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In-situ measurement of microwave absorption properties at 2.45 GHz for the polycondensation of lactic acid

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ABSTRACT

For the construction of a microwave-assisted organic synthesis plant, it is necessary to know the dielectric properties of the reaction system. Measurements of the dielectric properties of lactic acid aqueous solution, anhydrated lactic acid, oligo(lactic acid) and water, which are constituent materials in the polycondensation of lactic acid, confirm that dielectric properties decrease as reaction progresses. Calculated microwave penetration depths, obtained from the dielectric properties, show that microwaves penetrate deeply into the reaction system. This work should be useful for the development of microwave-assisted organic syntheses in the chemical industry.

1. Introduction

Microwave-assisted organic synthesis was first reported, in 1986, independently by Gedye et al. [1] and Giguere et al. [2] using domestic microwave ovens. Thousands of reports have since been published on microwave-assisted organic synthesis using desktop-level synthesis devices [3–7]. Recently, based on results obtained with these smaller devices, technology for scaling up the reaction vessel to a size suitable for industrial production is also of interest [8–10]. For large microwave-assisted organic synthesis plants, knowledge of the dielectric properties of reaction materials that are to be heated by microwave is essential for effective use of energy and safe operation of the plant. In particular, knowledge of power dissipation and microwave penetration depth is important.

Since the 1950s, microwave heating at 2.45 GHz has been widely used in the rubber and food industry [11]. In the latter, microwave absorption properties that depend on water content [12] or salt [13] have been studied. However, studies of dielectric properties as a function of reaction progress for organic and polymer syntheses at 2.45 GHz have not been reported, to the author's knowledge. In the food industry, although heating instruments have been designed based on such physicochemical data, this is not yet the case for reaction instruments for microwave-assisted organic and polymer synthesis.

Polycondensation is a basic reaction for the synthesis of polyester [14]. We have reported that microwave heating accelerates the synthesis of polyesters such as poly(lactic acid) [15] and aliphatic polyesters [16] by a factor of 10 compared to conventional heating. Based on the result of polycondensation of lactic acid by microwave heating, we developed a pilot-level microwave reactor. For it to be used effectively, it is necessary that we know the dielectric properties of materials involved in the polycondensation system.

The complex dielectric constant is given by the following equation [11]:

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \tag{1}$$

where $j = \sqrt{-1}$, ε' is the dielectric constant, and ε'' is the dielectric loss. Dielectric properties depend on the microwave frequency and temperature. In addition, the dielectric properties of a reaction system as a whole change as the reaction progresses because of the changing constituent materials in the system. Water in the system strongly influences the absorption properties of the system due to its high dielectric loss.

Power dissipation by microwave energy is given by the following equation:

$$P = \omega\varepsilon_0\varepsilon'' E^2 V \tag{2}$$

where ω is the angular frequency, ε_0 is the permittivity of free space, E is the electric field strength and V is the volume. Dielectric loss is related to heat generation by microwave energy. Thus it is

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important to measure the dielectric loss of heated materials as a function of temperature to predict overheating and prevent consequent runaway behaviour in a reaction system.

The penetration depth (at half power) of microwave energy is also a key factor in predicting efficient heating. This factor is given by the following equation:

$$D = \frac{\lambda}{2\pi\sqrt{\epsilon'}\tan\delta} \tag{3}$$

where $\tan\delta = \varepsilon''/\varepsilon'$ is the loss tangent and $\lambda = c/f$ is the microwave wavelength. Thus, the ratio of ε'' to ε' is related to the penetration depth. For the design of a microwave reaction plant, it is necessary to know the penetration depth as a function of temperature.

For this report, we measured the dielectric properties of the chemical materials involved in the polycondensation of lactic acid at 2.45 GHz as a function of temperature. The chemical materials are lactic acid aqueous solution, anhydrated lactic acid, oligo(lactic acid) and water—which are, respectively, the reaction substrate, intermediate, resultant and by-product. In addition, we estimated the penetration depth and attenuation curve of the microwaves. We also measured the water content in the materials and their average molecular weights to characterize the materials. Finally, we considered how microwave attenuation and dielectric properties change during the course of the polycondensation.

