

# **Laser desorption/ionization on the layer of graphene nanoparticles coupled with mass spectrometry for characterization of polymer**

**Minghua Lu,<sup>a</sup> Yongquan Lai,<sup>a</sup> Guonan Chen,<sup>b</sup> and Zongwei Cai<sup>\*a</sup>**

<sup>a</sup> *Department of Chemistry, Hong Kong Baptist University, Kowloon Tong, Kowloon, Hong Kong  
SAR, China*

<sup>b</sup> *Ministry of Education Key Laboratory of Analysis and Detection for Food Safety, Fuzhou  
University, Fuzhou 350002, Fujian, China*

Supplementary Information

## EXPERIMENTAL SECTION

**Chemicals and materials.** PPG standard samples including average molecular weight of 425 Da (PPG-425), 1000 Da (PPG-1000), 2000 Da (PPG-2000) and 3500 Da (PPG-3500) were purchased from Sigma-Aldrich (St. Louis, MO). PS with average molecular weight of 500 Da (PS-500) and 2500 (PS-2500) Da were supplied by Sigma-Aldrich (St. Louis, MO) and Sigma-Aldrich (Bellefonte, PA), respectively. PMMA samples with average molecular weight of 720 Da (PMMA-720) and 2000 Da (PMMA-2000) were obtained from American Polymer Standards (Mentor, OH). Silver trifluoroacetate (AgTFA),  $\alpha$ -cyano-4-hydroxycinnamic acid (CHCA) and 2,5-dihydroxy-benzoic acid (DHB) were purchased from Sigma-Aldrich (St. Louis, MO). Methanol, ACN and acetone, and Tetrahydrofuran (THF) were of HPLC grade and supplied by TEDIA (Fairfield, OH). Anhydrous ethanol was provided by Acros Organics (New Jersey). Peptide calibration standard II used for calibration of TOFMS instrument was obtained from Bruker Daltonics (Bruker, Germany). The water used in all experiments was prepared from a Milli-Q water purification system (Millipore, Milford, MA). Graphene nanopowder was obtained from Graphene Laboratories Inc. (Reading, MA).

**Sample preparation.** Unless otherwise stated, the polymer samples of PPG including PPG-425, PPG-1000, PPG-2000 and PPG-3500 were individually dissolved in a mixture of acetone/water (4/1, v/v) with concentration from 0.1 to 0.8 mg/mL. PS-500 and PS-2500 were prepared at concentration of 0.8 mg/mL by dissolving corresponding chemical in a mixture of THF/water (4/1, v/v). The acetone was used as solvent for the preparation of PMMA-720 and PMMA-2000 at concentration of 1.0 and 4.0 mg/mL, respectively. The conventional matrix solutions including DBH and CHCA were prepared by dissolving a matrix material into the same solvent with polymers at concentration of 10 mg/mL. The cationization reagent AgTFA used for PS was prepared at 1.0 mg/mL in THF. Graphene nanopowder (2 mg) was dispersed in a 1 mL solution of ethanol/water (1:1, v/v) and sonicated for 5 min prior to use. Graphene coating was prepared by applying 1  $\mu$ L suspension of graphene to a MALDI target plate and allowing the droplets to dry. PPG and PMMA samples were analyzed by pipetting 1  $\mu$ L solution of samples onto the graphene coating and allowed to dry under ambient conditions. PS samples were analyzed by pipetting 1  $\mu$ L mixture solution of polymer and AgTFA onto the graphene coating and allowed to dry under ambient

conditions. For the analysis of PPG by conventional MALDI method, NaCl was added to the sample solution to enhance cationization.

**Mass spectrometry analysis.** LDI on graphene coating and MALDI time-of-flight MS (TOFMS) analysis were performed on a Bruker Autoflex II mass spectrometer (Bruker Daltonics, Germany) equipped with a nitrogen laser (337 nm wavelength; 3 ns pulse width). The laser power energy was adjusted between 0% and 100% to provide the laser pulse energy between 93.8 and 121.8  $\mu\text{J}$ . Typical laser pulse energy from 10% (96.60  $\mu\text{J}$ ) to 20% (99.4  $\mu\text{J}$ ) were applied in the experiments, except where otherwise stated. The graphene coating was prepared on a MTP 384 massive target (S/N 03798) from Bruker Daltonics. Except where otherwise stated, the instrument was operated in reflectron mode with accelerating voltage, grid voltage and delayed extraction time set to 19 kV, 90% and 120 ns, respectively. Each mass spectrum was acquired as an average of 200 laser shots at 10.0 Hz frequency.

