

# End-Group Analysis of Blue Light-Emitting Polymers Using Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry

Hui Chen,<sup>†</sup> Meiyu He,<sup>\*,†</sup> Jian Pei,<sup>†</sup> and Bin Liu<sup>‡</sup>

Department of Chemistry, Peking University, Beijing, 100871, China, and Institute of Materials Research and Engineering, National University of Singapore, 117602, Singapore

**An analytical method based on matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) has been applied to provide information on the structure of a copolymer, e.g., repeat unit and end group. Seven conjugated polymers, which have been demonstrated as the active component in blue light-emitting diodes, were synthesized through Suzuki polycondensation reaction in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> catalyst. Their molecular weights were obtained using gel permeation chromatography analysis. MALDI-TOF MS was used to investigate the structure information in detail. The proposed end-group structures were confirmed by the identity between the observed and the simulated isotopic distribution of each polymer. The results demonstrate that these synthetic polymers possess various end groups and even contain macrocycles. The catalyst Pd(PPh<sub>3</sub>)<sub>4</sub> was found to introduce phenyl end groups via aryl–aryl exchange between the catalytic palladium intermediate and the triphenylphosphine ligand. All these results are based on the analysis of the mass spectrum data, which suggests that MALDI-TOF MS is an extraordinarily strong tool in synthetic polymer structure analysis.**

In the past decade, great efforts have been devoted to the analysis of synthetic polymers for their weight-average ( $M_w$ ), number-average ( $M_n$ ), polydispersity (PD), repeat units, and end group.<sup>1–15</sup> These kinds of polymer information, especially the end-group information, can afford a deeper insight into polymer

structures, reaction mechanisms, and side reactions. Furthermore, more and more studies have demonstrated that the end group of a polymer can affect the physical and chemical properties of that polymer, e.g., surface activity,<sup>10</sup> phase behavior,<sup>11</sup> and light-emitting.<sup>12</sup>

The typical methods of polymer analysis include size exclusion chromatography (SEC),<sup>13</sup> NMR,<sup>14</sup> laser light scattering,<sup>15</sup> and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) MS. All the methods have their own advantage in polymer analysis and the ability of obtaining the  $M_w$ ,  $M_n$ , and PD of the polymer. However, they are not so suitable for identifying the exact end group of polymer in the complex polymer system with the exception of MALDI-TOF MS. MALDI-TOF MS is thought to be the strongest tool for polymer analysis among the present polymer analysis methods because of the simplicity of the mass spectra, which shows mainly single-charged quasi-molecular ions with hardly any fragmentation; the time-of-flight analyzer in which very high molecular mass polymers can be analyzed beyond 1 MDa has been demonstrated, and the state-of-the-art reflection instruments allowing the determination of the repeat unit and the end group.

Recently, significant process has been achieved in the development of light-emitting diodes (LEDs) based on conjugated polymers.<sup>17–19</sup> Although all three primary colors (red, green, blue) required by full color display have been demonstrated in PLEDs, only red and green PLEDs have sufficient efficiencies and lifetimes to be of commercial value.<sup>20</sup> Pursuing efficient and stable blue LEDs based on conjugated polymers remains a challenge for research workers.

In this paper, we synthesized a series of conjugated polymers from P1 to P7 (Chart 1) by palladium-catalyzed Suzuki coupling reaction, which had the band gaps corresponding to blue light

\* Corresponding author. E-mail: myhe@chem.pku.edu.cn. Phone: (86-10)-62754181. Fax: (86-10)-62751708.

