

Monitoring Nonisothermal Crystallization of Thermoplastic Polymers Using a Quartz Crystal Resonator

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ABSTRACT: A new monitoring device for the nonisothermal crystallization of thermoplastic polymers, polyethylene, polypropylene, polystyrene, and polyamide, is developed utilizing a quartz crystal resonator, and its performance is evaluated by comparing the measurements with the results of DSC thermoanalysis and microscopic observation. The experimental results of four different polymers indicate that the variation of resonant frequency of the quartz crystal resonator is a good means to monitor the crystallization process. Though the measurements of melting and crystallization are close to the DSC outcome, more deviation is observed with the new device. The change in crystalline morphology dur-

ing the crystallization process is also detected from the slope changes of the frequency decrease. In comparison with the microscopic observation of polymer films, it is found that the processes of nucleation and crystal growth in nonisothermal crystallization can be explained with the variation of the resonant frequency of the quartz crystal resonator. In addition, crystallization kinetics is modeled with the Avrami equation. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 3370–3380, 2011

Key words: crystallization measurement; polymer crystallization; quartz crystal resonator; thermoplastic polymer

INTRODUCTION

The physical and mechanical properties of polymer are directly related to its structure and morphology, which are in turn influenced by the processing condition of the polymer. Crystallization is an important procedure for obtaining a desired polymer product having a particular specification of properties. Finding the crystallization condition for the specific structure and morphology of polymer is important when it comes to fabricate the desired polymer product. Differential scanning calorimetry (DSC) has been a useful tool to determine whether the properties of the polymer product satisfy the specific requirements. Despite that DSC is good for measuring the polymer properties, its availability is limited due to the cost and size of the equipment. It is necessary to develop a small and readily available device to determine the polymer properties.

The crystallization and melting behavior of copolyesters was examined by DSC and wide-angle X-ray diffraction.¹ The relation between molecular characteristics and crystallization kinetics of syn-

diotactic polypropylene has been determined with DSC.² The procedure was also applied for ethylene-acrylic copolymers and ethylene-methyl acrylate-acrylic acid terpolymers,³ polystyrene-*b*-poly(ethylene-*co*-butene) block copolymers⁴ and poly(ethylene terephthalate)/poly(trimethylene terephthalate) blends.⁵ Recently the crystallinity of isotactic polypropylene fiber has been examined by DSC, wide-angle X-ray diffraction, density gradient analysis and extension stress-strain measurement.⁶ Also, ultrasonic measurement has been used in the characterization of crystallinity, crystallite size and amorphousness.⁷

A quartz crystal resonator comprises a thin quartz crystal sandwiched between two metal electrodes that establish an alternating electric field across the crystal, causing vibrational motion of the crystal at its resonant frequency. This frequency is sensitive to mass changes due to loading on one of the electrodes and the viscoelastic property at the interface of the crystal and its electrode.⁸ For example, a 9-MHz resonator detects a mass variation of 1.4 ng/Hz from resonant frequency measurement⁹ and a viscosity change of 4.3×10^{-6} Pa s/ Ω from resonant resistance.¹⁰ Crystal formation and growth in the cooling crystallization of salt has been investigated with a quartz crystal resonator to determine a metastable zone width¹¹ and hysteresis.¹² The resonator was also used to monitor crystalline nucleation¹³ and growth.¹⁴ For the measurement of

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polymerization, the resonator has been implemented in the monitoring of UV photopolymerization.¹⁵ It has also been utilized in the measurement of adsorption.¹⁶

In this study, the quartz crystal resonator is applied to monitor the nonisothermal crystallization of polyethylene, polypropylene, polystyrene, and polyamide. A small amount of the polymer sample is placed on the electrode of the resonator, and its resonant frequency is traced during crystallization at a given cooling rate. The slope change of frequency variation at a certain temperature of the sample indicates the phase transition and change of crystalline morphology during the crystallization process. The measured results with the resonator are compared with the measurements from DSC and the microscopic observation of polymer films prepared at different quenching temperatures. The Avrami parameters of the crystallization kinetics are also estimated from the measurements.

EXPERIMENTAL

Materials

Polyethylene (Sigma-Aldrich Inc., Code No. 427799) in fine particles having a weight-average molecular weight of about 35,000 and a melting point of 90°C, syndiotactic polypropylene (Sigma-Aldrich Inc., Code No. 452149) having a number-average molecular weight of about 75,000 and a melting point of about 125°C, isotactic polystyrene (Sigma-Aldrich Inc., Code No. 450383) having a weight-average molecular weight of about 400,000 and a melting point

of 212°C, and polyamide (Sigma-Aldrich Inc., Code No. 181110) having a viscosity-average molecular weight of about 100,000 and a melting temperature of 220°C, were used as received. The samples of low melting point polyethylene and polypropylene were selected for the convenience of experiment, when the proposed device was first developed.

Analytical instruments

Thermal analysis was conducted with a differential scanning calorimeter (TA Instruments Inc., Model Q-10).

Resonator and frequency counter

An AT-cut quartz crystal resonator having a base frequency of 8 MHz (Sunny Electronics Co., Korea) was utilized in this experiment. The electrodes of the resonator were silver finished. Figure 1(a) shows the resonator. The resonant frequency, resonant resistance, and the temperature of the oil bath were measured using home-made devices, and an A/D converter was employed for signal processing. The digital signals of the resonant frequency, resonant resistance and temperature were provided to a PC for the data analysis.

Experimental procedure

The cell module holding the quartz crystal resonator shown in Figure 1(a) is illustrated in Figure 1(b). It is composed of two glass holders, two o-rings, two bakelite brackets, and four screws. The dimensions

