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## Molecular mass determination of polyamic acid ionic salt by size-exclusion chromatography

P. Santhana Gopala Krishnan<sup>a</sup>, S. Veeramani<sup>a</sup>, Rohit H. Vora<sup>a,b,\*</sup>, Tai-Shung Chung<sup>a,c</sup>,  
Shun-Ichiro Uchimura<sup>d</sup>, Hatsuo Sugitani<sup>e</sup>

<sup>a</sup>*Polyimide Group: Advanced Polymers and Chemicals Cluster, Institute of Materials Research and Engineering, 3 Research Link, Singapore 117 602, Singapore*

<sup>b</sup>*Department of Materials Science, National University of Singapore, 10 Kent Ridge Crescent, Singapore 129260, Singapore*

<sup>c</sup>*Department of Chemical & Environmental Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore 129260, Singapore*

<sup>d</sup>*HD Micro Systems, Yamazaki R&D Center, 13-1, Higashi-cho-4-chome, Hitachi-shi, Ibaraki, 317-8555, Japan*

<sup>e</sup>*Chemical and Physical Analysis Center, Nikka Techno Service Co., Ltd, 13-1, Higashi-cho-4-chome, Hitachi-shi, Ibaraki, 317-8555, Japan*

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### Abstract

A methodology was developed for the determination of molecular weight averages of polyamic acid ionic salt (PAS) by size-exclusion chromatography (SEC). Polystyrene standards were used for calibration and THF-DMF 1:1 by volume containing 0.06 M LiBr and 0.06 M H<sub>3</sub>PO<sub>4</sub> was used as the mobile phase. The proposed methodology was found to be reproducible.

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### 1. Introduction

Aromatic polyimides are extensively used in the microelectronics industry as interdielectric layers, passivation layers and  $\alpha$ -particle barriers, because of their excellent chemical and physical properties [1–4]. Most aromatic polyimides are not processable due to their inability to dissolve in organic solvents and high glass transition temperature or high melting point. Therefore, they are usually processed in soluble precursor form, such as polyamic acid,

polyamic ester or polyamic acid ionic salt (PAS) containing (meth)acrylate moiety, followed by chemical or thermal imidisation or by UV curing depending upon the precursor chosen. Both solution viscosity and molecular weight of these precursors, in particular polyamic acid and PAS, vary depending upon the storage conditions and moisture present in the solutions, thus causing serious problems in quality control and fabrication process. Therefore, it is necessary to determine the molecular weight of these precursors. Methods for determining the molecular weights of both polyamic acid [5–8] (Fig. 1a) and polyamic acid ester [9–13] (Fig. 1b) have been extensively studied. Size-exclusion chromatography

\*Corresponding author. Fax: +65-6776-3604.

E-mail address: rohitvora@nus.edu.sg (R.H. Vora).

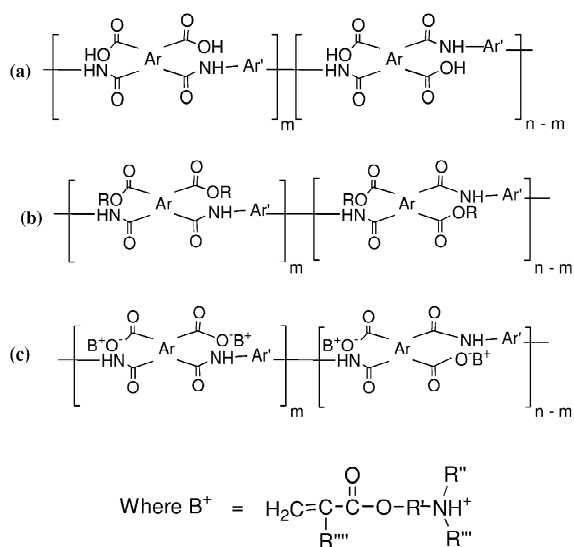


Fig. 1. Structure of (a) polyamic acid, (b) polyamic acid ester, and (c) polyamic acid ionic salt (PAS).

(SEC) for determining the molecular weight of PAS (Fig. 1c) has not yet been reported. The objective of this study was to propose a methodology for the molecular weight determination of PAS and to check its reproducibility.

