Interaction Between Unlike Macromolecules: A New Method Based on the Motional Resistance Response of a Piezoelectric Quartz Crystal

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ABSTRACT: A new method for the study of the interaction between unlike macromolecules was developed, based on the motional resistance (R_m) response of a piezoelectric quartz crystal sensor to viscosity change in a contacting dilute polymer solution. The experimental setup, constructed with a 9-MHz AT-cut quartz crystal, a flowthrough detection cell, and an impedance analyzer, was shown to provide highly reproducible data at 25°C and a fluid flow rate of 1.3–1.6 mL/min. A quantitative relationship between R_m and the relative viscosity of the dilute polymer solution was derived. A model for using R_m to study the interaction was proposed. The interaction between polyethylene glycol (PEG) and poly(vinyl alcohol) (PVAL) was studied by this method with a thermodynamic parameter α. Experimental results indicated that the values of α for the blend PEG/PVAL were 0.094 and 0.086, corresponding to molecular weights of PEG of 10,000 and 20,000, respectively, and in agreement with those of capillary viscometry. The positive value of α showed that an attractive interaction existed between PEG and PVAL. An important feature of the new method was that it could be used in continuous measurement. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2528–2534, 2002

Key words: intermolecular interaction; macromolecule; motional resistance (R_m); piezoelectric quartz crystal

INTRODUCTION

The study of the thermodynamic interaction between different kinds of macromolecules in blend is of great importance in the molecular design of polymer materials and in the development of new materials. The interaction can be studied by several techniques, including differential scanning calorimetry, ultraviolet–visible spectroscopy, inverse gas chromatography, and viscometry.[1] Most of these techniques require expensive equipment. The viscometry is based on measurement of the viscosity of dilute polymer solutions. Although some automatic viscometers, such as the Schott AVS system and differential viscometer from Viscotek,[2] are available, 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 important, the ac-

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curacy 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 and convenient method for the study of polymer–polymer intermolecular interaction.

The piezoelectric quartz crystal (PQC) sensor has been extensively used in liquid analysis since the AT-cut quartz crystal achieved stable oscillation in solution.[3–5] As a fast, convenient, and sensitive analytical tool, it has attracted wide attention from analysts. Its numerous applications include the determination of pharmaceutical compounds[6] and biomacromolecules,[7] and the monitoring of blood clotting.[8] However, to the best of our knowledge, few reports have been published on its application in polymer analysis and characterization, and no report has been issued on its application in the study of intermolecular interaction for polymers.

In this report, a new method for the study of polymer–polymer intermolecular interaction based on the motional resistance of the PQC sensor in response to viscosity changes in contacting dilute polymer solutions was proposed. The corresponding experimental setup was constructed. The related theoretical model was established. The interaction between polyethylene glycol (PEG) and poly(vinyl alcohol) (PVAL) was studied by the new method, the results of which were satisfactory.

THEORY

The PQC sensor is an electromechanical transducer. There are two methods to generate a signal using the PQC sensor.[9,10] One of them is referred to as quartz crystal impedance analysis, in which the crystal is connected to an impedance analyzer that applies an alternating voltage at various frequencies across the crystal. The quartz crystal impedance analysis is often based on the Butterworth–van Dyke equivalent electrical circuit composed of a motional arm and a static arm in parallel. The motional arm contains three equivalent circuit parameters in series, that is, motional resistance R_m, motional inductance L_m, and motional capacitance C_m, whereas the static arm contains only the static capacitance C_0. All four equivalent circuit parameters have distinct physical meanings.[11–13] R_m corresponds to the loss in mechanical energy mainly dissipated to the surrounding medium and quartz interior. R_m is of special significance for the study of the properties of the medium surrounding the sensor.

Several groups investigated the relationship between R_m and the properties of the PQC sensor's liquid loading.[9,11,12,14] Taking into account the energy losses in the electrodes, leads, and contacts, we describe the unperturbed (without surface loading, i.e., in vacuum) motional resistance R_1' as the following:

$$R_1' = \frac{(N\pi)^2 \eta_Q h}{8\mu_Q K^2 \varepsilon_{22} A} \left(\frac{\omega}{\omega_s}\right)^2 + \Delta R \tag{1}$$

where N is the harmonic number ($N = 1$ for fundamental mode), η_Q is the effective quartz viscosity, h is the thickness of the quartz crystal disc, μ_Q is the quartz elastic constant, K is the electromechanical coupling factor of the quartz, ϵ_{22} is the quartz permittivity, A is the electrode surface area, ω is the angular excitation frequency, ω_s is series resonant angular frequency, and ΔR presents the energy losses in the electrodes and the mounting. If the liquid detection cell is so designed that only one side of the quartz crystal is in contact with the dilute polymer solutions, the liquid loading can be treated as a semi-infinite Newtonian fluid. Then R_m, the total motional resistance, when the PQC sensor is loaded with such a fluid, is expressed as

