

# Relationship Between Dielectric Behaviors and Conversion of MMA during Polymerization Process

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**ABSTRACT:** Poly(methyl methacrylate), which is prepared by polymerization of methyl methacrylate (MMA), is widely used in the fabrication of polymer optical fiber and devices. In this article, a dielectric measurement method was proposed to monitor the polymerization process. The measurement result is compared with that obtained by the traditional Abbe's refractometer method. By monitoring the dielectric behaviors of polymerization system, the correlation between dielectric properties of reacting bulk and conversion of MMA was established. The influence of reactive temperature, reactive time, con-

version rate of prepolymerization, and oxygen environment was discussed. It was shown that the gel effect occurred at 2 h at the reactive temperature of 50°C when the conversion of prepolymer was about 24% with the absence of oxygen. The conversion rate obtained by Abbe's refractometer method was larger than that measured by dielectric method in the reaction metaphase. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** high-performance polymers; fibers; radical polymerization; dielectric properties; refractive index

## INTRODUCTION

Polymer optical fiber (POF), which has advantages including easy fabrication, good flexibility, large numerical aperture, and convenient connection, has shown potential application within the field of short-distance communication and local area network. Currently, poly(methyl methacrylate) (PMMA), a bulk polymer of free radical polymerization from highly pure MMA, is mostly used to fabricate the core of POF.<sup>1</sup> The performance of POF depends on the polymerization process of methyl methacrylate (MMA). Effective control of the polymerization process will favor the production of high-performance PMMA.

In conventional polymerization process, the monomer MMA triggered by initiators is polymerized to PMMA at the presence of chain transfer agent and appropriate conditions. As the polymerization progresses, the major component MMA is gradually replaced by PMMA. Noticeably, the gel effect always accelerates polymerization reaction and releases abundant heat,<sup>2</sup> which probably leads to implosion and poor-quality PMMA. Hereby, a feasible way of monitoring and controlling the monomer conversion is extremely important for the fabrication of PMMA.

There are several traditional methods of measuring the monomer conversion of MMA in polymerization, such as spectrum analysis,<sup>3</sup> Abbe's refractometer method,<sup>4</sup> and viscosimetry. However, the actual transition from liquid monomer to solid polymer cannot be measured and it is impossible to accomplish real-time online monitoring.

In this article, the change of relative permittivity of the reaction bulk is detected using a dielectric measurement method. The conversion rate of MMA is computed from a two-phase dielectric model. Then the relationship between the conversion of MMA and the bulk dielectric properties is revealed, which shows that the real-time monitoring of polymerization process is applicable. The experimental results are in good agreement with data obtained from Abbe's refractometer method. Furthermore, the influence of reactive temperature, reactive time, conversion of prepolymerization, and oxygen environment on polymerization process is discussed as well. It means that the dielectric measurement might become a new method for monitoring polymerization process, which is nondestructive, real time, and pollution free.

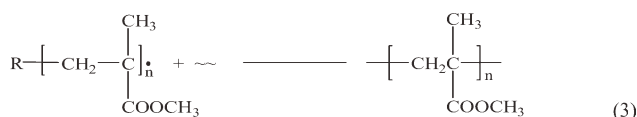
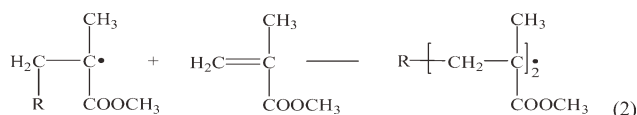
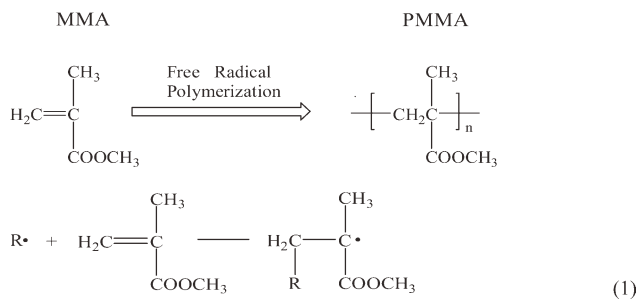
## PRINCIPLE AND EXPERIMENTAL

### Polymerization of MMA

PMMA is a bulk polymer of free radical polymerization from the monomer MMA. The polymerization progresses with three stages: chain initiation, chain

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propagation, and chain termination, which are shown in eqs. (1)–(3), respectively<sup>5</sup>:

