

Characterization of novel liquid crystalline polymers of polyacetylenes having a comb-like structure via SEC/RI/RALLS/DV

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Summary

Novel liquid crystalline polymers comprised of polyacetylenes having a comb-like structure were studied by size exclusion chromatography (SEC) with refractive index, right angle laser light scattering, and differential viscometry detectors (RI/RALLS/DV). This combination of SEC detectors is known as triple detector SEC, or simply SEC³. Based upon the data generated for these materials, the relationship between molecular size and the polymer structure was investigated, SEC universal calibration was shown to be valid, Flory's characteristic ratio (C_{∞}) was estimated, and the effect of the size of the side group on chain flexibility was elucidated. These results demonstrate that the technique of SEC³ is a powerful mean for characterizing polymers that cannot be effectively characterized by conventional SEC, such as the liquid crystalline polymers of this study.

Key Words: multi-detector SEC, liquid crystalline polymer, polyacetylene, comb-like structure, characteristic ratio

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Introduction

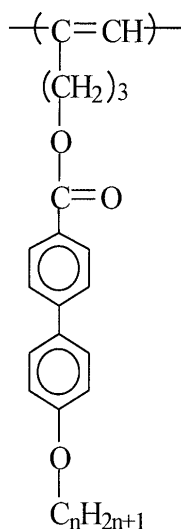
Size exclusion chromatography (SEC) is a powerful method for determining molecular weight (MW) and molecular weight distribution (MWD) of polymers. However, chromatographic columns in conventional SEC, where only one concentration detector is used, must be calibrated with standards of known molecular weight. For most polymers, direct calibration is not possible due to the lack of standards of known molecular weight and narrow MWD, having the same structure as the samples to be analyzed. Therefore, in most instances, only relative molecular weight information is obtained from conventional SEC. The generation of a meaningful calibration curve for a particular polymer, especially for newly synthesized polymers, is thus a major limitation of SEC. To overcome this problem in characterizing novel liquid crystalline polymers with a polyacetylene backbone and comb-like side chains, we have combined conventional SEC (refractive index detection, or RI) with a right angle laser light scattering photometer (RALLS) and a four-capillary bridge design differential viscometer (DV). With this triple-detector SEC (SEC³) technology, a DV detector is used to monitor polymer solution viscosity, a light scattering detector is used to measure the polymer molecular weight across the SEC chromatogram, and a RI detector measures polymer concentration. The enhanced capabilities and reliability of SEC with triple detection (RI/RALLS/DV) have been previously described (1-4). The purpose of the present work is to use triple detector

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SEC to characterize the molecular weights and study the dilute solution properties of novel liquid crystalline polymers.

Experimental Section

Samples: All the polymerization reactions and manipulations were carried out under a nitrogen atmosphere using an inert-atmosphere glove box or Schlenk techniques, except for the purification of the polymers, which was done in a fume hood in an open atmosphere. A typical experimental procedure for polymerization of A3E04, the monomer that leads to PA3E04 (Scheme 1), is as follows. Into a baked 20 mL Schlenk tube, with a three-way stopcock on the side arm, 273.1 mg of monomer was added (5), The tube was evacuated and then flushed with dry nitrogen three times. 2 mL of dioxane was injected into the tube in order to dissolve the monomer. The catalyst was prepared in another tube by dissolving 15.9 mg Of WCl_6 and 17.2 mg of Ph_4Sn in 2 mL of dioxane. After aging the two tubes at 60 °C for 15 min, the monomer solution was transferred into the catalyst solution using a syringe. The polymerization mixture was stirred under nitrogen at room temperature for 24 h. The mixture was then diluted with 5 mL of dioxane and added drop-wise to 500 mL acetone through a cotton filter with stirring. The precipitate was allowed to settle overnight, filtered using a Gooch crucible, washed with acetone and dried in a vacuum oven to constant weight. Other polymers were synthesized following similar procedures. The structure of PA3E0n is shown in Scheme 1:



Scheme 1. Structure of PA3E0n.