2. Experimental

2.1. Polycondensation of lactic acid

L-lactic acid (LA_{aq}, 90% aqueous solution) was purchased from Wako Chemical Industry and used without further purification. Lactic acid (2 mol) in a cylindrical reactor glass was set into a multimode microwave reactor (SMW-101, Shikoku Instruments, 2.45 GHz, max. power 1.5 kW). Temperature was measured by a fiber-optic thermometer (AMOTH FL-2000, Anritsu Meter Co.). A fiber-optic sensor was immersed into the reaction mixture through a glass tube.

Anhydrated lactic acid (LA_{an}) was prepared as follows: reaction temperature of the lactic acid aqueous solution was increased from room temperature to 180 °C for 5 min and then kept at that temperature for 30 min under atmospheric pressure.

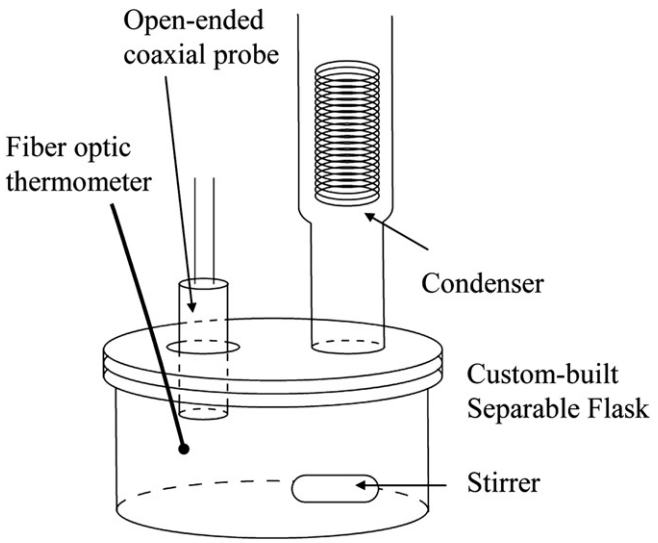


Fig. 1. Schematic illustration of a set for open-ended coaxial probe measurement.

Table 1
Symbols and characterizations of measured materials.

Material	Symbol	Average molecular weight[a]		Water content (%)
		M_n	M_w	
Lactic acid aqueous solution	LA_{aq}	(90.08)[b]	(90.08)	14.551
Anhydrated lactic acid	LA_{an}	607	622	2.038
Oligo(lactic acid)	LA_{oligo}	1480	2240	0.118

[a] Polystyrene was used as a standard.
[b] Molecular weight of lactic acid.

Oligo(lactic acid) (LA_{oligo}) was prepared as follows: anhydrated lactic acid was additionally heated at 180 °C for 90 min under vacuum at 200 Pa. The pressure was gradually decreased from atmospheric pressure to 200 Pa for 30 min.

2.2. Measurement of dielectric properties

Dielectric properties were measured using an open-ended coaxial probe [17,18]. The measurement system consisted of a custom-build separable flask (Fig. 1), high-temperature dielectric probe (85070E, Agilent Technologies) and vector network analyzer (8720ES, Agilent Technologies). The vector network analyzer operates over the frequency range 0.2–20 GHz. The probe operates over the temperature range −40 to 200 °C. The vector network analyzer was connected by a PCMCIA-GPIB interface (National Instruments) to a laptop PC that ran a software program (85070, Agilent Technologies) that calculates dielectric properties from reflected signals (S_{11}) from the vector network analyzer. The flask was heated from the bottom and stirred by a stirring hotplate. Measurements were carried out at any interval of temperatures after stabilization for >3 min (It was previously confirmed that obtained data are not affected by the presence or absence of stirring.) This system is suitable for measurements at temperatures up to 160 °C.

