

# Characterization of Novel Optically Active Conjugated Polyarylenes and Poly(aryleneethynylene)s by a Combination of Off-Line Static and Dynamic Light Scattering with Gel Permeation Chromatography

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**ABSTRACT:** By combining the offline static and dynamic laser light scattering (LLS) and gel permeation chromatography (GPC) results of a broadly distributed polymer sample, we were able to characterize a series of chiral binaphthyl-based polyarylenes and poly(aryleneethynylene)s in THF at 25°C. For each of the samples, we obtained not only the weight-average molar mass  $M_w$ , the second virial coefficient  $A_2$  and the z-average translational diffusion coefficient  $\langle D \rangle$ , but also two calibrations:  $V = A + B \log(M)$  and  $D = k_D M^{-\alpha_D}$ , where  $V$ ,  $D$ , and  $M$  are the elution volume, the translational diffusion coefficient and the molar mass for monodisperse polymer chains, respectively, and  $A$ ,  $B$ ,  $k_D$ , and  $\alpha_D$  are four calibration constants. Using these calibrations, we estimated the molar mass distributions of these novel polymers. We showed that using polystyrene to calibrate the GPC columns could lead to a smaller  $M_w$ . Our results indicate that all the polymers studied have a rigid chain conformation in THF at 25°C and the introduction of the  $-\text{NO}_2$  groups into the monomer can greatly promote the polymer solubility in THF. © 1998 John Wiley & Sons, Inc. *J Polym Sci B: Polym Phys* 36: 2615–2622, 1998

**Keywords:** optically active polymers; gel permeation chromatography; laser light scattering; GPC calibration; rodlike conformation

## INTRODUCTION

Recently, the investigation of conjugated polymers has attracted much interest because of their useful properties, such as electroluminescence, nonlinear optical properties, and high conductivity upon doping.<sup>1</sup> However, only lim-

ited studies of optically active conjugated polymers in solution have been reported.<sup>2–4</sup> In the past, the chirality of most optically active conjugated polymers was attributed to their optically active side groups, such as a polyacetylene with optically active alkyl groups.<sup>2</sup> In this study, several novel soluble optically active conjugated polyarylenes and poly(aryleneethynylene)s, which were prepared through a coupling of chiral binaphthyl monomers with various linkers,<sup>5–7</sup> were studied. The chirality is originated from a restricted rotation of the binaphthyl units in their backbone chains.

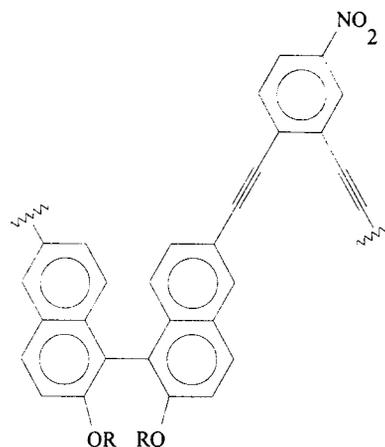
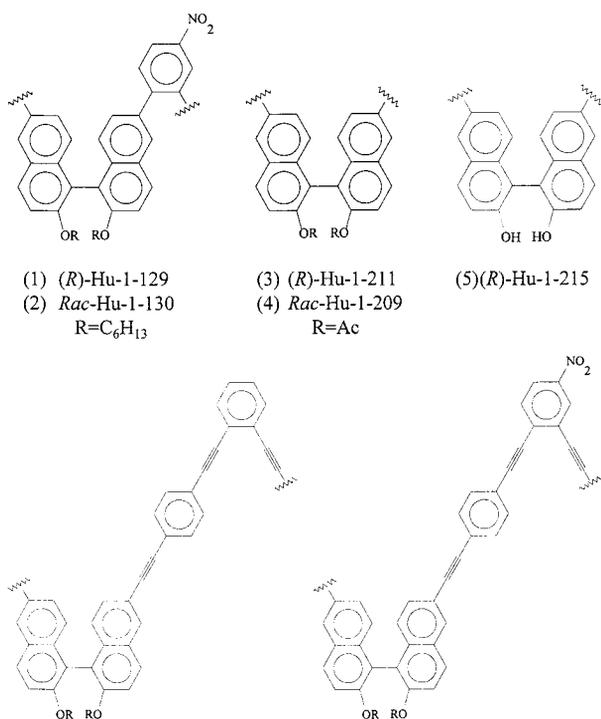
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These novel polymers have a high thermal stability. Moreover, they are highly fluorescent and able to emit blue light when irradiated. Recently, a highly enantioselective polybinaphthyl catalyst has been developed for the asymmetric reactions of aldehydes with alkyl zincs.<sup>8</sup> The optimization of the synthesis and development of various applications of the novel polymers requires the characterization of their molecular parameters, such as molar mass distribution and chain flexibility.

