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Self-diffusion of poly(*p*-phenyleneethynylene)s in dilute solution determined by pulsed-field-gradient NMR

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Abstract

Self-diffusion of poly[(2,5-didodecyl-*p*-phenylene)ethynylene]s (didodecyl-PPE) was measured in dilute $CDCl_3$ by pulsed-field-gradient NMR spectroscopy. The reduced versions of these didodecyl-PPEs, poly[2,5-didodecyl-*p*-xylylene]s (didodecyl-PPX), were also examined as random-coil analogs of equivalent chain lengths (14–120 repeat units). The coefficients for infinite-dilution self-diffusion (D_0) and their concentration dependence (k_F) were determined from plots of the self-diffusion coefficients versus concentration. These quantities were fit to power laws with molecular weight (M_0) and their scaling constants determined from double-logarithmic plots. For didodecyl-PPX, D_0 scales with M_0 by -0.50 ± 0.03 (ν) and k_F scales with M_0 by 0.51 ± 0.08 (α), consistent with a random-coil conformation for this polymer in solution. For didodecyl-PPE, D_0 scales with M_0 by -0.71 ± 0.06 (ν) and k_F scales with M_0 by 0.96 ± 0.06 (α), indicative of a semiflexible rod-like macromolecule.

Keywords: Self-diffusion; Pulsed-field-gradient NMR; Polyphenyleneethynylene

1. Introduction

Given their rod-like molecular structure, poly(*p*-phenyleneethynylene)s (PPEs) [1] might be expected to exhibit dynamics characteristic of rigid rods. Cotts et al. [2] used light scattering to determine the dilute-solution root-mean-square radii (R_g) for polydisperse PPE derivatives containing molecular weights between 100 and 2000 kg mol^{-1}. They found that a plot of R_g versus molecular weight could be fit using the Kratky–Porod worm-like chain model with a statistical segment length of about 30 nm. This corresponds to a persistence length of 15 nm or 20 phenyleneethynylene repeat units. Thus, for chain lengths of about 100 phenyleneethynylene units and greater, these rod-like macromolecules are better described as expanded random coils in solution [2]. For chain lengths below 20 repeat units, PPEs should exhibit more rod-like behavior in solution. Although the side chains are different for the PPEs of Cotts et al., Ricks et al. [3] have prepared didodecyl-PPEs with 14–120 phenyleneethynylene units. Thus, it should be interesting to see whether these didodecyl-PPEs exhibit rod-like or more flexible conformations in dilute solution.

Poly(*p*-phenyleneethynylene) (PPE) derivatives can be hydrogenated to their corresponding poly(*p*-xylylene)s (PPX), [4,5] to provide random-coil polymers with the same exact degree of polymerization as their rod-like precursors (Fig. 1). This has been demonstrated with both poly[(2,5-dialkyl-*p*-phenylene)ethynylene]s [4] and poly[(2,5-dialkoxy-*p*-phenylene)ethynylene]s [5]. The ability to modify the molecular shape through a chemical transformation makes these materials potentially useful in polymer-based nanotechnologies [6–8]. Ricks et al. [3] have reduced poly[(2,5-didodecyl-*p*-phenylene)ethynylene]s (didodecyl-PPE) with apparent molecular weights from 1 to 60 kg mol^{-1} to the corresponding poly[2,5-didodecyl-*p*-xylylene]s (didodecyl-PPX). The transformation occurs without a significant change in molecular weight (<1%) but considerable increase in chain flexibility. Using gel

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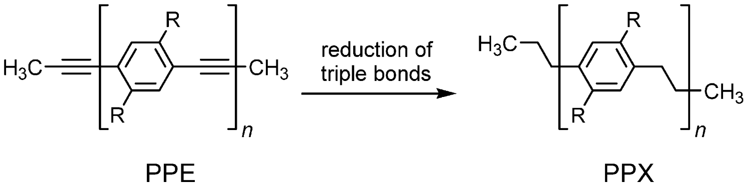