$$R_m = R_1' + R_2 = R_1' + R_c(\rho_L \eta_L)^{1/2} \tag{2a}$$

where R_2 is the added motional resistance attributed to surface liquid loading; ρ_L and η_L are the density and viscosity of the liquid, respectively; and

$$R_c = \frac{N\pi h}{4K^2 \omega_s \varepsilon_{22} A} \left(\frac{\omega}{2\rho_Q \mu_Q}\right)^{1/2} \tag{2b}$$

where ρ_Q is the quartz mass density. When the experimental setup has been constructed and experimental conditions, such as temperature and scanning frequency, are given, R_1' and R_c will be constants, and R_m is a linear function of $(\rho_L \eta_L)^{1/2}$.

Generally, dilute polymer solutions (concentration < 0.01 g/mL) can be considered as Newtonian fluids. Thus eqs. (2a) and (2b) can be used to describe the relationship between R_m and the properties of the dilute polymer solution with which the PQC sensor is in contact. Assuming that the value of R_1' is equal to the value of motional resistance in air, $R_{m(a)}$, we can measure

the value of R_1'. Placing the PQC in contact with the solvent and the dilute polymer solution allows measurement of the corresponding responses $R_{m(0)}$ and $R_{m(p)}$. According to eq. (2a),

$$R_{m(0)} = R_{m(a)} + R_c(\rho_{L(0)}\eta_{L(0)})^{1/2} \tag{3a}$$

$$R_{m(p)} = R_{m(a)} + R_c(\rho_{L(p)}\eta_{L(p)})^{1/2} \tag{3b}$$

where $\rho_{L(0)}$ and $\eta_{L(0)}$ are the density and viscosity of the solvent, respectively; and $\rho_{L(p)}$ and $\eta_{L(p)}$ are those of the dilute polymer solution. The following equation can be derived from eqs. (3a) and (3b):

$$\frac{R_{m(p)} - R_{m(a)}}{R_{m(0)} - R_{m(a)}} = \left(\frac{\rho_{L(p)}\eta_{L(p)}}{\rho_{L(O)}\eta_{L(O)}}\right)^{1/2} \tag{4}$$

For dilute polymer solutions, $\rho_{L(p)} \approx \rho_{L(0)}$. Therefore, we can predict the relative viscosity $\eta_r = \eta_{L(p)}/\eta_{L(0)}$ of dilute polymer solutions from the above R_m responses:

$$\eta_r = \left(\frac{R_{m(p)} - R_{m(a)}}{R_{m(0)} - R_{m(a)}}\right)^2 \tag{5}$$

Then the Huggins equation for dilute polymer solutions can be written as

$$\left[\left(\frac{R_{m(p)} - R_{m(a)}}{R_{m(0)} - R_{m(a)}}\right)^2 - 1\right]\frac{1}{c} = [\eta] + k[\eta]^2 c \tag{6}$$

where $[\eta]$ is intrinsic viscosity, c is polymer concentration, and k is the Huggins parameter. For nonelectrolyte dilute solutions, a plot of the left side of eq. (6) versus c should yield a straight line with intercept and slope corresponding to $[\eta]$ and $k[\eta]^2$, respectively. Theoretically, the parameter $[\eta]$ measures the effective hydrodynamic specific volume of an isolated polymer molecule, whereas the quantity k reflects the binary interactions between polymer segments.

Equation (6) can be readily adapted to a ternary system containing a solvent and two kinds of polymers.[15] The analog of eq. (6) for the mixture polymer solution is

$$\left[\left(\frac{R_{m(m)} - R_{m(a)}}{R_{m(0)} - R_{m(a)}}\right)^2 - 1\right]\frac{1}{c_1 + c_2} = [\eta]_m + k_m[\eta]_m^2(c_1 + c_2) \tag{7}$$

where $R_{m(m)}$ is the response when the blend solution is measured; c_1 and c_2 are the concentrations of polymer 1 and polymer 2 in the blend, respectively; and $[\eta]_m$ and k_m are the intrinsic viscosity and the Huggins parameter of the blend system, respectively.