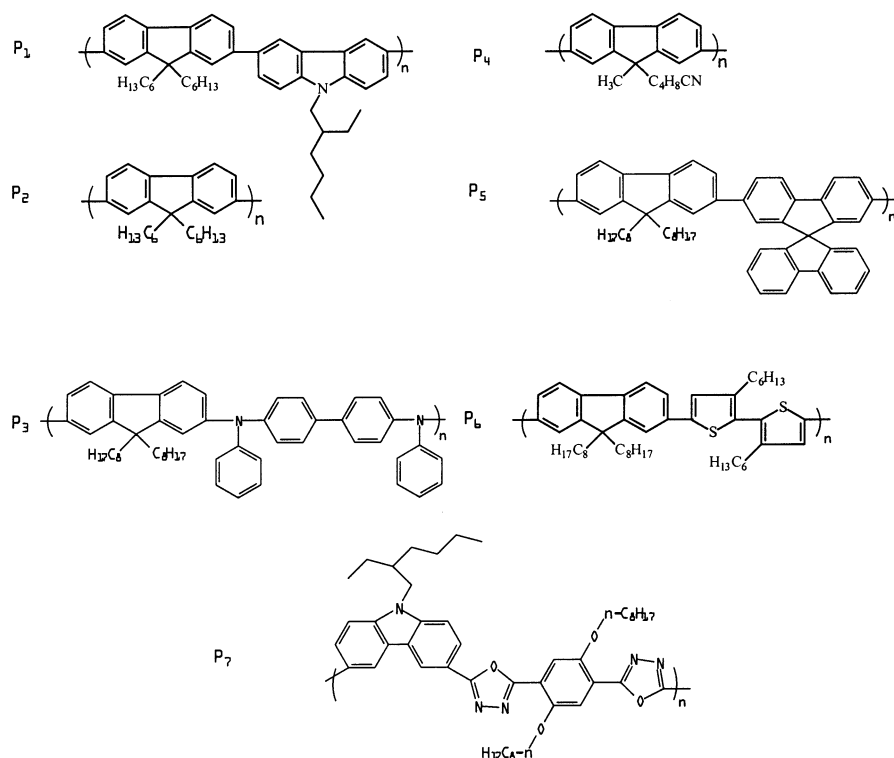
<sup>†</sup> Peking University.

<sup>‡</sup> National University of Singapore.

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Chart 1. Structures of the Seven Polymers

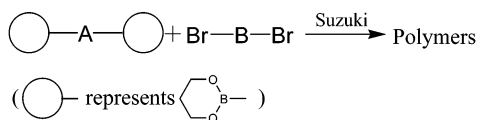


emission. Using MALDI-TOF MS, we readily obtained the polymer's structural information, which is important for polymer characterization in a single fast analysis. From the reflectron mode MALDI data, we acquired the information of repeat unit and end group of each polymer from polymer P1 to P7. By comparison between the observed isotopic distribution and the simulated isotopic distribution on XMASS (software provided by Bruker), we can confirm that our proposed end-group structures for the seven polymers are correct. Interestingly, we found that the phenyl in the catalyst  $\text{Pd}(\text{PPh}_3)_4$  can terminate the polymerization reaction by acting as the end group itself.

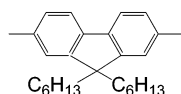
## EXPERIMENTAL SECTION

**Polymerizations.** All the seven polymers were synthesized by the Suzuki polycondensation reaction.<sup>21,22</sup>

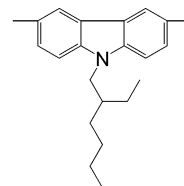
Target molecules were produced through the reaction between two factors A and B:



For P1, factor A is



and factor B is



**General Instrumentation and Conditions.** MALDI experiments were carried out using a Bruker Biflex III time-of-flight mass spectrometer (Bruker Daltonics, Billerica, MA). The instrument is equipped with a  $\text{N}_2$  laser emitting at 337 nm (Laser Sciences Inc., Cambridge, MA), a 1-GHz sampling rate digitizer, a pulsed ion extraction source, and an electrostatic reflectron. The laser pulse width is 3 ns, and its maximum power is 200  $\mu\text{J}$ . Spectra were acquired in the positive-ion mode using the reflectron. The acceleration voltage was 19 kV. The delay voltage was 14.3 kV, the delay time 200 ns, and the reflectron voltage was 20 kV. Typically, 40 single-shot mass spectra were summed to give a composite spectrum. All data were reprocessed using the Bruker XTOF software. The mass scale was calibrated externally, using the peptides angiotensin II, bovine insulin b-chain, bovine insulin, and equine cytochrome *c* (Sigma, St. Louis, MO) as mass standards. GPC analysis was conducted with a Waters 2690 separation module equipped with a Waters 410 differential refractometer HPLC system and Waters Styragel HR4E columns using polystyrene as the standard and THF as the eluant.