## 2. Experimental

### 2.1. Materials

Formulated PAS solution containing photosensitiser and other ingredients was obtained from Hitachi-DuPont MicroSystems, Japan. The generic structure of the PAS is shown in Fig. 1c. Anhydrous lithium bromide (LiBr, 99.995+ %) and phosphoric acid ( $\text{H}_3\text{PO}_4$ , 85%) were received from Aldrich and Ashland, respectively. HPLC grade tetrahydrofuran (THF), *N,N*-dimethyl formamide (DMF) and 4A molecular sieves were from Fisher Scientific. All chemicals were used as received except molecular sieves and lithium bromide, which were dried at 200 °C for 48 h in an air-circulating oven.

### 2.2. Characterisation

Solubility was evaluated using the following method. PAS was added into the solvent and dispersed thoroughly. After the mixture was swayed continuously for ~1 h at room temperature, solubility was characterised. Flow time was measured using an Ubbelohde viscometer by measuring the time taken for a fixed volume of the solvent to flow at 25 °C.

The molecular weight of PAS was determined using a Waters system containing a Waters 2690 separation module and a Waters 2487 UV detector. A series of ten narrow distribution polystyrene (PS) standards (Polyscience Inc. and Polymer Laboratories) was employed to generate the calibration plot. The peak molecular weights of these standards were 2 000 000, 900 000, 488 400, 400 000, 320 000, 200 000, 80 000, 30 000, 12 900 and 4000. Polymer concentrations of 2.5 mg/ml (for 4000 and 12 900 MW standards), 1.0 mg/ml (for 30 000, 80 000 and 200 000 MW standards) and 0.5 mg/ml (for the remaining standards) were used. Gelpack GL-S 300 MDT-5 (Hitachi) columns packed with PS gel having an exclusion limit of  $2 \times 10^8$  PS molecular weight (column of size 8 mm I.D.  $\times$  300 mm) were used. Three columns were used in series and were housed in an oven maintained at 40 °C. Exclusion ( $V_0$ ) and total retention ( $V_t$ ) volumes are about 19 and 39 ml, respectively, for both eluents. The number of theoretical plates was determined by using 0.25% (w/v) anisol and are 25 698 and 16 275 for the THF:DMF and THF eluent systems, respectively. The wavelength of UV detector was 270 nm and a flow-rate 1 ml/min was used. Based on our experience, for the THF:DMF eluent mixture, a UV detector is to be preferred over RI detector because of its high sensitivity, high resolution and stability of the base line. SEC solvents were filtered through a 0.2- $\mu\text{m}$  Teflon filter (Millipore). PAS solutions were filtered through 0.45  $\mu\text{m}$  (PTFE PP 13-mm filter; Lida Manufacturing) before injection. Sample concentration, injection volume and mobile phase are discussed in the following section. Elution curves are not adjusted for minor rate fluctuations detected using a flow-rate marker. All the molecular weights reported in this paper are in equivalent to polystyrene.

### 3. Results and discussion

PAS at 0.5% (w/v) concentration was found to be completely soluble in DMF alone but insoluble in THF, which is widely used in SEC measurements as a mobile phase (Table 1). Even though DMF is a good solvent for PAS, it was found to cause high column pressure ( $>950$  p.s.i. is not recommended by the column manufacturer) because of its viscous nature as also evident from the flow time measurements (Table 1). This necessitated a search for a solvent mixture which causes optimum column pressure at the same time as dissolving PAS completely. THF:DMF (1:1, v/v) solvent mixture was found to cause less column pressure ( $\sim 650$  p.s.i.) when compared to DMF alone without compromising the solubility of PAS. This solvent mixture was also reported to be a suitable mobile phase for polyamic acid [14].

Viscosity–concentration profiles ( $\eta_{inh}$  vs.  $C$ ) of PAS in this solvent mixture showed a linear relationship between 0.2 and 0.5 g/dl, but showed a positive deviation from linearity upon further dilution as shown in Fig. 2. This indicated that PAS exhibited typical polyelectrolyte effect similar to polyamic acids. Upon very large dilution, trace amount of moisture present in the solvent mixture might have hydrolysed the polymer chain, which resulted in the formation of new carboxylic acid groups. Furthermore, trace amount of amine present in the solvent mixture might have removed protons from these newly formed carboxylic acid groups resulting in uncompensated carboxylate anions. This might have caused repulsion between the like charges leading to chain expansion resulting in polyelectrolyte effect. To verify the above argument,  $\eta_{inh}$  versus concen-

Table 1  
Flow time of solvents and solubility of PAS

Solvent	Flow time (s)	SD	Solubility <sup>a</sup>
DMF	93.3	0.0071	Soluble
THF	59.8	0.0057	Insoluble
THF:DMF (1:1)	73.2	0.0141	Soluble

<sup>a</sup> 5 mg of PAS in 1 ml.

