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Analysis of the phase transition of polymer blends using quartz crystal analyser

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In this communication we show that an AT-cut quartz crystal analyser (QCA) can be applied to the investigation of the phase transition of polymer blend thin films. The phase transition phenomena of blend films of poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVAc) have been elucidated by simultaneous measurement of the resonant frequency and resonant admittance of the QCA. The PMMA/PVAc blend cast from ethyl acetate exhibited critical changes of resonant frequency and resonant admittance at the glass transition point. Copyright © 1996 Elsevier Science Ltd.

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The quartz crystal analyser (QCA) is known to be a sensitive device for detecting mass changes and monitoring liquid viscosity[1–3]. A large number of analytical applications in areas such as gas sensing, trace ion determination, immunoassay, gelation monitoring and electrochemical examination have been reported[1–5]. Phase-transition phenomena of liquid crystals[6,7], lipid multi-bilayer films[8] and Langmuir–Blodgett (LB) films[2] have been studied using the resonant frequency change on the quartz crystal and the surface acoustic device. The importance of studying viscoelastic phenomena in coating films has been emphasized, especially in the field of electrochemical analysis[9,10]. This can be done by measuring the resonant resistance (or the admittance) of the quartz crystal coated with polymer thin films[11–17]. Then, the mass and viscoelastic changes of polymer blend thin films can be analysed by simultaneous measurement of changes of the resonant frequency and resonant resistance of the quartz crystal.

The purpose of this communication is to present a preliminary report on the applicability of the quartz crystal to analyse viscoelastic changes during the phase transition of polymer blends by *in situ* measurement of the resonant frequency and the resonant resistance as a function of temperature.

The polymers used in this study were poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVAc). PMMA ($M_n = 78\,000$, $M_w = 90\,000$) and PVAc ($M_n = 81\,000$, $M_w = 110\,000$) were purchased from Aldrich Chemical Co. Both polymers were characterized by gel permeation chromatography (g.p.c.) and differential scanning calorimeter (d.s.c.) measurements. PMMA/PVAc blend solutions with various blend ratios were prepared by dissolving 3 wt% of total polymers in ethyl acetate. The blend samples are designated as A/B PMMA/PVAc by weight%. The 50/50 blend, for instance, denotes that the blend contains 50 wt% of PMMA and 50 wt% of PVAc. The solid blend films were prepared by casting the solutions on glass plates, followed by drying to constant weight. The glass transition temperatures of the films were measured using a Perkin–Elmer DSC 7 at a heating rate of $10°\mathrm{C\,min^{-1}}$ on the second run.

The principle of measuring the resonant frequency and resonant resistance changes of the quartz crystal simultaneously is shown in *Figure 1*. A signal with constant amplitude voltage (V_i) was applied from the terminal of the oscillating circuit. The current through the AT-cut quartz crystal is determined by the impedance of the quartz crystal (R_q) and the input impedance of the other terminal of the oscillating circuit (R_i). By measuring the voltage amplitude of the other terminal (V_q), the impedance of the quartz crystal is determined by the relation $R_q = (V_i/V_q - 1)R_i$. The equations for the resonant frequency change, and the resonant resistance of the quartz crystal with a coating film and the quartz crystal in contact with liquid, have been derived from theoretical models[4,5]. Possible deleterious crystal growth defects are known to have effects on quartz resonators[18]. Our previous works[1–3,5,7,10,11,14], however, have verified already that such effects are negligible, since special care has been always taken to avoid the effect of possible crystal defects on the data interpretation, if any.

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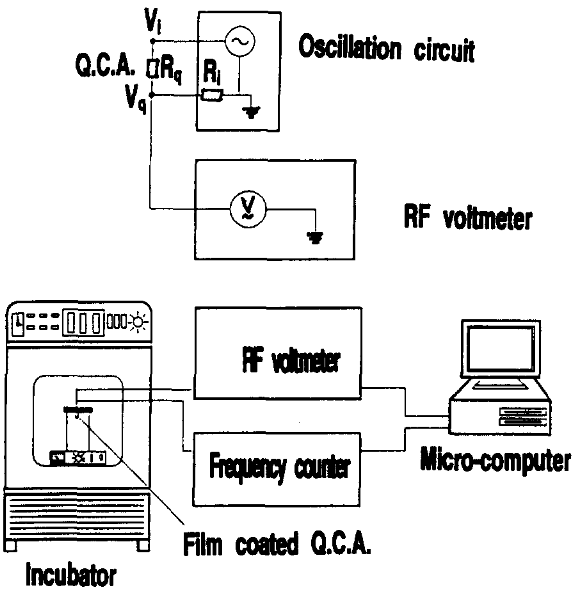

Figure 1 Schematic diagram of measuring system of resonant admittance (or resonant resistance)

The films were heated at a heating rate of 10°C $\min^{-1}$, quenched at the same cooling rate, and heated again at the same heating rate. The transition temperature was taken at the inflection point on the resonant resistance or the resonant frequency as a function of temperature on the second heating runs, where the inflection point was taken as the initial onset of the change of slope in the resonant resistance or the resonant frequency curve on the second run. The precision in the measurements was ±1.5°C. Six measurements were averaged with the confidence limit of 95%.