The number average molecular weight ( $M_n$ ), the weight average molecular weight ( $M_w$ ) and the degree of dispersity ( $D$ ) for all polymer samples were calculated by using the following formulas:

$$M_n = \sum (M_i N_i) / N_i \quad (\text{SE1})$$

$$M_w = \sum (M_i^2 N_i) / (M_i N_i) \quad (\text{SE2})$$

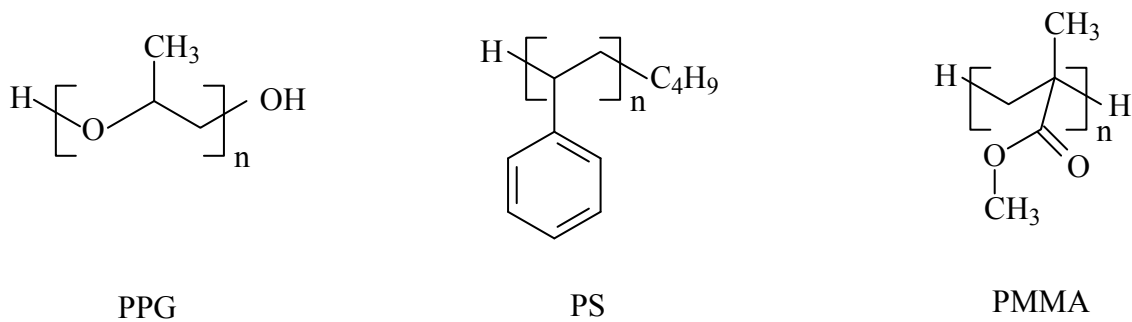
$$D = M_w / M_n \quad (\text{SE3})$$

Where  $M_i$  is the mass of oligomer  $i$ , and  $N_i$  is the peak area of oligomer  $i$  in the mass spectrum. Average molecular weights were corrected for the contribution of the cation.

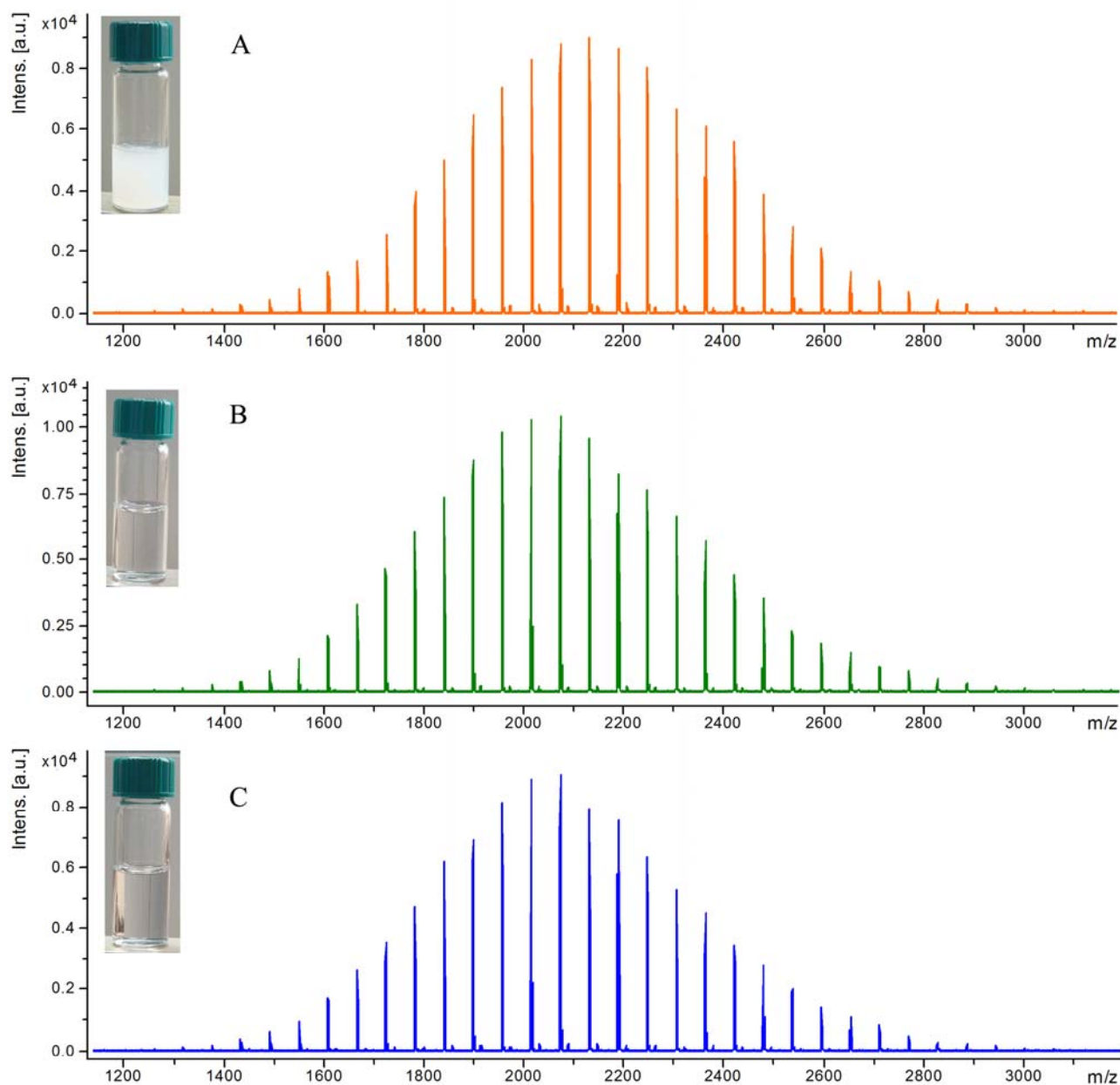
**Table S1** Molecular weight distribution of PPG and PS measured by LDI on the layer of graphene nanoparticles coupled with time-of-flight mass spectrometry.