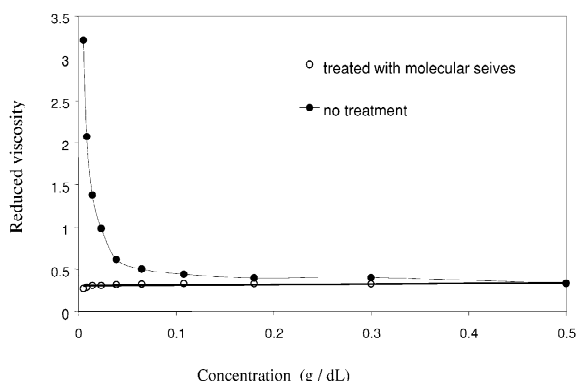


Fig. 2. Plot of inherent viscosity versus concentration of PAS.

tration of PAS was plotted using THF:DMF solvent mixture (1:1, v/v) (without LiBr and  $H_3PO_4$ ) which was stored in molecular sieves of 4A for few days. In this case, no polyelectrolyte effect was observed and intrinsic viscosity was found to be 0.31 dl/g at 25 °C (Fig. 2). This behavior could be explained on the basis that the treatment of molecular sieves might have removed not only moisture but also basic impurities present in the solvent mixture. As a result, the formation of new carboxylic acid groups or its anion (uncompensated) was prevented. It has been reported in the literature [14] that the polyelectrolyte effect in polyamic acid can be eliminated by the addition of 0.06 M LiBr and 0.06 M  $H_3PO_4$ . This was found to hold good for PAS also (Fig. 3).

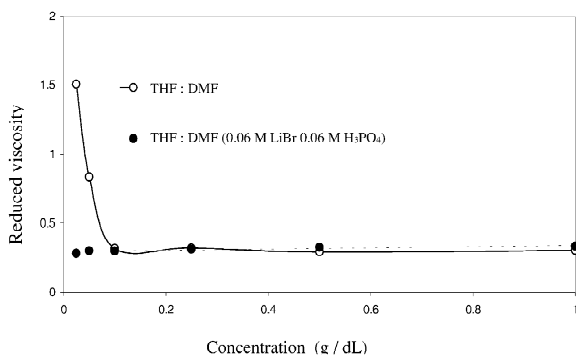


Fig. 3. Plot of inherent viscosity versus concentration of PAS.

Table 2  
Solubility of PAS in THF:DMF (1:1) containing 0.06 M LiBr and 0.06 M H<sub>3</sub>PO<sub>4</sub>

Sample concentration, mg/ml	Observation
5.0	Partially soluble
4.0	Partially soluble
3.0	Partially soluble
2.0	Partially soluble
1.0	Completely soluble

THF:DMF 1:1 (v/v) containing 0.06 M LiBr and 0.06 M H<sub>3</sub>PO<sub>4</sub> was used as the mobile phase for this study and intrinsic viscosity was found to be 0.34 dl/g at 25 °C.

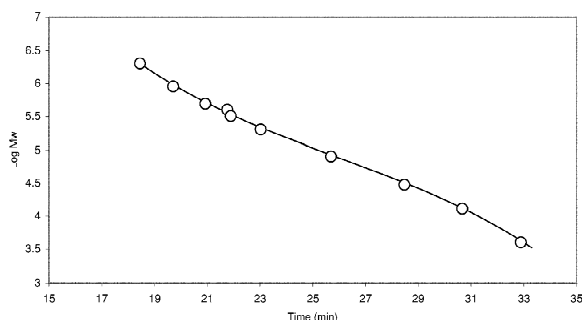


Fig. 4. SEC calibration graph for PS standards.

The solubility of PAS at various concentrations in THF:DMF (1:1, v/v) solvent mixture containing 0.06 M LiBr and 0.06 M H<sub>3</sub>PO<sub>4</sub> is given in Table 2. PAS was found to be completely soluble at a concentration of 1 mg/ml. Therefore, this sample concentration was used for SEC analysis.