Here n=4, 5, 7, 9

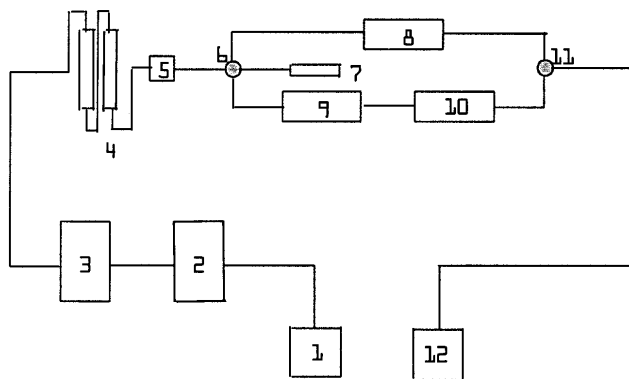


Fig. 1 A schematic diagram of SEC³ configuration

1. Solvent; 2. Pump; 3. Injector; 4. Columns; 5. Filter; 6. Valve; 7. Dampener; 8. RI; 9. RALLS; 10. DV; 11. Valve; 12. Waste.

Size Exclusion Chromatography: All analyses were run in THF at 25°C on two AE Gel Linear/5 Mixed Bed SEC columns (American Polymer Standards Corp.), measuring 30 cm in length and packed with 5µm diameter PS Gel. The solvent was degassed before use. A programmable HPLC pump (Waters, Model 590) was used for eluent delivery at 1.0 mL/min. The effluent was split into two equal volume streams in order to accommodate three detectors with minimum band broadening. One flow path was equipped with a Waters 410 differential refractometer. The other flow path was equipped with a Viscotek Model T60 dual detector module with RALLS and DV in series. Samples

were dissolved in THF at a concentration of 2.000 mg/mL and were filtered with 0.2 μ m pore size poly(tetrafluoroethylene) membrane filters. Injection volumes of 100 μ L were used. TriSEC software (Viscotek Co.) was used for data treatment. Fig. 1 shows a schematic diagram of the SEC³ system. During the measurement, the stability of the instrument is controlled to DV baseline noise < 0.3 mV and RALLS baseline noise < 3.0 mV. A series of eleven polystyrene (PS) standards from American Polymer Standards (Mentor, OH), having molecular weights ranging from 1800 to 300,000, were used for calibration. In addition, a series of PS solutions having different concentrations were used to calibrate the RI response. The dn/dc of PS/THF was taken as 0.185 mL/g, as prescribed in the instrument manual. Assuming that 100% mass was recovered from the RI detector during the measurement and using the RI response calibration, dn/dc of unknown samples may be determined and used to determine true molecular weights via RALLS.

Results and Discussion

Differences in SEC methods

Conventional SEC (SEC¹) generates number-average (M_n) and weight-average (M_w) molecular weights based on the PS calibration. These MWs are related to the values of PS with same hydrodynamic volume. The true molecular weights of the analyzed specimens are different from their relative molecular weights, owing to the differences in chain flexibility and local structure of the polyacetylenes and linear PS standards. Thus, true molecular weights of the liquid crystalline polyacetylenes could not be measured by conventional SEC¹. In addition, sample overloading, band-broadening and flow rate fluctuation factors may influence the accuracy of measurement.

An improved method for analysis of molecular weights of the specimens is to use the RI and DV combination (SEC²). In this approach, the viscosity chromatogram in units of specific viscosity (η_{sp}) and relative viscosity (η_r) can be obtained and used to derive specific and inherent viscosity distribution. The intrinsic viscosity $[\eta]$ distribution then be derived from the Solomon-Ciuta equation (6):

$$[\eta] = \frac{\sqrt{2(\eta_{sp} - \ln \eta_r)}}{C} \quad (1)$$

Here, C is the local concentration determined by RI detector. If M-H coefficients of the sample are known, MW of each individual slice is calculated from the MHS equation so both MW and MWD can be obtained from the instrument measurement without applying retention calibration. Otherwise, a universal calibration method should be used to calculate the average molecular weights and the other parameters. A universal calibration curve ($\log([\eta]^*MW)$ vs. Retention Volume (RV)) is established from a series of narrow PS standards. Assuming $\log([\eta]^*MW)$ for PS standard is same as that for unknown polymer with the same RV, MW of unknown polymer can be derived from the difference between the sample $[\eta]$ and the calibration curve,

$$\log(MW) = \log([\eta]^*MW) - \log([\eta]) \quad (2)$$

Radius of gyration (R_g) is calculated from the molecular weight and the intrinsic viscosity, using the Flory-Fox equation, assuming a linear flexible chain molecule,

$$R_g = \frac{1}{\sqrt{6}} \left(\frac{[\eta] \cdot MW}{\Phi_0} \right)^{\frac{1}{3}} \quad (3)$$

where, Φ_0 is the Flory constant (7).