Gel permeation chromatography (GPC) as a convenient analytical method has been widely used in polymer research and development to determine the molar mass distribution of a given polymer. The calibration of a GPC column normally requires a set of narrowly distributed polymer samples that are rather difficult, if not impossible, to obtain in practice. This is why polystyrene standards are often used if the polymer studied has a similar chain conformation in solution. However, in this study, the chain conformations of polyarylenes and poly(aryleneethynylene)s are expected to be quite different from that of polystyrene. Therefore, a recently developed method of combining the LLS and GPC results of only one sample was adopted to calibrate the GPC columns. Eight different polyarylenes and poly(aryleneethynylene) samples were investigated and their molecular structures are as follows:



(8)*(R)*-Ma-1-148  
R=C<sub>18</sub>H<sub>37</sub>

The *R* polymers are made of *R* binaphthyl units and the *Rac* polymers are made of racemic binaphthyl units. Polyarylenes and poly(aryleneethynylene)s except *(R)*-Hu-1-215, which is soluble in DMSO and basic water solution, are soluble in various organic solvents such as THF and chloroform in spite of their rigid backbone chain structure, which is due to the reduction of the  $\pi$ - $\pi$  stacking by the nonplanarity of the binaphthyl groups.

## EXPERIMENTAL

### Solution Preparation

The sample synthesis has been detailed before.<sup>9-11</sup> Analytical grade THF dried by sodium immediately prior to the sample preparation was used as solvent for all the polymers except for *(R)*-Hu-1-215, where 1 *M* NaOH was used as solvent because it is insoluble in THF. The solution concentration was in the range  $4 \times 10^{-4}$  to  $3 \times 10^{-3}$  g/mL. All the polymer solutions were clarified by 0.5  $\mu$ m PTFE filters at room temperature.

### Laser Light Scattering (LLS)

A modified commercial LLS spectrometer (ALV/SP-125) equipped with an ALV-5000 multi- $\tau$  digital time correlator and a He-Ne laser (Spectra-Physics Model 127, output power 40 mW at  $\lambda_0 = 632.8$  nm) as the light source was used. The primary beam is vertically polarized with respect to the scattering plane. The instrument was cal-

**Table I.** Summary of Static and Dynamic Laser Light-Scattering Results of Polyarylenes and Poly(aryleneethynylene)s in THF at 25°C

Sample	$M_w$ (g/mol)	$10^3 A_2$ (mol · cm <sup>3</sup> /g <sup>2</sup> )	$10^8 \langle D \rangle$ (cm <sup>2</sup> /s)	$\langle R_h \rangle$ (nm)	$dn/dC$ (mL/g)	$M_{w,SEC}$ (g/mol)
(R)-Hu-1-129	12200	~ 0	178	2.59	0.250	10100
Rac-Hu-1-130	7780	1.40	232	1.98	0.250	6300
(R)-Hu-1-211	7130	-2.86	202	2.28	0.291	6400
Rac-Hu-1-209	5930	-6.27	205	2.24	0.291	7400
Rac-Ma-1-159	13800	-6.24	168	2.74	0.255	11600
Rac-Ma-1-157	12400	2.66	142	3.24	0.267	10500
(R)-Ma-1-148	22000	5.15	210	2.19	0.215	7200

The relative errors:  $M_w$ ,  $\pm 5\%$ ;  $A_2$ ,  $\pm 20\%$ ;  $\langle D \rangle$  and  $\langle R_h \rangle$ ,  $\pm 5\%$ ;  $dn/dC$ ,  $\pm 1\%$ .