The SEC calibration graph for PS standards in THF:DMF (1:1, v/v) solvent mixture is given in Fig. 4. This calibration plot was used to calculate the molecular weights of PAS samples. When PAS was eluted in THF:DMF alone, an additional peak appeared and eluted at longer time than in THF:DMF containing LiBr and H<sub>3</sub>PO<sub>4</sub> (Fig. 5). It was attributed to the adsorption of PAS in the column. Similar adsorption on GPC column was reported for polyamic acids [7,15,16]. Nefedov [17] has reported that addition of LiBr and H<sub>3</sub>PO<sub>4</sub> to the mobile phase suppressed the polyelectrolyte, adsorption and electrostatic repulsion effects. It is also evident from Fig. 5 that LiBr and H<sub>3</sub>PO<sub>4</sub> are essential for better chromatogram of PAS.

Figs. 6 and 7 show the effect of injection volume and sample concentration on SEC curves. Even though the concentration dependence in SEC is anticipated, it is especially significant for polymers having molecular weights greater than 10<sup>6</sup>. As the molecular weight of PAS used in this experiment is less than 10<sup>5</sup>, the concentration dependence was not predominant. This is evident from the same retention volume (Figs. 6 and 7) irrespective of the amount of

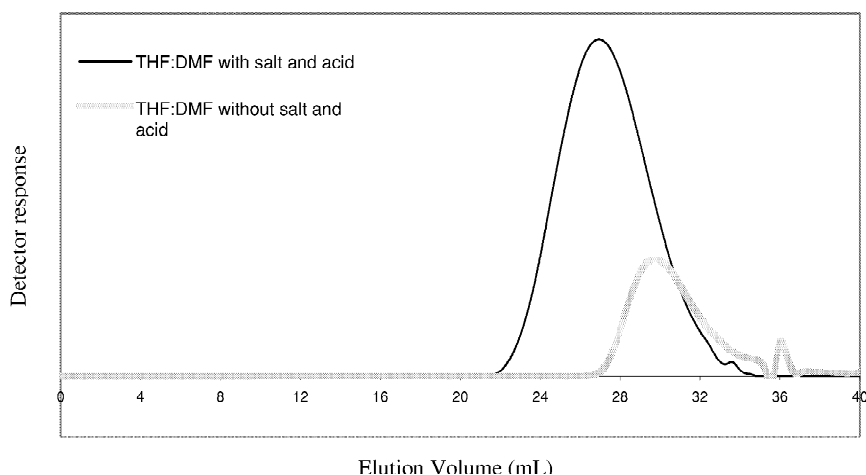


Fig. 5. Effect of LiBr and H<sub>3</sub>PO<sub>4</sub> on SEC curves of PAS.

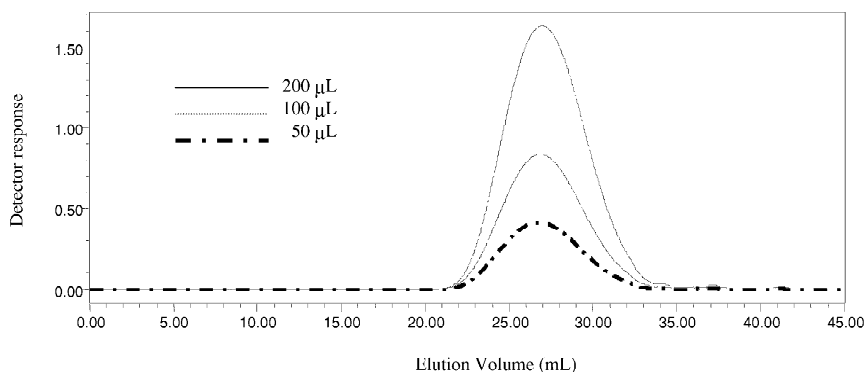


Fig. 6. Effect of injection volume on SEC curves of PAS.

