau) are also in reasonable agreement with the predictions of $G_0N$ from BoB, as expected for polymers whose entanglements are governed by Rouse motion. Values of $G_0N$, $M_e$, and $\tau_e$ can be seen in Table 1.
Figure 3. Master-curves of a) RRa P3BT and b) PCT6BT. Master-curves were generated using tTs and were horizontally shifted to reference temperatures of 240 °C, and 140 °C respectively, using shift factors $a_T$ as shown in SI 6-9. The open symbols are experimental data and the solid black curves are the fits to $G'$ and $G''$, generated from the BoB tube model, inputting the molecular mass distribution from GPC and assuming all chains are linear. The master-curves for the other 10 polymers tested can be seen in SI 3-5. c) Ratio of the reptation time, $\tau_{rep}$, and Rouse time of an entanglement strand, $\tau_e$, as a function of the number of entanglements along the chain for all 12 conjugated polymers.
Table 1. Chain dimensions, polymer properties, and plateau moduli for various conjugated polymers.

| Polymer    | $l_k$ [nm] | $l_k$ [nm] | $T$ [°C] | $v_0$ [nm] | $f_k^3/v_0$ | $\sigma_{0N}$ [MPa] | $M_e$ [kg/mol] | $\tau_e$ [μs] | $\rho$ [g/cm$^3$] | $M_w$ [kg/mol] | D |
|------------|------------|------------|----------|------------|-------------|-----------------------|----------------|-------------|----------------|----------------|---|
| PmmpP10   | 1.8        | 1.9 ± 0.5  | 200      | 1.45       | 4.7         | 0.29                  | 13.0           | 5.0         | 0.96          | 76             | 1.8 |
| PmmpP8    | 1.8        | 200        | 1.30     | 5.3        | 0.48        | 7.9                   | 10            | 0.96        | 73            | 2.1            |    |
| PmmpP6    | 1.8        | 240        | 1.15     | 6.0        | 0.85        | 4.8                   | 2.8           | 0.96        | 109           | 2.1            |    |
| RRa P3DDT | 5.6        | 200        | 6.0 ± 1.5| 5.99       | 29          | 0.46                  | 8.4           | 0.3         | 0.98          | 79             | 1.8 |
| RRa P3OT  | 5.6        | 240        | 5.24     | 34         | 0.67        | 5.6                   | 0.16          | 0.87        | 62            | 2.8            |    |
| RRa P3HT  | 5.6        | 240        | 5.3 ± 0.9| 3.55       | 49          | 0.81                  | 5.8           | 0.7         | 1.1           | 110            | 3.1 |
| RRa P3BT  | 5.6        | 240        | 3.27     | 52         | 1.01        | 4.1                   | 0.7           | 0.98        | 72            | 2.5            |    |
| PFT6BT    | 11         | 240        | 7.99     | 167        | 0.75        | 5.3                   | 60            | 0.94        | 66            | 2.3            |    |
| PFTBT     | 11         | 300        | 4.47     | 298        | 0.43        | 15                    | 100           | 1.35        | 135           | 4.2            |    |
| PCT6BT    | 12         | 140        | 8.42     | 195        | 0.55        | 6.1                   | 12000         | 0.98        | 36            | 1.8            |    |
| PCDTBT    | 12         | 300        | 5.55     | 296        | 0.21        | 27                    | 430           | 1.2         | 200           | 3.7            |    |
| PPT6BT    | 17         | 15 ± 1.7   | 200      | 11.6       | 304         | 0.46                  | 8.0           | 500         | 0.94          | 49             | 1.6 |

