

A Novel Determination Technique of Polymer Viscosity-Average Molecular Weights with Flow Piezoelectric Quartz Crystal Viscosity Sensing

YOUAN MAO,* WANZHI WEI, JINZHONG ZHANG, YIJIN LI

College of Chemistry and Chemical Engineering, Hunan University, Changsha, 410082, China

Received 13 July 2000; revised 24 September 2000; accepted 15 October 2000

ABSTRACT: A new method for the determination of polymer viscosity-average molecular weights was developed with flow piezoelectric quartz crystal (PQC) viscosity sensing. The experimental setup with a 9 MHz AT-cut quartz crystal and a flow detection cell was constructed and shown to be able to give highly reproducible data under the temperature of $25 \pm 0.1^\circ\text{C}$ and the fluid flow rate of 1.3–1.6 mL/min. A response model for PQC in contact with dilute polymer solutions (concentration <0.01 g/mL) was proposed in which the frequency change from the pure solvent, Δf_s , follows $\Delta f_s = -k_6\eta^{1/2} + k_7$, where η is the absolute viscosity of dilute polymer solution and k_6 and k_7 are the proportionality constants. This model was examined with poly(ethylene glycol) samples (PEG-20000 and PEG-10000) under the aforementioned experimental conditions using water as solvent. The result was $\Delta f_s = -1587\eta^{1/2} + 1443$. Based on this model, the method for the determination of polymer viscosity-average molecular weights, M_η , by flow PQC viscosity sensing was described and examined with an unknown poly(vinyl alcohol) (PVAL) sample. The new method proved to be an attractive and promising alternative for the determination of polymer molecular weights based on the good agreement between the molecular weight determined by the new method ($M_\eta = 58600$) for the unknown PVAL sample with that determined by the conventional capillary viscosity method. The new method has some advantages over the conventional viscosity method; for examples, operation is simpler and more rapid; the instruments required are cheaper and portable; the needed sample quantity is smaller; and the experimental setup constructed can be used in continuous measurement. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 63–69, 2001

Key words: piezoelectric quartz crystal (PQC); viscosity sensing; flow determination; polymer viscosity-average molecular weight; dilute polymer solution

INTRODUCTION

The determination of polymer molecular weights is of great importance in polymer science and engineering. There are various techniques for

measuring polymer molecular weights, including end group analysis, membrane osmometry, light scattering, ultracentrifugation, gel permeation chromatography, viscometry, etc.,¹ and new methods are still being developed. For instance, Oh et al.² recently proposed to determine molecular weight and distribution of rigid-rod polymers by the phase-modulated flow birefringence. However, most of those methods require expensive equipment. In practical applications, the viscosity

Correspondence to: W. Wei (youanmao@cmmail.com).

*On leave from National University of Defense Technology.

method is one of the most commonly used, but it is only a relative method and has some serious shortcomings. The determination of molecular weight by the viscosity method involves measurement of the viscosity of dilute polymer solutions. Although some automatic viscometers are available, such as the Schott AVS system and Differential Viscometer from Viscotek,³ conventional capillary viscometers (Ubbelohde or Ostwald) are often used because the automatic viscometers are more complex and more expensive than ordinary glass viscometers. However, it is well known that such capillary viscometers cannot be used for continuous viscosity measurement and their cleaning is a very tedious task; therefore, the capillary viscosity method is time consuming and very inconvenient. Furthermore, and more importantly, the accuracy of the method depends on the worker's proficiency in operation. These shortcomings in currently available methods indicate that it is necessary to develop a rapid, convenient, and low cost instrumental method for the determination of polymer viscosity-average molecular weights.

Extensive attention has been paid to piezoelectric quartz crystal (PQC) liquid sensing, since AT-cut quartz crystals achieved stable oscillation in solution.⁴ Furthermore, there is increasing interest in utilization of PQC because of its easy use, low detection limit, and continuous operation.⁵⁻⁸ However, to our knowledge, application of PQC in polymer analysis and characterization has not been reported.

