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An Apparent Size-Exclusion Quantification Limit Reveals a Molecular Weight Limit in the Synthesis of Externally Initiated Polythiophenes

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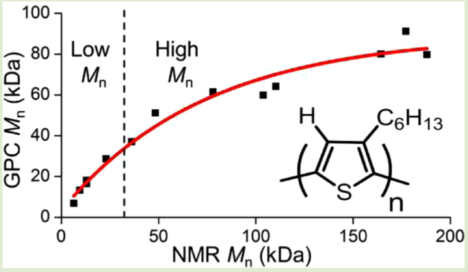
Supporting Information

ABSTRACT: We report the linear and nonlinear regions of the relationship between number average molecular weight determined by gel permeation chromatography (GPC) and ^{1}H NMR end-group analysis for a series of *o*-tolyl-initiated poly(3-hexylthiophene)s (P3HTs). For conjugated polymers with chains that are 39−138 repeat units in length (6.5−23 kDa), GPC systematically overestimates the number average molecular weight (M_n) by a factor of 1.3 ± 0.1 (standard error), and GPC and ^{1}H NMR end-group analysis correlate in a linear manner. For chains 138−1130 (23−188 kDa) repeat units in length, we observe a nonlinear relationship between GPC and end-group analysis. Static light-scattering experiments confirm that at high molecular weight (>70 kDa) decreasing the catalyst loading does not appreciably increase the polymer chain length. Thus, we conclude that there is a molecular weight limit in the synthesis of externally initiated polythiophenes and a propensity for the growth of nonexternally initiated chains which increases as a function of M_n. This is significant as external initiation has been reported to result in nearly 100% externally initiated chains as well as reduce the possibility of chain−chain coupling in a typical synthesis. Our data show that 100% external initiation only holds true for polymers that are less than 40 kDa and encourages caution when determining M_n by NMR using this synthetic methodology at high molecular weights.



Regioregular poly(3-hexylthiophene) (P3HT) is one of the most widely studied among current conjugated polymers (CPs).[1−13] One of the hallmarks of P3HT is that it can be synthesized under quasi-living conditions, allowing control of the polymer length by varying the catalyst loading (catalyst to monomer ratio). This has allowed researchers to conclude that the opto-electronic properties of P3HT, and CPs in general, are strongly tied to polymer molecular weight.[1,14,15] Despite intense focus on developing structure−property−function relationships in CPs, the molecular weights of these batch-synthesized polymers are still not certain due to the lack of reliable methods to determine them. The systematic error in molecular weight measurements for CPs requires significant attention to determine the discrepancy between the values that are measured using commonly employed methods and the true molecular weight of CPs.

Gel permeation chromatography (GPC) is the most widely used technique for measuring polymer molecular weight. In this case, it is common to estimate CP molecular weight using GPC relative to polystyrene (PS) standards while making two assumptions: (1) that the hydrodynamic radii of the two polymers are the same at equivalent chain length and (2) the retention volume in which the polymers elute out of the column decreases as a function of chain length at the same rate. In general, assumption (1) qualifies GPC as a size-exclusion method that determines size or, more accurately, the hydrodynamic radius of polymers by filtration elution time relative to those of known standards. The problem is that CPs are mostly rigid and rod-like, whereas common standards (PS, for example) are coil-like; therefore, comparing rod-like CPs with coil-like PS causes a great deal of uncertainty in this important measurement. We and others have hypothesized that the systematic errors in GPC measurements result in molecular weight overestimation for CPs. Investigations using matrix-assisted laser desorption ionization−time-of-flight mass spectrometry (MALDI−TOF) on poly(alkylthiophene)s revealed that the extent of overestimation by GPC ranges between 1.2 and 2.3, depending on the molecular weight.[16] Hiorns et al. suggest dividing molecular weight by 1.6 to produce an approximate true molecular weight when analyzing P3HT.[2] Moreover, at a certain chain length, GPC can no longer be used to adequately estimate polymer length due to the size exclusion limit of the column.[17]

Herein, we systematically compare the M_n of P3HT determined by size-exclusion chromatography with ^{1}H NMR end-group analysis for polymers with a wide range of expected molecular weights (6.9−166 kDa). We synthesize polymers functionalized with an *o*-tolyl group that provides a distinct ^{1}H NMR end-group resonance signal, which is compared with the resonance signal of the polymer repeat unit. To the best of our knowledge, this is the first systematic GPC and end-group study of a series of externally initiated CPs. We adhere to two