For the SEC3 configuration, in addition to the direct measurement of $[\eta]$, Mw of each individual slice is obtained from the RALLS detector directly,

$$Mw = R_{\theta} / KC \quad (4)$$

Here R_{θ} is the Rayleigh ratio, K is an optical constant and C is the local concentration obtained from RI detector. Mw and Rg are obtained after correcting the MW for angular dependence of scattered light. Initially, the particle scattering function at 90° , $P(90)$, is assigned a value of 1.0. An estimated molecular weight, Mw_{est} , is calculated from Eq. 4, and then an estimated radius of gyration, Rg_{est} is calculated from Eq. 3. An updated $P(90)$ is then calculated from the following Debye $P(90)$ function (8),

$$P(90) = \frac{2 * [e^{-x} - (1-x)]}{x^2} \quad (5)$$

where, at 90° ,

$$\sqrt{x} = \left(\frac{4\pi n_o}{\lambda_o} \right) Rg \quad (6)$$

where n_o is the solvent refractive index and λ_o is the wavelength of the incident light.

A new estimate of molecular weight is calculated from,

$$Mw_{est} = Mw_{est} / P(90) \quad (7)$$

The above steps are repeated using refined estimates of molecular weight to calculate Rg and $P(90)$ until the molecular weight and Rg values no longer change. In SEC³, both $[\eta]$ and MW do not rely on the retention calibration. This unique feature gives SEC³ a great advantage over the other methods.

SEC/RI(SEC¹), SEC/RI/DV(SEC²), and SEC³ Characterization.

Characterization data obtained via conventional SEC¹, SEC² and SEC³ are listed in Table 1. Here $[\eta]_n$ and $[\eta]_w$; Rg_n and Rg_w are number-average and weight-average intrinsic viscosities and radii of gyration, respectively.

Table I Characterization data via SEC¹, SEC² and SEC³ for liquid crystalline polyacetylenes

Samples	Method	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n	$[\eta]_n \times 10^2$ (dL/g)	$[\eta]_w \times 10^2$ (dL/g)	Rg_n (nm)	Rg_w (nm)
PA3E04	SEC ¹	1.3	3.0	2.3	/	/	/	/
	SEC ²	1.4	4.5	/	6.4	7.2	3.4	4.5
	SEC ³	2.4	5.0	/	6.1	7.1	4.0	4.7
PA3E05	SEC ¹	1.9	4.1	2.2	/	/	/	/
	SEC ²	2.6	6.5	/	8.7	10.0	4.4	5.8
	SEC ³	3.5	7.0	/	8.1	9.8	5.0	5.9
PA3E07	SEC ¹	2.2	5.0	2.3	/	/	/	/
	SEC ²	3.1	7.3	2.3	8.2	9.9	4.6	6.0
	SEC ³	3.7	7.7	2.1	7.4	9.7	5.0	6.1
PA3E09	SEC ¹	1.9	4.0	2.1	/	/	/	/
	SEC ²	3.9	6.4	1.6	7.0	7.8	4.8	5.4
	SEC ³	3.7	6.3	1.7	7.0	7.8	4.7	5.4

From Table 1, we can see that SEC¹ can only give values of M_n and M_w relative to PS standards, not the true average molecular weights. It is thus not the most effective method for characterizing these liquid crystalline polymers.

M_n , M_w , $[\eta]_w$ and Rg_w values can be obtained via SEC² and SEC³ simultaneously. For the high molecular weight samples, SEC² and SEC³ generate almost identical values. The small difference in the viscosity values indicates different data smoothing/data reduction algorithms used by the software. Overall, the agreement of molecular weight and radius of gyration provides assurance that correct values are generated by these methods.

