**Preparation of Polymethylacrylic Acid Standard Samples for
GPC Applications via a Precipitation Fractionation-Separated
Step Hydrolysis Method**

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Preparation of PMAA standard samples—Running Title

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17 **Abstract:** *A series of polymethylacrylic acid (PMAA) standard samples were prepared*
18 *from fractionated PMMA samples followed by a two-step hydrolysis. The six PMMA*
19 *standard samples with narrow molecular weight distributions were produced by free*
20 *radical polymerization and fractionated with toluene-petroleum ether. Their average*
21 *molecular weights ranged from 3.1×10^3 to 4.3×10^4 , dispersion coefficients were less*
22 *than 1.5, and their gel permeation chromatography (GPC) peak shapes were symmetrical.*
23 *The PMMA standard samples were dissolved in dioxane, and then hydrolyzed in a*
24 *saturated NaOH-methanol solution for 24 h, the methanol then evaporated, and after that*
25 *the PMMA samples were hydrolyzed in a 2 mol/L NaOH aqueous solution for 24 h. The*
26 *^1H -NMR results showed that the two-step hydrolysis degree was higher than 98.70%. The*
27 *PMAA standard samples were obtained after acidifying the hydrolysates, namely*
28 *polymethacrylic acid sodium salt, and their molecular weights were constant during the*
29 *separation process. The acid-base titration results showed the purities of the PMAA*
30 *samples were greater than 98.6%, and their molecular weight distributions were*
31 *symmetrical and narrow. The molecular weights of the PMAA were determined by the*
32 *stoichiometric relationship of the hydrolysis reaction. Compared with viscosimetry, the*
33 *results of both methods were basically the same, and their errors were less than 10%.*

34 **Keywords:** GPC, polyelectrolyte, molecular weight standard samples, polymethyl
35 methacrylate, polymethylacrylic acid

37 Introduction

38 The molecular weights and the molecular weight distributions of polyelectrolytes can
39 affect their performances.^[1, 2] Normally, they are measured using gel permeation
40 chromatography (GPC). However, the standard samples of polyelectrolytes are hard to be
41 prepared, so non-electrolyte standard samples, such as polyethylene glycol (PEG) and
42 dextran, are often applied in the determination, resulting in deviations in the

43 measurements.^[3, 4]

44 Monodisperse polymer standards can be easily obtained by living polymerization, and
45 their molecular weights can be measured by static light scattering and membrane
46 permeation.^[5] However, the synthesis of polyelectrolytes by living polymerization as
47 well as the precise determination of their molecular weights is not easy. As a result,
48 polyelectrolyte standard samples can only be obtained by indirect methods at present. In
49 1992, Mykytiuk et al.^[6] used 1-methoxy-1-trimethylsilyloxy-2-methyl propylene (MTS)
50 as the initiator and tetrabutylammonium fluoride (TBAF) as the catalyst to prepare
51 several different monodisperse polybenzyl methacrylates (PBzMA) by group transfer
52 polymerization and used GPC to measure the molecular weights. The catalytic
53 hydrogenation process of polybenzyl methacrylate was proceeded with Pd/C as the
54 catalyst in an ethyl acetate-methanol mixed solution under an atmosphere of H₂ at room
55 temperature to obtain monodisperse PMAA. In 1996, Kawaguchi et al.^[7] produced
56 poly(tertiary butyl methacrylate) by anionic polymerization in the presence of LiCl,
57 followed by a two-step hydrolysis with Si(CH₃)₃I and HBr; then the poly(tertiary butyl
58 methacrylate) was hydrolyzed to obtain monodisperse PMAA. The predecessor,
59 monodisperse poly(tertiary butyl methacrylate) was easy to synthesize, but difficult to
60 hydrolyze. So until now, commercialized polyelectrolyte standard samples are still rare.