Fig. 1. Hydrogenation of rod-like poly(*p*-phenyleneethynylene) (PPE) derivatives gives the more flexible poly(*p*-xylylene)s (PPX). This has been demonstrated for R = alkyl [4] and alkoxy [5] groups. For the materials studied here, $R = C_{12}H_{25}$.

permeation chromatography (GPC) with polystyrene standards, they reported apparent molecular weights for didodecyl-PPXs that are an average of 1.4-fold lower than the apparent molecular weights of the corresponding didodecyl-PPEs of equivalent chain length [3]. While PPE derivatives exhibit GPC molecular weights that are greater than their actual molecular weights due to their rod-like nature [9–11] the high-molecular-weight PPEs are not true rigid rods.

For didodecyl-PPEs, aggregation limits their study in solution to the dilute regime. We attempted to examine the didodecyl-PPEs in dilute chloroform using light scattering, but were unsuccessful due to insufficient scattering intensities at the low concentrations required to prevent aggregation. We were successful, however, using pulsed-field-gradient (PFG) NMR spectroscopy. PFG NMR has been widely and successfully applied to provide self-diffusion coefficients of linear, [12] cyclic, [13] star-branched [14] and rod-like [15] polymers in solution and in the melt. Here, we report the self-diffusion coefficients versus molecular weight for didodecyl-PPE and didodecyl-PPX in dilute solution. This work was aimed at clarifying the dilute-solution conformation of the didodecyl-PPEs and further exploring the influence of molecular architecture on polymer hydrodynamics. The diffusion measurements are interpreted in terms of dilute-solution theories with scaling relations.

2. Background

Polymer self-diffusion behavior in dilute solution is connected to the size and shape of a single chain. The size is directly related to the diffusion coefficient, while the shape can be inferred by how the diffusion coefficient changes with the size (i.e. molecular weight). In the infinite-dilution limit, the self-diffusion coefficient (D_0) of a polymer chain can be correlated to its hydrodynamic radius (R_H) by the Einstein–Stokes relation [16]:

$$D_0 = \frac{k_B T}{6\pi\eta R_H} \tag{1}$$

where k_B is the Boltzmann constant, T is the absolute temperature and η is the solvent viscosity. The hydrodynamic radius, and thus D_0, for an isolated polymer in solution scales with molecular weight [17]:

$$D_0 \sim M^{\nu} \tag{2}$$

where ν is the scaling constant. The polymer chain conformation in solution is reflected in the value of ν with -0.6 to -0.5 for flexible linear random coils [12,18], around -0.33 for highly branched or collapsed linear polymers [19,20], and approaching -1 for rigid rods.

The self-diffusion coefficient at infinite dilution (D_0) is accessible by measuring the self-diffusion coefficient (D_s) at finite concentrations (c) in the dilute regime and then fitting to this power series expression [12,14,18]:

$$D_s^{-1}(c) = D_0^{-1}(1 + k_F c + \ldots) \tag{3}$$

where k_F is a molecular-weight-dependent coefficient used to describe the concentration dependence of the translational friction opposing self-diffusion. The concentration dependence of the friction factor has been treated by Pyun and Fixman for spherical polymers [21], $k_F \sim M^{-1}D_0^{-3}$, and by Peterson [22] and Itou et al. [23] for rod-like polymers, $k_F \sim M^{1/3}/D_0$. Thus, similar to Eq. (2), a scaling relation between k_F and molecular weight may be written:

$$k_F \sim M^{\alpha} \tag{4}$$

where $\alpha = -1-3\nu$ for spheres and $\alpha = (1/3) - \nu$ for rods in solution (ν is defined in Eq. (2)). The Pyun/Fixman model has been applied to some flexible linear and star polymers [14,18,24,25], while the Peterson/Itou et al. model has been used for rod-like polymers such as polyglutamate [26]. The correlation between α and ν can thus be used as another practical test for models of polymer conformation in solution.