The RALLS signal response of SEC³ depends not only on sample concentration but also on sample molecular weight. The RALLS signal may easily fall below the detection limit in the low molecular weight tail of SEC peaks. In this instance, MW of the individual slice is underestimated. In ignoring the contribution of low molecular weight fractions, the calculated M_n of a polydisperse sample will be much higher than the true value, since the low molecular weight components are very important in the M_n calculation. Here we see that M_n of PA3E04 measured using the SEC³ method was overestimated. The DV method has better capabilities at low MW than the RALLS method. This is because the viscometer has better sensitivity at low MW than the light scattering detector. A RALLS signal is proportional to MW to the first power, whereas the sensitivity of the viscometer scales with MW^α , where α is the M-H coefficient. However the DV method, like the conventional method, depends on the retention volume calibration.

The inaccuracy of MW measurements using RALLS in the low MW regime does not significantly affect the M_w measurement for polydisperse samples because the low molecular weight components do not contribute much to the calculation of weight-average molecular weight.

MWD of samples can be generated from SEC² or SEC³ if both M_n and M_w can be determined accurately. Otherwise, the ratio of M_w over M_n from RI results would give better insight into MWD (although not necessarily quantitatively).

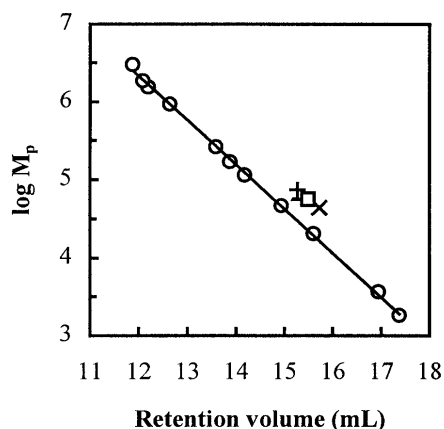


Fig.2 Plot of Log M_w (from RALLS) as a function of retention volume

PS: o; PA3E04: x; PA3E05: Δ
PA3E07: +; PA3E09: □

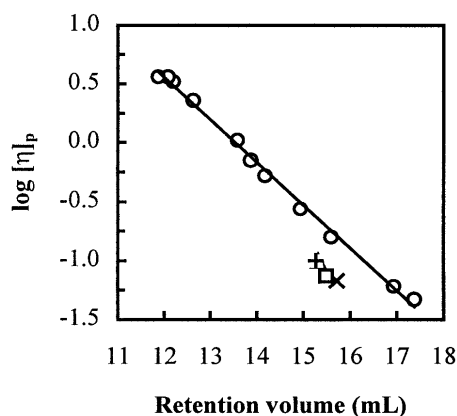


Fig.3 Plot of $[\eta]_p$ (from DV) as a function of retention volume

PS: o; PA3E04: x; PA3E05: Δ
PA3E07: +; PA3E09: □

Figure 2 shows the plot of retention volume against peak molecular weight of both PS standards and the liquid crystalline polyacetylenes. Figure 3 shows a plot of retention volume versus peak intrinsic viscosity for these polymers. We find that points corresponding to liquid crystalline polymers fall to the right of the M_p -- RV curve of PS but to the left of the $[\eta]_p$ -- RV curve of PS. This indicates that in comparison to PS with same molecular weight, the polyacetylenes exhibit relatively compact conformations of

higher density and smaller $[\eta]_p$. This observation explains why MW values obtained via SEC¹ for the liquid crystalline polymers are smaller than their true MW values, as obtained via SEC² and SEC³. Relatively compact molecular structures in solution are a characteristic of branched polymers. Since the polyacetylenes of this work contain no long chain branches, they can be characterized as having a local "comb-like" structure, with short branches pendant from each repeating unit.

