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Mark−Houwink−Sakurada Constants for the Methoxy Precursor of Poly(2,5-thienylenevinylene)

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Introduction

Organic π-conjugated compounds are nowadays widely investigated as new, advanced materials for electrooptical applications. The polymeric nature of some of them is considered an additional advantage. For example, for poly(thiophene-2,5-diylvinylene)—better known as poly(2,5-thienylenevinylene) (PTV)—an ingenious synthetic route (see Figure 1) has been designed, during which a chloroform—soluble methoxy precursor polymer (MeO−PTV) can be isolated. At this stage processing and characterization can be conveniently performed. In this context, it is somewhat surprising how little attention has been paid to the determination of true molecular weights and molecular weight distributions of conducting polymers,[1] compared to the efforts spent to optimize the polymerization procedures to PTV.[2−11]

Gel permeation chromatography (GPC) is an efficient technique to determine molecular weights and molecular weight distributions. Being a relative method, a calibration is necessary to convert retention times to molecular weights. Polystyrene calibration curves are often used for this purpose. While this might give good estimates of the relative magnitude of molecular weights, better values can be obtained only if the relation between the hydrodynamic volumes of the polymer under investigation and the calibration standard is known.[12−14] Thus, one objective of the present work is to find this relation by determining the Mark−Houwink−Sakurada constants for MeO−PTV in chloroform solution from a combination of viscosity measurements and GPC data. The other is to evaluate better molecular weights for MeO−PTV by gel permeation chromatography. Obviously, at this stage the values obtained by this technique are still to be substantiated by an absolute method (e.g., light scattering or osmometry). In fact, size exclusion may not be the only mechanism governing the elution of MeO−PTV. Other factors such as chemical affinity cannot be excluded.

Theory

The Mark−Houwink−Sakurada (MHS) relation (eq 1) links

$$[\eta] = KM_v^{\alpha} \qquad (1)$$

the viscosity-average molecular weight, M_v, to the intrinsic viscosity, $[\eta]$, of a polymer solution through the constants α and K. The latter constants may be obtained accurately from two samples of the same polymer/solvent system with different intrinsic viscosities. It has been shown[15,16] that α follows from eq 2, when the other parameters are known. Once α is found, K follows from eq 3. In eq 2 the primed and unprimed

$$[\eta]'/[\eta] = \sum w_i' J_i'^{\alpha/(\alpha+1)} / \sum w_i J_i^{\alpha/(\alpha+1)} \qquad (2)$$

$$K = \left\{ \frac{[\eta]}{\sum w_i J_i^{\alpha/(\alpha+1)}} \right\}^{\alpha+1} \qquad (3)$$

terms refer to different samples of the same polymer. The polydisperse polymer is considered as a mixture of monodisperse species each with molecular weight M_i, weight fraction w_i, intrinsic viscosity $[\eta]_i$, and a parameter J_i ($J_i \equiv [\eta]_i M_i$) related to the hydrodynamic volume.

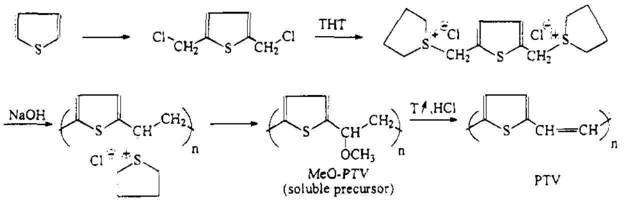

Figure 1. Synthetic route to PTV via the $CHCl_3$-soluble precursor polymer MeO−PTV.

A gel permeation chromatogram yields w_i values after normalization and J_i values, $J_i = K\{M_i(\text{polystyrene})\}^{\alpha+1}$, after calibration of the column with monodisperse polystyrene standards.[12]

A number of extrapolation methods are available in the literature to determine the intrinsic viscosity of a polymer solution.[17−21] Of these, the one of Heller[19] gives the most reproducible values. In this method, $[\eta]$ is taken as the inverse mean of the inherent and reduced viscosity in the limit of infinite dilution. We employed the approximate relation, shown in eq 4, which works well for "good" solvents. Here, c denotes concentration

$$\frac{1}{[\eta]} = \lim_{c \to 0} \left\{ \frac{c}{\eta_{\text{spec}}} + \frac{c}{\ln \eta_{\text{rel}}} \right\} / 2 \qquad (4)$$

in g/mL of solvent, η_{spec} the specific viscosity, and η_{rel} the relative viscosity.