**Samples and Reagents.** The total seven polymers were synthesized by the palladium-catalyzed Suzuki coupling reaction. MALDI analysis of the polymers utilized the following compounds

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Table 1. Experimental Conditions of the Polymers<sup>a</sup>

polymers	matrix	C <sub>1</sub> (mg/mL)	C <sub>2</sub> (mg/mL)	C <sub>1</sub> /C <sub>2</sub>
P1	DI	10	5	2:1
P2	IAA	10	5	2:1
P3	IAA	10	5	2:1
P4	IAA	10	5	2:1
P5	DI	10	5	2:1
P6	DI	10	5	2:1
P7	DI	10	2	2:1

<sup>a</sup>C<sub>1</sub>, concentration of the matrix; C<sub>2</sub>, concentration of the polymer.

Table 2. Molecular Weight Distribution of the Polymers

polymers	M <sub>n</sub>	M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>
P1	8900	15600	1.7
P2	6060	8250	1.3
P3	7950	9080	1.1
P4	11800	20300	1.7
P5	11600	33600	2.9
P6	26500	50200	1.9
P7	2793	3135	1.1

as matrixes: 3-indoleacrylic acid (IAA; Acros) and dithranol (DI; Aldrich, Milwaukee, WI). The solvent, inhibitor-free tetrahydrofuran (THF; Aldrich), stored in a Sure/Seal bottle, was used as received.

**Sample Preparation.** In MALDI experiments it is well known that the sample preparation protocol influences the sensitivity, selectivity, and mass resolution.<sup>23–25</sup> So we tried to find the best condition for each polymer by varying the matrixes, the cationization salts, and the ratio of sample and matrix. Detailed experimental conditions are shown in Table 1. We used a dried droplet method<sup>26</sup> to prepare sample target: 3  $\mu$ L of sample mixture was applied to the sample target and air-dried.

## RESULTS AND DISCUSSION

**GPC Analysis.** In MALDI-TOF MS on polymers, there is a discrimination against higher molecular weight species in samples with a polydispersity of more than 1.2,<sup>27</sup> and an accurate determination of the molecular weight distribution from MALDI-TOF MS can only be obtained in combination with a GPC fractionation to analyze wide-dispersity samples. Therefore, the molecular weights of these seven polymers were measured by means of gel permeation chromatography (GPC) using THF as the eluant and polystyrene as the standards. A summary of the molecular weights and the polydispersity indexes is listed in Table 2 (the molecular weight of P7 was obtained by MALDI-TOF).

All these polymers readily dissolve in common organic solvents, such as chloroform, THF, toluene, and xylene. The number-average molecular weights of the polymers determined by GPC ranged from ~6000 to ~51 000 with polydispersity

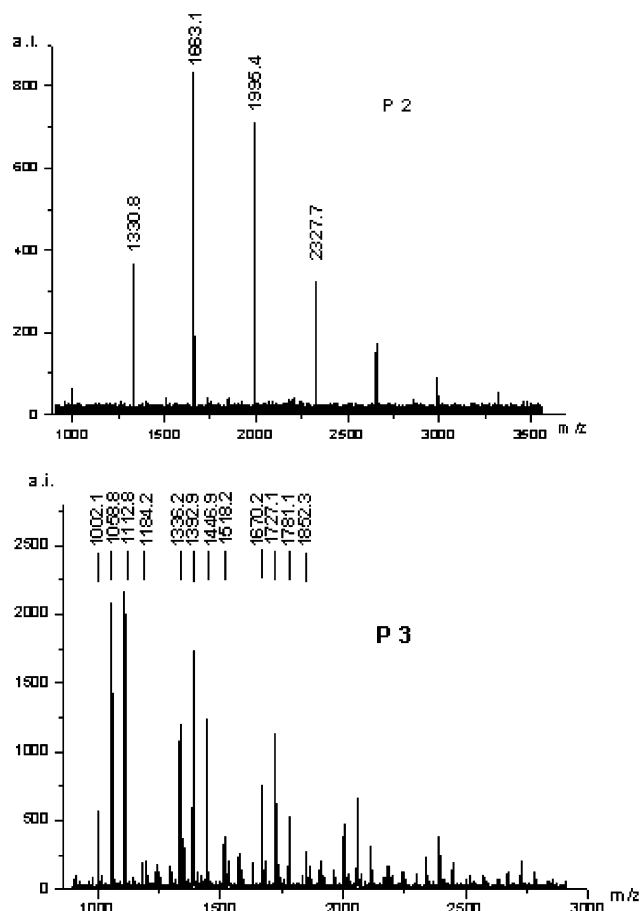


Figure 1. MALDI mass spectra (reflectron mode) of P2 and P3.