Before measurement, the network analyzer was warmed up for at least 1 h. All electrical connections were checked and cleaned with ethanol to remove any residue. The system was calibrated before each measurement because small variations in cable position, connections, ambient temperature and other factors can affect system performance. The testing probe was calibrated using a short circuit (a gold-plated precision shorting block included in the 85070E probe kit), open circuit (air) and known load (pure water at 25 °C). The dielectric properties of water, methanol and ethanol at 25 °C were measured and compared with data published by Agilent Technologies.

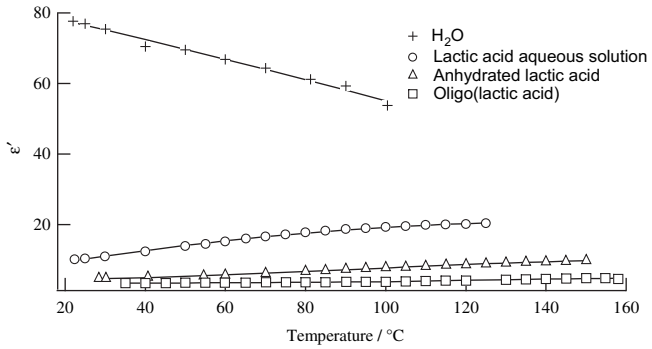


Fig. 2. Dielectric constants of samples as a function of temperature.

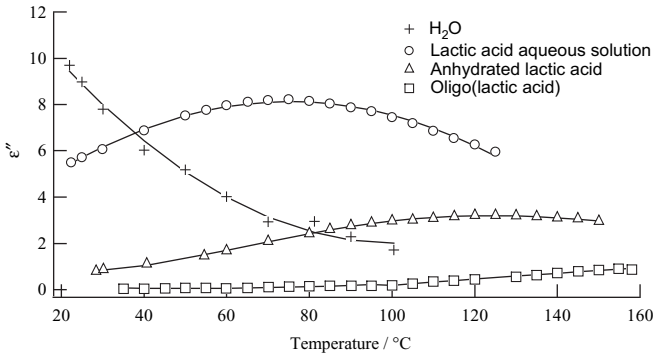


Fig. 3. Dielectric loss factors of samples as a function of temperature.

2.3. Measurement of average molecular weight

Molecular weights were measured by size exclusion chromatography (SEC; 8020 series, Tosoh Bioscience) under the following conditions: column oven temperature = 40 °C; elutant = chloroform; flow rate = 1 mL/min; standard for calculation of average molecular weight = poly(styrene).

2.4. Measurement of water content

Water content was measured by the Karl Fisher (KF) titration method [19] using a coulometer (DL31, Mettler Toledo). KF solution was purchased from Sigma–Aldrich Laborchemikalien GmbH. The instrument was allowed to stabilize until the drift was 9 μg min^{-1}, a value that was no hindrance for KF measurements.

Lactic acid aqueous solution was injected directly into the coulometer by a dried glass syringe through a silicon septum. For measurements of anhydrated lactic acid and oligo(lactic acid), chloroform solutions of these samples were previously prepared at 30 w/v%. The water content of these samples was estimated by subtracting the water content of the chloroform used as solvent from the measured water content.

3. Results and discussion

3.1. Characterizations of materials

Average molecular weights and water content of the measured materials are listed in Table 1. The number average molecular weights of LA_{an} and LA_{oligo} were 610 and 1480, respectively. These values correspond to those of the linked lactic acids, which are around 8 and 20, respectively. The water content in LA_{aq}, LA_{an} and LA_{oligo} was 14.551, 2.038 and 0.118%, respectively. Water content decreases with increasing average molecular weight. The progression of polycondensation is thus in the order LA_{aq}, LA_{an}, LA_{oligo}.

3.2. Measurements of dielectric properties as a function of temperature

Measured dielectric constants at 2.45 GHz as a function of temperature are shown in Fig. 2. Water has the highest dielectric constant among the measured samples. Dielectric constants for LA_{aq}, LA_{an} and LA_{oligo} decrease in an order corresponding to progression of the polycondensation. The degree of polycondensation also affects changes in the dielectric constant of the reaction mixture.