ibrated with toluene to make sure that the scattering intensity from toluene has no angular dependence in the range of 15–150°. The details of the LLS instrumentation and theory can be found elsewhere.<sup>12,13</sup> All specific refractive index increments ( $dn/dC$ ) were determined by using a novel differential refractometer,<sup>14</sup> which are listed in Table I. There is no difference in  $dn/dC$  between the optically active and inactive samples in each pair. All the LLS measurements were carried out at  $25.0 \pm 0.1^\circ\text{C}$ .

In Static LLS, the angular dependence of the excess absolute time-averaged scattered intensity, known as the excess Rayleigh ratio ( $R_{vv}(\theta)$ ), was measured. For a dilute polymer solution measured at a small scattering angle ( $\theta$ ),  $R_{vv}(\theta)$  can be related to the weight-average molar mass  $M_w$ , the second virial coefficient  $A_2$ , and the root-mean-square  $z$ -average radius of gyration  $\langle R_g^2 \rangle_z^{1/2}$  (or simply  $\langle R_g \rangle$ ) as<sup>15</sup>

$$\frac{KC}{R_{vv}(q)} \approx \frac{1}{M_w} \left( 1 + \frac{1}{3} \langle R_g^2 \rangle_z q^2 \right) + 2A_2 C \quad (1)$$

where  $K = 4\pi^2 n^2 (dn/dC)^2 / N_A \lambda_0^4$  and  $q = (4\pi n / \lambda_0) \sin(\theta/2)$  with  $N_A$ ,  $dn/dC$ ,  $n$ , and  $\lambda_0$  being Avogadro number, the specific refractive index increment, the solvent refractive index and the wavelength of light in vacuum, respectively.

In Dynamic LLS, a precise intensity–intensity time correlation function  $G^{(2)}(t, q)$  in the self-beating mode was measured.  $G^{(2)}(t, q)$  is related to the normalized first-order electric field time correlation function  $g^{(1)}(t, q)$  as<sup>12</sup>

$$G^{(2)}(t, q) = \langle I(t, q) I(0, q) \rangle = A [1 + \beta |g^{(1)}(t, q)|^2] \quad (2)$$

where  $A$  is a measured base line;  $\beta$ , a parameter depending on the coherence of the detection; and  $t$ , the delay time. For a polydisperse sample,  $g^{(1)}(t, q)$  is related to the line-width distribution  $G(\Gamma)$  by<sup>12</sup>

$$g^{(1)}(t, q) = \langle E(t, q) E^*(0, q) \rangle = \int_0^\infty G(\Gamma) e^{-\Gamma t} d\Gamma \quad (3)$$

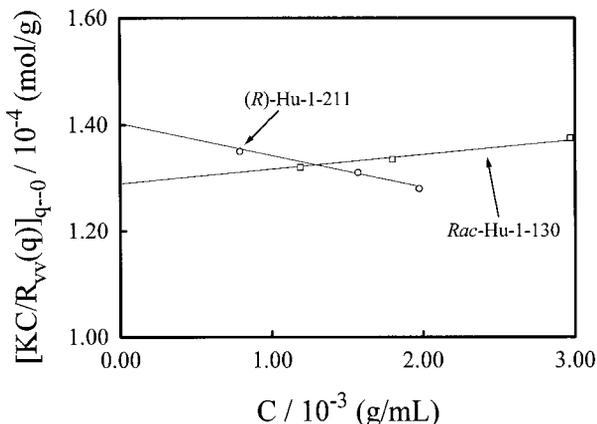
The Laplace inversion of  $g^{(1)}(t, q)$ , using the CONTIN analysis program,<sup>16</sup> can lead to  $G(\Gamma)$  on the basis of eqs. (2) and (3). The line width  $\Gamma$  usually depends on both  $C$  and  $\theta$  as<sup>17,18</sup>

$$\Gamma/q^2 = D(1 + k_d C)(1 + f \langle R_g^2 \rangle_z q^2) \quad (4)$$

where  $D$  is the translational diffusion coefficient;  $f$ , a dimensionless number; and  $k_d$ , the diffusion second virial coefficient.  $f$  depends on the chain structure, polydispersity and solvent quality.  $D$ ,  $f$ , and  $k_d$  can be obtained from the plots of  $(\Gamma/q^2)_{C \rightarrow 0, \theta \rightarrow 0}$  ( $\Gamma/q^2$ ) <sub>$\rightarrow 0$</sub>  vs.  $q^2$  and  $(\Gamma/q^2)_{\theta \rightarrow 0}$  vs.  $C$ , respectively.