Several groups provided detailed theoretical explanations for the behavior of PQC in contact with liquids. Kanazawa and Gordon⁹ developed a simple physical model in which the coupling of the shear wave in the quartz to a damped shear wave in the fluid was considered, assuming negligible fluid elasticity. This model allowed the following relationship to be derived, relating the change in oscillation frequency of the crystal to the material parameters describing the liquid and the quartz:

$$\Delta f = -f_b^{3/2}(\eta_l \rho_l / (\pi \rho_q \mu_q))^{1/2} \quad (1)$$

where Δf is the frequency change oscillating in the liquid relative to that in air, f_b is the basic oscillation frequency of the dry crystal, η_l and ρ_l are the absolute viscosity and density of the liquid, respectively, and μ_q and ρ_q are the elastic modulus and the density of the quartz, respectively. Bruckenstein and Shay¹⁰ derived a simi-

lar, though not identical, expression based on an analogy between the oscillating boundary layer adjacent to each crystal face and the thickness of an alternating current (ac) polarographic diffusion layer. Hager¹¹ developed a slightly different equation by considering the viscous energy losses and fluid velocity at the crystal surface:

$$\Delta f = -k_1(\eta_l \rho_l)^{1/2} + k_2 \varepsilon_1 \quad (2)$$

where k_1 and k_2 are proportionality constants and ε_1 is the dielectric constant of the liquid. Taking a more empirical approach, Nomura and Okuhara¹² suggested that the following relationship most appropriately described the frequency change:

$$\Delta f = -k_3 \rho_l^{1/2} - k_4 \eta_l^{1/2} + k_5 \quad (3)$$

where k_3 , k_4 , and k_5 are empirical proportionality constants. Yao and Zhou⁴ observed a relationship resembling eq.3, with the exception that two additional terms were included to take into account dielectric and conductance effects. Later work⁸ identified that not only did the viscosity, density, conductivity, and permittivity of the liquid influence the frequency, but also other factors associated with the physical and chemical nature of the interfacial environment. For examples, the frequency response was mediated by interfacial interactions, such as the structure of solid-solution interface with respect to surface roughness and surface stress, interfacial viscosity, surface free energy, as well as the extent of crystal contact with the solution phase. To date, no unifying equation has been developed to describe the piezoelectric crystal response in liquid. Generally, the predictions of Kanazawa et al.⁹ and Bruckenstein et al.¹⁰ could be in good agreement with experiments except for the high viscosity solutions, salt solutions, and polymer solutions.^{8,13} To apply PQC sensing in polymer analysis and characterization, investigation of the response behavior of PQC in polymer solutions is needed.

In this paper, a response model for PQC in contact with dilute polymer solutions and a novel method for the determination of polymer viscosity-average molecular weights are proposed. The corresponding experimental setup is constructed, and the model and the new method are experimentally examined. The results are satisfactory.

THEORY

In the derivation process of eq.1, Kanazawa and Gordon⁹ used the Newtonian viscosity fluid law to

describe the stress relation for the fluid. Other authors¹⁴ also utilized this law in their works. Use of this law means that the solution used should be a Newtonian viscous fluid. However, most of polymer solutions, especially the concentrated ones, are not Newtonian fluids. Thus, the relationship between the frequency change and the viscosity and density for concentrated polymer solutions cannot be expressed as eq.1 or other similar equations. However, for dilute polymer solutions, the relation between Δf and $(\eta_1\rho_1)^{1/2}$ will be linear because the Newton law holds in that case.

If the detection cell is so designed that only one side of the quartz crystal is in contact with liquid, the conductivity and permittivity of the liquid will have little effect on the frequency change because there exists no liquid return circuit between the two metal electrodes deposited on the crystal in such a situation. Moreover, if the flow detection cell is used, the properties of solid–solution interface, such as interfacial structure, and their effect on frequency change will remain constant. Under these conditions, the relation between Δf and the properties of dilute polymer solutions can be described as follows

$$\Delta f = -k'_1(\eta_1\rho_1)^{1/2} + k'_2 \quad (4)$$

where k'_1 and k'_2 are proportionality constants.