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important requirements which enable accurate quantification of polymers by this process: (1) the pertinent NMR end-group and repeat unit resonance signals must be free from signal contamination caused by other resonance signals, and (2) the resonance signals of interest, especially the end-group signal, must be quantifiable. Requirement (2) is especially important for extremely high molecular weight polymers.[18] We focus this study on the low and high M_n regions, which we define as lesser than and greater than 40 kDa, respectively. The trends at low M_n and high M_n are likely applicable to other conjugated polymers synthesized by similar methods.[19−25]

o-Tolyl-initiated P3HT was synthesized as previously described and then characterized by NMR spectroscopy and gel permeation chromatography with polystyrene standards (Scheme 1).[26,27] This method has been shown to produce end-functionalized P3HT, with nearly 100% end-group functionalization,[26] as well as the controlled polymerization of copolymers.[28] MALDI−TOF experiments indicate complete *o*-tolyl functionalization for the low molecular weight polymers (P3HT-4, see Table 1 for naming conventions); however, higher molecular weight polymers cannot be quantified using this method [see Supporting Information (SI), Figure S1]. ^{31}P NMR analysis of the catalyst complex indicates the presence of only the *o*-tolyl-initiated species present in the reaction mixture (see SI Figure S2).

Scheme 1. Synthetic Route to *o*-Tolyl-Initiated P3HT[26]

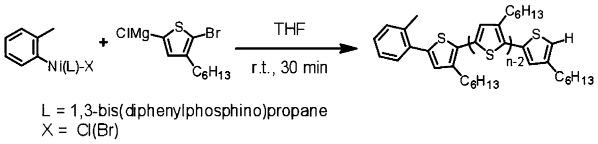

Table 1. Summary of P3HT Synthesized at Indicated Catalyst Loading

entry[a]	GPC PDI[b]	GPC M_n[b,c]	NMR M_n[c]
P3HT-4	1.31	6.9	6.5
P3HT-3	1.32	13.2	9.5
P3HT-2a	1.35	16.8	13.0
P3HT-2b	1.33	18.1	13.0
P3HT-2c	1.36	16.5	13.1
P3HT-1	1.29	28.7	23.1
P3HT-0.5a	1.40	37.1	36.1
P3HT-0.5b	1.30	51.2	48.4
P3HT-0.25	1.42	61.5	78.0
P3HT-0.2a	1.80	64.1	110.4
P3HT-0.2b	1.55	59.9	103.8
P3HT-0.1a	1.86	79.8	188.0
P3HT-0.1b	1.53	91.2	177.2
P3HT-0.1c	1.71	80.1	164.4

[a] The number after the dash (-) refers to the catalyst loading, in mol % monomer. The letter after the number refers to a particular replicate at the same catalyst loading. For example, P3HT-2a denotes the first of a triplicate set (a, b, c) of P3HT synthesized with 2% catalyst loading. [b] GPC was performed at 140 °C in 1,2,4-trichlorobenzene and calibrated to PS standards. [c] The number average molecular weight (M_n) was determined by GPC and NMR and is reported in kDa.

To prepare a set of *o*-tolyl-initiated P3HT with different molecular weights, the catalyst loading was varied between 4 and 0.1 mol % with respect to the monomer. For this study, 14 different reaction conditions were used to synthesize P3HTs, including two duplicates (0.5% and 0.2% catalyst loading) plus two triplicates (2% and 0.1% catalyst loading) (Table 1).

We first determine the relationship between reaction time and polymer polydispersity by GPC analysis. Reaction time is a significant contributor to polymer chain coupling by disproportionation of Ni(dppp)Br chain ends for a typical P3HT synthesis. When polymerization was allowed to proceed for 12 h, the corresponding GPC traces reveal a shoulder in the elution peak that is approximately as large as the main peak and approximately twice its molecular weight (as determined by peak molecular weight, M_p), which we interpret as the chain−chain coupled product (see SI Figure S3). To circumvent this, we shortened the reaction time to 30 min and observe that the shoulder is significantly less pronounced (see SI Figure S4). Finally, the reaction concentration was adjusted by modifying the total volume when the reaction was carried out with 2 mol % catalyst for 30 min (see SI Figure S5).

GPC analysis of the polymers reveals that most polymers have a low polydispersity (≤1.4 PDI), with the exception of the high M_n polymers (>60 kDa, PDI 1.5−1.9). As noted above, minor coupling of P3HT chains accounts for the slight shoulder peaks observed in the GPC analyses (Figure 1 and see SI Figure S6).