### Gel Permeation Chromatography (GPC)

One Ultrastyrigel 500A (7.8 × 300 mm, Part No. 10571) and two Ultrastyrigel linear (7.8 × 300 mm, Part No. 10681) GPC columns calibrated by polystyrene standards together with a Waters 510 HPLC Pump and a Waters 410 Differential Refractometer were used. THF was used as eluent and the flow rate was 1.23 mL/min. The concentration of the samples are ca. 2–5 mg polymer in 5 mL THF. The temperature of the columns was kept at 40°C.



**Figure 1.** Concentration dependence of  $[KC/R_{vv}(\theta)]_{q \rightarrow 0}$  of *Rac*-Hu-1-130 and *(R)*-Hu-1-211 in THF at  $T = 25^\circ\text{C}$ .

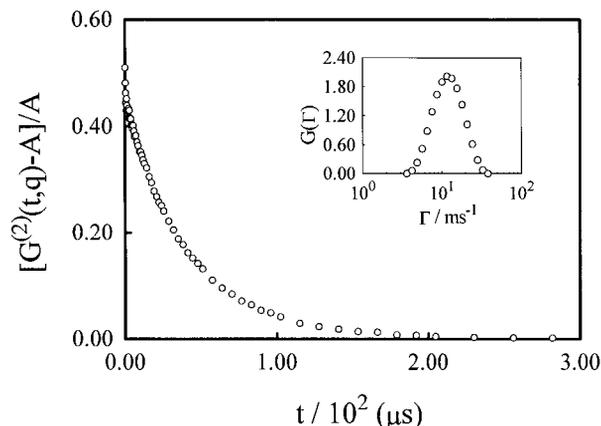
## RESULTS AND DISCUSSION

Figure 1 shows the concentration dependence of  $[KC/R_{vv}(q)]_{q \rightarrow 0}$  of *Rac*-Hu-1-130 and *(R)*-Hu-1-211. On the basis of eq. (1),  $M_w$ ,  $\langle R_g \rangle$ , and  $A_2$  can be obtained from the extrapolation of  $[KC/R_{vv}(q)]_{c \rightarrow 0, q \rightarrow 0}$ ,  $[KC/R_{vv}(q)]_{c \rightarrow 0}$  vs.  $q^2$  and  $[KC/R_{vv}(q)]_{c \rightarrow 0}$  vs.  $C$ , respectively. The LLS results are summarized in Table I. In this study,  $\langle R_g \rangle$  is so small that  $[KC/R_{vv}(q)]$  has nearly no angular dependence and no accurate values of  $\langle R_g \rangle$  were obtained. The positive and negative values of  $A_2$  respectively indicate that THF is a good solvent for *(Rac)*-Hu-1-130 and *Rac*-Ma-1-157, and *(R)*-Ma-1-148; and a poor solvent for *(R)*-Hu-1-211, *Rac*-Hu-1-209, and *Rac*-Ma-1-159. It is clear that introducing the  $-\text{NO}_2$  groups can promote the polymer solubility in THF at  $25^\circ\text{C}$ .