The oscillation frequency is quite sensitive to stresses caused by mounting and to changes in the hydrostatic pressure of the solution. Consequently, we use the frequency change relative to pure solvent rather than to air or vacuum as the response signal of piezoelectric crystals. When pure solvent passes through the detection cell, according to eq.4, the frequency change, Δf_0 , will be

$$\Delta f_0 = -k'_1(\eta_0\rho_0)^{1/2} + k'_2 \quad (5)$$

where η_0 and ρ_0 are the viscosity and density, respectively, of the solvent used, and $\rho_1 = \rho_0$ can be assumed because the liquid is a dilute polymer solution (generally, its concentration is $<0.01\text{g/mL}$). Let $\Delta f'_s = \Delta f - \Delta f_0$, then

$$\Delta f'_s = -k_6(\eta_1)^{1/2} + k_7 \quad (6)$$

where $\Delta f'_s$ is the frequency change relative to solvent, and k_6 and k_7 are the proportionality constants that are related to the properties of the

crystal and solvent, the conditions of solid/solution interface, the mounting of experimental setup, etc. Equation 6 is the response model proposed here for PQC in contact with dilute polymer solutions.

From eq.6, we can obtain η_1 as follows:

$$\eta_1 = ((k_7 - \Delta f'_s)/k_6)^2 \quad (7)$$

Thus we can predict the viscosity of dilute polymer solutions by $\Delta f'_s$. In the study of polymer solution, what we are interested in is the change of liquid viscosity caused when polymers enter the solution. The viscosity change can be evaluated in several parameters, such as relative viscosity increment (η_{sp}) and intrinsic viscosity ($[\eta]$). The term η_{sp} can be expressed as follows:

$$\eta_{sp} = (k_7 - \Delta f'_s)^2/(k_6^2\eta_0) - 1 \quad (8)$$

Thus, η_{sp} also can be predicted by $\Delta f'_s$. From the Schulz–Blaschke equation,¹

$$\eta_{sp}/C = [\eta] + k_8[\eta]\eta_{sp} \quad (9)$$

where C is the concentration of dilute polymer solution and k_8 is a constant not related to the concentrations, $[\eta]$ can be defined as follows:

$$[\eta] = \{[(k_7 - \Delta f'_s)^2/(k_6^2\eta_0) - 1]/C\}_{\eta_{sp} \rightarrow 0} \quad (10)$$

According to eq.10, after $\Delta f'_s$ values are measured for a variety of different concentrations of dilute polymer solutions, the values of $[(k_7 - \Delta f'_s)^2/(k_6^2\eta_0) - 1]/C$ can be calculated and plotted against the corresponding values of η_{sp} , or $[(k_7 - \Delta f'_s)^2/(k_6^2\eta_0) - 1]$. Then $[\eta]$ can be determined by extrapolation to $\eta_{sp} \rightarrow 0$. The value of intrinsic viscosity only depends on polymer molecular weights when the polymer, solvent, and temperature are assigned. The relation between $[\eta]$ and the polymer viscosity-average molecular weight, M_η , could be expressed by the famous Mark–Houwink equation

$$[\eta] = KM_\eta^\alpha \quad (11)$$

where K and α are constants in a given range of molecular weights. Therefore,

$$M_\eta = (\{[(k_7 - \Delta f'_s)^2/(k_6^2\eta_0) - 1]/C\}_{\eta_{sp} \rightarrow 0}/K)^{1/\alpha} \quad (12)$$

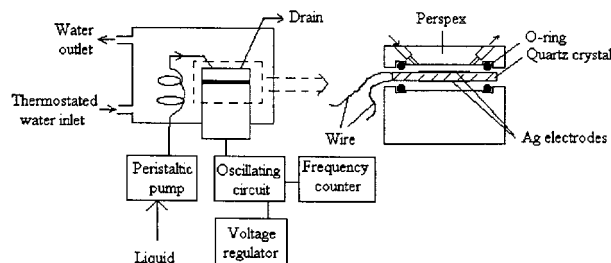


Figure 1 Schematic diagram of experimental setup.

and M_η can be determined by PQC viscosity sensing as long as K and α are known.