Figure 2 shows the change in the resonant resistance of dried 50/50 blend films after complete removal of solvents. In this figure, part a shows the change in the resonant resistance and b exhibits the change in the resonant frequency. One can see that there are clear inflection points around 44 and 66°C in the plots of both resonant resistance and resonant frequency as a function of temperature, regardless of the number of heating cycles. In particular, much clearer changes are observed in the case of the plot of the resonant frequency *versus* temperature, as illustrated by arrows in the figure. It may be assumed that these critical changes of resonant frequency and resonant admittance during heating cycles can be attributed to some type of transition temperature. The data are summarized in *Table 1*. The data showed hysteresis on the first and second heating cycles but were always identical within experimental error after the second heating cycle. Thus, the data shown in *Table 1* were taken from the second heating cycle. Similar data on the second heating cycle are also shown for the 30/70 blend and PVAc homopolymer films in *Table 1*. It is seen that two transition temperatures were observed for the blends, meaning that the blend is immiscible, whereas one transition temperature was observed for the homopolymer, PVAc. This result is in agreement with our previous work[19] where it was found that PMMA/PVAc blend films showed phase separation when they were cast from ethyl acetate over the whole composition range.

In *Table 1* the glass transition temperatures obtained from d.s.c. thermograms are also listed for comparison.

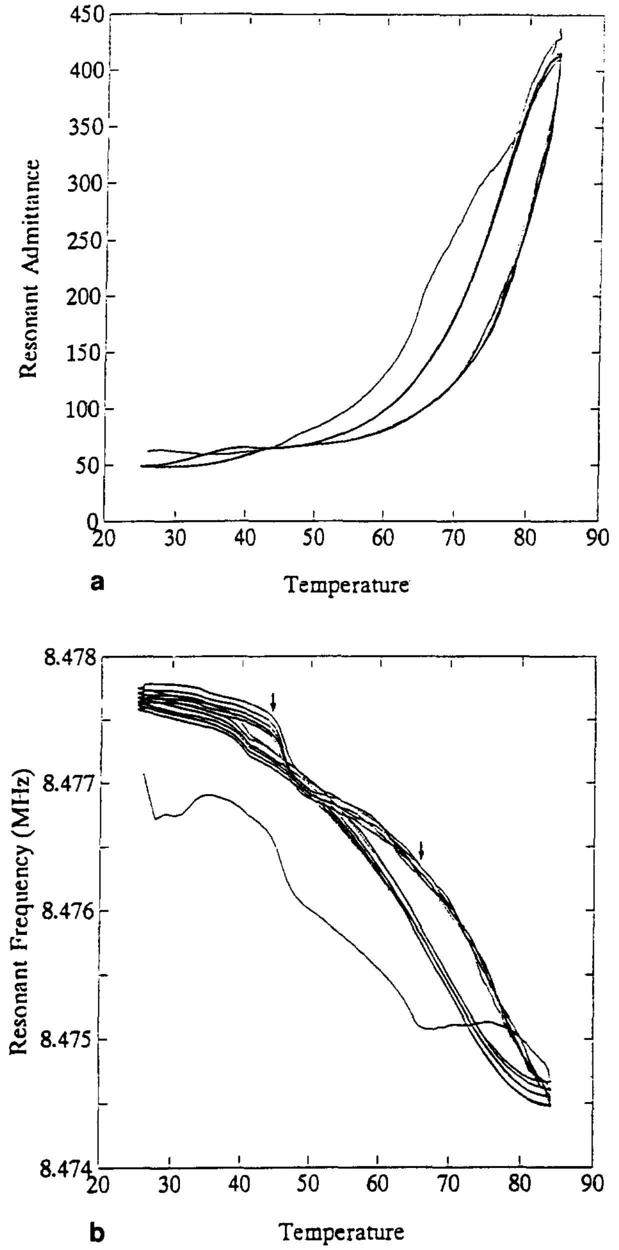

Figure 2 Resonant admittance (a) and resonant frequency (b) profiles of 50/50 PMMA/PVAc blend-coated AT-cut crystal as a function of temperature; the inflection points in (b) are shown by arrows

Table 1 Comparison of phase transition temperatures measured by QCA with T_g point measured by d.s.c. thermograms

	QCA (°C)		D.s.c. (°C)	
PMMA	–		100	
50/50 (PMMA/PVAc)	44	66	35	85
30/70	36	59	38	70
PVAc	39		35	

Comparison of the QCA and d.s.c. data indicates that the transition temperatures from the QCA are indicative of the glass transition temperatures of blend films as well as homopolymers. It should be noted that there is a reasonable correspondence between the glass transition temperatures by d.s.c. and the transition temperatures from the QCA, although there are noticeable differences in the sense of the absolute values. Careful inspection of *Table 1* indicates that the differences are much larger for the PMMA than for the PVAc component in the blends, and the transition temperatures of PMMA measured by the QCA are always lower than the glass transition temperatures of the homopolymer measured by d.s.c.

The discrepancy between the d.s.c. and QCA measurements may result from the thin film nature of the QCA samples compared with the d.s.c. samples. Recently, Mayes reported that the near-surface region of glassy polymers in coatings or thin films exhibits a significant depression in the glass transition due to chain-end enrichment[20]. Since thin films are used for QCA measurements, the results in *Table 1* may therefore be related to the surface-reduced glass transition temperature behaviour of the PMMA component. The transition temperature of PMMA itself, however, was not detected from QCA measurement, since the temperature range of QCA measurement in this study was below 90°C. Therefore, from the data in *Table 1* we conclude that the QCA technique can be successfully applied to investigate the phase transition behaviour of polymer blends by measuring the transition temperature, as well as to measure directly the glass transition temperatures of polymers. Furthermore, it is noteworthy that QCA measurements can detect the phase transition temperature of polymer thin films prepared from solutions containing very small amounts of sample (ca. 0.5–1.0 μg), whereas relatively larger amounts (ca. 5–10 mg) of sample are necessary to measure the phase transition behaviour in bulk by d.s.c. More experiments are in progress and will be reported at a later date.

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