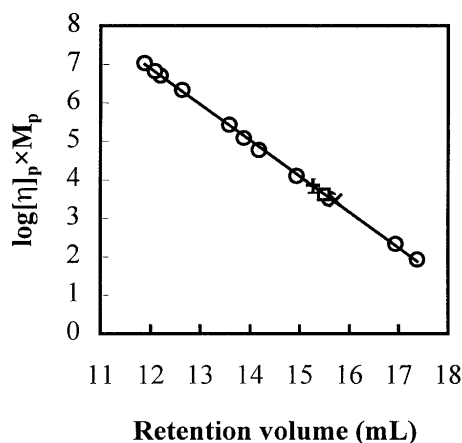


Fig. 4 Plot of $\log[\eta]_p \times M_p$ as function of retention volume
PS: o; PA3E04: ×; PA3E05: Δ;
PA3E07: +; PA3E09: □

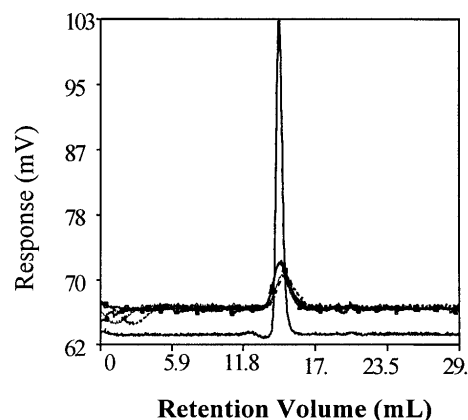


Fig.5 DV response of an LC polymer and a PS standard with similar MW

Data from SEC³ for these polymers are fit to a universal calibration curve in Fig. 4. The data points for the liquid crystalline polymers and PS standards fall on a common line. This indicates the validity of universal calibration for the polymer under investigation. In addition, the validity of universal calibration suggests that viscosity and molecular weight data obtained via multidetector SEC are reliable. DV response of four samples, compared with PS standard (MW of 46,000) with similar concentration at the same response factors, is shown in Figure 5. Again, the low magnitude of DV response of liquid crystalline polymers, compared with that of PS with similar molecular weight and concentration, reflects the tightly coiled structures of these materials. This shows that qualitative insight into molecular conformation in solution can be obtained from inspection of SEC³ chromatograms.

Flory's Characteristic Ratio (C_∞) and Unperturbed Dimensions ($\langle r_0^2 \rangle / M$)^{1/2}

Polymers exhibit conformations ranging from tight coils to highly extended structures in solution. The most commonly used parameter (9) for flexible polymers is Flory's characteristic ratio C_∞ , defined as

$$C_\infty = \lim_{N \rightarrow \infty} \frac{\langle r_0^2 \rangle}{Nl^2} \quad (8)$$

where $\langle r_0^2 \rangle$ is the mean-square unperturbed (theta condition) end-to-end distance in cm², N is the number of main chain bonds, and l is the average bond length. The determination of C_∞ is easily accomplished by combining the measurement of M and $[\eta]$. Values of $[\eta]$ can be measured either in thermodynamically good solvents or under theta conditions. The most commonly used method for estimating K_θ from good solvent data is based upon the Burchard-Stockmayer-Fixman relationship (10-11), shown in Eq. 9, in which K_θ can

be obtained as an intercept by extrapolating good solvent values of $[\eta]/M_w^{1/2}$ versus $M_w^{1/2}$ to $M_w^{1/2} \rightarrow \text{zero}$.

$$[\eta] M_w^{-1/2} = K_\theta + 0.51B \Phi_0 M_w^{1/2} \quad (9)$$

where

$$K_\theta = \Phi_0 (\langle r_0^2 \rangle / M)^{3/2} \quad (10)$$

C_∞ can then be determined using the following equation:

$$C_\infty = \lim_{N \rightarrow \infty} \frac{\langle r_0^2 \rangle / M}{\left(N' / M_0 \right) l^2} \quad (11)$$

where N' denotes the number of backbone bonds per repeat unit and M_0 is the mass per repeat unit.

Using Eq. 9, we generated a plot of $[\eta]/M_w^{1/2}$ versus $M_w^{1/2}$ with K_θ as an intercept as shown in Fig. 6. The slopes for the PA3E04 and PA3E09 samples are approximately zero, which means that THF at 25°C is a near theta solvent for these polymers. Unperturbed dimensions and C_∞ values for the four polymers are listed in Table II.