Finally, once the MHS constants α and K are established, the molecular weights of the polymer under investigation, M_{2i}, are connected via eq 5 to the known molecular weights, M_{1i}, of monodisperse polystyrene standards used in the universal calibration of a GPC column. in which α_1, K_1 and α_2, K_2 are the MHS

$$\log M_{2i} = \frac{1}{1 + \alpha_2} \log\left(\frac{K_1}{K_2}\right) + \left(\frac{1 + \alpha_1}{1 + \alpha_2}\right) \log M_{1i} \qquad (5)$$

constants of the polystyrene standards and of the polymer, respectively. For polystyrene in chloroform at 25 °C we used:[12] $\alpha_1 = 0.76$ and $K_1 = 7.16 \times 10^{-3}$ cm^3/g.

Experimental Section

MeO−PTV is synthesized via the modified precursor route[7,11] (see Figure 1). The starting product thiophene is bis(chloromethyl)ated and the product converted into the bis-tetrahydrothiophenium salt. The latter is polymerized in a methanol/water (2/1, v/v) solution for about 20 h at about −45 °C by addition of an equimolar amount of NaOH. The resulting sulfonium precursor polymer solution is allowed to warm to room temperature, at which time the sulfonium groups are substituted by methoxy groups. The formed MeO−PTV precipitates and is dissolved in chloroform for further processing. The synthetic procedure has been optimized[22,23] to reproducibly synthesize MeO−PTV of excellent chemical quality,

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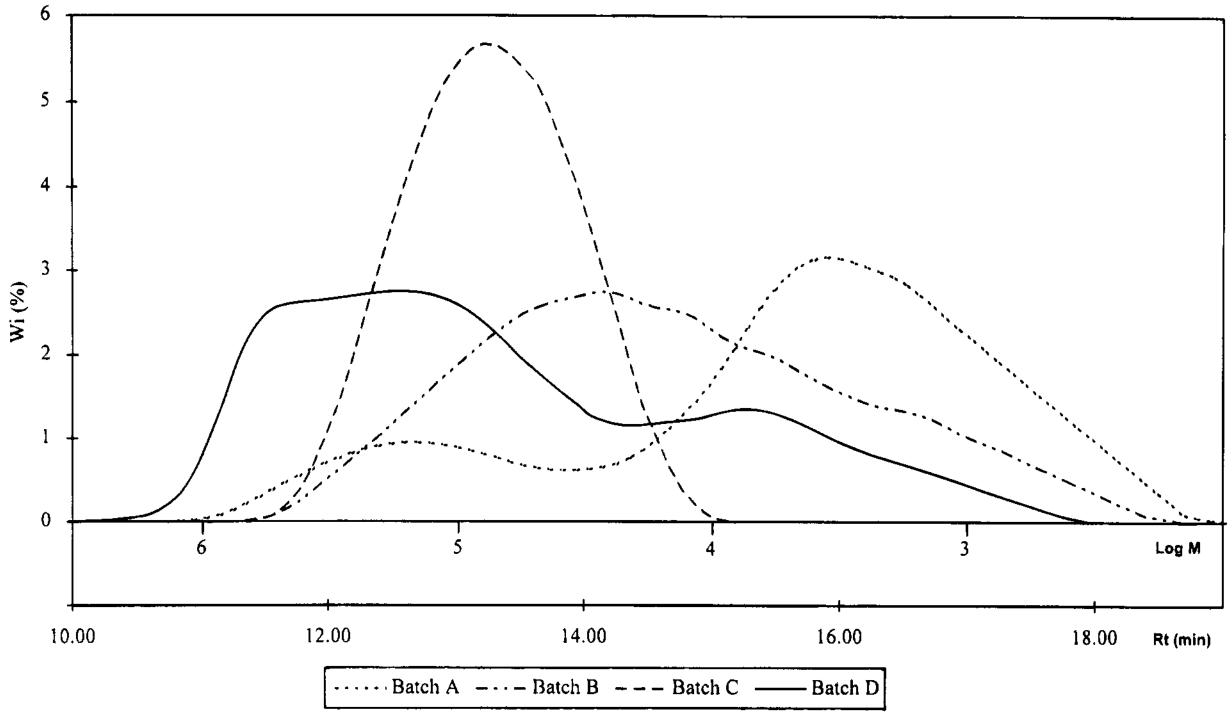

Figure 2. Gel permeation chromatograms of MeO–PTV batches, A–D, obtained from four synthetic runs. Weight fractions, w_i, after normalization are plotted against retention times (Rt) as well as against log M after calibration with MeO–PTV.