Table 3. Peak Information of the Seven Polymers

polymers	peak series (monoisotopic mass)
P1	1035.7, 1645.1, 2254.4; 1095.7, 1705.1, 2314.5; 1296.9, 1906.2, 2515.6; 1218.8, 1828.1, 2437.6; 888.5, 1497.9, 2107.2; 1236.8, 1846.2, 2455.6
P2	1663.1, 1995.4, 2327.7, 2660.1
P3	1002.1, 1336.2, 1670.2; 1058.8, 1392.9, 1727.1; 1112.8, 1446.9, 1781.1; 1184.2, 1518.2, 1852.3
P4	1106.4, 1365.4, 1624.5; 1129.2, 1388.3, 1647.4; 1038.3, 1297.6, 1556.6; 1072.4, 1331.4, 1590.6
P5	1093.1, 1795.5, 2497.9; 1406.9, 2109.3, 2811.8; 1485.8, 2188.2, 2890.6
P6	1443.0, 2163.4, 2883.9, 3604.4
P7	1491.0, 2236.4, 2981.8, 3727.3

indexes of 1.1–2.9 using polystyrene as standards. It was found that for those comonomers that are electron deficient or with electron-withdrawing groups, the molecular weights are relatively higher, since they favor the Suzuki coupling reaction.<sup>28</sup>

**Repeat-Unit Analysis by MALDI-TOF MS.** Some of the polymers' spectra are shown in Figure 1. (P2, P3). The peak series information for the seven polymers was listed in Table 3. From the spectra, different peak series were found and we can readily count out the masses of the repeat unit of each polymer by subtracting a peak's mass value from the next peak in the same series. The observed and the calculated masses of the polymers' repeat unit are shown in Table 4. The fairly matching data suggest

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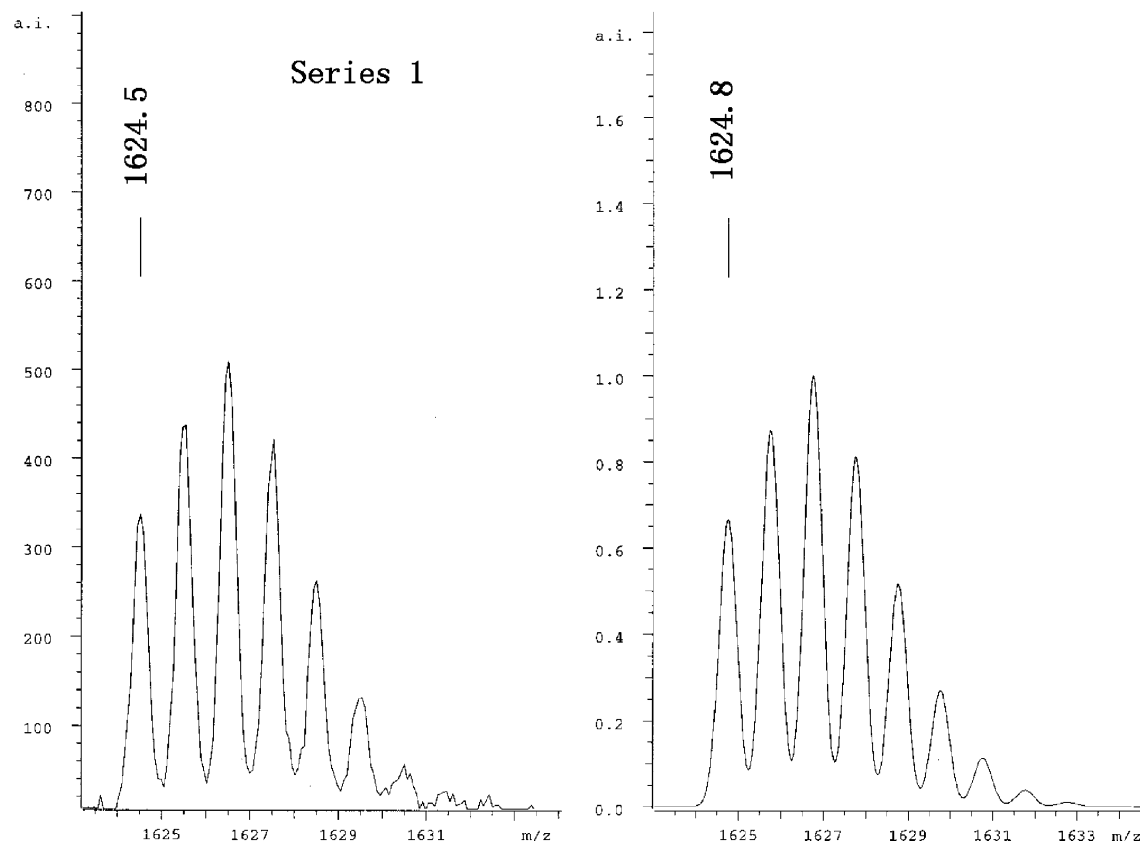


Figure 2. Experimental (left) and theoretical (right) isotope pattern for P4,  $C_{114}H_{102}N_6Cl_2$ .