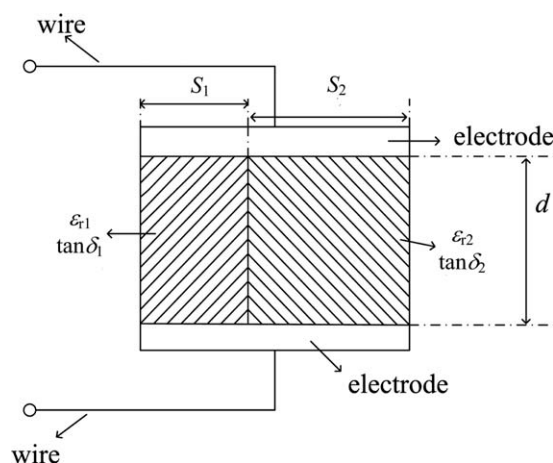


where R· represents free radical created by initiators. The continuous addition reaction of R· and the monomer MMA creates longer chain radicals. They finally terminate by chain transfer agents or inter-chain termination conditions as conversion of MMA increases, eventually PMMA is obtained. The variation of component proportion, molecular structures, and molecular weight from MMA to PMMA result in the change of the dielectric and physical/chemical properties of reaction system. Therefore, the variation of dielectric properties of reaction bulk could indicate the polymerization process.

### Two-phase dielectric model

Both PMMA and MMA are polar dielectrics. Their permittivity is mainly contributed by electronic/ionic displacement polarization and dipole orientation polarization. However, PMMA is solid and MMA is liquid. The molecular structure of monomer MMA is organized more loosely than that of the polymer. Accordingly molecular dipole in MMA would be polarized more easily than PMMA. As there are mainly two components in the polymerization system, that is, MMA and PMMA,<sup>6</sup> the reactive system can be considered as a dynamic two-phase composite; the conversion of MMA is a variable parameter. Therefore, polymerization process can be described by the relative changes of mass proportion of two components.

If the relative permittivity  $\epsilon_r$  and dielectric loss  $\tan \delta$  of each component are given, the mixture's equivalent parameter  $\epsilon_r$  would be determined by an equivalent circuit method rather than micromechanism of composite dielectrics system.<sup>7</sup> The common model of



**Figure 1** Parallel model of the two-component mixing composite.

the two-component mixing composite can be classified into three types: parallel, series, and uniform mixing.

### Parallel model

The equivalent model is shown in Figure 1. Both MMA and PMMA are considered to be composites in parallel sandwiched between two-plate electrodes. They have the same thickness  $d$ .  $\epsilon_r$ ,  $\epsilon_{r1}$ , and  $\epsilon_{r2}$  are the permittivities of reaction system, MMA, and PMMA, respectively.  $S_1$  and  $S_2$  are the cross-sectional areas of MMA and PMMA, respectively. Capacitance of the mixture can be described by the capacitances of MMA and PMMA by the following equation:

$$C = C_1 + C_2 \quad (4)$$

Two parameters  $X_1$  and  $X_2$  are introduced to represent the mass percentage of MMA and PMMA.

$$X_1 + X_2 = 1 \quad (5)$$

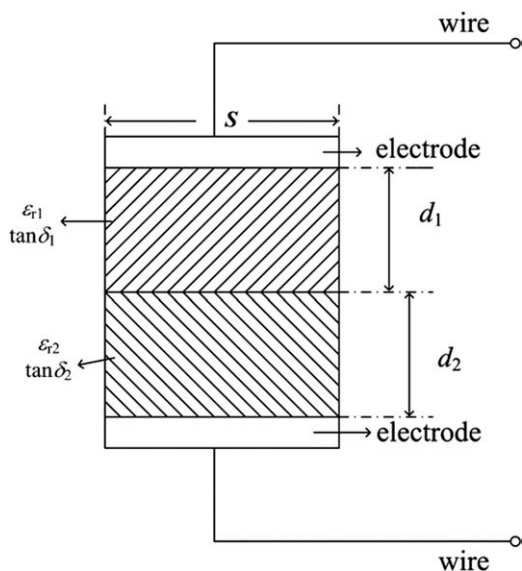
The permittivity of the mixture  $\epsilon_r$  can be described by the following equation:

$$\epsilon_r = X_1 \epsilon_{r1} + X_2 \epsilon_{r2} \quad (6)$$

Meanwhile,  $X_2$  also means the monomer conversion of MMA, which can be described by the following equation:

$$X_2 = \frac{\epsilon_r - \epsilon_{r1}}{\epsilon_{r2} - \epsilon_{r1}} \quad (7)$$

The permittivity  $\epsilon_r$  of reaction system could be calculated by measuring the parameter capacitance ( $C$ ) in the polymerization process. The permittivities of MMA and PMMA, that is,  $\epsilon_{r1}$  and  $\epsilon_{r2}$ , are known.



**Figure 2** Series model of the two-component mixing composite.

Provided that the space between electrode and the cross-sectional area are constant, PMMA volume percentage of the reaction, that is, the conversion rate of MMA, can also be obtained.