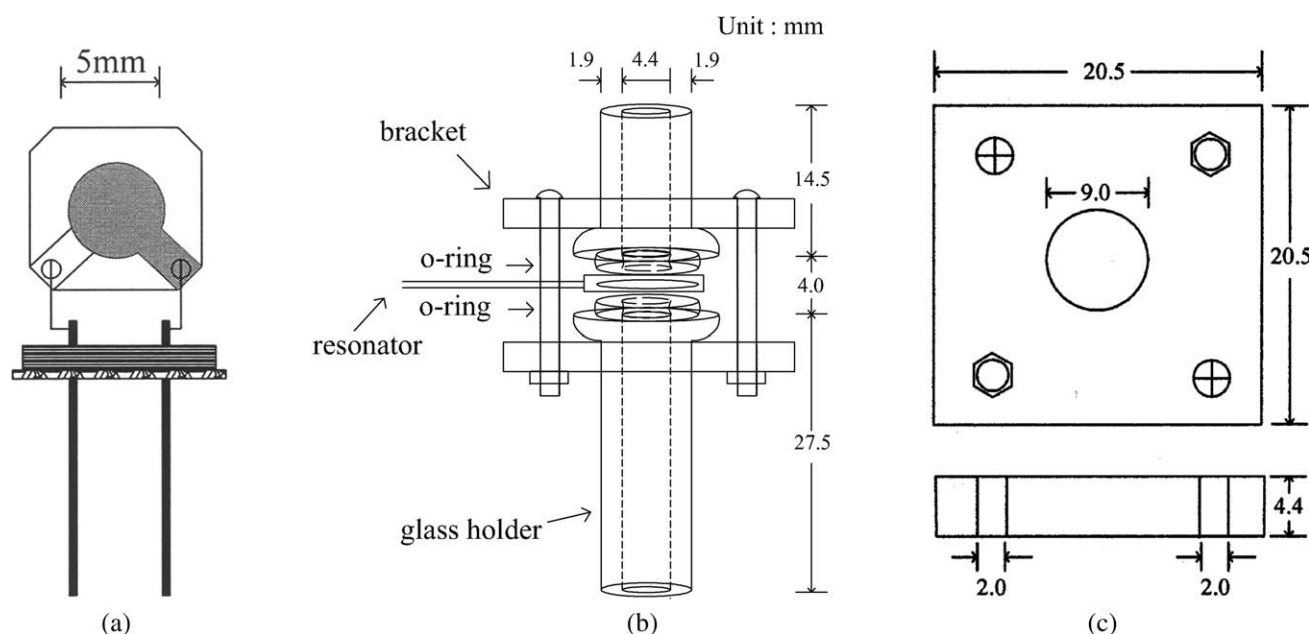


Figure 1 Schematic diagrams of quartz crystal resonator (a), resonator cell module (b), and holding bracket (c).

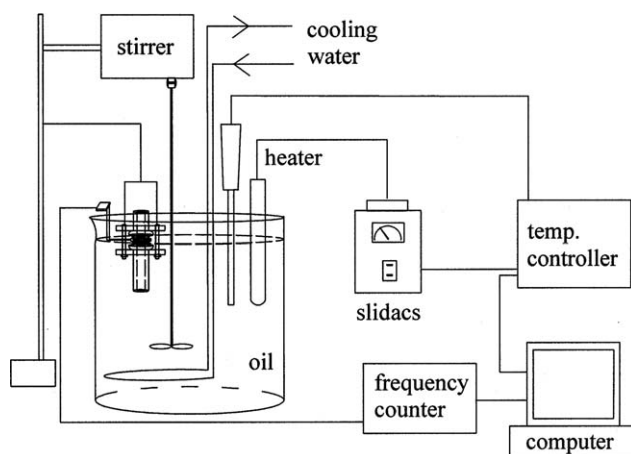


Figure 2 A schematic diagram of the experimental setup.

of the brackets are given in Figure 1(c). The resonator is placed between two glass holders, and the two *o*-rings keep the oil from wetting the electrode surface. The brackets tighten the glass holders with four screws. The detailed dimensions of the cell are given in the Figure 1. After the module was assembled, fine particles of polyethylene were obtained by sieving the powder with a sieve of 250 μm . About one third of 0.1 mg of the polyethylene powder was placed on the top electrode of the resonator. The amount was adequate for the measurement of resonant frequency. The module was put in an oil bath, illustrated in Figure 2. Touching the polymer sample with the heating medium of silicone could affect the thermal property of the polymer. Therefore, a careful placement of the resonator in the oil bath was necessary. For better control of resonator temperature, the module was immersed to the level of the upper *o*-ring in the bath. The bath temperature was adjusted by electric heating, and water cooling was also provided for the cooling process in the experiment. The electric heater was controlled by means of a programmable temperature controller (Hanyoung Electronic Co., Korea, Model NP-200).

The experiment began at a temperature of about 40°C. After the experimental setup was stabilized for an hour, the bath temperature was raised at a rate of 1.5°C/min up to 100°C, and was cooled at a rate of 1°C/min. In two separate runs, the cooling cycles were manipulated at rates of 0.5°C/min and 2°C/min, respectively. Though the highest temperature of heating was 100°C for polyethylene, it was 160°C, 260°C, and 250°C for polypropylene, polystyrene, and polyamide respectively. While the temperature increase was at a rate of 2°C/min, the decrease for the crystallization was at a rate of 2°C/min for polypropylene and polystyrene, and at a rate of 1.5°C/min for polyamide. The polyethylene sample was not melted completely until the top heating temperature of 100°C was reached. The measurement was

conducted in air. In the cooling process, the sample was gradually crystallized. The resonator can be heated up to 500°C in a nitrogen atmosphere, and therefore the viscosity of actual industrial polymers with high molecular weights can be measured by raising the measuring temperature. A PC collected the data of resonant frequency, resonant resistance and bath temperature during the experiment, and the stored data was analyzed following the experiment. For comparison of the crystallization measurements, the thermoanalytic experiments were conducted using DSC with the same temperature manipulation as in the frequency measurement. Because the sample amount is so small, the sample may not be representative of the tested polymer, and repeated measurements with different samples are necessary.

To examine the crystallization measurements with the resonant frequency variation, separate film samples prepared from the crystallization using similar temperature manipulation were observed with a microscope (Olympus, Japan, Model BH-2). Twenty milligrams of polyethylene was placed on a slide glass, and was heated up to 130°C at a rate of 2°C/min in an oven. When the polyethylene had melted completely, a cover glass and a weight were placed on the sample to make a film specimen. The film was cooled at a rate of 1°C/min until the temperature reached 90°C, and then was quenched with tap water. In the same manner, two more films, with temperatures of 73°C and 60°C, were prepared.

Frequency and physical property variation

The frequency variation due to the viscosity change of the polymer sample placed on the electrode surface of a quartz crystal resonator is computed from the following equation.^{17,18}

$$\Delta f \approx \frac{1}{2\pi\rho_0 h_0} \sqrt{\frac{\rho\eta\omega}{2}} \quad (1)$$

where f is the resonant frequency, ρ is density, h is thickness, η is viscosity, ω is angular velocity, and the subscript denotes the quartz plate. The subscript 0 denotes the properties of quartz plate, and the properties of the polymer sample are represented without the subscript. In the cooling process of the polymer sample the polymer crystallizes. As the polymer crystallization proceeds, the viscosity increases to result in a steady decrease of the resonant frequency. Therefore, monitoring the frequency can serve to trace the crystallization process of the polymer sample.