Measured dielectric losses at 2.45 GHz as a function of temperature are shown in Fig. 3. Water has a high loss factor at room temperature. However, with heating to above 90 °C, its loss factor decreases by 80%. At above 35 °C, LA_{aq} has a greater loss factor than does water. LA_{aq} has a loss factor of >6 in the temperature range 25–120 °C and is thus heated by microwave with greater efficiency than is water. LA_{an} and LA_{oligo}, both resultants of polycondensation, have lower loss factors than does LA_{aq}. At 120 °C, in a comparison of loss factors for the various materials, loss factors are seen to decrease as the polycondensation progresses. The loss factors for LA_{an} and LA_{oligo} decrease by 48.8 and 93.1%, respectively.

3.3. Regression analysis for prediction of dielectric properties

Previously, we reported the microwave-accelerated polycondensation of lactic acid [15]. For that report, poly(lactic acid) was synthesized at 180 °C. We carried out a regression analysis to estimate the dielectric constants and dielectric loss factors for LA_{an} and LA_{oligo} at 180 °C. We should apply a theoretical model concerned with dielectric properties as a function of temperature to estimate the dielectric constant and losses, however no available model have ever been reported. The results are listed in Tables 2 and 3. The analysis was deemed accurate because of the high value of the coefficient of determination ($R_2 > 0.98$). For fitting observed data of the dielectric constant and losses of LA_{an}, third and fourth order polynomial were applied, respectively, because of higher determination coefficient than second order polynomials. The R_2 of dielectric constant and losses of LA_{an} were 0.9957 and 0.9796, respectively. These values were inadequate to estimate the

Table 2
Equation constants for regression analysis of dielectric constants and coefficients of determination (R^2).

	Dielectric constant				Polynomial order	R^2
	$a_1X^3 + b_1X^2 + c_1X + d_1$					
	a_1	b_1	c_1	d_1		
Anhydrated lactic acid	−2.6144e-06	7.1856e-04	−0.014384	4.535	3	0.9996
Oligo(lactic acid)	–	−8.8297e-05	0.040505	0.57404	2	0.9810

Table 3
Equation constants for regression analysis of dielectric losses and coefficients of determination (R^2).

	Dielectric loss constant					Polynomial order	R^2
	$a_2X^4 + b_2X^3 + c_2X^2 + d_2X + e_2$						
	a_2	b_2	c_2	d_2	e_2		
Anhydrated lactic acid	3.0788e-08	−1.3736e-05	0.001873	−0.06589	1.479	4	0.9985
Oligo(lactic acid)	–	–	7.4876e-05	−0.0072672	0.2278	2	0.9889

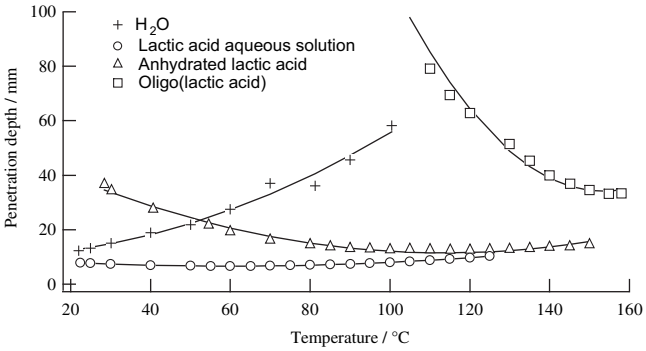


Fig. 4. Calculated penetration depths of samples as a function of temperature.

dielectric constant and losses at 180 °C. The estimated dielectric constants and loss factors at that temperature for LA_{an}, LA_{oligo}, LA_{an} and LA_{oligo} are 9.98, 5.00, 2.52 and 1.35, respectively.