	Measured data			Manufacturer data		
	$M_n$	$M_w$	$PD$	$M_n$	$M_w$	$PD$
PPG-425	447	460	1.03		N*	
PPG-1000	1061	1081	1.02		N	
PPG-2000	2077	2108	1.01		N	
PPG-3500	3702	3739	1.01		N	
PS-500	640	684	1.07	470	520	1.11
PS-2500	2178	2245	1.03	2440	2460	1.01

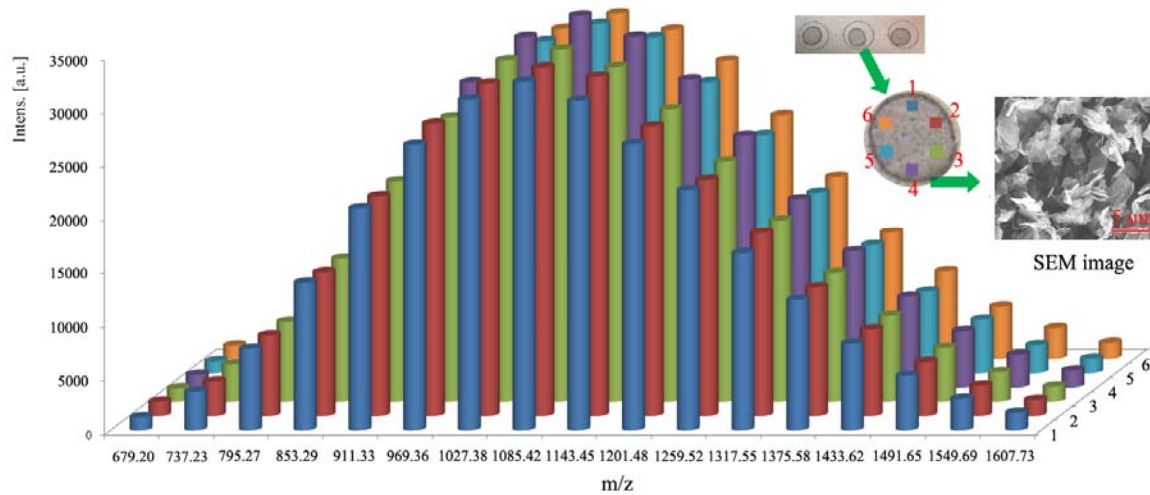
\* N represents the data not provided by manufacture.