The change of viscosity of thermoplastic polymers, polyethylene, polypropylene, polystyrene and

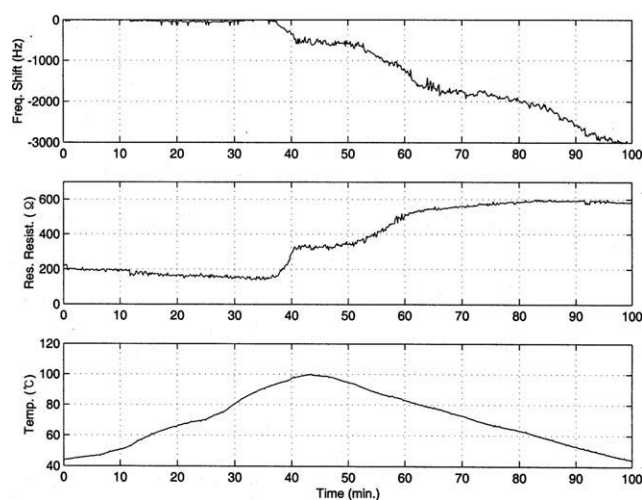


Figure 3 Variations of resonant frequency, resonant resistance, and temperature of polyethylene at a cooling rate of $1^{\circ}\text{C}/\text{min}$.

polyamide during nonisothermal crystallization was monitored from the variation of resonant frequency of the quartz crystal resonator. A small amount of polymer sample was placed on the electrode of the resonator having a thin, tiny quartz plate. The results of the examination of frequency variation are explained below.

RESULTS AND DISCUSSION

Monitoring crystallization with frequency

Figure 3 shows the variations of the resonant frequency, resonant resistance and temperature while the temperature of the polyethylene sample is raised from 40 to 100°C at an average rate of $1.5^{\circ}\text{C}/\text{min}$ and cooled to 40°C at a rate of $1^{\circ}\text{C}/\text{min}$. During the temperature elevation up to 90°C no significant change in the frequency was observed, but a slow reduction of resonant resistance was detected. Because the sample was powder, no surface contact of the sample on the electrode was made until it melted, keeping the resonant frequency steady. When the sample began to melt, surface contact was partially made, and the frequency also decreased until the sample melted completely. In the beginning the sample particles were put on the electrode surface, and the contact area between the sample and electrode was limited. During the melting of the sample the area continuously broadened to reduce the frequency and to raise the resistance. After the melting was completed, frequency and resistance were stable until crystallization started. As the crystallization proceeded, the frequency steadily dropped and the resistance rose. The frequency decrease and the resistance elevation are due to the increase of rigidity from the crystallization on the

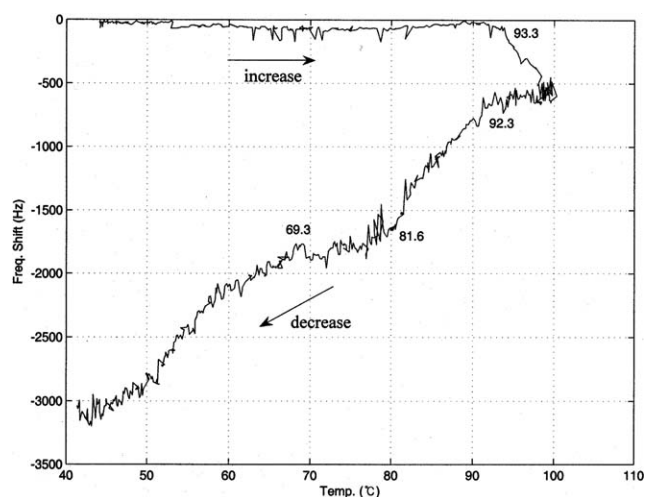


Figure 4 Variation of resonant frequency with temperature of polyethylene at a cooling rate of $1^{\circ}\text{C}/\text{min}$. The numbers are the temperatures at the moment of slope change in the frequency variation.

electrode surface of the resonator as indicated in eq. (1). A slope change of frequency variation indicates the variation of sample viscosity representing phase transition and the alteration of crystalline morphology of the polymer sample. For better examination of frequency variation, Figure 4 is provided as a plot of the frequency and sample temperature changes of the polyethylene sample. The arrows show the direction of temperature variation, and the numbers indicate the temperatures of slope change of the frequency variation. The measurements were conducted with different rates of cooling for polyethylene samples. In Figures 5 and 6, the cooling rates were $0.5^{\circ}\text{C}/\text{min}$ and $2^{\circ}\text{C}/\text{min}$, respectively, while

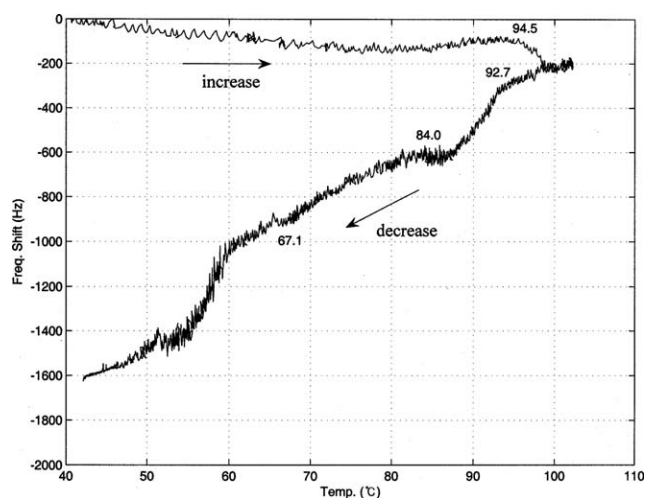


Figure 5 Variation of resonant frequency of polyethylene with temperature at a cooling rate of $0.5^{\circ}\text{C}/\text{min}$. The numbers indicate the temperatures at the moment of slope change in the frequency variation.