Table II Unperturbed Dimensions, Characteristic Ratios, and MHS Constants

Samples	M_0 (g/mol)	$K_\theta \times 10^4$ (dL/g)	$(\langle r_0^2 \rangle / M)^{1/2}$ (nm)	C_∞	α	K
PA3E04	336	3.3	0.051	21.0	0.50	3.1
PA3E05	350	3.0	0.050	21.0	0.60	1.2
PA3E07	378	1.9	0.042	16.0	0.75	0.23
PA3E09	406	2.9	0.049	24.0	0.53	2.20

The flexibility of a polymer chain is strongly related to chain structure. For a freely jointed chain, which has neither rotational hindrances nor bond angle restrictions, $\langle r_0^2 \rangle = Nl^2$. Thus C_∞ is equal to 1 for the freely jointed chain, whereas larger C_∞ reflects diminished flexibility owing to fixed bond angles and rotational hindrances. Therefore, the C_∞ value is a quantitative indication of polymer chain flexibility, i.e. the larger the characteristic ratio, the less flexible the chain. The main chain of polyacetylene exhibits rigidity because of its double bond, but flexibility of the substituent also plays a very important role in determining C_∞ . The biphenyl substituent is rigid but these side groups also contain $-\text{COO}$ and $-\text{CO}$ bonds, alkylene spacers, and alkyl groups, which impart these polymers with flexibility because of the relative ease of rotation about some of these bonds. The C_∞ values initially decrease from 21 to 16 as the number of methylene groups in the side chain increases, as indicated in Table II. This trend appears to reflect an increase in flexibility of the side group as the alkyl chain becomes longer. However, C_∞ then increases to 24 as the length of the alkyl group is further increased. This reduction in chain flexibility could reflect an increased hindrance of rotation around backbone bonds caused by this very large substituent. It thus appears that for PA3E09 its large size offsets the effect of the side group flexibility with regard to conformational flexibility. MHS plots can also be generated using data from SEC³ (Fig. 7 and Table II).

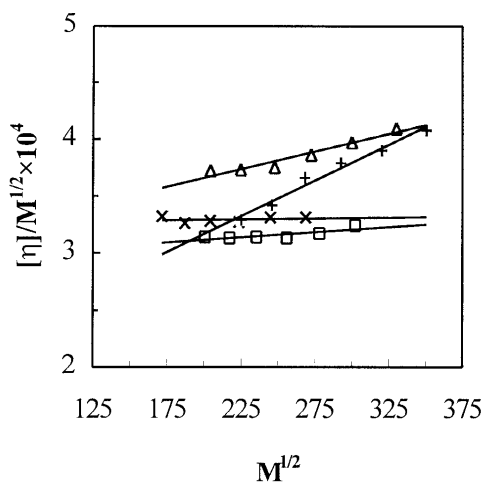


Fig. 6 Plot of $[\eta]/M^{1/2}$ as a function of $M^{1/2}$
 PA3E04: ×; PA3E05: Δ; PA3E07: +; PA3E09: □

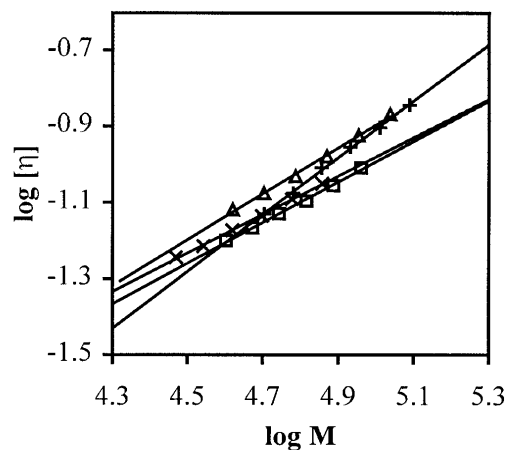


Fig. 7 MHS plot of M_p vs $[\eta]$
 PA3E04: ×; PA3E05: Δ;
 PA3E07: +; PA3E09: □

Conclusions

Novel liquid crystalline polymer based on polyacetylene backbones with biphenyl-containing side groups could not be effectively characterized by conventional SEC. However, information on molecular weight, polydispersity, polymer size and polymer chain flexibility could all be obtained by multidetector size exclusion chromatography techniques (SEC/RI/RALLS/DV). Increasing the length of alkyl substituents present in the side groups initially increases chain flexibility. However, when these alkyl groups become very large chain flexibility is diminished.

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