Figure 2 shows a typical intensity–intensity time correlation function of *(R)*-Hu-1-129 in THF at  $25^\circ\text{C}$ , where the insert shows a corresponding line width distribution  $G(\Gamma)$  calculated on the basis of eq. (3) by using the CONTIN program in the correlator.  $G(\Gamma)$ s are relatively narrowly distributed for all the polymers studied, and the relative width  $\mu_2/\langle \Gamma \rangle^2$  is in the range of 0.2–0.3, where

$$\mu_2 = \int_0^\infty G(\Gamma)(\Gamma - \langle \Gamma \rangle)^2 d\Gamma \quad \text{and} \quad \langle \Gamma \rangle = \int_0^\infty G(\Gamma)\Gamma d\Gamma.$$

The line width  $\Gamma$  can be further converted to the translational diffusion coefficient  $D$  on the basis of eq. (4). In the case of  $C \sim 10^{-4}$  g/mL and  $\theta = 30^\circ$ ,  $(1 + k_d C)(1 + f \langle R_g^2 \rangle_z q^2) \sim 1$  so that  $\Gamma/q^2$

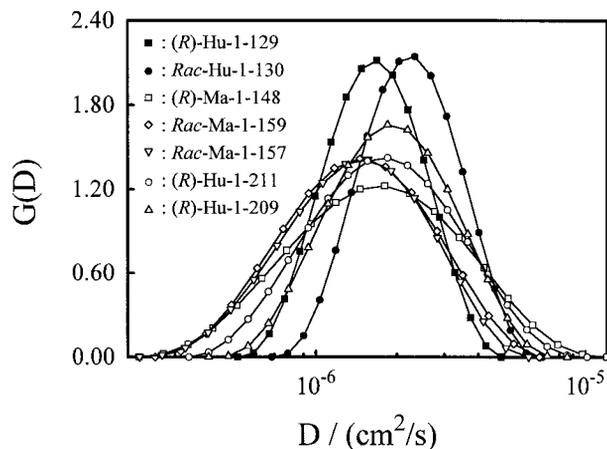


**Figure 2.** Typical intensity–intensity time correlation function of *(R)*-Hu-1-129 in THF at  $\theta = 30^\circ$  and  $T = 25^\circ\text{C}$ , where the insert shows a corresponding line width distribution  $G(\Gamma)$  calculated from  $G^{(2)}(t, q)$  on the basis of eqs. (2) and (3).

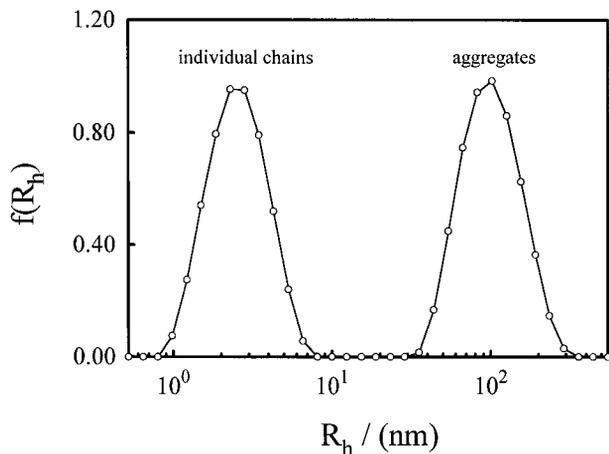
$= D$  and each  $G(\Gamma)$  can be directly converted into a translational diffusion coefficient distribution  $G(D)$ .

Figure 3 shows the translational diffusion coefficient distributions  $G(D)$  of polyarylenes and poly(aryleneethynylene)s in THF at  $25^\circ\text{C}$ . Each  $G(D)$  can be further related to a hydrodynamic radius distribution  $f(R_h)$  using the Stokes–Einstein equation:  $D = k_B T / 6\pi\eta R_h$ , where  $k_B$ ,  $T$ , and  $\eta$  are the Boltzmann constant, the absolute temperature, and solvent viscosity, respectively. All the dynamic LLS results are also summarized in Table I, where

$$\langle D \rangle = \left[ \int_0^\infty G(D)D dD \right] \quad \text{and} \quad \langle R_h \rangle = k_B T / 6\pi\eta \langle D \rangle.$$



**Figure 3.** Translational diffusion coefficient distributions of seven polyarylene and poly(aryleneethynylene) samples in THF at  $25^\circ\text{C}$ .



**Figure 4.** Hydrodynamic radius distribution of (*R*)-Hu-1-215 in 1 *M* NaOH at 25°C.

The small values of  $\langle R_h \rangle$  indicate that all the polymer chains are short, which are consistent with their low molar masses.

