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

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A series of polymethylacrylic acid (PMAA) standard samples were prepared from fractionated PMMA samples followed by a two-step hydrolysis. The six PMMA standard samples with narrow molecular weight distributions were produced by free radical polymerization and fractionated with toluene-petroleum ether. Their average molecular weights ranged from $3.1 \times 10^3$ to $4.3 \times 10^4$, dispersion coefficients were less than 1.5, and their gel permeation chromatography (GPC) peak shapes were symmetrical. The PMMA standard samples were dissolved in dioxane, and then hydrolyzed in a saturated NaOH-methanol solution for 24 h, the methanol then evaporated, and after that the PMMA samples were hydrolyzed in a 2 mol·L$^{-1}$ NaOH aqueous solution for 24 h. The $^1$H-NMR results showed that the two-step hydrolysis degree was higher than 98.70%. The PMAA standard samples were obtained after acidifying the hydrolysates, namely polymethacrylic acid sodium salt, and their molecular weights were constant during the separation process. The acid–base titration results showed the purities of the PMAA samples were greater than 98.6%, and their molecular weight distributions were symmetrical and narrow. The molecular weights of the PMAA were determined by the stoichiometric relationship of the hydrolysis reaction. Compared with viscometry, the results of both methods were basically the same, and their errors were less than 10%.

Keywords  GPC, molecular weight standard samples, polyelectrolyte, polymethyl methacrylate, polymethylacrylic acid

Introduction

The molecular weights and the molecular weight distributions of polyelectrolytes can affect their performances.\[1,2\] Normally, they are measured using gel permeation chromatography (GPC). However, the standard samples of polyelectrolytes are hard to be prepared, so non-electrolyte standard samples, such as polyethylene glycol (PEG) and dextran, are often applied in the determination, resulting in deviations in the measurements.\[3,4\]

Monodisperse polymer standards can be easily obtained by living polymerization, and their molecular weights can be measured by static light scattering and membrane permeation.\[5\] However, the synthesis of polyelectrolytes by living polymerization as well as the precise determination of their molecular weights is not easy. As a result, polyelectrolyte
standard samples can only be obtained by indirect methods at present. In 1992, Mykytiuk et al.\cite{6} used 1-methoxy-1-trimethylsilyloxy-2-methyl propylene (MTS) as the initiator and tetrabutylammonium fluoride (TBAF) as the catalyst to prepare several different monodisperse polybenzyl methacrylates (PBzMA) by group transfer polymerization and used GPC to measure the molecular weights. The catalytic hydrogenation process of PBzMA was proceeded with Pd/C as the catalyst in an ethyl acetate-methanol mixed solution under an atmosphere of H$_2$ at room temperature to obtain monodisperse polymethylacrylic acid (PMAA). In 1996, Kawaguchi et al.\cite{7} produced poly(tertiary butyl methacrylate) by anionic polymerization in the presence of LiCl, followed by a two-step hydrolysis with Si(CH$_3$)$_3$I and HBr; then the poly(tertiary butyl methacrylate) was hydrolyzed to obtain monodisperse PMAA. The predecessor, monodisperse poly(tertiary butyl methacrylate) was easy to synthesize, but difficult to hydrolyze. So until now, commercialized polyelectrolyte standard samples are still rare.

The molecular weights of the monodisperse polyelectrolytes produced by the methods mentioned above were calculated from the molecular weights of the predecessors. So it’s important to determine the molecular weight of the predecessors accurately. PMMA standard samples have been commercialized. It’s thus easy and accurate to determine the molecular weights if we choose PMMA standard samples as predecessors to produce PMAA by hydrolysis. But PMMA is hard to hydrolyze. Erhardt et al.\cite{8} used crown ether as the phase transfer catalyst to improve the rate of hydrolysis, but it’s toxic and environmentally unfriendly.

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

**Experimental**

**Materials**

All reagents used in the synthesis were of analytical grade. MMA was distilled under vacuum before use. The PMMA standard samples were provided by the Polymer Lab, UK (Chromatograms are shown in Fig. 1). The internal diameter and the viscometer constant of Ubbelohde capillary viscometer were 0.6 mm and 0.006861 mm$^2$·S$^{-2}$, respectively. The GPC analysis used an Agilent-1100 chromatography system (Agilent Co., USA). The $^1$H-NMR analysis used an Inova-600 nuclear magnetic resonance apparatus (Varian Co., USA).
Figure 1. Chromatograms of PMMA standard samples from Polymer Lab, the peak molecular weights are (1) \(1.44 \times 10^6\), (2) \(4.39 \times 10^5\), (3) \(7.36 \times 10^4\), (4) \(1.24 \times 10^4\), (5) \(3.09 \times 10^3\), (6) \(1.40 \times 10^3\); the dispersion coefficients are (1) 1.08, (2) 1.09, (3) 1.04, (4) 1.05, (5) 1.05, (6) 1.20.