Cragg and Bigelow[16] studied the intermolecular interaction in solution by the Huggins coefficient k_m in a ternary system (polymer–polymer–solvent). On the basis of Cragg and Bigelow's work, Sun et al.[17] proposed a thermodynamic coefficient α to characterize the interaction between unlike macromolecules, defined as

$$\alpha = k_m - \frac{k_1x_1^2[\eta]_1^2 + 2(k_1k_2)^{1/2}x_1x_2[\eta]_1[\eta]_2 + k_2x_2^2[\eta]_2^2}{[\eta]_m^2} \tag{8}$$

where x is the weight fraction of the two polymers in blend. Subscripts 1 and 2 correspond to polymer 1 and polymer 2, respectively. If there is an attractive interaction other than hydrodynamic between the unlike macromolecules, $\alpha > 0$; if repulsion, $\alpha < 0$, else $\alpha = 0$.

According to eqs. (6) and (7), a series of experiments can be designed to determine the values of $[\eta]_1$, $[\eta]_2$, k_1, k_2, $[\eta]_m$, and k_m. Then eq. (8) can be used to calculate the value of α, which can be used to describe the interaction of the unlike macromolecules.

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 a silver electrode (6 mm in diameter) on each side was used. The crystal was placed inside a flowthrough detection cell made of cast polymethylmethacrylate ("perspex"). Only one side of the crystal was exposed to the liquid (50 μL). The crystal electrodes were directly connected to an HP 4192A LF impedance analyzer (Hewlett–Packard, Palo Alto, CA). The values of the equivalent circuit parameters of the quartz crystal were calculated internally by the HP 4192A from the measured impedance data. Test solutions were pumped through the cell with an electronic peristaltic pump (Model LDB-M, China). The cell and the crystal holder were

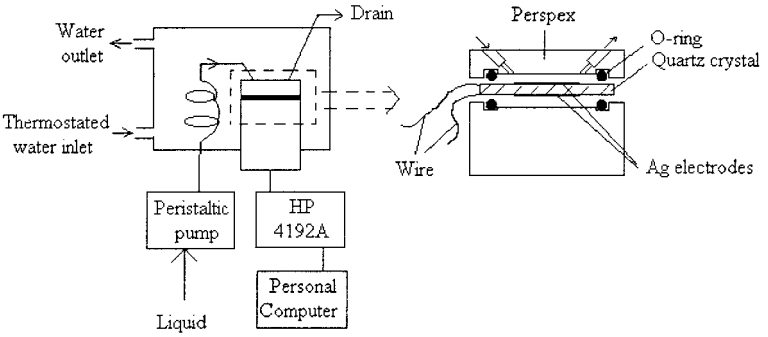

Figure 1 Schematic diagram of the experimental setup.

placed in a thermostatic water bath. A computer was used to control the HP 4192A and to acquire and analyze data.

Two kinds of PEG, PEG-20K and PEG-10K, were supplied by Chemical Reagent Company of Shanghai (China). Their viscosity molecular weights were 20,000 and 10,000, respectively. The sample of poly(vinyl alcohol) was purchased from Kanto Kagaku (Tokyo, Japan). Its degree of polymerization was 500. All test solutions were prepared from double-distilled deionized water, and such water was used throughout.

Procedure

The measurement conditions with the HP 4192A impedance analyzer were as follows: 201 points, a frequency span of 30 kHz covering the resonant frequency of the PQC sensor, IF BW of 10 kHz, and source power of 0.5 dBm.

Before the measurement, 30 min was needed to stabilize the whole experimental setup. In each set of experiments, the motional resistance in air was first determined. Second, the solvent (water) was applied. Then dilute polymer solutions were applied and the concentrations of the solutions were increased stepwise. At last, water was applied again to check the reversibility of the response. Five sets of experiments were performed, three of which were for three single-polymer solution systems (PEG-10K, PEG-20K, and PVAL) and the other two of which were for two-polymer blend systems (PEG-10K/PVAL and PEG-20K/PVAL with $x = 0.5$).

The viscosity of the above-mentioned dilute polymer solutions was also measured with a Ubbelohde viscometer at the temperature 25 $\pm$ 0.1°C.

RESULTS AND DISCUSSION

Main Experimental Conditions and Data Reproducibility

The R_m response of the PQC sensor in liquid is sensitive to system temperature because the viscosity and density of a liquid are related to the temperature. To select an appropriate test temperature, we studied the effect of temperature on the stability of the R_m response in the range 20–32°C. Experimental results showed that a stable R_m response could be obtained under any temperature in this range. In the following experiments, the system temperature was controlled to be 25 $\pm$ 0.1°C.

The flow rate of the fluid has an effect on the properties of the crystal/solution interface. Accordingly, it is also necessary to study the effect of the fluid flow rate on the stability of the R_m response. Experiments showed that no dependency of the R_m response on the flow rate was found in the range 1.3–1.6 mL/min. Hence, the flow rate was controlled to be 1.3–1.6 mL/min in the following experiments.