61 The molecular weights of the monodisperse polyelectrolytes produced by the methods
62 mentioned above were calculated from the molecular weights of the predecessors. So it's
63 important to determine the molecular weight of the predecessors accurately. PMMA
64 standard samples have been commercialized. It's thus easy and accurate to determine the
65 molecular weights if we choose PMMA standard samples as predecessors to produce
66 PMAA by hydrolysis. But PMMA is hard to hydrolyze. Erhardt et al.^[8] used crown ether
67 as the phase transfer catalyst to improve the rate of hydrolysis, but it's toxic and
68 environmentally unfriendly.

69 In this article, the PMMA crude products were prepared by free radical polymerization
70 and then the crude PMMA products were precipitated and fractionated by a
71 toluene-petroleum ether separation system to get narrow distribution PMMA. Their
72 molecular weights were accurately determined by GPC. The ester groups of the narrow
73 distribution PMMA were hydrolyzed to obtain narrow distribution PMAA standard
74 samples (Scheme 1, described below). The stoichiometric relationship of the hydrolysis
75 was applied to the calibration of the PMAA standard samples. This method was simple,
76 low-cost, practical, and could yield large volumes of the standard samples.

77

78 **Experimental**

79 *Materials*

80 All reagents used in the synthesis were of analytical grade. MMA was distilled under
81 vacuum before use. The PMMA standard samples were provided by the Polymer Lab,
82 UK (Chromatograms are shown in Fig. 1). The internal diameter and the viscometer
83 constant of Ubbelohde capillary viscometer were 0.6 mm and $0.006861 \text{ mm}^2 \cdot \text{S}^2$,
84 respectively. The GPC analysis used an Agilent-1100 chromatography system (Agilent
85 Co., USA). The $^1\text{H-NMR}$ analysis used an Inova-600 nuclear magnetic resonance
86 apparatus (Varian Co., USA).

87 GPC conditions for PMMA: PLGEL mixed-C ($7.8\text{mm} \times 300\text{mm}$, $5\mu\text{m}$) GPC column.
88 RID detector. The mobile phase was tetrahydrofuran (THF). The flow rate was 1.0
89 $\text{mL} \cdot \text{min}^{-1}$. Column temperature was 25.0°C . The concentration of the sample was 1.0
90 $\text{g} \cdot \text{L}^{-1}$ (solvent was THF), injection volume was $50\mu\text{L}$.

91 GPC conditions for PMAA: PL AQUAGEL-OH mixed-M ($7.5\text{mm} \times 300\text{mm}$, $8\mu\text{m}$,
92 double column series) GPC column. RID detector. The mobile phase was phosphate
93 buffer solution ($0.10 \text{ mol} \cdot \text{L}^{-1}$, $\text{pH}=6.86$). The flow rate was $1.0 \text{ mL} \cdot \text{min}^{-1}$. The column
94 temperature was 25.0°C . The PMAA samples were dissolved in the mobile phase, and the

95 concentration of the samples were $1.0 \text{ g} \cdot \text{L}^{-1}$, injection volume was $50 \mu\text{L}$.

96

97 ***Preparation of PMMA Crude Products***

98 0.8 g azobisisobutyronitrile, 40 g methyl methacrylate and 200 g toluene were mixed
99 in a constant pressure dropping funnel, and added dropwise to a three-neck flask
100 containing 80 mL of toluene; the mixture was heated at 70°C for 2 h and then allowed
101 to cool. Three times the volume of the mixture of petroleum ether was added to
102 precipitate the PMMA completely. The PMMA precipitates were dried under vacuum at
103 60°C , yielding the largest average molecular weight PMMA crude products. Smaller
104 average molecular weights of PMMA were synthesized in the same way at 80°C and
105 90°C , respectively.