Table 4. Observed and Calculated Monoisotopic Masses of the Polymers' Repeat Unit

polymers	elemental composition	$M_{cal}^a$	$M_{obs}^b$
P1	$C_{45}H_{55}N_1$	609.4	609.4 (six series observed)
P2	$C_{25}H_{32}$	332.3	332.3 (one series observed)
P3	$C_{53}H_{58}N_2$	722.5	334.1 (four series observed)
P4	$C_{19}H_{17}N_1$	259.1	259.1 (four series observed)
P5	$C_{54}H_{54}$	702.4	702.4 (three series observed)
P6	$C_{49}H_{68}S_2$	720.5	720.5 (one series observed)
P7	$C_{46}H_{59}N_5O_4$	745.5	745.5 (one series observed)

<sup>a</sup> Calculated value. <sup>b</sup> Observed value.

that the polymers we synthesized are the same as what we expected except for P3 (see latter part). Repeat-unit information renders MALDI-TOF MS much easier in identifying a polymer compared with other polymer identification methods such as NMR. The former can make it only by counting out the difference between two nearby peaks of a same series in seconds while the latter does it by searching for the characteristic peaks of the target polymer in a rather complex NMR spectrum.<sup>29</sup>

**End-Group Analysis by MALDI-TOF MS.** Although the molecular weight values from MALDI-TOF probably do not represent the actual molecular weight distribution, they do allow us to assess the mechanism of the different polymerization reactions, such as the formation of the end group. Typically, we

conduct the end-group analysis using formula 1, where  $M_{end}$

$$M_{end} = M_{peak} - M_{cat} - nM_{re} \quad (1)$$

represents the mass of the end group,  $M_{peak}$  represents the mass of the selected peak,  $M_{cat}$  represents the mass of cation ion, and  $nM_{re}$  represents  $n$  times the mass of the repeat unit.

In the case of our polymers, something has changed. Contrary to the normal soft ionization MALDI mechanism, where the analyte has no absorption at 337 nm and ionization usually takes place via cation attachment,<sup>30</sup> our conjugated polymers show resonant absorption. This may lead to the formation of radical ions  $[M]^{\cdot+}$  by photoionization instead of cationized species, e.g.,  $[M + Na]^+$ ,  $[M + K]^+$ , or  $[M + H]^+$ . It is in accordance with other groups' studies on poly(*p*-phenylenes)<sup>31</sup> and polythiophenes.<sup>32,33</sup> Therefore, in some of these seven polymers formula 1 changes into formula 2, where  $M_{elec}$  represents the mass of an

$$M_{end} = M_{peak} - M_{elec} - nM_{re} \quad (2)$$

electron, which is so tiny that can be neglected.

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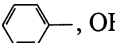

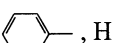
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(32) Langeveld, B. M. W.; Janssen, R. A. J.; Spiering, A. J. H.; Dongen, J. L. J. *Chem. Commun.* **2000**, 81.

(33) Jayakannan, M.; Dongen, J.; Janssen, R. A. J. *Macromolecules* **2001**, *34*, 5386.

(29) Robinson, K. L.; Vamvakaki, M.; Lascelles, S. F.; Armes, S. P. *Polymer* **2000**, *41* (24), 8501.