3. Experimental section

Didodecyl-PPEs were prepared according to published methods [27]. Didodecyl-PPXs were synthesized by hydrogenation of didodecyl-PPEs [4]. The GPC data for these materials in $CHCl_3$ using polystyrene standards have been published [3]. The GPC peak molecular weight of the didodecyl-PPXs varies from 6.4 to 52 kg mol^{-1} (between 14 and 120 repeat units), with M_w/M_n ratios from 1.5 to 2.5. The molecular weights of the didodecyl-PPEs are taken here as the GPC peak molecular weights of the corresponding didodecyl-PPXs. For NMR analysis, each sample was dissolved into $CDCl_3$ (Aldrich, 99.9%) at concentrations around 0.8, 2 and 5 mg ml^{-1}. These concentrations are less than 0.1 wt%. Even for monodisperse polymers, it has been shown that concentrations greater than 0.1 wt% lead to curvature in double-logarithmic plots of self-diffusion coefficients versus molecular weight, and thus deviations from the scaling law of Eq. (2). At each concentration, two samples were prepared and tested.

All NMR experiments were performed in 5-mm NMR tubes at a constant temperature of 25 °C using a Bruker DRX 500 spectrometer. The pulsed-field-gradient (PFG) NMR experiments were carried out using the double-stimulated-echo (DSTE) sequence with monopolar gradients [28]. Field gradient calibration was accomplished using the self-diffusion coefficient of pure water at 25 °C (2.299×10^{-9} m^2 s^{-1}) [29]. The diffusion time (Δ) was varied from 40 to 250 ms, depending on the sample molecular weight and concentration, so that the PPE/PPX resonances were attenuated to approximately 5% of their original intensities. The gradients (g) were applied for 4 ms (δ) and incremented 16 times from 1.7 to 63.0 G cm^{-1}. Gradient settling times were 1 ms and the eddy current elimination duration was 50 ms. Homospoil gradients (1 ms) were applied during the diffusion and eddy current settling durations to destroy signals from unwanted coherence paths. A total of 16 free induction decays containing 8k complex data points were collected at each gradient amplitude. The delay between each scan was 12 s and 16 dummy scans were applied before the first data were collected.

For molecules experiencing Brownian motion, the echo amplitude decay, $I(g)$, can be described as:

$$I(g) = I(0)\int_0^\infty P(D)\exp(-kD)\mathrm{d}D \tag{5}$$

where $P(D)$ is a relaxation-weighted self-diffusion-coefficient distribution function. For a given gradient duration (δ), $k=(\gamma g\delta)^2(\Delta-\delta/3)$, where γ is the magnetogyric ratio of the nucleus under observation (^{1}H for this study).

For polydisperse samples, the diffusion decay curve can be analyzed by model-free inverse Laplace transforms (ILT) [30,31] or by assuming a specific model distribution. Model-free fitting enjoys the great advantage of no assumptions. However, it normally requires high signal-to-noise ratios due to ill-posed conditions associated with the ILT. In contrast, when a diffusion-coefficient distribution function is assumed or known, the fit of the diffusion decay curve provides relatively small uncertainties due to the limited number of adjustable parameters. For the experimental settings described above for this study, the signal-to-noise ratios were typically not sufficient for accurate model-free analyses. Thus, the diffusion decay curves were fitted to a log-normal distribution, which has been used successfully for PFG NMR analyses of other polymers [32–34]. This choice of a log-normal function for a model diffusion-coefficient distribution is based on its common use to describe polymer molecular weight distributions:

$$P(M) = \frac{1}{M\sigma_M\sqrt{2\pi}}\exp\left(-\frac{[\ln(M)-\ln(M_0)]^2}{2\sigma_M^2}\right) \tag{6}$$

where M_0 is the median molecular weight and σ_M is a measure of the width of the molecular weight distribution. If the scaling law shown in Eq. (2) holds for the polymer, the $P(D)$ in Eq. (5) can be written:

$$P(D) = \frac{1}{D\sigma_D\sqrt{2\pi}}\exp\left(-\frac{[\ln(D)-\ln(D_s)]^2}{2\sigma_D^2}\right) \tag{7}$$

where D_s is the peak diffusion coefficient and $\sigma_D(=\nu\sigma_M)$ is the measure of the width of the self-diffusion-coefficient distribution. In this analysis, NMR relaxation weighting was ignored, including its possible variation among different-sized species of the same sample. The log-normal analysis was carried out using Matlab.