Table 1. Intrinsic Viscosities (cm^3/g) of MeO–PTV Batches A–D Obtained after Heller[19]

batch	[η]	batch	[η]
A	26.0	C	52.5
B	37.5	D	76.0

Table 2. Mark–Houwink–Sakurada Constants Obtained from Equations 2 and 3

polymer pair	α	K (cm^3/g)
A/B	0.55	0.0928
A/C	0.62	0.0457
A/D	0.60	0.0504
B/C	0.68	0.0191
B/D	0.61	0.0457
C/D	0.60	0.0551

i.e., without sulfonium remnants, premature elimination, and C=O defects. Nevertheless, seemingly small variations in polymerization conditions (purity of bis-tetrahydrothiophenium salt, time, and constancy of temperature during polymerization to sulfonium precursor) result in rather large variations of the molecular weight distribution of MeO–PTV. While this may pose problems when producing PTV films of reproducible optical and mechanical quality, it is of benefit to us here; the four synthetic runs turned out to be different enough to be useful in the evaluation of the MHS constants. The GPC and viscosity experiments were performed with the chloroform solutions of these four MeO–PTV batches (see Figure 2). GPC experiments were carried out at 25 °C using a Polymer Labs 60-cm mixed C column. Polymers were eluted with chloroform at the flow rate of 1 mL/min. A UV–vis spectrometer operating at the fixed wavelength λ = 260 nm was used as the detector. The system was equipped with a Spectra Physics SP 4200 GPC integrator for data acquisition and processing. Monodisperse polystyrene standards ranging from 580 to 960 000 were used to calibrate the system.

Using an Ubbelohde-type viscosimeter, the viscosities were measured of the solvent $CHCl_3$ and of four solutions ranging in concentration from 1 to 10 mg/mL of each of the four MeO–PTV batches. The temperature was maintained at 25 ± 0.01 °C. Efflux times were measured to 0.001-s accuracy. Intrinsic viscosities, [η], were obtained by the method of Heller[19] using eq 4 (Table 1).

Results and Discussion

The six [η] ratios—resulting from the pairwise combination of the polymer batches A–D—were taken together with their GPC data to calculate values of α and K using eqs 2 and 3. The results are given in Table 2. The approach is known to give unreliable α and K values when the molecular weights of a polymer pair are similar.[1,24] Hence, we excluded the pairs A/B and B/C and arrived at the following averaged Mark–Houwink–Sakurada constants at 25 °C for MeO–PTV in a $CHCl_3$ solution:

$$\alpha = 0.61 \pm 0.01$$

$$K = 0.048 \pm 0.005\ \mathrm{cm^3/g}$$

These values are in-between values usually observed in other linear polymer/solvent systems. In fact, α = 0.61 is half-way between α = 0.5 for a randomly coiled polymer under Θ conditions (solvent and temperature) and α = 0.75–0.80 for a good solvent. Yet, in our opinion, it points to a flexible-chain structure of the MeO–PTV precursor polymer brought about by the $-CH(OCH_3)CH_2-$ spacers between the thiophene rings. The absence of such spacers results in strong π-orbital interactions between thiophene rings and hence in much stiffer chains, as shown in α = 0.97 found[1] for poly(3-hexylthiophene) in tetrahydrofuran.

Furthermore, using eq 5 a new calibration curve was made relating the retention times of MeO–PTV solutions in a Polymer Labs 60-cm mixed C column to their true molecular weights. Figure 2 gives the distribution of weight fractions w_i of the batches A–D and better estimates of their molecular weight range.

Finally, Table 3 shows the comparison of weight-average and number-average molecular weights of MeO–PTV, evaluated using the MeO–PTV and polystyrene calibration curves. If the new calibration curve is correct (i.e., elution dominated by size exclusion), then

Table 3. Number-Average (M_n), Weight-Average (M_w), and Viscosity-Average (M_v) Molecular Weights and Polydispersity Degrees (Pd) of MeO–PTV Batches A–D from GPC Experiments Using Polystyrene and MeO–PTV Calibration Curves

	PS calibration			MeO–PTV calibration			
batch	M_n	M_w	Pd	M_n	M_w	Pd	M_v
A	3 600	67 000	19	880	33 000	38	15 000
B	5 900	94 000	16	2200	50 000	23	33 000
C	51 000	144 000	2.8	21 000	71 000	3.4	59 000
D	18 000	248 000	14	5000	140 000	28	104 000

the data show that the use of the polystyrene calibration curve overestimates M_w and M_n by factors of 2–3 due to the difference in MHS constants.

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