106

107 ***Precipitation Fractionation and Calibration of PMMA***

108 The PMMA crude products were dissolved in toluene (2.0%), followed by the
109 successive additions of petroleum ether with volume fractions of 0.26, 0.31, 0.39, 0.44,
110 0.50, and 0.60 of the toluene- petroleum ether separation system. The mixture was left to
111 stand for 24 h at 15°C and then separated by centrifugation. The precipitate was washed
112 twice with petroleum ether and dried under vacuum at 60°C to get the largest molecular
113 weight PMMA fraction. The supernatant was then diluted by petroleum ether again and
114 the above operations repeated to get the smaller molecular weight PMMA fractions, 6
115 from each of the three samples. The obtained PMMA fractions were fractionated
116 repeatedly until each PMMA fraction complied with the requirement of a narrow
117 molecular weight distribution ($M_w/M_n < 1.5$), with the 18 samples being combined to give
118 6 final samples.

119 The molecular weight distributions of the PMMA fractions were measured by GPC.

120 The calibration curve equation was based on PMMA standard samples.

121

122 *Hydrolysis of PMMA Standard Samples and Calibration of PMAA Standard Samples*

123 The 6 fractionated PMMA standard samples with narrow weight distributions were
124 dissolved in dioxane (10%). Then saturated NaOH-methanol was added into 50 mL of
125 the solution by the molar ratio of $n(\text{NaOH}):n(\text{ester group})$ equals 1:2. The mixture was
126 refluxed for 24 h under the protection of pure N_2 . The solvent was then evaporated, 50
127 mL NaOH aqueous solution ($2 \text{ mol} \cdot \text{L}^{-1}$) was added in and the mixture was refluxed for
128 another 24 h to complete the hydrolysis. Every 12 hours after the hydrolysis started, the
129 samples were taken to detect the extent of hydrolysis by $^1\text{H-NMR}$. The $^1\text{H-NMR}$
130 spectroscopy was carried out at 600 MHz, using a Varian Inova-600 nuclear magnetic
131 resonance apparatus. Three times the volume of methanol was added into the hydrolysate
132 to precipitate the PMAA-Na. The PMAA-Na samples were washed with methanol and
133 dissolved in 30 mL water, and then NaCl was added until the solution was saturated. 30
134 mL concentrated HCl was added into the solution to precipitate the PMAA. The
135 precipitates were then washed with HCl (6 mol/L), dried under vacuum at 60°C and the
136 PMAA standard samples were obtained. The purity of the PMAA was measured by
137 acid-base titration. 0.10g accurately weighed lab-made PMAA samples were dissolved in
138 0.10 mol/L NaOH aqueous solutions, and a few drops of phenolphthalein indicator added;
139 after that the solutions were titrated by 0.10 mol/L HCl until the color of the solution
140 changed from red to colourless. The purity value of the PMAA could be calculated
141 according to the following formula:

$$142 \quad \omega\%(\text{PMAA}) = \frac{(V(\text{NaOH}) \times c(\text{NaOH}) - V(\text{HCl}) \times c(\text{HCl})) \times M(\text{MAA})}{m(\text{PMAA})} \times 100\% \quad . \quad \text{The}$$

143 molecular weights of the lab-made PMAA standard samples were computed by the
144 hydrolysis equation and compared with experimental values measured by viscometry.