EXPERIMENTAL

Apparatus and Materials

The experimental setup is schematically shown in Figure 1. A 9 MHz AT-cut quartz crystal wafer (12.5 mm in diameter) with silver electrodes (6 mm in diameter) on each side was used. The crystal was placed inside a flow detection cell made of cast polymethylmethacrylate ("Perspex"). Only one side of the crystal was exposed to the liquid (50 μL). The crystal holder was directly connected to a laboratory-made IC-TTL oscillating circuit. A direct current (dc) voltage regulator (Model JWY-30B, China) supplied the circuit, and the working voltage was set at 5 V. A universal frequency counter (Model SC-7201, Iwatsu, Japan) was employed to record the oscillating frequency. Test solutions were applied in a flow detection cell, propelled by an electronic peristaltic pump (Model LDB-M, Zhejiang, China). The flow rate was controlled at 1.3–1.6 mL/min; in this range, no dependence of the frequency change on the flow rate was found. The crystal, the crystal holder, and the detection cell were placed in a thermostatic water bath (25 ± 0.1 °C). The entire apparatus just described was accommodated in a chamber in which temperature was kept at 25 ± 1 °C. A computer was used for data analysis.

Poly(ethylene glycol) 20000 (PEG-20000) and poly(ethylene glycol) 10000 (PEG-10000) used in this work was obtained from commercial sources. Poly(vinyl alcohol) (PVAL), the average molecular weight of which is unknown, was from Guangzhou Chemicals Company, China. All test polymer solutions were prepared from double-distilled deionized water, which was used throughout.

Procedure

Before the experiment, 30 min were required to allow the oscillator to stabilize. Water was first applied because, as described in eq. 6, the reference state was oscillation in pure solvent. After stabilization of the frequency with water, test solutions were used. The concentrations of the test solutions were increased in a stepwise manner. At the end of each experimental run, water was applied to check the reversibility of the frequency.

The viscosity of PEG solutions was determined with an Ubbelohde viscometer at the 25 ± 0.1 °C.

RESULTS AND DISCUSSION

Data Reproducibility

The viscosity and density of a liquid are sensitive to the system temperature. Thus, the frequency change is also sensitive to the temperature. On the other hand, the flow rate of the fluid has an effect on the properties of the crystal–solution interface, and the latter affects the frequency. Accordingly, it is necessary to maintain the temperature and the flow rate of the fluid constant as far as possible to achieve high reproducibility in the experiment. Good reproducibility was obtained at temperatures $<25 \pm 0.1$ °C and solution flow rates of 1.3–1.6 mL/min, as described next.

A typical recording of frequency change by application of various concentrations of a polymer is shown in Figure 2. The oscillating frequency in water was taken as a reference value, as described in eq. 6. After application of a solution with a different concentration of the polymer, the oscillating frequency stabilized within a few minutes. Finally, water was applied, and the application reversed the oscillating frequency to the original level. Values of Δf_s caused by varying the concentrations of polymer were very reproducible: the coefficients of variation (five independent experiments) were 3.5% for 0.001g/mL, 3.0% for 0.002g/mL, 2.7% for 0.003g/mL, 1.9% for 0.004g/mL, and 1.1% for 0.006g/mL PEG-20000 solutions.