4. Results and discussion

Dilute solutions of poly[(2,5-didodecyl-*p*-phenylene)ethynylene]s (didodecyl-PPE) and their corresponding poly[2,5-didodecyl-*p*-xylylene]s (didodecyl-PPX) were examined by pulsed-field-gradient NMR spectroscopy. The normalized NMR signal decays were non-linear due to the sample polydispersity in plots of $\ln[I(g)/I(0)]$ versus k. These echo decay curves were fit to Eq. (5) where $P(D)$, shown as Eq. (7), was assumed to be a log-normal distribution. A representative set of data are shown in Fig. 2 along with their respective fits for 15 kg mol^{-1} didodecyl-PPE. Through this fitting, D_s and σ_D were obtained. The D_s was determined for each sample at three concentrations; the D_s-versus-concentration data were then fitted by Eq. (3) to determine the infinite-dilution self-diffusion coefficients,

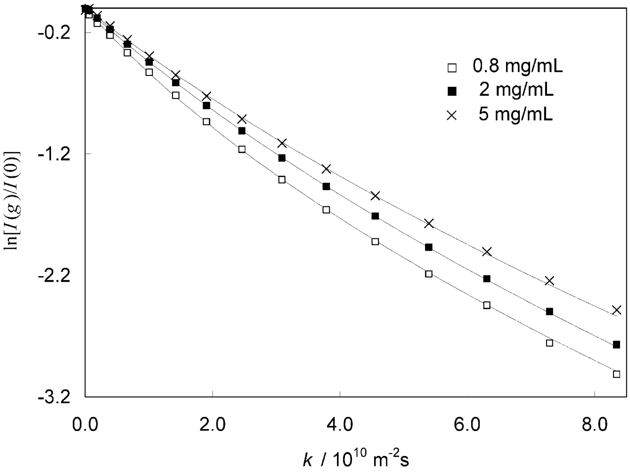

Fig. 2. Normalized NMR signal intensity versus $k=(\gamma g\delta)^2(\Delta-\delta/3)$ for 15 kg mol^{-1} didodecyl-PPE in CDCl$_3$ at three different concentrations: 0.8 mg ml^{-1} (□), 2 mg ml^{-1} (■), and 5 mg ml^{-1} (×). The solid lines are non-linear least-squares fits to the data using Eq. (5) with $P(D)$ as Eq. (7). From the fitting, a peak self-diffusion coefficient was obtained, D_s, along with the width of the self-diffusion coefficient distribution, σ_D.

D_0, and the concentration coefficients of the translational friction, k_F.

The infinite-dilution self-diffusion coefficients of didodecyl-PPX and didodecyl-PPE versus their respective GPC peak molecular weights are shown in a double-logarithmic plot in Fig. 3. Both sets of data easily fit straight lines, indicating their adherence to the scaling law shown in Eq. (2). To use Eq. (2) with polydisperse samples like those examined here, the scaling exponent must be constant over the entire molecular-weight distribution. The data shown in Fig. 3 are consistent with this assumption.