145

146 *Molecular Weight Test of Lab-made PMAA Standard Samples*

147 The six PMMA standard samples provided by the Polymer Lab, UK were hydrolyzed
148 to prepare six monodisperse PMAA standard samples in the same way. The
149 monodisperse PMAA standard samples were used to compare with the lab-made PMAA
150 standard samples. The molecular weight M_n could be calculated according to the
151 Mark-Houwink equation: $[\eta] = KM_n^a$. The efflux time of the solution, which was t , and
152 the efflux time of the solvent, which was t_0 , were measured in the Ubbelohde capillary
153 viscometer. The relative viscosity, η_r , was calculated with the formula $\eta_r = \eta / \eta_0 = t/t_0$.
154 Then the specific viscosity, η_{sp} , could be calculated with the formula $\eta_{sp} = \eta_r - 1$. After
155 that, two graphs were plotted in the same coordinate system according to the Kraemer
156 equation $\frac{\ln \eta_r}{c} = [\eta] - K' [\eta]^2 c$ and the Huggins equation $\frac{\ln \eta_{sp}}{c} = [\eta] + K'' [\eta]^2 c$.
157 One of the graphs was plotted as η_{sp}/C against C , the other was η_{sp}/C against C . These 2
158 graphs shared the same X axis, and the Y axis intercept. The value of the Y axis intercept
159 was the intrinsic viscosity, $[\eta]$, and the M_n could be calculated. Viscometry is a mature
160 method to measure the M_n , hence it was regarded as the exact value of the molecular
161 weight. The M_n was calculated with the formula $M_n = (\sum w_i M_i^0)^{1/0}$, using the results
162 from the GPC analysis.

163

164 **Results and Discussion**

165 *Precipitation Fractionation Effects of Different Average Molecular Weights of PMMA*

166 Studies have shown that the solubility of PMMA with different molecular weights is
167 related to the temperature and solvent.^[9] According to this feature, we fractionated
168 different average molecular weight PMMA crude products by isothermal precipitation.
169 The selected solvent was toluene and the precipitant was petroleum ether. 6 fractions

170 from each of the 3 samples (70, 80, and 90 °C) were obtained, namely 18 samples, and
171 then the PMMA samples with nearly the same molecular weight were put together,
172 yielding 6 final samples. The dependency relationship between PMMA molecular weight
173 and the volume fraction of petroleum ether in a toluene-petroleum ether separation
174 system is shown in Fig. 2. As indicated above, we chose petroleum ether volume
175 fractions 0.26, 0.31, 0.39, 0.44, 0.50 and 0.60 as the fractionation points and obtained 6
176 fractions from each preparation with uniform, evenly spaced molecular weights and
177 narrow distributions, resulting in the final 6 samples also having the same values and
178 distributions.

179

180 *Molecular Weights and Distribution Coefficients of Different Fractions of PMMA*

181 Figure 1 shows the chromatograms of the PMMA standard samples provided by the
182 Polymer Lab, UK. Figure 3 shows the chromatograms of the lab-made PMMA standard
183 samples. The $\lg M_p$ - V_e calibration curve equation is based on the relationship of peak
184 elution volume and peak molecular weight of the PMMA standard samples.

$$185 \quad \lg M_p = 10.206 - 0.8611V_e$$

186 The correlation coefficient of its regression equation was 0.9996. According to this
187 equation, the relative molecular mass and its distribution for the lab-made narrow
188 molecular weight distribution PMMA standard samples could be calculated. The results
189 are shown in Table 1.

190 The peak molecular weights of the six narrow molecular weight distributions PMMA
191 standard samples were between 3.1×10^3 and 4.3×10^4 (Table 1). The molecular weights
192 were evenly distributed, and the dispersion coefficients were less than 1.5. It is noted the
193 molecular weight distributions of the lab-made samples were broader than those of the
194 Polymer Lab samples, this is partly due to combining 3 samples for each of the 6 final
195 samples. Despite the greater distribution breadth, the M_w/M_n were still less than 1.5, with

196 most near 1.25 and the volume of the samples were much larger for equivalent cost.

197

198 *Hydrolysis conditions of PMMA standard samples and the purity of PMAA standard*
199 *samples*

200 The numbers of methoxy-H and methyl-H of PMMA molecules are equal. After the
201 hydrolysis of the ester group, the number of methoxy-H decreased. The hydrolysis degree
202 of PMMA was calculated by the peak area ratio of methoxy-H and methyl-H in the
203 ^1H -NMR spectra. The ^1H -NMR results of PMMA sample 1 and a PMAA sample which
204 was hydrolyzed from sample 1 are shown in Figs 4 and 5, respectively. The relationship
205 between the hydrolysis degree and the reaction time of sample 1 is shown in Table 2. The
206 result shows that the initial reaction was fast when the hydrolysis was carried out in the
207 organic system. However, the hydrolysate was gradually precipitated from the organic
208 phase so that the further hydrolysis reaction was hindered. The hydrolysis degree can
209 only reach about 95%. When the sample was subjected to the second hydrolysis in
210 aqueous solution, the hydrolysis degree could reach more than 98%. After the two-step
211 hydrolysis, the final hydrolysis degrees of the six narrow distribution PMAA samples
212 reached 98.7%–98.9% (Table 3).