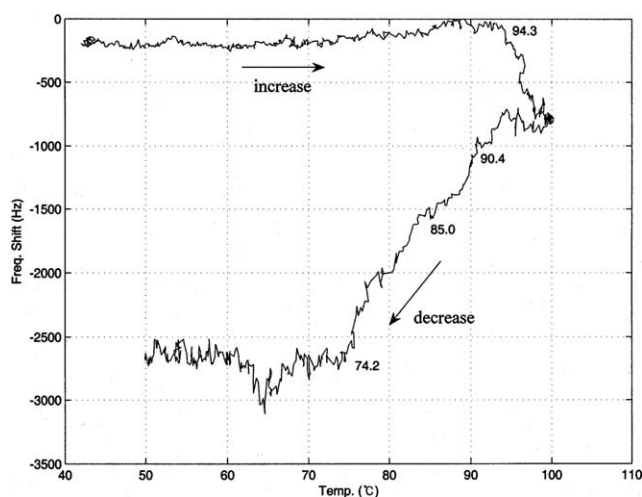


Figure 6 Variation of resonant frequency of polyethylene with temperature at a cooling rate of 2°C/min. The numbers indicate the temperatures at the moment of slope change in the frequency variation.

the heating rate was the same as in the previous measurement. Similar processes of melting and crystallization were observed for the three different rates of cooling. The absolute value of frequency shift depends on the sample amount. Because the exact amounts are different for the measurements in various cooling rates, the different frequency shifts are observed.

The same procedure of melting and crystallization of polyethylene was applied to the polypropylene sample, and the variation of resonant frequency along with temperature manipulation is shown in Figure 7. The sample temperature was raised up to 165°C at a rate of 2°C/min, and reduced at the same rate. The procedure was also applied to the polysty-

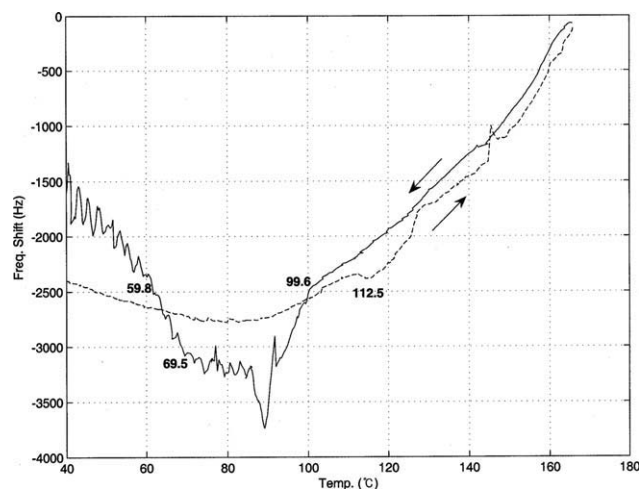


Figure 7 Variation of resonant frequency of polypropylene with temperature at a cooling rate of 2°C/min. The numbers indicate the temperatures at the moment of slope change in the frequency variation.

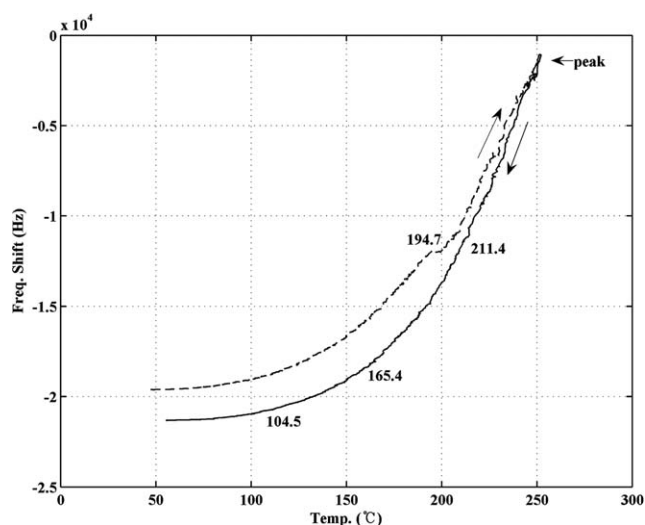


Figure 8 Variation of resonant frequency of polystyrene with temperature at a cooling rate of 2°C/min. The numbers indicate the temperatures at the moment of slope change in the frequency variation.

rene and polyamide samples, and the frequency variations of these samples with temperature are given in Figures 8 and 9 respectively. In these measurements, the temperature was elevated up to 250°C. The temperatures of the slope change of frequency variation are indicated in the plots, and they are summarized in Table I. The sample melts as the temperature elevates, and crystallizes as lowers. The headings in the Table I follow the sequence of the sample changes. The peak frequency observed in the cooling process of Figure 8—others are in the heating process—is presumed to be an experimental error. The readings are compared with the DSC measurements in the next section.

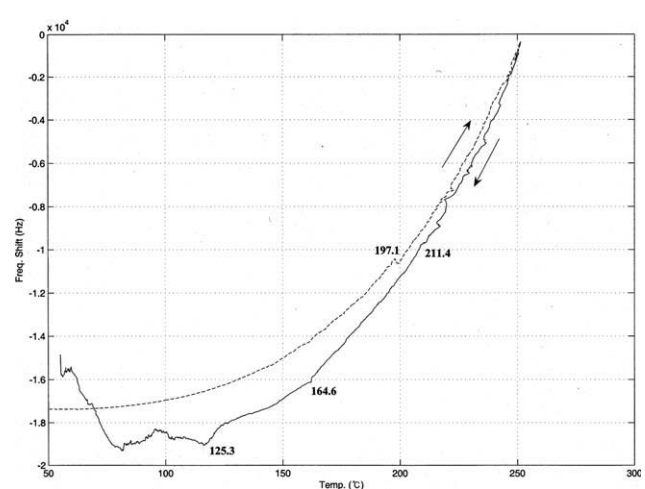


Figure 9 Variation of resonant frequency of polyamide with temperature at a cooling rate of 1.5°C/min. The numbers indicate the temperatures at the moment of slope change in the frequency variation.

TABLE I
Measured Temperatures of Melting, Solidification, Nucleation and Crystal Growth Using the Quartz Crystal Resonator and the DSC at Different Cooling Rates

Polymer	Cooling rate (°C/min)	Quartz crystal resonator				DSC	
		Melting	Solidification	Nucleation growth		Melting	Solidification
PE	0.5	94.5	92.7	84.0	67.1	94.8	92.9
	1.0	93.3	92.3	81.6	69.3	93.1	92.1
	2.0	94.3	90.4	85.0	74.2	94.3	91.1
PP	2.0	112.5	99.6	69.5	59.8	112.8	96.4
PS	2.0	194.7	211.4	165.4	104.5	195.1	211.1
PA	1.5	197.1	211.4	164.6	125.3	199.7	206.9

Unless the resonant frequency suddenly decreases by a large amount during crystallization, the measurement is valid. When the sample amount was too much, or the sample was detached from the resonator surface, the frequency dropped abruptly and the measurement was no longer available. This unsuccessful measurement happened once out of about five measurements. The measurements listed in Table I were from the single measurement. For the analysis of measurement deviation, the results of three measurements for different cooling rates are listed in Table II. The errors were computed from the average of three measurements of a cooling rate, and the largest error among the three cooling rates is listed in the Table II. While the temperature of crystal growth gives the highest error of +3.17°C, others are less than 2°C. As shown in Table II the measurement error increases with higher cooling rates, but the difference is not significant. A lower cooling rate gives less noise in the frequency measurement, and more distinct observation of the slope change is available. While the repeatability of measurement was good at a low cooling rate, low repeatability was observed due to the fast temperature variation in the measurement of high cooling rates. The measured melting temperature is compared with the temperature provided by the polymer manufacturer in Table III. The measurement of

melting temperature depends upon the heating rate and amount of sample. The difference of the melting points listed in the Table III is from the different heating rate and sample amount. Change of viscosity in the amorphous phase was also detected with the proposed device, when it gave the variation of slope in the viscosity increase with cooling.