Table 5. End-Group Analysis of Polymers Studied

Polymer	Residual mass	Proposed end-group	Configuration	Remarks
P1	(1)94	 , OH	E-A(BA) <sub>n</sub> -E	[M] <sup>+</sup>
	(2)154	2 	E-A(BA) <sub>n</sub> -E	[M] <sup>+</sup>
	(3)78	 , H	E-(AB) <sub>n</sub> -E	[M] <sup>+</sup>
	(4)0	-----	(AB) <sub>n</sub>	[M] <sup>+</sup>
	(5)2	2H	E-B(AB) <sub>n</sub> -E	[M] <sup>+</sup>
	(6)18	H, OH	E-(AB) <sub>n</sub> -E	[M] <sup>+</sup>
P2	2	2H	E-(AB) <sub>n</sub> -E	[M] <sup>+</sup>
P3	(1)0	-----	(B) <sub>n</sub>	[M] <sup>+</sup>
	(2)390	2H	E-A(B) <sub>n</sub> -E	[M] <sup>+</sup>
	(3)778	2H	E-A(B) <sub>n</sub> A-E	[M] <sup>+</sup>
	(4)516	H, I	E-A(B) <sub>n</sub> -E	[M] <sup>+</sup>
P4	(1)70	2Cl	E-(A) <sub>n</sub> -E	[M] <sup>+</sup>
	(2)93	2Cl	E-(A) <sub>n</sub> -E	[M+Na] <sup>+</sup>
	(3)36	H, Cl	E-(A) <sub>n</sub> -E	[M] <sup>+</sup>
	(4)2	2H	E-(A) <sub>n</sub> -E	[M] <sup>+</sup>
P5	(1)2	2H	E-A(BA) <sub>n</sub> -E	[M] <sup>+</sup>
	(2)2	2H	E-(AB) <sub>n</sub> -E	[M] <sup>+</sup>
	(3)81	H, Br	E-(AB) <sub>n</sub> -E	[M+H] <sup>+</sup>
P6	2	2H	E-(AB) <sub>n</sub> -E	[M] <sup>+</sup>
P7	0	-----	(AB) <sub>n</sub>	[M] <sup>+</sup>

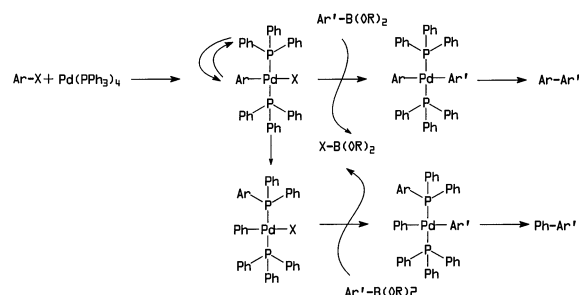
On the basis of the spectrum, we conducted end-group analysis of polymer P1: six series of peaks are observed in the spectrum with the same repeat-unit mass ( $m/z$  609). We chose the peak of  $m/z$  1645.1 first. It is considered to be a  $n = 2$  oligomer. Thus, the mass of the end group is calculated using formula 2:  $M_{\text{end}} = 1645.1 - 2 \times 609.4 = 426.3$ , which is composed of 332.3 (mass of coupling part A), 17, and 77. Therefore, we deduced the actual mass of end group is 17 and 77, and the polycondensation configuration of this series is E-A(BA)<sub>n</sub>-E, where E represents

the end group and A and B represent the two coupling parts.. The peaks  $m/z$  1705.1, 1906.2, 1828.1, 1497.9, and 1846.2 are of series 2–6, respectively. Through the similar process above, we obtained their end groups and configurations (see Table 5.). This is the usual way of end-group analysis by which we determined all of the seven polymers' end groups. The results are shown in Table 5.

When the elemental composition of a compound is fixed, its isotopic distribution is ascertainable. Different elemental composi-



Scheme 1. Mechanism of Aryl–Aryl Exchange in the Suzuki Coupling Reaction



tions have different distributions although they may have the same accurate mass. On the other hand, isomers may also obscure one's deduction for end groups. However, there are specific end groups in the specific synthetic reaction. The knowledge of the synthetic procedure and precursor compounds greatly helps in deducing end-group structures. For example, the end groups of the P1 series(1) could be  $-H$  and  $-C_6H_5$  or their isobaric structures such as two  $-C\equiv C-CH_3$ . It is reasonable for  $-C_6H_5$  coming from the aryl–aryl exchange while the latter could find its origin from neither synthetic reaction nor precursor compounds. So we can confirm the proposed end groups by comparing the observed isotopic distribution with the theoretical one. The theoretical and the observed isotopic distributions of P4 end group are shown in Figure 2.