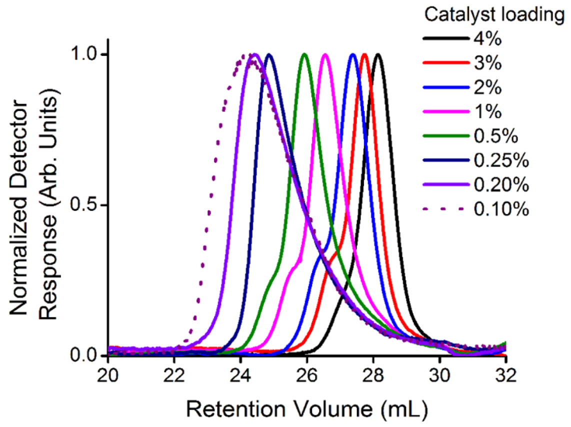

Figure 1. GPC elution profiles of *o*-tolyl-initiated P3HT synthesized at indicated catalyst loadings.

To obtain quantitative NMR data, the ^1H nuclear spins must be completely relaxed prior to each excitation pulse. This relaxation time is typically accommodated during a combination of the acquisition period, when the receiver is turned on, and a delay period that is inserted prior to each excitation pulse. In this study, the delay time was chosen by measuring the relative peak area integrations of the proton on the aromatic repeat unit (6.98 ppm, see Figure S7, SI) to those of the methyl protons on the *o*-tolyl end group (2.49 ppm, see SI Figure S7) for P3HT-0.2, P3HT-1, and P3HT-2c (see SI Figures S8−S16). A combined acquisition and delay time of 8 s or longer yielded integral ratios that did not significantly change (see SI Table S1), which suggested that at least 8 s will accommodate complete relaxation of the ^1H signals. Thus, all subsequent spectra were acquired with a combined 8 s acquisition and delay time. The integrated area of the *o*-tolyl methyl resonances was normalized to 3 (as there are three protons in the methyl group), after which the normalized integrated area of the aromatic repeat resonance was assessed. The latter value was representative of the degree of polymerization, and from this the M_n was calculated.

To assess the reproducibility of the measurement, we performed our first total analysis (NMR M_n vs GPC M_n) in triplicate at 2% catalyst loading, that is, three separately synthesized and isolated polymers prepared under identical conditions (P3HT-2{a–c}). Our results indicate that our synthesis and analysis is very reproducible with a GPC-determined M_n of 17.1 ± 0.5 kDa (standard error) (see SI Figure S17). The end-group analysis shows improved precision for the triplicate, with an M_n of 13.04 ± 0.01 kDa (see SI Figures S8, S18, and S19). Importantly, this single-point analysis confirms the systematic GPC overestimation of M_n, in this case by a factor of 1.3, for these polymer samples. We also synthesized a set of triplicates at the lowest catalyst loading corresponding to the highest molecular weights in our set. The variation in this case is larger relative to the triplicate at 2% catalyst loading. We find that the M_n for P3HT synthesized at 0.1% catalyst loading is 83.7 ± 3.7 kDa as measured by GPC (see SI Figure S20) and 176.5 ± 6.8 kDa as measured by NMR (see SI Figures S21–S23).[29] This dissimilarity (GPC M_n vs NMR M_n) for the high molecular weight polymers will be described in detail below. Low and intermediate molecular weight polymers were also analyzed by NMR (see SI Figures S24–S29; Table 1). The regioregularity for all polymers is greater than or equal to 97%.

We observe a linear relationship between NMR M_n and GPC M_n between 6.5 and 23.1 kDa (NMR M_n). In our instrumentation, which we note operates at 140 °C, overestimation occurs by a factor of 1.3 ± 0.1 (Figure 2). This factor is notably lower than the extent of overestimation by 1.7 as reported by Zhang et al.,[6] possibly due to our specific chromatographic conditions and analysis at high temperatures.

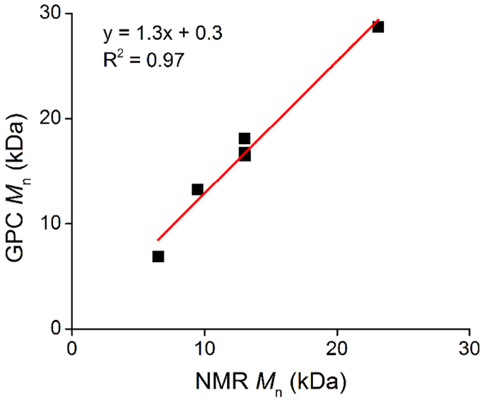

Figure 2. Relationship between GPC M_n and NMR M_n for P3HT synthesized with catalyst loadings between 1% and 4%.

The relationship between NMR and GPC M_n appears nonlinear in very long polymers (M_n > 40 kDa) (Figure 3). Diminishing increases in GPC M_n with respect to increasing NMR M_n suggest plateauing behavior. The curve plateaus at high molecular weight, which can be fit with an exponential function with an asymptote at 89.6 ± 6.5 kDa. We found this result surprising, as our high-temperature GPC was calibrated with a set of polystyrene standards containing polymers of M_n up to 1136 kDa. To our knowledge, this result is the first report of an apparent systematic *underestimation* of molecular weight by GPC measurement for P3HT. It is noteworthy that as the predicted M_n of the polymer increases the elution curve appears to asymmetrically broaden. Interestingly, the predicted M_n based on monomer:catalyst ratio correlates linearly with the NMR M_n at all weights (Figure 4).