To examine the accuracy of the proposed device, measurement of indium crystallization was conducted, but the resonant frequency suddenly dropped during the measurement due to the sample melting and metal-metal adhesion on the silver electrode of the resonator. This test was attempted with potassium thiocyanate—a nonmetallic compound having a relatively sharp melting point, and the sudden frequency drop made the test impossible.

Comparison with DSC measurements

Phase transition was detected from the change of frequency variation slope in the plot of sample temperature and frequency, and the results were compared with DSC measurements. Figures 4 through 9 are the plots of polyethylene, polypropylene, polystyrene, and polyamide, and the temperatures of the slope change listed in Table I are interpreted for the phase transition and morphological change. For the evaluation of the temperature measurements,

TABLE II
Measured Temperatures of Melting, Solidification, Nucleation and Crystal Growth Using the Quartz Crystal Resonator at Different Cooling Rates for Performance Evaluation

Polymer	Cooling rate (°C/min)	Quartz crystal resonator			
		Melting	Solidification	Nucleation	Growth
PE	5	86.7	87.8	82.7	46.2
	5	86.5	88.0	81.5	42.4
	5	85.2	87.6	81.5	43.7
PE	7	86.6	87.8	83.4	46.2
	7	85.9	87.8	81.6	50.7
	7	84.1	86.5	80.9	48.1
PE	10	84.7	84.7	79.6	37.4
	10	86.5	87.8	80.2	35.5
	10	86.5	86.6	82.8	41.2
Max. error from average		-1.43	-1.67	+1.93	+3.17

TABLE III
Measured and Manufacturer's Temperatures of Melting.
Measured Temperature is at a Cooling Rate of
2.0 °C/min Except PA at 1.5 °C/min. Units Are in °C

Polymer	Measured	Manufacturer's
PE	94.3	90
PP	112.5	125
PS	194.7	212
PA	197.1	220

DSC thermoanalysis was conducted with the same sample and temperature variation. Figure 10 shows the result for polyethylene at a cooling rate of 1°C/min in the dashed line. The beginning temperatures of melting and crystallization are close to the measurements, except for polypropylene and polyamide as given in Table I. Note that the DSC analysis does not show the temperature of the morphological change. The DSC measurement was conducted with different rates of cooling for the polyethylene sample. In the solid line of Figure 10 the cooling rate was 0.5°C/min, while the heating was the same as in the frequency measurement. Similar processes of melting and crystallization are observed. Again, the measurements of the proposed device and DSC are close. The same

measurement was carried out with a cooling rate of 2°C/min as demonstrated in the double dashed line of Figure 10, and a similar comparison result was obtained to the previous two experiments. Though the heating rate is same in Figure 10, the difference in heat flow is due to different samples used and measurement error. The crystalline polymer is more stable than the amorphous, and it releases more heat during crystallization.

DSC thermoanalysis was conducted with different samples of polypropylene, polyamide, and polystyrene, and the results are shown in Figures 11 and 12. The temperature variation was the same as in the frequency measurements. Though the measurements of the proposed device give some error from the results of the DSC as listed in Table I, they are acceptable. Two peaks in the melting process of the double dashed line of Figure 11 are presumed to be two particles of sample having slightly different properties placed on the sample holder. The large temperature difference between the measurements of the proposed technique and the DSC in polypropylene and polyamide is due to the limit of the new device. The measurement results of phase transition temperature from the proposed device using a quartz crystal resonator and of DSC indicate that the