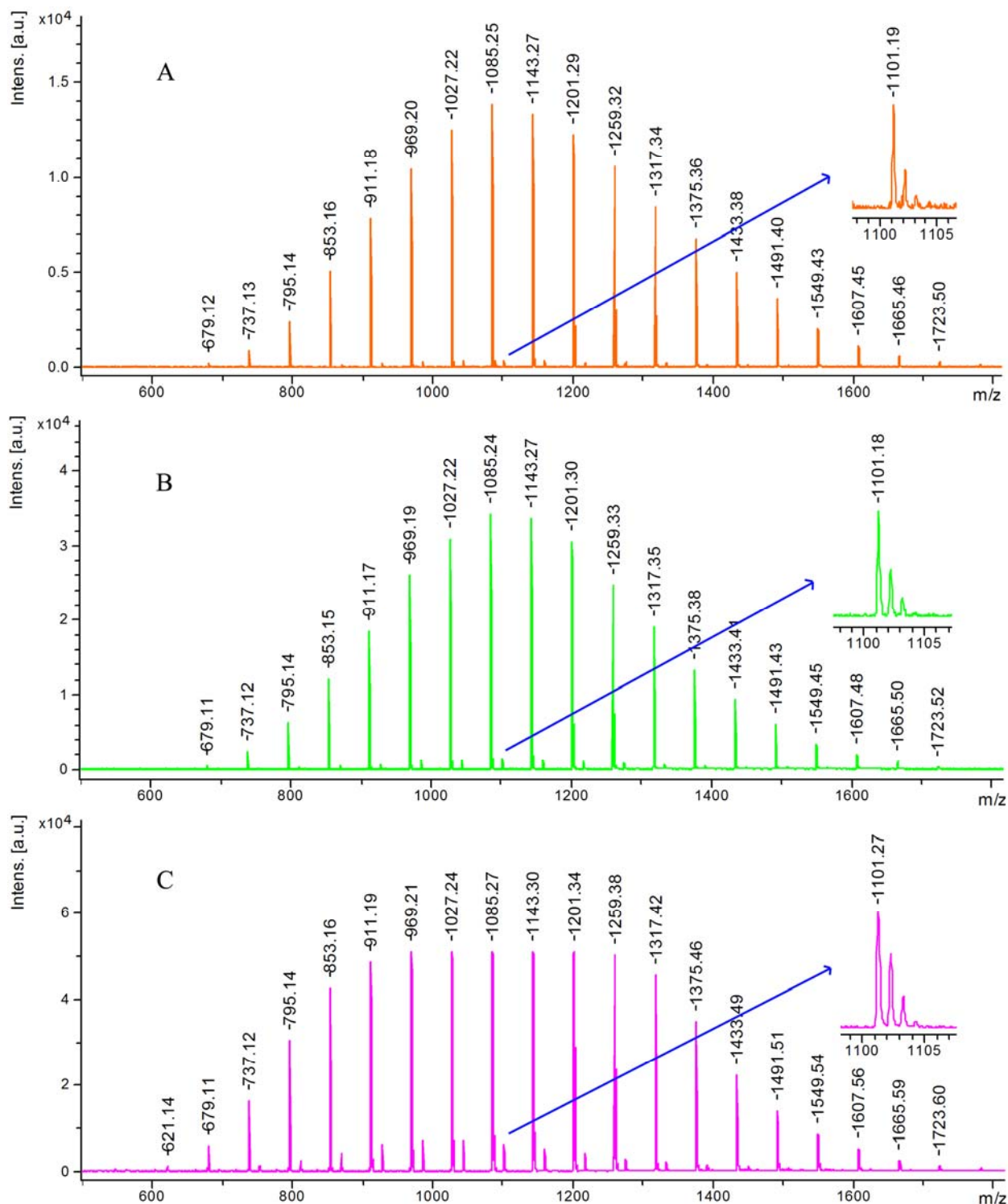
**Fig. S1** Chemical structures of the measured polymers with possible end groups.



**Fig. S2** TOFMS spectra of PPG-2000 obtained with developed method by using different solvents for sample preparation: (A) water; (B) methanol; and (C) acetone. The analysis was performed under same experimental conditions except the solvent used in sample preparation.