Dependence of Frequency Decrease on $\eta_l^{1/2}$

Equation 6 implies that the frequency change is proportional to $\eta_l^{1/2}$. This relationship was checked using PEG-20000 and PEG-10000 samples. We prepared PEG-20000 aqueous solutions of five different concentrations and PEG-10000

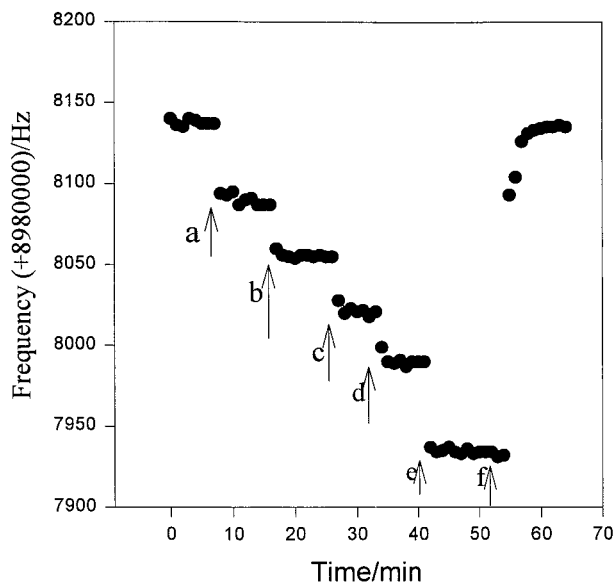


Figure 2 Typical responses of the frequency for dilute polymer solutions. Arrows show the times when test solutions were replaced. Concentrations of PEG-20000: (a) 0.001; (b) 0.002; (c) 0.003; (d) 0.004; (e) 0.006; (f) 0.0 g/mL.

solutions of six different concentrations. The piezoelectric responses, Δf_s , of these high polymer solutions were measured with our experimental setup under the aforementioned conditions. The results are listed in Table I. We also detected the viscosity of these high polymer solutions with an Ubbelohde viscometer, and the viscosity values also are in Table I. A plot of the frequency change versus $\eta_1^{1/2}$ using PEG-20000 and PEG-10000 solutions is shown in Figure 3. It is clear that the expected linear relationship of eq. 6 holds for the PEG-20000 and PEG-10000 samples.

Table I Values of Δf_s for Dilute Polymer Aqueous Solutions

Sample	C (g/mL)	$-\Delta f_s$ (Hz)	η_1 (cp)
PEG-20000	0.001	50	0.8888
	0.002	82	0.9224
	0.003	116	0.9624
	0.004	147	1.0018
	0.006	203	1.0796
	0.008	238	1.1584
PEG-10000	0.001	38	0.8722
	0.002	54	0.8893
	0.003	76	0.9150
	0.004	96	0.9407
	0.006	131	0.9834
	0.008	185	1.0518

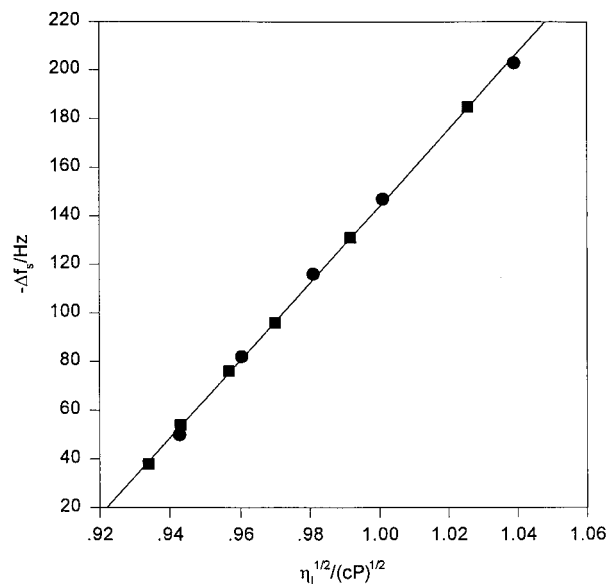


Figure 3 Plot of Δf_s versus $\eta_1^{1/2}$ for PEG-20000 (●) and PEG-10000 (■) aqueous solutions.