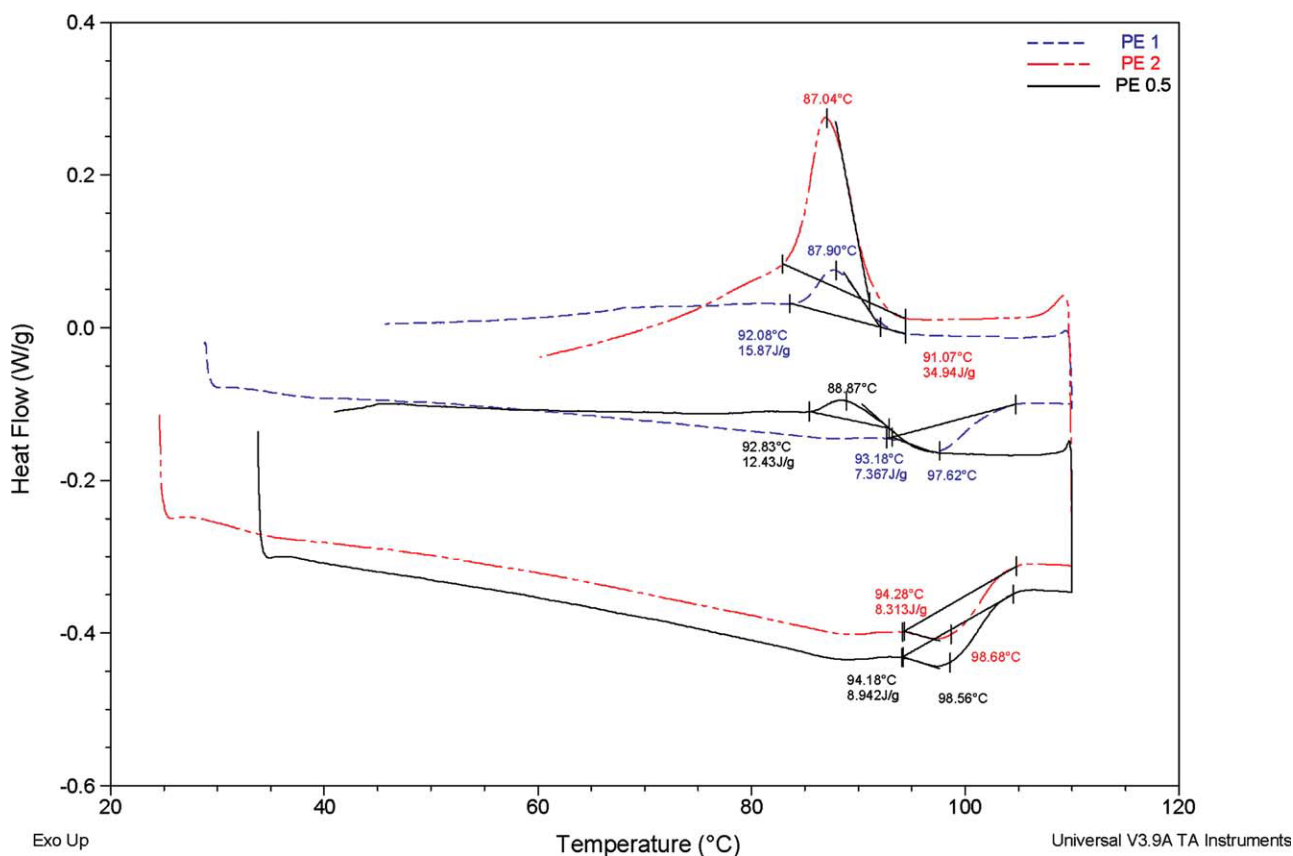


Figure 10 Plot of DSC thermoanalysis of polyethylene at different cooling rates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

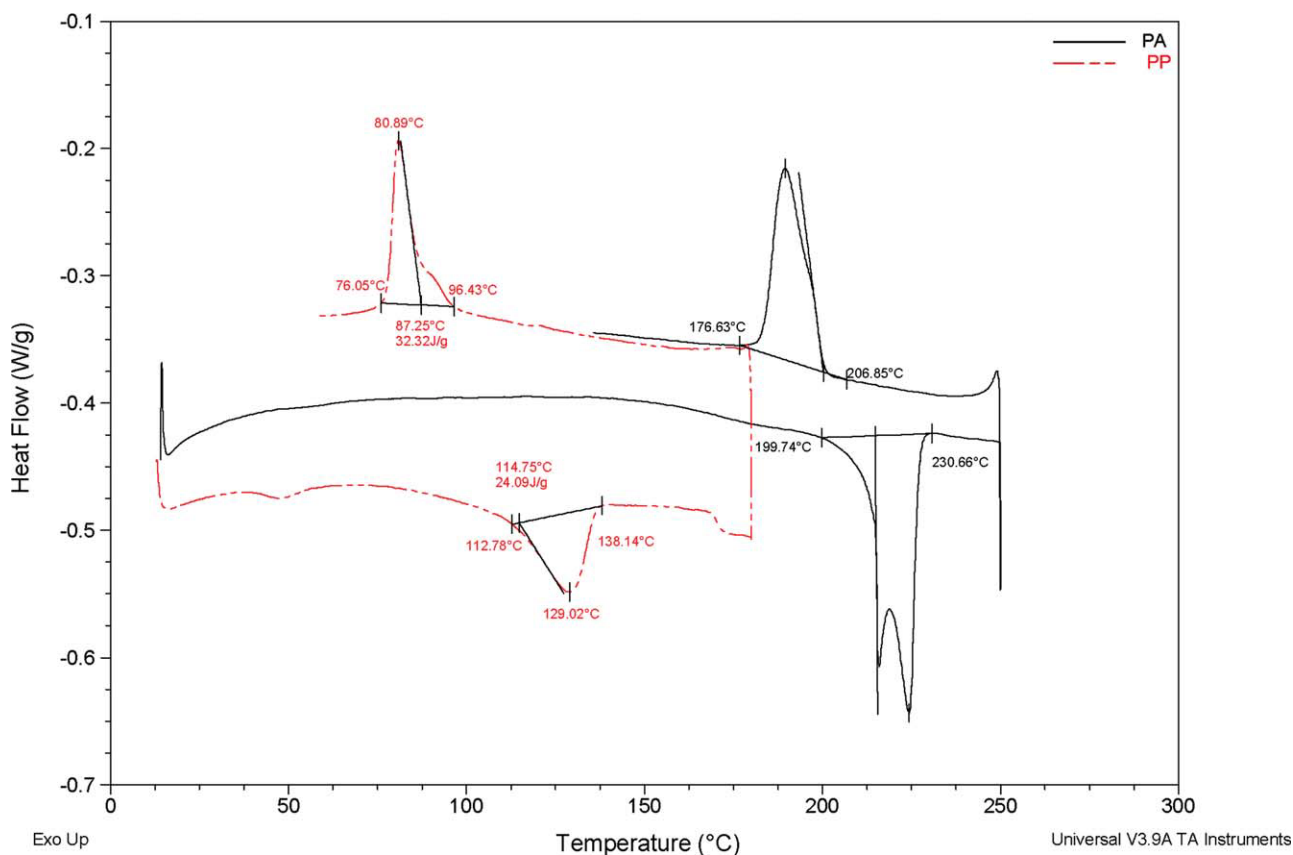


Figure 11 Plot of DSC thermoanalysis of polypropylene and polyamide at cooling rates of 2°C/min and 1.5°C/min, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

monitoring performance of the proposed device is acceptable. Yet further improvement of the new device is necessary.

The change of crystalline morphology was also determined from the change of frequency variation slope in the plot of temperature and frequency, and the result was compared with microscopic observation. For close examination of the frequency variation along with the sample temperature, variation for the polyethylene at a cooling rate of 1°C/min is plotted in Figure 4. The arrows of increase and decrease indicate the direction of temperature variation. The steady frequency during the temperature elevation suddenly dropped at a temperature of 93.3°C, at which the melting of the polyethylene sample began. The frequency reduction stopped at 100°C when the melting was completed, and slowly lowered when the cooling began. As seen in the top plot of Figure 3, the drop of frequency stopped above around 93°C, and the supplier of the sample polyethylene indicated that the melting point was 90°C. Therefore, the sample was heated up to 100°C. At a temperature of 92.3°C the slope of frequency reduction became larger due to the initia-

tion of crystallization of the molten sample. These temperatures of melting and crystallization were close to the results of DSC measurement as demonstrated in Figure 10.