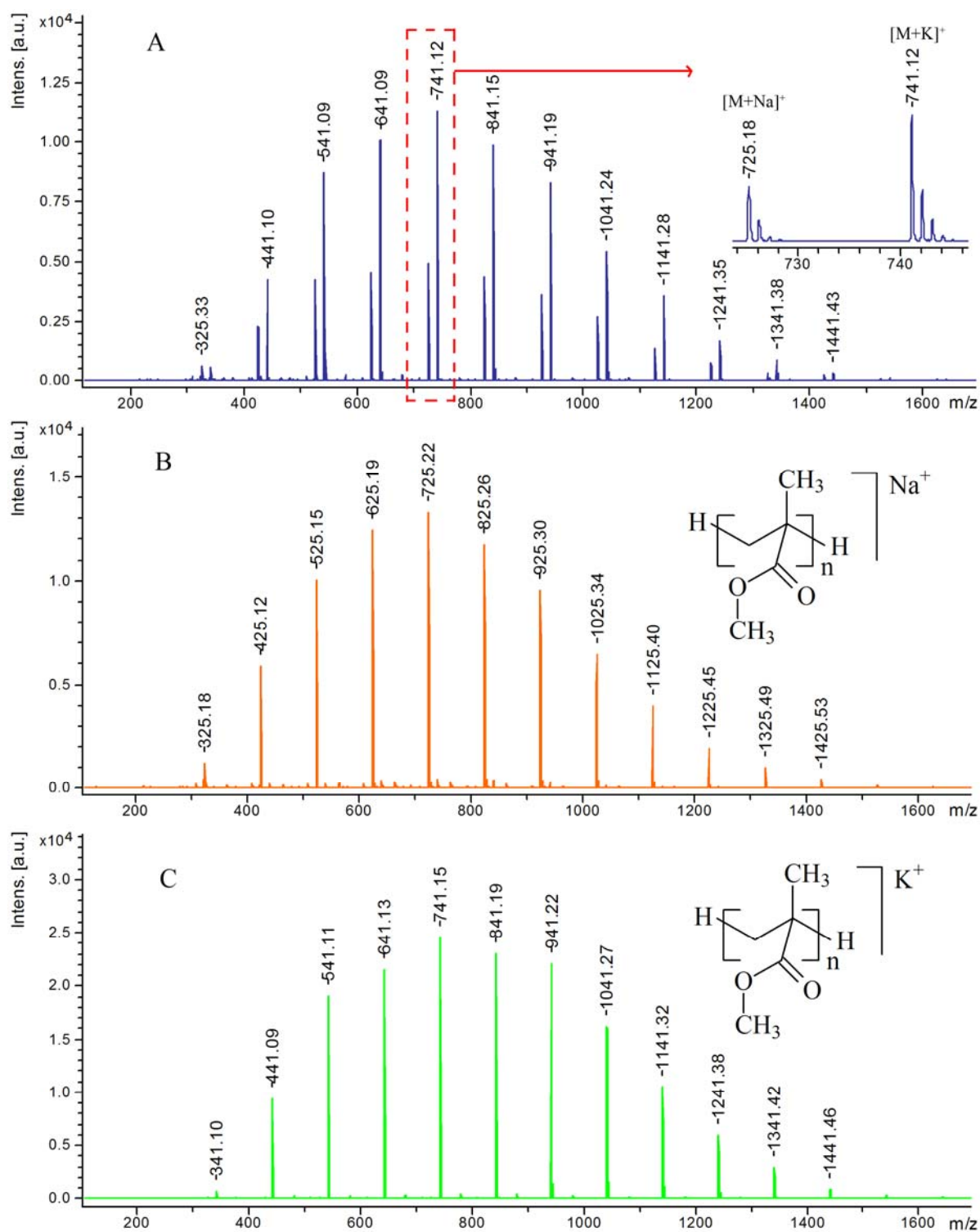


**Fig. S3** Shot-to-shot reproducibility obtained for the analysis of PPG-1000 from the analyses with LDI on the layer of graphene nanoparticles.