(*R*)-Hu-1-215 is insoluble in THF, but is partially soluble in 1 *M* NaOH aqueous solution, evidenced by a bimodal hydrodynamic radius distribution shown in Figure 4. The first peak located in the range of 1–9 nm represents individual polymer chains and the second peak located at 100 nm could be attributed to either the aggregation of individual polymer chains or possible electrostatic interaction between the hydroxyl groups ionized in the strong base solution. However, we found that adding 0.1 *M* NaCl into the solution to increase the ionic strength of the solution has no effect on  $f(R_h)$ , which indirectly indicates that the second peak is related to the aggregation. It is interesting to note that the only difference between (*R*)-Hu-1-211 and (*R*)-Hu-1-215 is that the —OAc groups have been replaced by the —OH groups.

For comparison, the values of  $M_w$  from GPC in which polystyrene standards were used to calibrate the columns are also listed in Table I. Except in the case of (*R*)-Ma-1-148, LLS gives a larger  $M_w$  than SEC, indicating that using polystyrene to calibrate the GPC columns is not quite right because polyarylene and poly(aryleneethynylene) have a different chain conformation. The LLS study of other poly(aryleneethynylene)s showed a similar result.<sup>19</sup> However, it should be noted that in the studied molar mass range, polystyrene chains are so short that they are not as flexible as long polystyrene chains. This may be why the values of  $M_w$  from GPC and LLS are not

very much different. Considering the results of (*R*)-Hu-1-211 and *Rac*-Hu-1-209, we think that the LLS results are more reasonable because the variation of  $M_w$ ,  $A_2$ , and  $\langle R_h \rangle$  in each pair of polymers is consistent; namely,  $A_2$  increases as  $M_w$  decreases, and  $R_h$  increases as  $M_w$  increases. Ideally, we should use a set of narrowly distributed samples with the same chemical structure, but different molar masses, to calibrate the GPC columns. However, in this study, we were not able to obtain the fractions with different molar masses.

To obtain a proper calibration of the GPC columns from only one polymer sample, we used a method of combining the off-line LLS and GPC results.<sup>20</sup> For the convenience of discussion, its basic principle is outlined as follows: it is known that for a given polymer chain both the elution volume  $V$  in GPC and the translational diffusion coefficient  $D$  in dynamic LLS are related to its hydrodynamic size, so that  $V$  and  $D$  are interconnected. If we have either the calibration of

$$V = A + B \log(M) \quad (5)$$

or

$$D = k_D M^{-\alpha_D} \quad \text{or written as}$$

$$\log(D) = \log(k_D) - \alpha_D \log(M) \quad (6)$$

we are able to transform  $C(V)$  or  $G(D)$  into its corresponding molar mass distribution, where  $A$ ,  $B$ ,  $k_D$ , and  $\alpha_D$  are four calibration constants. A combination of eqs. (5) and (6) leads to

$$V = \mathbf{A} + \mathbf{B} \log(D) \quad (7)$$

where  $\mathbf{A} = A + B \log(k_D) \alpha_D$  and  $\mathbf{B} = -B/\alpha_D$ . Squaring both sides of eq. (7) leads to

$$V^2 = \mathbf{A}^2 + 2\mathbf{A}\mathbf{B} \log(D) + \mathbf{B}^2 \log^2(D) \quad (8)$$

After respectively integrating the both sides of eqs. (7) and (8), we have

$$\langle V \rangle = \mathbf{A} + \mathbf{B} \langle \log(D) \rangle \quad (9)$$

and

$$\langle V^2 \rangle = \mathbf{A}^2 + 2\mathbf{A}\mathbf{B} \langle \log(D) \rangle + \mathbf{B}^2 \langle \log^2(D) \rangle \quad (10)$$