Microscopic observation

In the process of further temperature decrease as given in Figure 4, the slope changes of frequency variation were observed at temperatures of 81.6°C and 69.3°C. These slope changes are presumed to indicate different processes of crystallization, though the DSC result does not show the changes. In the crystallization of polyethylene, it has been reported that the equilibrium phase transition temperature from the monoclinic to the hexagonal phase is approximately 80°C during heating, and the phase transition of monoclinic to hexagonal phase in annealing occurs at a temperature of 68°C.¹⁹ Because direct observation of the different processes of crystallization was not available with the polyethylene sample on the resonator surface in this study, separate film specimens were prepared to examine the difference of crystalline morphology. The detailed

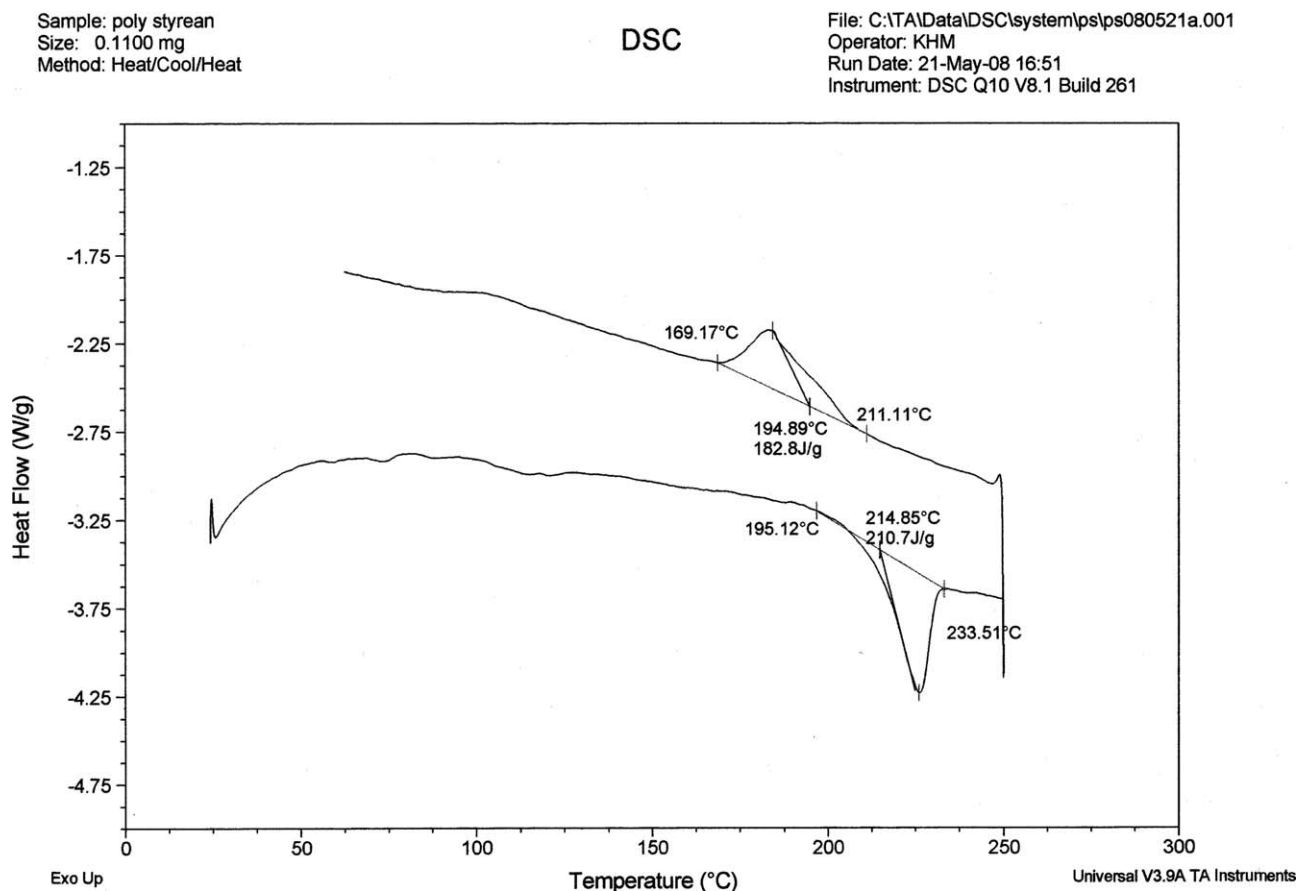


Figure 12 Plot of DSC thermoanalysis of polystyrene at a cooling rate of 2°C/min.

procedure of film preparation has been given in the experimental section. Figure 13 demonstrates the nucleation and crystal growth observed with a microscope having a magnification of 400 \times . Between Figure 13(a,b), the number of white dots rises significantly. This indicates that the nucleation occurs during the period at a temperature between 92.3°C and 69.3°C. Note that Figure 13(a) shows the film quenched at a temperature of 90°C and Figure 13(b), at 73°C. When the film is prepared at a temperature of 60°C as illustrated in Figure 13(c), the size of crystals is much bigger than that appearing in Figure 13(b). This indicates that the crystal growth occurs below the temperature of 69.3°C. Though the DSC result does not show any of these observations of crystalline variation, the proposed device of this study monitors not only the phase changes but also the processes of crystallization. The beginning of crystallization is observed at the first change of the slope of resonant frequency decrease, and the final change of the slope indicates the end of the crystallization. Between the temperatures the processes of nucleation and crystal growth are demonstrated.

Crystallization kinetics

The kinetics of polymer crystallization is commonly described with the following Avrami model.^{2,20–22}

$$\theta(t) = 1 - \exp(-K_A t^{n_A}) \quad (2)$$

where θ is the relative crystallinity, a function of time t , and K_A and n_A are the Avrami parameters. Though the Avrami equation was used for isothermal crystallization, the simplified assumption that crystallization occurs under constant temperature was applied for the modeling.^{2,5} As the crystallization of the polyethylene sample placed on the resonator surface proceeds, the sample viscosity increases and the resonant frequency drops more as given in eq. (1). Therefore, the relative crystallinity is related to the frequency decrease. The parameters were obtained from the experimental results of the frequency variation with regression, and are listed in Table IV.