The self-diffusion coefficients of didodecyl-PPE are smaller than those of the corresponding didodecyl-PPX with the same molecular weight. Thus, for a given chain length, the hydrodynamic radius of didodecyl-PPE is larger than the hydrodynamic radius of didodecyl-PPX. This can be attributed to the rigid nature of didodecyl-PPE, which expands the chain beyond that of a random-coil structure. The double-logarithmic plots of D_0 versus M_0 for both didodecyl-PPX and didodecyl-PPE are adequately described by linear relations for the molecular weight range covered. Linear least-squares-fitting results can be written in the form of Eqs. (8) and (9):

$$D_{0,\mathrm{PPX}}/\mathrm{m}^2\ \mathrm{s}^{-1} = (6.7 \pm 0.5) \times 10^{-9} M_0^{-0.50 \pm 0.03} \quad (8)$$

$$D_{0,\mathrm{PPE}}/\mathrm{m}^2\ \mathrm{s}^{-1} = (3.8 \pm 1.0) \times 10^{-8} M_0^{-0.71 \pm 0.06} \quad (9)$$

The scaling constant, ν, of didodecyl-PPX is around -0.50, indicative of a random-coil polymer in dilute solution ($-0.60 \leq \nu \leq -0.50$). For didodecyl-PPE, ν is about -0.71, which is considerably smaller than the lower limit for a random coil (-0.60 in good solvent). This clearly demonstrates that didodecyl-PPE cannot be described by a random-coil structure. On the other hand, it is also significantly different from the asymptotical limit of -1 for a rigid rod. For the well known rod-like poly (γ-benzyl-α,L-glutamate) (PBLG), the reported scaling constant is -0.70 ± 0.1 from fluorescence photobleaching recovery [35] or -0.78 ± 0.05 from dynamic light scattering [36,37]. Thus, the ν value for the didodecyl-PPE indicates these polymers behave more like semiflexible PBLG than like strictly rigid rods for molecular weights of 6.4–52 kg mol^{-1} (between 14 and 120 repeat units).

Chu et al. [38] synthesized PPEs containing a *m*-phenylene between every three *p*-phenylene groups along its backbone and studied it with GPC using a viscosity detector. Their plot of log[η] versus log(M_w) yielded a Mark–Houwink exponent of 0.78 for samples with number-average degrees of polymerization of 13 and 27. This Mark–Houwink exponent corresponds to $\nu = -0.59$, consistent with a random-coil conformation for these PPE copolymers. Using GPC data collected with a light scattering detector, Moroni et al. [39] plotted estimated intrinsic viscosities [η] versus weight-average molecular weights (M_w) for a didodecyloxy-PPE. For molecular weights between 25 and 100 kg mol^{-1} (53–214 PPE repeat units), they reported a Mark–Houwink exponent of 1.92; this corresponds to a $\nu = -0.97$ and is probably too high (*p* 1625 of Ref. [1]). Using their [η]-versus-M_w data (Fig. 2 in Ref. [39]), we found a Mark–Houwink exponent of 2.5 from the slope. The corresponding ν is less than the asymptotic limit of -1, clearly indicating that these data are incorrect.

Concentration coefficients of the translational friction (k_F) are shown for didodecyl-PPX and didodecyl-PPE versus their respective GPC peak molecular weights in the double-logarithmic plot of Fig. 4. The k_F for both polymers increases with molecular weight, with the k_F for didodecyl-PPE consistently larger than that of didodecyl-PPX with the same degree of polymerization. This is simply related to the inverse relationship of the concentration to diffusion

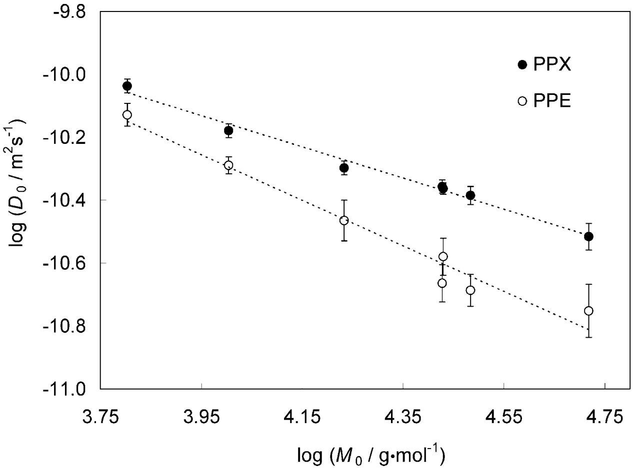

Fig. 3. Double-logarithmic plot of the infinite-dilution self-diffusion coefficients (D_0) versus the peak molecular weight (M_0) from GPC for didodecyl-PPX (●) and didodecyl-PPE (○). Dashed lines are linear least-squares fits to the data.