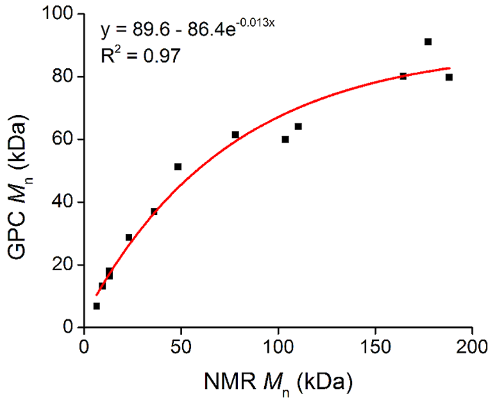

Figure 3. Relationship between GPC M_n and NMR M_n.

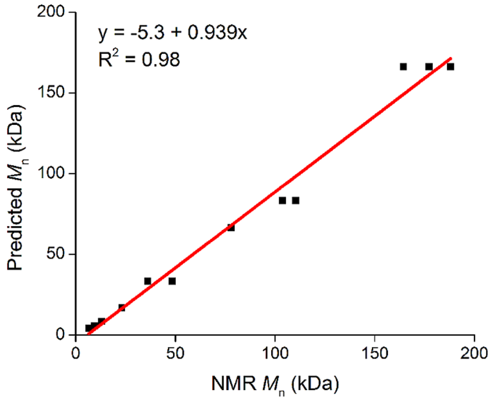

Figure 4. Relationship between predicted M_n (from catalyst loading) and NMR M_n.

While the GPC-based overestimation at the low M_n regime could be attributed to the dissimilarity in polymer type with PS standards, at the high M_n regime GPC produces a lower M_n than measured by NMR. The exponential fit in Figure 3 indicates that the error in GPC measurement, relative to the NMR measurement, is not constant in the high M_n regime. One explanation for this could be that Assumption 2 (the retention volume in which the polymers elute out of the column decreases as a function of chain length at the same rate) does not hold especially for high molecular weight P3HT. A second explanation is that the synthesis is not consistent as a function of molecular weight; for example, while we have confirmed that nearly all chains are fully *o*-tolyl initiated at low molecular weights and that a single initiating species is present in the beginning of all reactions, at higher molecular weights this may not hold true. This scenario would lead to polymer chains without the *o*-tolyl end group but would still increase the intensity of the thiophene aromatic resonance at 6.98 ppm, thus leading to an increase in NMR M_n that is consistent with a monomer:catalyst ratio.

To distinguish between these two effects, we carried out static light scattering (SLS) measurements on high M_n P3HT to determine if catalyst loading had an effect after the observed point of GPC saturation. SLS also indicates that the size of the polymers does not drastically change once the catalyst reaches

0.2% or lower (see SI Figure S30). This suggests that indeed there is a molecular weight limit to this synthetic method and that once this limit is reached new chains are initiated that do not contain the *o*-tolyl end group, leading to erroneous NMR M_n measurements. A similar feature was observed in previous work on nonexternally initiated polythiophenes showing a constant polymer chain length with continued consumption of monomer from solution by new chain initiation.[30] This theory is further supported by the broad GPC peaks that are skewed toward low molecular weight polymers by new chain growth.

In conclusion, our data indicate a nonlinear relationship between GPC M_n and NMR M_n for P3HT that begins around M_n = 40 kDa. However, SLS experiments confirm that decreasing the catalyst loading below 0.2% does not increase the polymer chain length, and for externally initiated P3HTs, very high molecular weights (>100 kDa) will be challenging to achieve. This is especially important when considering that for optoelectronic uses CPs with high M_n are often desirable. Our results show that end-group analysis cannot be used reliably for determining the M_n of high M_n CPs with externally initiated end groups, even when the NMR spectra can be reproducibly integrated, due to the propensity for the growth of uninitiated chains which increases as a function of M_n. This is significant as external initiation has been reported to lead to nearly 100% externally initiated chains as well as to reduce the possibility of chain−chain coupling in a typical synthesis. Our data show that nearly 100% external initiation likely only holds true for polymers that are less than approximately 40 kDa.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis of *o*-tolyl-initiated P3HT, instrumentation, sample preparation, additional data, and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

D.S.S. designed the study; M.W., J.H., L.M.K., Y.L., and D.C.B. conducted experiments; and all authors contributed to write the manuscript.

Notes

The authors declare no competing financial interest.

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