213 As indicated, the PMAA samples were purified by precipitation with methanol and
214 HCl, in succession. The purity was measured by acid-base titration. The acid-base
215 titration results showed the purity of the PMAA was higher than 98.6%. The GPC results
216 proved the separation process did not affect the molecular weight of the polymer. Figure
217 6 shows the molecular weight distributions of the six PMAA standard samples. The
218 distributions were symmetrical and narrow.

219

220 *Molecular weight certification of PMAA standard samples*

221 Changes in molecular weight in the hydrolysis reaction were assumed to be identical

222 with the stoichiometric relationship. We calculated the molecular weights of the PMAA
223 standard samples according to the hydrolysis reaction equation shown in Scheme 1, and
224 the results are listed in Table 4.

225 We measured the viscosity-average molecular weights of the PMAA standard samples
226 by viscosity and compared them with the results calculated by the hydrolysis reaction
227 equation, based on the parameters listed in Table 1 and the M_n obtained from the GPC
228 measurements. The results show that they were basically the same and their relative
229 errors were less than 10%, which illustrates that the hydrolysis did not affect the
230 polymerization degree of PMAA. We thus suggest that it's reliable to calculate the
231 molecular weights of the PMAA standard samples according to the hydrolysis reaction
232 equation.

233

234 Conclusions

235 Six PMMA standard samples with narrow molecular weight distributions were
236 produced by free radical polymerization and fractionated with toluene-petroleum ether.
237 Their average molecular weights ranged from 3.1×10^3 to 4.3×10^4 , the dispersion
238 coefficients were less than 1.5 and the GPC peak shapes were symmetrical. The PMMA
239 samples were hydrolyzed in NaOH-methanol solution and NaOH aqueous solution, in
240 succession. The hydrolysis degrees reached more than 98%. The PMAA standard
241 samples were obtained after acidification and precipitation, and their molecular weights
242 were constant during the separation process. The acid-base titration results showed the
243 purities of the PMAA samples were greater than 98.6%. The molecular weight
244 distributions of PMAA were symmetrical and narrow. The molecular weight values of
245 the PMAA determined from the PMMA values by the stoichiometric relationship of the
246 hydrolysis reaction, were comparable with the viscosimetric measurements; the relative
247 errors were less than 10%, suggesting that the molecular weights results obtained by

248 calculation based on the previously measured PMMA values could be regarded as
249 accurate. The PMMA and PMAA standard samples could be obtained in large volumes at
250 relatively low cost compared with commercially available standards.

251

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256

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280

281

283 **Scheme 1.** The hydrolysis reaction equation of PMMA

284 **Figure 1.** Chromatograms of PMMA standard samples from Polymer Lab; the peak
285 molecular weights are (1) 1.44×10^6 , (2) 4.39×10^5 , (3) 7.36×10^4 , (4) 1.24×10^4 , (5)
286 3.09×10^3 , (6) 1.40×10^3 ; the dispersion coefficients are (1) 1.08, (2) 1.08, (3) 1.04, (4)
287 1.05, (5) 1.05, (6) 1.20

288 **Figure 2.** Relationship of PMMA peak molecular weights and petroleum ether volume
289 fractions

290 **Figure 3.** Chromatograms of lab-made PMMA standard samples

291 **Figure 4.** ^1H -NMR spectrum of PMMA before hydrolysis (Solvent was CDCl_3)