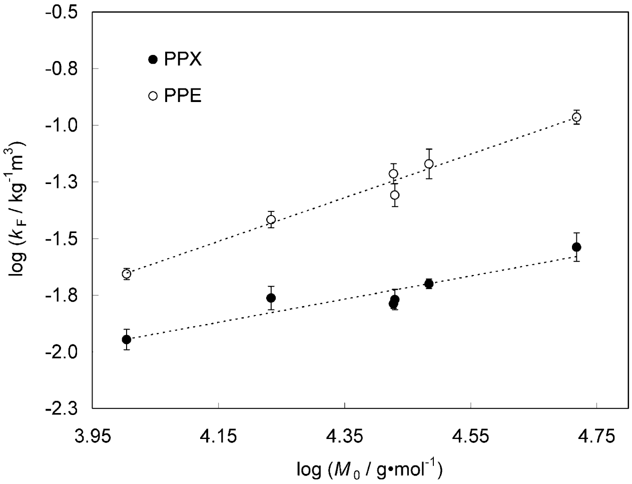

Fig. 4. Double-logarithmic plot of the coefficient describing the concentration dependence of the translational friction (k_F) versus the GPC peak molecular weight (M_0) for didodecyl-PPX (●) and didodecyl-PPE (○). Dashed lines are linear least-squares fits to the data.

coefficients (Eq. (3)) and the smaller relative diffusion coefficients of the didodecyl-PPE for a given chain length. As with the D_0-versus-M_0 data of Fig. 3, both sets of k_F data fit straight lines, indicating their adherence to the scaling law shown as Eq. (4). Similar to Eqs. (8) and (9) we find

$$k_{F,PPX}/\mathrm{kg}^{-1}\,\mathrm{m}^3 = (1.0\pm0.8)\times10^{-4}M_0^{0.51\pm0.08} \tag{10}$$

$$k_{F,PPE}/\mathrm{kg}^{-1}\,\mathrm{m}^3 = (3.2\pm0.5)\times10^{-6}M_0^{0.96\pm0.06} \tag{11}$$

where the scaling constant (α) is 0.51 for didodecyl-PPX and 0.96 for didodecyl-PPE. The self-diffusion coefficient of didodecyl-PPE thus shows much stronger concentration dependence than the self-diffusion coefficient of didodecyl-PPX. This is another indication of the more rigid nature of the didodecyl-PPE.

The scaling constants for the diffusion and concentration coefficients with molecular weight (Eqs. (8)–(11)) are collected in Table 1. In addition to the experimentally determined values of ν and α, we have provided the theoretical values of α for a random-coil model (Pyun/Fixman) [21] and for a rod-like model (Peterson/Itou et al.) [22,23]. These theoretical α values were calculated from the experimental ν values and are designated $\alpha_{\nu,\mathrm{coil}}$ and $\alpha_{\nu,\mathrm{rod}}$, respectively.

For random-coil chains in solution, the Pyun/Fixman model predicts that $\alpha_{\nu,\mathrm{coil}} = -1–3\nu$. Some data can be found in the literature to support this relation for linear or branched polymers [14,18,25,40]. For didodecyl-PPX, $\alpha_{\nu,\mathrm{coil}} = 0.50$ which is in excellent agreement with the experimental α value (0.51). This, together with the experimental ν value (−0.50), provides consistent and strong evidence that the didodecyl-PPX adopts a random-coil conformation in $CDCl_3$.