**Table II.** Summary of the Calibration Constants and the Parameters of the Molar Mass Distributions

Sample	A (cm <sup>3</sup> )	B (cm <sup>3</sup> )	10 <sup>2</sup> k <sub>D</sub> (cm <sup>2</sup> /s)	α <sub>D</sub>	From G(D)		From C(V)	
					M <sub>w</sub> (g/mol)	M <sub>w</sub> /M <sub>n</sub>	M <sub>w</sub> (g/mol)	M <sub>w</sub> /M <sub>n</sub>
(R)-Hu-1-129	45.8	-2.61	2.17	1	12200	1.16	12100	1.16
Rac-Hu-1-130	42.2	-2.28	1.82	1	7780	1.15	7760	1.15
(R)-Hu-1-211	42.6	-2.34	1.44	1	7130	1.14	7130	1.14
Rac-Hu-1-209	41.7	-2.31	1.22	1	5930	1.26	5890	1.25
Rac-Ma-1-159	36.7	-1.66	2.32	1	13800	1.35	13600	1.35
Rac-Ma-1-157	37.2	-1.72	1.77	1	12400	1.31	12200	1.31
(R)-Ma-1-148	32.5	-1.11	4.63	1	22000	1.50	21600	1.49

where  $\langle V \rangle$ ,  $\langle V^2 \rangle$ ,  $\langle \log(D) \rangle$  and  $\langle \log^2(D) \rangle$  can be calculated from  $G(D)$  and  $C(V)$ , so that **A** and **B** can be obtained on the basis of eqs. (9) and (10). On the other hand,  $M_w$  is defined as

$$\frac{\int_0^\infty MF_w(M)dM}{\int_0^\infty F_w(M)dM}, F_w(M) \propto \frac{G(D)D}{M^2} \text{ and } F_w(M) \propto \frac{C(V)}{M}$$

from our previous study,<sup>20</sup> so that we have

$$M_{w,DLS} = \frac{k_D^{1/\alpha_D} \int_0^\infty G(D)dD}{\int_0^\infty G(D)D^{1/\alpha_D}dD} \quad (11)$$

and

$$M_{w,SEC} = \frac{k_D^{1/\alpha_D} \int_0^\infty 10^{(A-V)/(\alpha_D B)} C(V)dV}{\int_0^\infty C(V)dV} \quad (12)$$

where we have used eqs. (6) and (7) and the relations among **A**, **B**,  $A$ ,  $B$ ,  $k_D$ , and  $\alpha_D$ . For a given sample, it is expected that  $M_{w,DLS} = M_{w,SEC} = M_w$ , i.e.,

$$\frac{\int_0^\infty G(D)dD}{\int_0^\infty G(D)D^{1/\alpha_D}dD} = \frac{\int_0^\infty 10^{(A-V)/(\alpha_D B)} C(V)dV}{\int_0^\infty C(V)dV} \quad (13)$$

where  $\alpha_D$  is the only unknown parameter. For a chosen  $\alpha_D$ , we can first calculate  $\langle V \rangle$ ,  $\langle V^2 \rangle$ ,  $\langle \log(D) \rangle$  and  $\langle \log^2(D) \rangle$ ; then obtain **A** and **B** on the basis of eqs. (9) and (10); and finally calculate the both sides of eq. (13). An iteration of the above procedure enables us to find a proper  $\alpha_D$  to minimize the difference between the both sides of eq. (13). With this  $\alpha_D$ , we can further calculate  $k_D$  from either eq. (11) or (12) by replacing the left-hand side of the equation with  $M_w$  from static LLS and using  $G(D)$  from dynamic LLS or  $C(V)$  from SEC; and finally get  $A$  and  $B$  from **A**, **B**,  $k_D$ , and  $\alpha_D$ , i.e., we can simultaneously obtain eqs. (5) and (6) by using only one polymer sample, plus a combination of LLS and GPC.