292 **Figure 5.** ^1H -NMR spectrum of PMAA by two-step hydrolysis (Solvent was D_2O)

293 **Figure 6.** Molecular weight distributions of lab-made PMAA standard samples

294

295

296 **Table 1** Molecular weights and molecular weight distribution coefficients of the
297 lab-made PMMA standard samples

298 **Table 2** Hydrolysis degrees of the lab-made PMMA standard samples under different
299 conditions (sample 1)

300 **Table 3** Hydrolysis degrees of the lab-made PMMA standard samples after two-step
301 hydrolysis

302 **Table 4** Comparison of the calculated molecular weights of the lab-made PMAA
303 standard samples and actual measured M_n

304

305
306

307

Scheme 1. The hydrolysis reaction equation of PMMA

308

309 **Figure 1.** Chromatograms of PMMA standard samples from Polymer Lab, the peak

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311 3.09×10^3 , (6) 1.40×10^3 ; the dispersion coefficients are (1) 1.08, (2) 1.09, (3) 1.04, (4)

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 316 fractions

317

Figure 3. Chromatograms of lab-made PMMA standard samples

323

324 **Figure 4.** ^1H -NMR spectrum of PMMA before hydrolysis (Solvent was CDCl_3)

325

326

Figure 5. $^1\text{H-NMR}$ spectrum of PMAA after preparation by a two-step hydrolysis
(Solvent was D_2O)

331

332

333 **Figure 6.** The molecular weight distributions of lab-made PMAA standard samples

334

335

Table 1

336

Molecular weights and molecular weight distribution coefficients of the lab-made

337

PMMA standard samples

PMMA	1	2	3	4	5	6
M_p	4.34×10^4	2.36×10^4	1.05×10^4	5.72×10^3	3.82×10^3	3.11×10^3
M_w	4.08×10^4	2.56×10^4	1.23×10^4	6.39×10^3	4.68×10^3	3.27×10^3
M_n	3.25×10^4	2.04×10^4	9.57×10^3	5.07×10^3	3.25×10^3	2.58×10^3
M_w/M_n	1.25	1.26	1.28	1.26	1.44	1.26

338

339

340

Table 2

341 Hydrolysis degrees of the lab-made PMMA standard samples under different conditions

342

(sample 1)

Hydrolysis step	Reaction time(h)	Hydrolysis degree (%)
Step 1	12	81.42
(Saturated	24	94.86
NaOH-	36	94.89
methanol	48	95.36
solution)		
	24+12	97.82
Step 2 (2mol/L	24+24	98.76
NaOH)	24+48	98.78
	24+72	98.97

343

344

345

Table 3

346 Hydrolysis degrees of the lab-made PMMA standard samples after two-step hydrolysis

Sample	1	2	3	4	5	6
Hydrolysis degree (%)	98.76	98.81	98.93	98.70	98.79	98.88

347

348

349

Table 4

350

Comparison of the calculated molecular weights of the lab-made PMAA standard

351

samples and actual measured M_n

Sample	Actual	The calculated molecular weight					Relative error
No.	measured M_n	M_w	M_n	M_p	M_n'	M_w/M_n	(%)
1	3.52×10^4	3.51×10^4	2.80×10^4	3.73×10^4	3.70×10^4	1.25	5.11
2	1.93×10^4	2.20×10^4	1.75×10^4	2.03×10^4	2.07×10^4	1.26	7.25
3	9.72×10^3	1.06×10^4	8.23×10^3	9.03×10^3	9.06×10^3	1.29	-6.80
4	4.46×10^3	5.50×10^3	4.36×10^3	4.93×10^3	4.88×10^3	1.26	9.42
5	3.54×10^3	4.02×10^3	2.80×10^3	3.28×10^3	3.20×10^3	1.43	-9.60
6	2.39×10^3	2.81×10^3	2.22×10^3	2.67×10^3	2.56×10^3	1.26	7.11

352