Kurosawa et al.¹³ examined the relationship between the piezoelectric responses and the products of viscosity and density for a series of aqueous solutions of several polymers. Their results showed that no linear relationship existed between Δf and $(\eta_1 \rho_1)^{1/2}$ for the solutions of high molecular weight polymers. They ascribed this phenomenon to the difference between static viscosity and viscosity at high frequency. However, the result in the present work does not support their view. Both PEG-20000 and PEG-10000 are high molecular weight polymers. In our opinion, the difference between our experiments and theirs lies mainly in the polymer solution concentration range used. In the present work, dilute polymer solutions were applied, whereas Kurosawa et al.¹³ used more concentrated solutions. It is known that the concentration has an important effect on the properties of polymer solutions. In the concentrated solutions, not only is there an interaction between polymer and solvent molecules but also a stronger interaction between polymer molecules. Therefore, the concentrated polymer solutions are highly viscous and not ideal solutions where the Newtonian viscosity fluid law does not hold. So, in the concentrated polymer solutions, there is no linear relation between Δf and $(\eta_1 \rho_1)^{1/2}$ because such a relation is based on the Newton law. On the other hand, the interaction between polymer molecules can be negligible in dilute polymer solutions. Generally, the dilute

Table II Predicted Values of η_1 and η_{sp} for Dilute PVA Solutions

C (g/mL)	$-\Delta f_s$ (Hz)	η_1 (cp)	η_{sp}
0.001	110	0.9576	0.0755
0.002	166	1.0279	0.1544
0.003	226	1.1060	0.2421
0.004	288	1.1897	0.3361
0.006	418	1.3751	0.5444

polymer solutions can be thought as ideal solution and there viscously flow behavior can be described by the Newton law; therefore we can expect a linear relation between Δf_s and $\eta_1^{1/2}$ in dilute polymer solutions. From Figure 3, we can obtain the following regression equation:

$$\Delta f_s = -1587\eta_1^{1/2} + 1443 \quad (13)$$

Comparing eq.13 with eq. 6, it is obvious that $k_6 = 1587 \text{ Hz}/(\text{cp})^{1/2}$ and $k_7 = 1443 \text{ Hz}$.

The obtained single composite linear line, shown in Figure 3, indicates that k_6 and k_7 are independent of the polymer, which is in agreement with the explanation for them in the Theory section. Therefore, we can predict the viscosity of other dilute solutions of polymers with the model. The prediction of viscosity of dilute polymer solutions will find applications in polymer analysis and characterization, such as in the determination of polymer viscosity-average molecular weights.

Determination of PVAL Viscosity-Average Molecular Weights

To determine the viscosity-average molecular weight of unknown PVAL sample, we prepared PVAL aqueous solutions of five different concentrations and measured the corresponding frequency changes. The results are shown in Table II. Using eqs.13, 7, and 8, η_1 and η_{sp} of these solutions were predicted, and are listed in Table II. The values of η_1 and η_{sp} of PVAL dilute solutions increased monotonously with their concentration increasing, which was in agreement with general observations.

Let

$$P(\Delta f_s, c) = [(k_7 - \Delta f_s)^2 / (k_6^2 \eta_0) - 1] / c \quad (14)$$

The linear plot of $P(\Delta f_s, C)$ versus η_{sp} is shown in Figure 4. According to eq.10, the intrinsic viscosity of PVAL solution can be obtained by extrapolation to $\eta_{sp} \rightarrow 0$, and here the value obtained was $[\eta] = 72.62 \text{ mL/g}$. Furthermore, the viscosity-average molecular weight can be calculated from eq. 12. The result was $M_\eta = 58600$ for the unknown PVAL sample where $K = 3.0 \times 10^{-1} \text{ mL/g}$ and $\alpha = 0.5$ at 25°C (from Brandrup and Immergut).¹⁵

We also measured the viscosity-average molecular weight of the same unknown PVAL sample by conventional capillary viscometry and the result obtained was $M\eta' = 58500$. It is evident that the result by the new method is in good agreement with that of the conventional method. Therefore, the new method can be used to determine the viscosity-average molecular weights of a polymer.

The new method proposed here has some advantages over the conventional viscosity method. For examples, the operation is simpler and more rapid, especially there is no need for tedious cleaning process; the instruments required are cheaper and portable, which is more attractive than the Schott AVS system and Differential Viscometer from Viscotek,³ the needed sample quantity is smaller; and, in particular, the experimental setup constructed can be used in continuous measurement.