To examine the effect of temperature change on the resonant frequency and resonant resistance, a blank test was conducted, and the results are shown in Figure 14. Whereas frequency variation

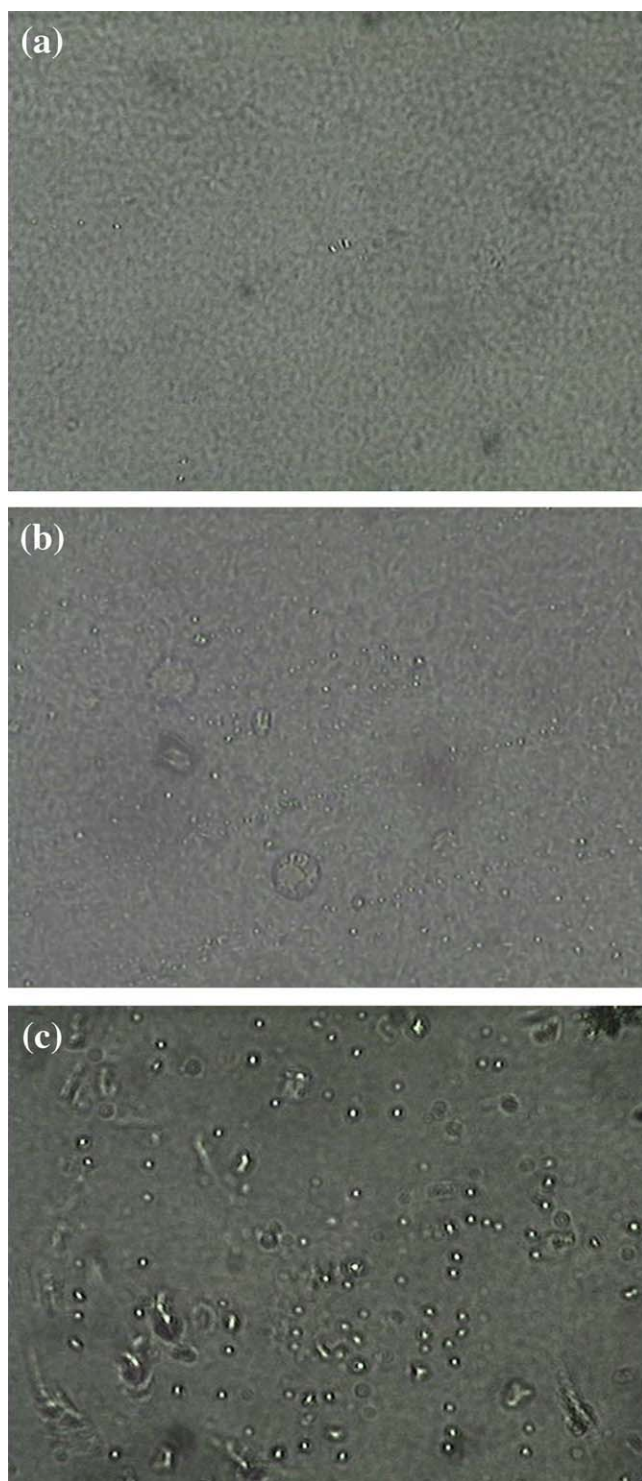


Figure 13 Microscopic photographs of polyethylene film quenched at temperatures of 90°C (a), 73°C (b), and 60°C (c) with a magnification of $\times 400$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was noticeable, resistance varied to a much smaller extent than the sample measurement shown in Figure 3. Almost a half of the total variation of the frequency occurred at the temperature of melting,

TABLE IV
Avrami Parameters

Polymer	Cooling rate (°C/min)	K_A	n_A	Corr. coef.
PE	0.5	0.0063	1.18	0.949
	1.0	0.0173	1.18	0.978
	2.0	0.0069	2.41	0.945
PP	2.0	0.0360	1.07	0.977
PS	2.0	0.0213	1.27	0.922
PA	1.5	0.0636	1.11	0.898

and the amount of variation was much smaller than that in the measurement of Figure 3. The oscillation frequency of the quartz crystal resonator is proportional to the square root of shear modulus of quartz.⁸ The modulus increases with temperature elevation resulting in the frequency increase. The resonant resistance is inversely proportional to the square of shear stiffness of the quartz. As temperature rises, the stiffness decreases and the resistance increases.²³ In the calculation of the parameters in eq. (2) the effect of temperature variation was eliminated by deducting the frequency variation of a blank resonator. The computed parameters are relatively even for different samples and cooling rates with an acceptable coefficient of correlation. This indicates that the proposed device is useful for monitoring the nonisothermal crystallization of polymer materials. The Avrami parameter n_A was between 1.0 and 2.7, and K_A was between 0.0012 and 0.48 for PET.²⁴ The n_A was between 2.01 and 3.27, and K_A was between 9×10^{-5} and 3.58 for PP.²⁵

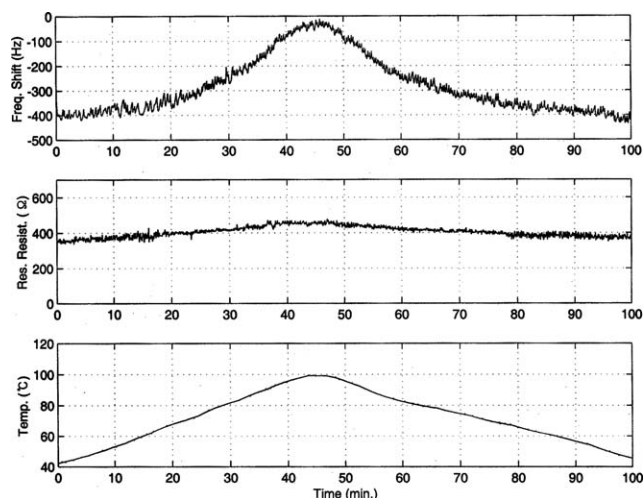


Figure 14 Variations of resonant frequency, resonant resistance, and temperature with a blank resonator at a cooling rate of 1°C/min.

The device of a quartz crystal resonator proposed in this study is quite simple and readily available compared with DSC equipment. It can give relatively good measurements of the phase transition temperature of polymer compared with the DSC analysis, and the temperature of crystalline morphology variation can be determined using the device. The proposed device can be utilized in monitoring the whole process of nonisothermal crystallization of polymer material, which is not possible with DSC. The continuous measurements of crystallinity are used to determine the kinetic parameters of crystallization model. In addition, the proposed device can be modified to a portable instrument having wide applications in practice, because it is simple and small. However, further improvement of the device is necessary.

CONCLUSIONS

A new monitoring device to observe the melting and crystallization of polymer materials is proposed, and its performance is examined and compared with the results from DSC and microscopy. The resonant frequency of the proposed device is utilized in the determination of melting and crystallization of polyethylene, polypropylene, polystyrene, and polyamide. The experimental results indicate that the measurements show some deviation from those of DSC, but monitoring of morphological change is possible. Though the measurements are acceptable, further improvement of the proposed device is necessary. From the frequency measurement, the crystallization kinetics is modeled using the Avrami equation. In spite of its limitations, the proposed device is simple and readily available, and its usefulness in the measurement of melting and crystallization of polymer material is demonstrated here.

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