The concentration of the polymer solution is also an important experimental condition. The concentrations of all polymer and blend solutions were designed to be lower than 0.01 g/mL in this work.

A typical recording of R_m responses by application of various concentrations of a polymer is shown in Figure 2. After the application of a solution with a different concentration of the polymer, the R_m response changed at once and stabilized within 1 min. This indicated that the experimental setup could respond rapidly and sensitively to a change in the viscosity of a dilute polymer solution. Thus, the technique is suitable for continuous measurement.

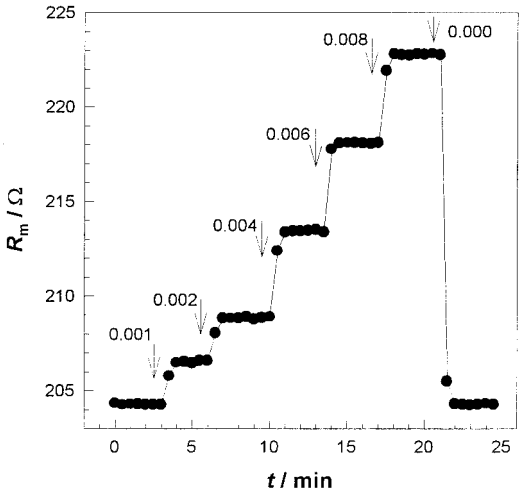

Figure 2 Typical responses of the motional resistance for dilute polymer solutions. Arrows show the times when test solutions were replaced. Concentrations of PEG-10K are 0.001, 0.002, 0.004, 0.006, 0.008, or 0.000 g/mL. [$R_{m(a)}$ = 11.5251 Ω].

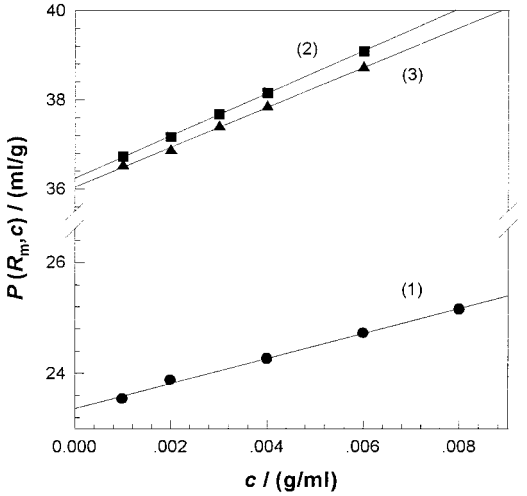

Figure 3 Huggins plots of three single-polymer systems: (1) PEG-10K; (2) PEG-20K; (3) PVAL.

At the end of the experiments, water was applied again, which very quickly reversed the R_m response to its original level. This indicated that no irreversible adsorption occurred on the crystal surface during the measurement. Therefore, the experimental setup can be used repeatedly.

Good data reproducibility was achieved under the experimental conditions mentioned above. The values of R_m caused by varying the concentrations of the polymer were very reproducible: the coefficients of variation (five independent experiments) were lower than 1.8% for all data. For example, the coefficients of variation were 0.8% for water, 1.0% for 0.001 g/mL, 0.9% for 0.002 g/mL, 1.2% for 0.004 g/mL, 1.4% for 0.006 g/mL, and 1.0% for 0.008 g/mL PEG-10K solutions.

Intrinsic Viscosity and Huggins Parameters

For the solutions of a single polymer, define

$$P(R_m,c) = \left[\left(\frac{R_{m(p)} - R_{m(a)}}{R_{m(0)} - R_{m(a)}}\right)^2 - 1\right]\frac{1}{c}$$

Then eq. (6) can be written as

$$P(R_m,c) = [\eta] + k[\eta]^2 c \qquad (9)$$

For dilute solutions of nonelectrolyte polymers, such as PEG and PVAL, a plot of $P(R_m, c)$ versus c should yield a straight line. We prepared aqueous solutions of PEG-10K (c: 0.001, 0.002, 0.004, 0.006, and 0.008 g/mL), PEG-20K (c: 0.001, 0.002, 0.003, 0.004, and 0.006 g/mL), and PVAL (c: 0.001, 0.002, 0.003, 0.004, and 0.006 g/mL). The piezoelectric responses R_m of these solutions were measured with our experimental setup under the above-mentioned conditions. The corresponding values of $P(R_m, c)$ were calculated. The plots of $P(R_m, c)$ versus c for these single-polymer systems are shown in Figure 3. It was evident that the expected linear relationship from eq. (9) held over the entire range of concentrations studied in this work. Results correlating with Huggins plots of these single-polymer systems are listed in Table I.