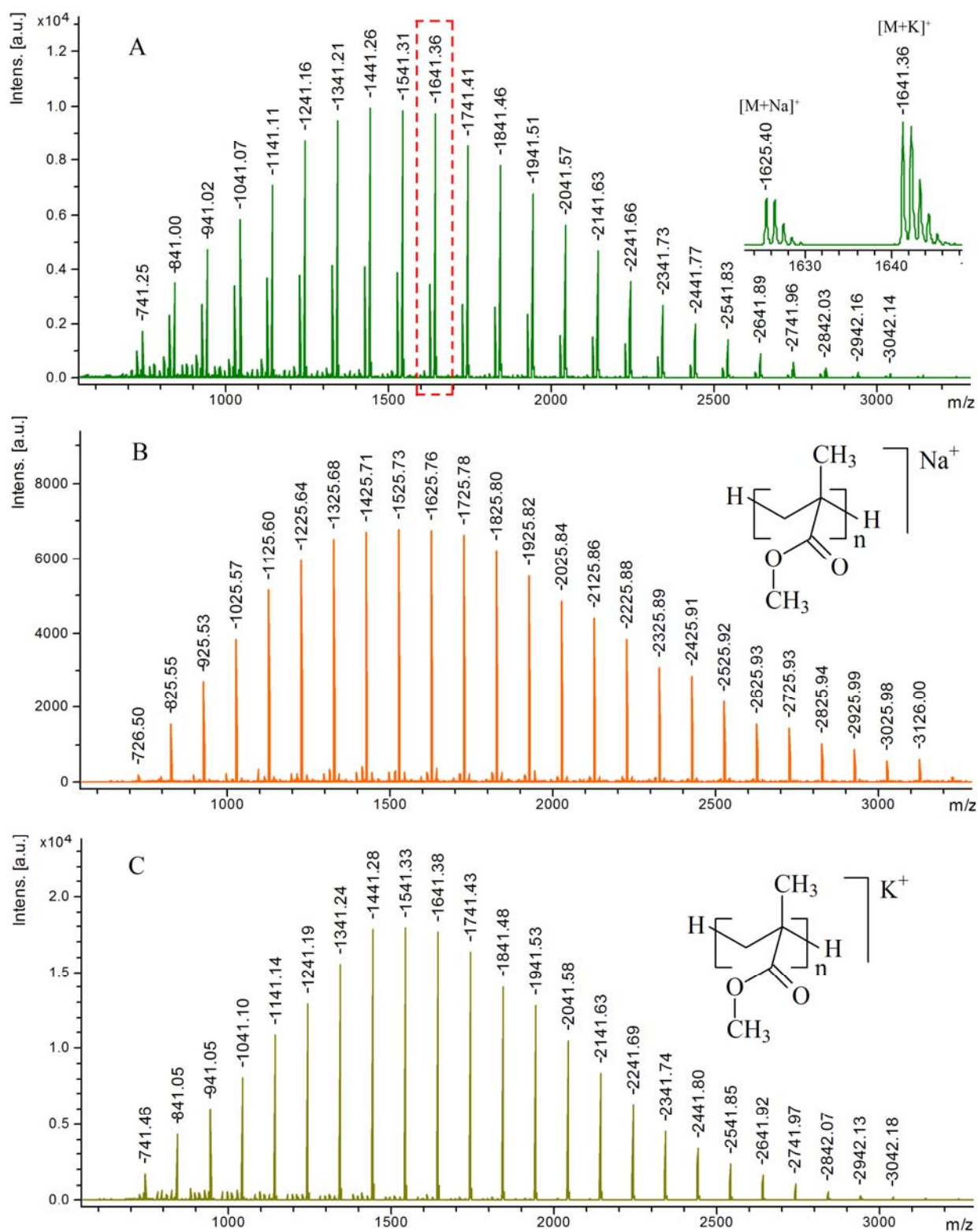


**Fig. S4** Mass spectra of PPG-1000 obtained by using LDI on the layer of graphene nanoparticles under different laser power energy: (A) 15% (98.00  $\mu$ J); (B) 20% (99.40  $\mu$ J); (C) 25% (100.8  $\mu$ J). The experiments were performed under the same conditions.





**Fig. S5** TOFMS spectra of PMMA-700 obtained by LDI on GC (A) without additional salt, (B) with sodium salt as additive, and (C) with potassium salt as additive. Laser power, accelerating voltage and delayed extraction time were set 20% (99.40  $\mu$ J), 19 kV and 60 ns, respectively.



**Fig. S6** TOFMS spectra of PMMA-700 obtained by LDI on GC (A) without additional salt, (B) with sodium salt as additive, and (C) with potassium salt as additive. Laser power, accelerating voltage and delayed extraction time were set 20% (99.40  $\mu$ J), 19 kV and 120 ns, respectively.