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

GPC conditions for PMAA: PL AQUAGEL-OH mixed-M (7.5 mm \(\times\) 300 mm, 8 \(\mu\)m, double column series) GPC column. RID detector. The mobile phase was phosphate buffer solution (0.10 mol-L\(^{-1}\), pH = 6.86). The flow rate was 1.0 mL-min\(^{-1}\). The column temperature was 25.0\(^\circ\)C. The PMAA samples were dissolved in the mobile phase, and the concentration of the samples were 1.0 g-L\(^{-1}\), injection volume was 50 \(\mu\)L.

**Preparation of PMMA Crude Products**

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

**Precipitation Fractionation and Calibration of PMMA**

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

The molecular weight distributions of the PMMA fractions were measured by GPC. The calibration curve equation was based on PMMA standard samples.

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

The 6 fractionated PMMA standard samples with narrow weight distributions were dissolved in dioxane (10%). Then saturated NaOH-methanol was added into 50 mL of the solution by the molar ratio of \(n(\text{NaOH}):n(\text{ester group}) = 1:2\). The mixture was refluxed for 24 h under the protection of pure N\(_2\). The solvent was then evaporated, 50 mL NaOH aqueous solution (2 mol L\(^{-1}\)) was added in and the mixture was refluxed for another 24 h to complete the hydrolysis. Every 12 hours after the hydrolysis started, the samples were taken to detect the extent of hydrolysis by \(^1\text{H-NMR}\). The \(^1\text{H-NMR}\) spectroscopy was carried out at 600 MHz, using a Varian Inova-600 nuclear magnetic resonance apparatus. Three times the volume of methanol was added into the hydrolysate to precipitate the PMAA-Na. The PMAA-Na samples were washed with methanol and dissolved in 30 mL water, and then NaCl was added until the solution was saturated. And 30 mL concentrated HCl was added into the solution to precipitate the PMAA. The precipitates were then washed with HCl (6 mol L\(^{-1}\)), dried under vacuum at 60\(^\circ\)C and the PMAA standard samples were obtained. The purity of the PMAA was measured by acid–base titration. 0.10 g accurately weighed lab-made PMAA samples were dissolved in 0.10 mol L\(^{-1}\) NaOH aqueous solutions, and a few drops of phenolphthalein indicator added; after that the solutions were titrated by 0.10 mol L\(^{-1}\) HCl until the color of the solution changed from red to colorless. The purity value of the PMAA could be calculated according to the following formula:

\[
\omega\%(\text{PMAA}) = \frac{(V(\text{NaOH}) \times c(\text{NaOH}) - V(\text{HCl}) \times c(\text{HCl})) \times M(\text{MAA})}{m(\text{PMAA})} \times 100\%.
\]

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

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

The six PMMA standard samples provided by the Polymer Lab, UK were hydrolyzed to prepare six monodisperse PMAA standard samples in the same way. The monodisperse PMAA standard samples were used to compare with the lab-made PMAA standard samples. The molecular weight \(M_\eta\) could be calculated according to the Mark-Houwink equation: \([\eta] = K M_\eta^\alpha\). The efflux time of the solution, which was \(t\), and the efflux time of the solvent, which was \(t_0\), were measured in the Ubbelohde capillary viscometer. The relative viscosity, \(\eta_r\), was calculated with the formula \(\eta_r = \eta/\eta_0 = t/t_0\). Then the specific viscosity, \(\eta_s\), could be calculated with the formula \(\eta_s = \eta_r - 1\). After that, two graphs were plotted in the same coordinate system according to the Kraemer equation \(\ln \eta_{sp}/C = [\eta] - K''[\eta]^2 C\) and the Huggins equation \(\ln \eta_{sp}/C = [\eta] + K''[\eta]^2 C\). One of the graphs was plotted as \(\eta_{sp}/C\) against \(C\), the other was \(\eta_s/C\) against \(C\). These 2 graphs shared the same X-axis, and the Y-axis intercept. The value of the Y-axis intercept was the intrinsic viscosity, \([\eta]\), and the \(M_\eta\) could be calculated. Viscometry is a mature method to measure the \(M_\eta\), hence it was regarded as the exact value of the molecular weight. The \(M'_\eta\) was calculated with the formula \(M'_\eta = (\sum w_i M_\eta^a) / \alpha\), using the results from the GPC analysis.
Results and Discussion

Precipitation Fractionation Effects of Different Average Molecular Weights of PMMA

Studies have shown that the solubility of PMMA with different molecular weights is related to the temperature and solvent. According to this feature, we fractionated different average molecular weight PMMA crude products by isothermal precipitation. The selected solvent was toluene and the precipitant was petroleum ether. And 6 fractions from each of the 3 samples (70, 80, and 90°C) were obtained, namely 18 samples, and then the PMMA samples with nearly the same molecular weight were put together, yielding 6 final samples. The dependency relationship between PMMA molecular weight and the volume fraction of petroleum ether in a toluene-petroleum ether separation system is shown in Fig. 2. As indicated above, we chose petroleum ether volume fractions 0.26, 0.31, 0.39, 0.44, 0.50, and 0.60 as the fractionation points and obtained 6 fractions from each preparation with

![Figure 2](image_url)

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

![Figure 3](image_url)

**Figure 3.** Chromatograms of lab-made PMMA standard samples.
Table 1
Molecular weights and molecular weight distribution coefficients of the lab-made PMMA standard samples

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

uniform, evenly spaced molecular weights and narrow distributions, resulting in the final 6 samples also having the same values and distributions.