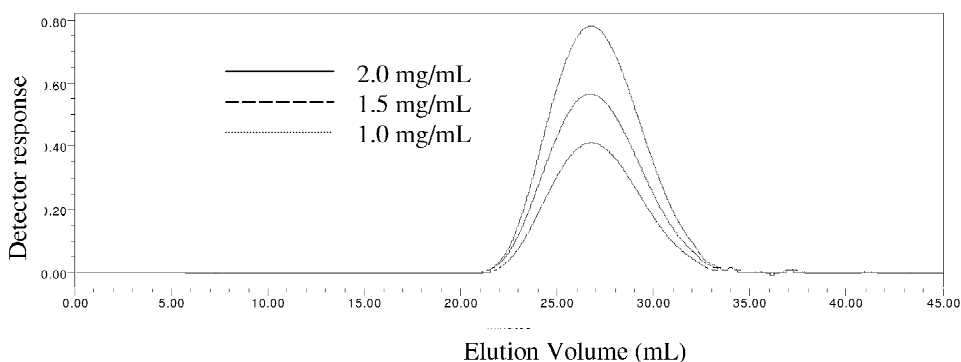


Fig. 7. Effect of sample concentration on SEC curves of PAS.

sample injected into SEC. However, peak area increased with increase in the amount of sample injected in both the cases. Molecular weight distribution (MWD) curves were found to be unimodal. Molecular weights of PAS determined at different injection volumes and concentrations are given in Tables 3 and 4, respectively, and were quite similar. Reproducibility of SEC results was checked by injecting 200 µl of sample (containing 1 mg of PAS per ml of SEC solvent mixture) three times and was found to produce similar chromatogram (Fig. 8).

Table 5 shows the PAS molecular weights of three runs, which are quite comparable. Table 6 shows the molecular weight of PAS stored at RT. Molecular weight was determined by injecting 200-µl sample (containing 1 mg of PAS per ml of SEC solvent mixture). Determined  $\bar{M}_n$ ,  $\bar{M}_w$  and  $\bar{M}_z$  were found to decrease with increasing storage time showing that they were not stable at RT.

The proposed methodology for the determination of molecular weight averages of PAS by SEC was found to be reproducible.

Table 3  
Molecular weights of PAS at 1-mg/ml concentration

Injection volume, µl	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_z$
50	55 260	32 140	84 720
100	53 880	31 420	82 440
200	51 900	30 030	79 560

Table 4  
Molecular weights of PAS at 50-µl injection volume

Concentration (mg/ml)	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_z$
1.0	55 260	32 140	84 720
1.5	56 400	33 100	86 220
2.0	55 350	32 400	84 530

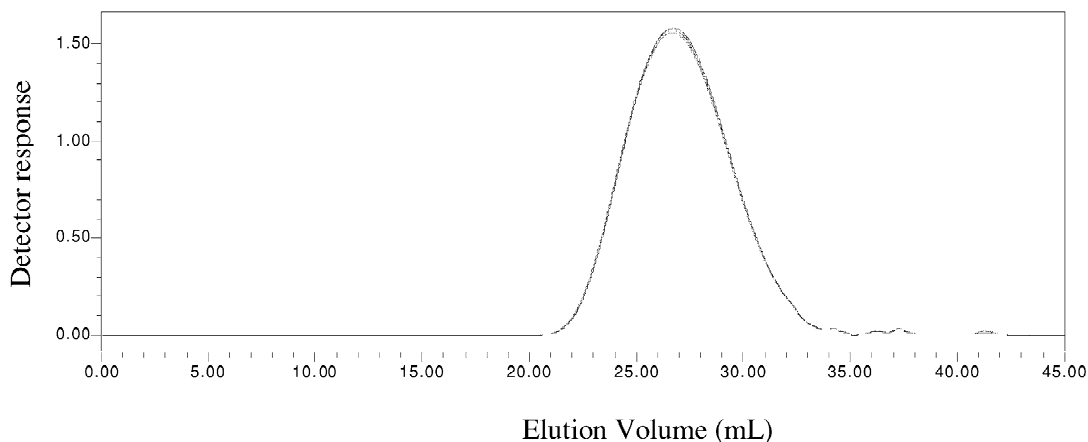


Fig. 8. SEC curves of PAS showing reproducibility.

Table 5  
Molecular weights of PAS at 1-mg/ml concentration and 200- $\mu$ l injection volume

Run No.	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_z$
1	57 050	32 230	89 200
2	57 060	32 360	89 000
3	56 160	31 970	87 300
SD	516.753	198.578	1044.03

Table 6  
Molecular weights of PAS stored at RT

Storage time (h)	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_z$
0	63 830	43 700	91 530
24	62 970	43 240	90 170
48	62 410	42 880	89 530
168	61 570	42 170	88 690

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