For a rod-like polymer, the Peterson/Itou et al. model predicts $\alpha_{\nu,\mathrm{rod}} = (1/3) - \nu$. Application of the rod model to the didodecyl-PPX yields $\alpha_{\nu,\mathrm{rod}} = 0.83$, which is far away from the experimental α value (0.51) and clearly proves that the rod model fails for the random-coil didodecyl-PPX. On the other hand, $\alpha_{\nu,\mathrm{rod}}$ of didodecyl-PPE is 1.04, which is quite close to the experimental α value (0.96) and certainly closer than the $\alpha_{\nu,\mathrm{coil}}$ of 1.13 calculated from the random-coil model. Thus, the rod-like model is a better fit for didodecyl-PPE, consistent with its semiflexible rod-like structure in solution revealed through its experimental ν value (−0.71). Since the previously reported persistence length for a similar PPE derivative is 20 repeat units [2], these results are quite reasonable.

The didodecyl-PPEs examined here are 2,5-disubstituted-*p*-phenylene derivatives containing between 14 and 120 repeat units. The shorter of these didodecyl-PPEs are below the persistence length (20 phenyleneethynylene repeat units) reported for the PPEs of Cotts et al. [2]. Note, however, that the diffusion coefficient for these shorter didodecyl-PPEs scales with the molecular weight in the same manner as the longer didodecyl-PPEs (Fig. 3). If the shorter didodecyl-PPEs were more rigid (i.e. scaled more steeply with M_0), a plot of $\log(D_0)$ versus $\log(M_0)$ should exhibit some curvature as opposed to the linear relation shown in Fig. 3. However, persistence lengths are affected by the size [41–43] and linear density [44] of side chains. The PPEs of Cotts et al. were also 2,5-disubstituted-*p*-phenylene derivatives but the side chains were dialkoxy alternating with di(amidodialkyl) groups. Thus, whereas polymers with contour lengths much smaller than their persistence lengths should exhibit rigid-rod behavior, the persistence length for these didodecyl-PPEs is not necessarily the same as that reported for the PPE derivatives of Cotts et al. [2]. Although, similar persistence lengths (13 nm) have been reported for rod-like polymers, poly(*p*-phenylenes), constructed of different backbones and side chains [45].

5. Summary

Self-diffusion coefficients of poly[(2,5-didodecyl-*p*-phenylene)ethynylene]s (didodecyl-PPE) were measured for three concentrations in dilute solution (<0.1 wt%) by pulsed-field-gradient NMR spectroscopy. The molecular weights of the didodecyl-PPEs were determined from GPC of the corresponding poly[2,5-didodecyl-*p*-xylylene]s (didodecyl-PPX) obtained by selective reduction of the backbone triple bonds. Plots of the self-diffusion coefficients versus concentration yielded infinite-dilution self-diffusion (D_0) and concentration (k_F) coefficients. These quantities were then fit to power laws with molecular weight (M_0) and the scaling constants determined from double-logarithmic plots. For didodecyl-PPE with 14–120 phenyleneethynylene repeat units, D_0 scales with M_0 by −0.71 ± 0.06 (α) and k_F scales with M_0 by 0.96 ± 0.06 (α), indicative of a semiflexible rod-like macromolecule.

Table 1
Experimental scaling constants (ν, α) and theoretical α_ν values

	ν	α	α_ν	
			$\alpha_{\nu,\mathrm{coil}} = -1–3\nu$[a]	$\alpha_{\nu,\mathrm{rod}} = (1/3) - \nu$[b]
PPX	−0.50 ± 0.03	0.51 ± 0.08	0.50 ± 0.09	0.83 ± 0.03
PPE	−0.71 ± 0.06	0.96 ± 0.06	1.13 ± 0.18	1.04 ± 0.06

[a] $\alpha_{\nu,\mathrm{coil}} = -1–3\nu$ for random coil in solution based on Pyun/Fixman [21]. Uncertainty of the $\alpha_{\nu,\mathrm{coil}}$ is three times the error of ν due to error propagation.

[b] $\alpha_{\nu,\mathrm{rod}} = (1/3) - \nu$ for a rod-like polymer in solution based on Peterson/Itou et al. [22,23].

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