Theoretically, the Huggins parameter of a flexible polymer should vary between 0.5 (for the θ temperature) and 0.3 (for very good solvent).[18,19] It is shown from Table I that the k value of flexible polymer PEG determined in this work indeed falls within this range, which confirms the reliability of the data.

For solutions of two polymers, define

$$W(R_m, c_1 + c_2) = \left[\left(\frac{R_{m(m)} - R_{m(a)}}{R_{m(0)} - R_{m(a)}}\right)^2 - 1\right]\frac{1}{c_1 + c_2}$$

Equation (7) can be changed into

$$W(R_m, c_1 + c_2) = [\eta]_m + k_m[\eta]_m^2(c_1 + c_2) \qquad (10)$$

We prepared PEG-10K/PVAL and PEG-20K/PVAL blend aqueous solutions, respectively. For both of them, x = 0.5, and the concentrations

Table I Intrinsic Viscosity Data and Intermolecular Interaction Parameters for the PEG/PVAL Blend at 298.15 K

Blend	PEG Fraction	$[\eta]$/(mL/g)	k	α
PEG-10K	1.000	23.36	0.412	—
PEG-20K	1.000	36.24	0.362	—
PVAL	0.000	36.03	0.344	—
PEG-10K/PVAL	0.500	29.68	0.465	0.094 (0.091)[a]
PEG-20K/PVAL	0.500	36.15	0.438	0.086 (0.087)

[a] The values in parenthesis were the results of capillary viscometry.

($c_1 + c_2$) were: 0.001, 0.002, 0.003, 0.004, and 0.005 g/mL. The plots of $W(R_m, c_1 + c_2)$ versus ($c_1 + c_2$) for both blend systems are shown in Figure 4. Each of them yields a straight line over the entire range of concentrations studied here. Results obtained from the plots are also summarized in Table I.

Estimation of Intermolecular Interaction in PEG/PVAL Blend

The values of parameter α for blend PEG/PVAL, calculated according to eq. (8), were 0.094 and 0.086, corresponding to PEG molecular weights of 10,000 and 20,000, respectively. We also determined the α values by capillary viscometry,[1] also listed in Table I. It was evident that the result of the new method was in agreement with that determined by capillary viscometry.

In the Huggins equation, the parameter k originates from a superposition of several types of interactions, that is, the hydrodynamic and thermodynamic contributions. The parameter α can be applied to describe the thermodynamic interaction between unlike macromolecules. The positive values of α here indicated that the intermolecular interaction of PEG and PVAL was attractive.

In a PEG/PVAL blend, several types of hydrogen bonds may be formed, both intra- and intermolecular hydrogen bonds. The latter may be helpful for the crosslinking of the blend, leading to the attractive interaction between PEG and PVAL molecules.

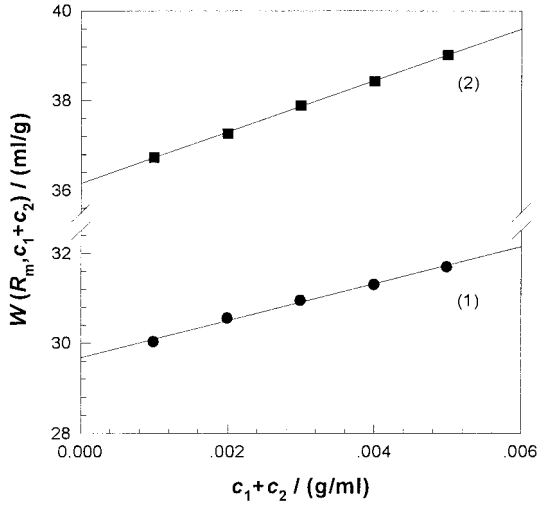

Figure 4 Huggins plots of two polymer blend systems: (1) PEG-10K/PVAL; (2) PEG-20K/PVAL.

CONCLUSIONS

The new method developed here was shown to be an attractive and promising alternative for the study of polymer–polymer intermolecular interaction. The experimental setup was able to provide highly reproducible data at 25°C and a fluid rate of 1.3–1.6 mL/min. The model proposed for the interaction study by R_m monitoring was shown to be valid. The experimental results indicated that there is an attractive intermolecular interaction between PEG and PVAL in the PEG/PVAL blend. An important feature of this method is that it can be used in continuous measurement. We concluded that this method would find more applications in polymer science in the future.

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