3.4. Penetration depth and attenuation curve of microwaves

From the obtained dielectric properties, we calculated microwave penetration depths by Equation (3). Depths for measured materials as a function of temperature are shown in Fig. 4. The depth for the reaction mixture increases as the polycondensation progresses. For reaction at 120 °C, the penetration depth for LA_{oligo} was 6 times greater than for LA_{aq}. For reaction at 180 °C, penetration depths for LA_{an} and LA_{oligo} were 17 and 23 mm, respectively.

From these penetration depths, we calculated attenuation curves for LA_{an} and LA_{oligo}. Starting with the following equation:

$$E = E_{max} e^{-\frac{1}{2D}z} e^{j(\omega t - \beta z)} \quad (4)$$

where E_{max} is the strength of the electric field before penetration, z is the depth of penetration, t is time and β is the phase constant, we set the phase change $e^{j(\omega t-\beta z)}$ to 1 to obtain the following simplified equation:

$$E = E_{max} e^{-\frac{1}{2D}z} \quad (5)$$

From Equation (5), we calculated attenuation curves for LA_{an} and LA_{oligo} (Fig. 5). The depths at which the strength of the electric field is 10% of its value at the surface for LA_{an} and LA_{oligo} were 80 and 110 mm, respectively. Thus, microwaves penetrate more deeply as the polycondensation progresses. The attenuation curve expressed that microwaves penetrate to matters 5 times as deep as compared with the half power penetration depth.

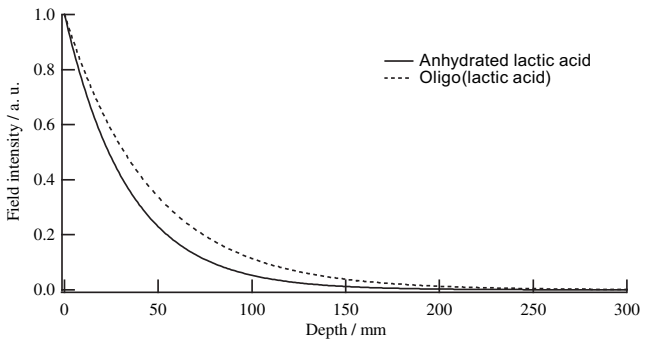
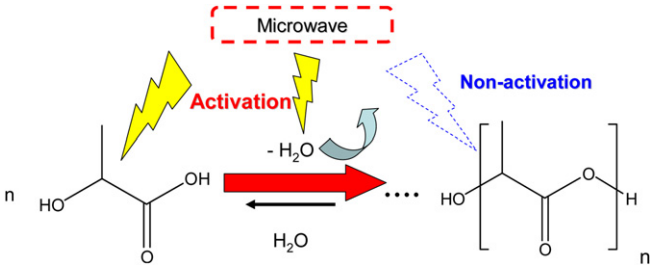


Fig. 5. Calculated attenuation curves for anhydrated lactic acid and oligo(lactic acid) at 180 °C.



Scheme 1. Image of accelerated polycondensation by microwave heating.

3.5. Microwave-accelerated polycondensation

These results suggest that the greater the average molecular weight polyester is difficult to absorb microwaves. That is, the resultant polyester is not activated by microwaves. In contrast, the substrate (lactic acid) and by-product (water) are activated by microwaves due to their high dielectric loss factors. Thus, chemical equilibrium shifts towards the resultant. This difference in absorption properties may cause the acceleration of the polycondensation that we observed in our previous work (Scheme 1) [15].

4. Conclusions

Dielectric properties were measured for water, lactic acid aqueous solution, anhydrated lactic acid and oligo(lactic acid), which are constitute elements in polycondensation, as a function of temperature up to 160 °C using an open-ended coaxial probe. The properties, having been shown to be a function of reaction temperature in our previous report, were estimated at 180 °C by regression analysis. The resulting values were used to calculate penetration depths of microwaves and attenuation curves for reaction materials.

These results confirm that the dielectric constant and dielectric loss in the reaction system decrease as the polycondensation progresses, and runaway reactions will not occur. This work can enable planners to predict the response of a chemical system to microwaves at 2.45 GHz, and can thus help guide the design and construction of safe, high-performance plants.

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