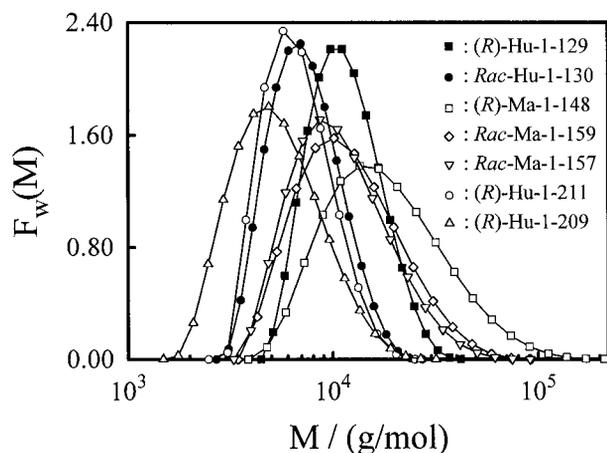
Table II summarizes the values of  $A$ ,  $B$ ,  $k_D$ , and  $\alpha_D$ . The fact that  $\alpha_D = 1$  indicates that the polymer chains have a rigid conformation. This is expected because the conjugated backbone chains with the bulk binaphthyl groups are so short (10–20 monomer units) that they are not flexible. Moreover, it is worth noting that the calibration parameters are similar, which can be attributed to a similar rodlike structure of these conjugated polymers.

Once having  $A$ ,  $B$ ,  $k_D$ , and  $\alpha_D$ , we were ready to convert either  $G(D)$  or  $C(V)$  into a corresponding molar mass distributions  $F_w(M)$ . Figures 5 and 6 respectively show such calculated molar mass distributions from  $G(D)$  and  $C(V)$ , respectively. It should be stated that the difference in the low

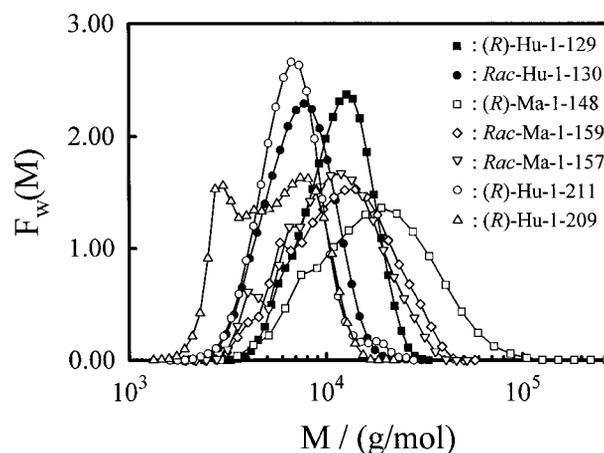
molar mass tail of the distributions presented in Figures 5 and 6 is due to the fact that the LLS detector is not able to "see" the lower molar mass portion because the scattered light intensity is proportional to  $M^2$ . This is why LLS normally leads to a narrower molar mass distribution. The polydispersity index ( $M_w/M_n$ ) calculated from the  $F_w(M)$ s in Figures 5 and 6 are also summarized in Table II. Both the values of  $M_w$  and  $M_w/M_n$  calculated from  $G(D)$  and  $C(V)$  agree satisfactorily well with each other.

## CONCLUSIONS

It is clear that using polystyrene standards to calibrate the GPC columns for the characterization of polyarylene or poly(aryleneethynylene) could lead to an improper  $M_w$ . As an alternative method, a combination of laser light scattering and gel permeation chromatography can simultaneously establish the two calibrations of  $V = A + B \log(M)$  and  $D = k_D M^{-\alpha_D}$  for the chiral binaphthyl-based polyarylene and poly(aryleneethynylene) in THF at 25°C. Our results revealed that these polymers have a rigid chain conformation in THF at 25°C and the introduction of the  $-\text{NO}_2$  groups into these chiral binaphthyl-based polymers increases its solubility in THF at 25°C. The calibrations of  $D = k_D M^{-\alpha_D}$  established in this study are independent of a particular laser light-scattering instrument and ready to be used in



**Figure 5.** Differential weight distributions of molar mass ( $F_w(M)$ ), calculated from the  $G(D)$ s from dynamic LLS shown in Figure 3, of seven polyarylene and poly(aryleneethynylene) samples.



**Figure 6.** Differential weight distributions of molar mass ( $F_w(M)$ ), calculated from the  $C(V)$ s from GPC, of seven polyarylene and poly(aryleneethynylene) samples.

future to characterize similar polyarylene and poly(aryleneethynylene) as long as THF is used as solvent and temperature is 25°C.

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