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

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

$$1gM_p = 10.206 - 0.8611V_e$$

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

The peak molecular weights of the six narrow molecular weight distributions PMMA standard samples were between $3.1 \times 10^3$ and $4.3 \times 10^4$ (Table 1). The molecular weights were evenly distributed, and the dispersion coefficients were less than 1.5. It is noted the

![1H-NMR spectrum of PMMA before hydrolysis (solvent was CDCl₃).](image)
molecular weight distributions of the lab-made samples were broader than those of the Polymer Lab samples, this is partly due to combining 3 samples for each of the 6 final samples. Despite the greater distribution breadth, the $M_w/M_n$ were still less than 1.5, with most near 1.25 and the volume of the samples were much larger for equivalent cost.

**Hydrolysis Conditions of PMMA Standard Samples and the Purity of PMAA Standard Samples**

The numbers of methoxy-H and methyl-H of PMMA molecules are equal. After the hydrolysis of the ester group, the number of methoxy-H decreased. The hydrolysis degree of PMMA was calculated by the peak area ratio of methoxy-H and methyl-H in the $^1$H-NMR spectra. The $^1$H-NMR results of PMMA sample 1 and a PMAA sample that was hydrolyzed from sample 1 are shown in Figs. 4 and 5, respectively. The relationship between the

**Table 2**

Hydrolysis degrees of the lab-made PMMA standard samples under different conditions (sample 1)

| Hydrolysis step | Reaction time(h) | Hydrolysis degree (%) |
|-----------------|------------------|-----------------------|
| Step 1 (Saturated NaOH- methanol solution) | | |
| | 12 | 81.42 |
| | 24 | 94.86 |
| | 36 | 94.89 |
| | 48 | 95.36 |
| Step 2 (2 mol/L NaOH) | 24 + 12 | 97.82 |
| | 24 + 24 | 98.76 |
| | 24 + 48 | 98.78 |
| | 24 + 72 | 98.97 |
Table 3

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 |

hydrolysis degree and the reaction time of sample 1 is shown in Table 2. The result shows that the initial reaction was fast when the hydrolysis was carried out in the organic system. However, the hydrolysate was gradually precipitated from the organic phase so that the further hydrolysis reaction was hindered. The hydrolysis degree can only reach about 95%. When the sample was subjected to the second hydrolysis in aqueous solution, the hydrolysis degree could reach more than 98%. After the two-step hydrolysis, the final hydrolysis degrees of the six narrow distribution PMAA samples reached 98.7%~98.9% (Table 3).

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

Molecular Weight Certification of PMAA Standard Samples

Changes in molecular weight in the hydrolysis reaction were assumed to be identical with the stoichiometric relationship. We calculated the molecular weights of the PMAA standard samples according to the hydrolysis reaction equation shown in Scheme 1, and the results are listed in Table 4.

We measured the viscosity-average molecular weights of the PMAA standard samples by viscosity and compared them with the results calculated by the hydrolysis reaction
table 4
Comparison of the calculated molecular weights of the lab-made PMAA standard samples and actual measured \(M_\eta\)

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

equation, based on the parameters listed in Table 1 and the \(M_\eta\) obtained from the GPC measurements. The results show that they were basically the same and their relative errors were less than 10%, which illustrates that the hydrolysis did not affect the polymerization degree of PMAA. We thus suggest that it’s reliable to calculate the molecular weights of the PMAA standard samples according to the hydrolysis reaction equation.

Conclusions

Six PMMA standard samples with narrow molecular weight distributions were produced by free radical polymerization and fractionated with toluene-petroleum ether. Their average molecular weights ranged from \(3.1 \times 10^3\) to \(4.3 \times 10^4\), the dispersion coefficients were less than 1.5 and the GPC peak shapes were symmetrical. The PMMA samples were hydrolyzed in NaOH-methanol solution and NaOH aqueous solution, in succession. The hydrolysis degrees reached more than 98%. The PMAA standard samples were obtained after acidification and precipitation, and their molecular weights were constant during the separation process. The acid–base titration results showed the purities of the PMAA samples were greater than 98.6%. The molecular weight distributions of PMAA were symmetrical and narrow. The molecular weight values of the PMAA determined from the PMMA values by the stoichiometric relationship of the hydrolysis reaction, were comparable with the viscosimetric measurements; the relative errors were less than 10%, suggesting that the molecular weights results obtained by calculation based on the previously measured PMMA values could be regarded as accurate. The PMMA and PMAA standard samples could be obtained in large volumes at relatively low cost compared with commercially available standards.

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