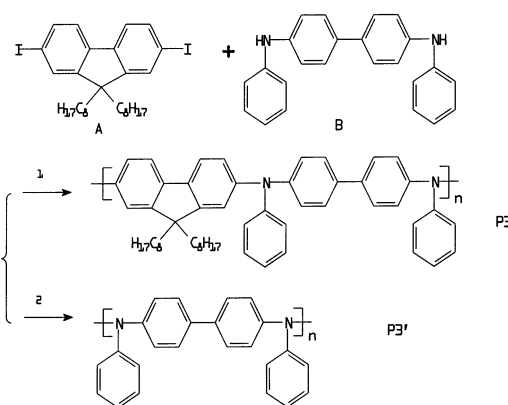
Typically, the Suzuki coupling reaction may have four polycondensation configurations:  $E-A(BA)_n-E$ ,  $E-(AB)_n-E$ ,  $E-B(AB)_n-E$ , and  $(AB)_n$  macrocycles. The detailed configurations of these seven polymers are shown in Table 5.

**Polymer 1.** Six series were observed. In three series, we found the existence of a phenyl group. We considered it came from the catalyst  $Pd(PPh_3)_4$ . The Suzuki coupling reaction occurs in three consecutive steps: oxidative additions of aryl halides to the palladium center, transmetalation of arylboronic derivatives, and reductive elimination of organic partners to yield biaryls ( $Ar-Ar'$ ).<sup>34</sup> Reports in the literature describe the occurrence of aryl–aryl exchange between the triphenylphosphine ligands and the palladium center in  $Ar-Pd(PPh_3)_2-X$  to produce  $Ph-Pd[(PPh_2Ar)(PPh_3)]-X$  (Scheme 1).<sup>33,35–37</sup> When the latter species reacts with  $Ar'-B(OR)_2$  during transmetalation, it results in the formation of unwanted  $Ph-Ar'$  instead of  $Ar-Ar'$ . In our study, this exchange resulted in production of chains with a phenyl end group. A macrocycle is found in series 4. Hydrogen and hydroxyl are common end groups in many polymers as well as in series 5 and 6.

**Polymers 2 and 6.** Only one series was observed in these two polymers and the end groups are two hydrogen atoms. The polymers formed a radical ion.

**Polymer 3.** There are four series in the spectrum. This is a special polymer in our study. We intended to synthesize the target polymer P3 following the route shown in Scheme 2.

Scheme 2. Synthetic Route for Polymer P3



The repeat-unit mass of wanted polymer P3 should be  $m/z$  722, but we observed  $m/z$  334 from the spectrum. We suggest that the reaction did not proceed following route 1 to produce target polymer P3 but produced P3' by route 2. Therefore, we deduced the end group on the basis of P3'. Series 1 is a macrocycle. The factor A did not act as the coupling factor but terminated the chain with the end groups 2H for series 2 and 3 and H and I for series 4 (Table 5.). The result came as a surprise to us. On the other hand, it deeply proved the outstanding capability of MALD-TOF MS in identifying unknown polymers.

**Polymer 4.** Four series were found. Three of the series contain chlorine atoms, which are considered to be introduced by the abundant  $Bu_4NCl$  in the previous preparation reaction. Series 1 is terminated with a radical cation while series 2 is the former's sodium cationized species. Series 3 is terminated with a hydrogen and chlorine atoms and series 4 with two hydrogen atoms.

**Polymer 5.** There are three series observed. Series 1 and 2 are terminated with two hydrogen atoms and series 3 is terminated with a hydrogen and bromine atoms. The ionization of series 3 is by protonation while series 1 and 2 are by radical cationization.

**Polymer 7.** One series was found whose residual mass is 0. This means the structure is a macrocycle, which is typical in the Suzuki coupling reaction.

## CONCLUSION

Seven polymers with blue light-emitting activity were synthesized by the Suzuki coupling reaction and studied. GPC was used to acquire the molecular weights and MALDI-TOF MS was used to obtain the repeat-unit and end-group structure information of the polymers. The experimental repeat units are the same as what we designed. Hydrogen is the most common end group in this series of polymers. Aryl–aryl exchange was found to introduce phenyl in the Suzuki coupling reaction to terminate the chain-growing reaction. We also identified an unexpected polymer. Our study confirms the usefulness of MALDI-TOF MS for polymer structure characterization. With the structure information deduced from MALDI-TOF spectra, we can understand more about the mechanism of polycondensation and gain a deeper insight in the limiting side reactions, which is helpful in improving material

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properties and enlightening the synthesis of new functional polymers. That will have great impact on the polymer industry.

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