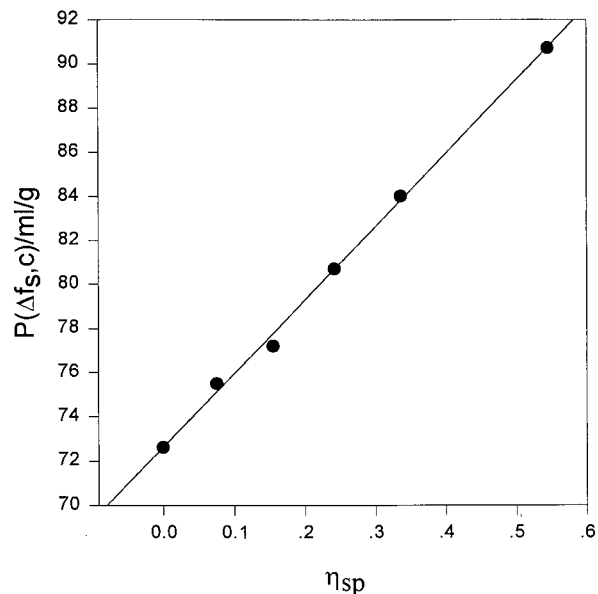


Figure 4 $P(\Delta f_s, c)$ plotted against η_{sp} for dilute PVAL solutions.

CONCLUSIONS

The response model proposed for PQC in contact with dilute polymer solutions was shown to be valid. Δf_s in dilute polymer solutions was a linear function of $\eta_l^{1/2}$. The method described here for the determination of polymer viscosity-average molecular weights by PQC viscosity sensing was preliminarily shown to be an attractive and promising alternative for the determination of polymer molecular weights. We are interested in application of this method in more polymer systems. In addition, the experimental setup constructed seems to be able to provide highly reproducible data.

This work was supported by the National Natural Science Foundation of China.

REFERENCES

1. Elias, H. G. *Macromolecules*; Second Ed.; Plenum Press: New York, 1984; Vol. 1, Chapter 9, pp. 345–368.
2. Oh, Y. R.; Lee, Y. S.; Kwon, M. H.; Park, O. O. *J Polym Sci, Part B: Polym Phys* 2000, 38, 509–515.
3. Mays, J. W.; Hadjichristidis, N. *Polymer Characterization Using Dilute Solution Viscometry*; In *Modern Methods of Polymer Characterization*, Barth, H. G., Mays, J. W., Eds. Wiley: New York, 1991; Chapter 7.
4. Yao, S.-Z.; Zhou, T.-A. *Anal Chim Acta* 1988, 212, 61–72.
5. Charlesworth, J. M. *Anal Chem.* 1990, 62, 76–81.
6. Cavic-Vlask, B. A.; Rajakovic, L. J. V. *Fresenius' J Anal Chem* 1992, 343, 339–347.
7. Nie, L.; Yao, S. *Fenxi Huaxue.* 1996, 24(2), 234–241.
8. Bunde, R. L.; Jarvi, E. J.; Resentreter, J. J. *Talanta.* 1998, 46, 1223–1236.
9. Kanazawa, K. K.; Gordon II, J. G. *Anal Chim Acta* 1985, 175, 99–105.
10. Bruckenstein, S.; Shay, M. *Electrochim Acta* 1985, 30, 1295–1300.
11. Hager, H. E. *Chem Eng Commun* 1986, 43, 25–38.
12. Nomura, T.; Okuhara, M. *Anal Chim Acta* 1982, 142, 281–284.
13. Kurosawa, S.; Tawara, E.; Kamo, N.; Kobatake, Y. *Anal Chim Acta* 1990, 230, 41–49.
14. Muramatsu, H.; Tamiya, E.; Karrube, I. *Anal Chem* 1988, 60, 2142–2146.
15. Brandrup, J.; Immergut, E. H. *Polymer Handbook*; Second Ed.; John Wiley & Sons, Inc.; New York, 1975; pp. VI-14.