$^a l_k$ from SANS obtained at 25 °C. $^b l_k$ from the FRC model. $^c G_{0N}$ for PFTBT and PCDTBT are taken from fitting the master-curves just above their $T_{NI}$’s, so some nematic behavior is expected. $^d$Isotropic $G_{0N}$ for PPT6BT was obtained by shifting to a reference temperature ≈60 °C above the $T_{NI}$. $^e G_{0N}$ for all polymers from fits to BoB.
Using Equation 1, we show that aromatic and conjugated polymers populate a wide range between the flexible and stiff regimes. In addition, we can explore whether previously reported scaling models\textsuperscript{12} represent the crossover regime between stiff and flexible chains. Aromatic P\textit{nnmpP} polymers follow Lin-Noolandi scaling with a power law exponent (see Equation 1) \( \alpha = 2 \), which suggests that these polymers are flexible.\textsuperscript{31, 32} The P3AT, PFT6BT and PCT6BT and PPT6BT polymers follow closer to the Morse scaling with a power law exponent \( \alpha = 2/5 \), indicating that these conjugated polymers are semiflexible and are a unique class of materials.\textsuperscript{33} Based on these data we propose a crossover equation between the two regimes (Equation 4), suggesting that the crossover between the flexible and stiff regimes is controlled by \( l_k \) and should occur at \( l_k^3 / \nu_0 = 11.7 \) with \( N_e = 5.8 \), significantly larger than unity.

\[
N_e = \frac{k_B T}{G_0 \nu_0} = 400 \left( \frac{l_i^3}{\nu_0} \right)^{-2} + 7.77 \left( \frac{l_i^3}{\nu_0} \right)^{-2/5} \tag{4}
\]

PFTBT and PCDTBT lie well below the prediction, which suggests that lingering local nematic alignment may persist in these materials slightly above their \( T_{NI} \). As the degradation temperature for many conjugated polymers begins just above 300 °C and the \( T_{NI} \) for both PFTBT and PCDTBT are both above 270 °C, it is likely that both polymers are not fully isotropic and therefore have reduced entanglements as previously shown.\textsuperscript{21} In the case of PPT6BT, which also has a nematic phase but does follow Everaers’ prediction, the \( T_{NI} \) is far below the degradation temperature. This allows us to measure the polymer well above its \( T_{NI} \), deep into the isotropic phase.
Figure 4. Conjugated polymer melts (circles) follow Everaers’ scaling predictions with dimensionless plateau modulus $G_0^N$ vs dimensionless Kuhn monomer volume $v_0$. a) The flexible melt data (solid green squares) were obtained from $^{15, 34}$, the flexible solution data (open green squares) from $^{35, 36}$, and the semiflexible solution data (open blue squares) was obtained from $^{37, 38}$. The solid black line is the proposed crossover given by Equation 4. The more flexible PmmpP polymers fit best with the flexible melt scaling argument $(l_k^3/v_0)^2$ while P3AT, PFT6BT and PCT6BT and PPT6BT fit best with the semiflexible scaling argument of $(l_k^3/v_0)^{2/5}$. The PFTBT and PCDTBT polymers lie well below the prediction, this is hypothesized to be due to lingering nematic domains slightly above their $T_{NI}$. The tube model for a semiflexible and flexible polymer can be seen in insets a) and b), respectively. b) An expanded view of the crossover region.

3. Conclusions

We have verified the use of the FRC model and experimentally populated the previously empty crossover between flexible and stiff polymers, thereby validating scaling theories in this region and demonstrating that the Everaers relationship can be used to predict $G_0^N$ of conjugated polymers from their structure. Conjugated polymers are semiflexible, enabling our study of the crossover between the flexible and stiff regimes. These results re-emphasize the importance of identifying how nematic phases can affect not only the charge transport properties of conjugated polymers but also entanglements, and therefore mechanical properties as well. Figure 4 provides a universal curve that allows predictions of mechanical moduli for chains of various backbone stiffnesses from $l_k$. Furthermore, in conjunction with linear
viscoelastic descriptions (such as BoB), Figure 4 can allow the generation of rheological spectra that would provide insight to other mechanical aspects of any polymer, such as relaxation and terminal behavior. Ultimately, this work helps enable the prediction of mechanical properties of isotropic conjugated polymers to support the design of stretchable and biocompatible electronics.

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5. Disclaimer

Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure accurately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.
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