#### Series model

Two components are considered to be composite in series between the electrodes. They have same cross-sectional area  $S$ .  $d_1$  and  $d_2$  are the thickness of the two dielectrics, respectively. The equivalent model is shown in Figure 2. Capacitance of the mixture can be described by the capacitances of MMA and PMMA as follows:

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} \quad (8)$$

The mass percentage of MMA and PMMA,  $X_1$  and  $X_2$ , could be obtained; the mixture's permittivity  $\epsilon_r$  can be described by the following equation:

$$\epsilon_r^{-1} = X_1 \epsilon_{r1}^{-1} + X_2 \epsilon_{r2}^{-1} \quad (9)$$

#### Uniform mixing

Actually for a two-component composite system, parallel model and series model are both ideal cases. A uniform mixing model might represent the real reactive system.

According to eqs. (6) and (9), relative permittivity  $\epsilon_r$  can be described by the following equation:

$$\epsilon_r^K = X_1 \epsilon_{r1}^K + X_2 \epsilon_{r2}^K \quad (10)$$

where  $X_1$  and  $X_2$  are the mass percentage of MMA and PMMA, respectively.

In the parallel model,  $K = 1$ , whereas in the series model,  $K = -1$ . In the two-component uniform mixing model,  $K$  ranges from  $-1$  to  $1$ .

The total differential of eq. (10) is calculated in the following equation:

$$K \epsilon_r^{K-1} d\epsilon_r = K X_1 \epsilon_{r1}^{K-1} d\epsilon_{r1} + K X_2 \epsilon_{r2}^{K-1} d\epsilon_{r2} \quad (11)$$

When  $K$  approaches zero,

$$\frac{d\epsilon_r}{\epsilon_r} = X_1 \frac{d\epsilon_{r1}}{\epsilon_{r1}} + X_2 \frac{d\epsilon_{r2}}{\epsilon_{r2}} \quad (12)$$

The relative permittivity of the mixture  $\epsilon_r$  can be integrated from above equation:

$$\ln \epsilon_r = X_1 \ln \epsilon_{r1} + X_2 \ln \epsilon_{r2} \quad (13)$$

Moreover, the monomer conversion of MMA  $X_2$  can be described by the following equation:

$$X_2 = \frac{\ln(\epsilon_r/\epsilon_{r1})}{\ln(\epsilon_{r2}/\epsilon_{r1})} \quad (14)$$

Taking into account the solubility of MMA and PMMA and experimental situation, mixing model is more suitable.

#### Theoretical model of Abbe's refractometer method

By the Lorentz-Loren's equation,

$$\left(\frac{n^2 - 1}{n^2 + 2}\right) \left(\frac{M}{\rho}\right) = \frac{N_0 \alpha_e}{3\epsilon_0} \quad (15)$$

where  $n$  is the sample refractive index,  $M$  is the weight (kg),  $\rho$  is material density,  $N_0$  is Avogadro constant, and  $\alpha_e$  is electronic displacement polarization.

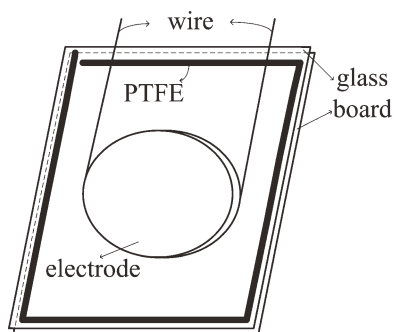
At optical frequency, only electronic displacement polarization exists. By substituting eq. (15) into eq. (7), PMMA volume percentage of the reaction, that is, the conversion rate of MMA, can be obtained:

$$X_2 = \frac{n - n_1}{n_2 - n_1} \quad (16)$$

where  $n$  is the sample refractive index,  $n_1$  is the refractive index of MMA, and  $n_2$  is the refractive index of PMMA.

#### Experimental method

Raw MMA produced by Shanghai Organic Chemical Factory (Shanghai, China) was cleaned using NaOH solution and distilled water twice under the pressure



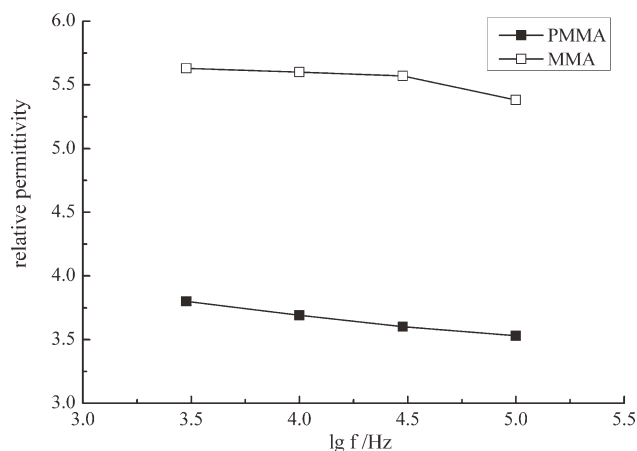
**Figure 3** Polymerization container with two electrodes.

of 0.086 MPa and 55°C to obtain pure MMA. The azobisisobutyronitrile (AIBN) was used as the initiator.

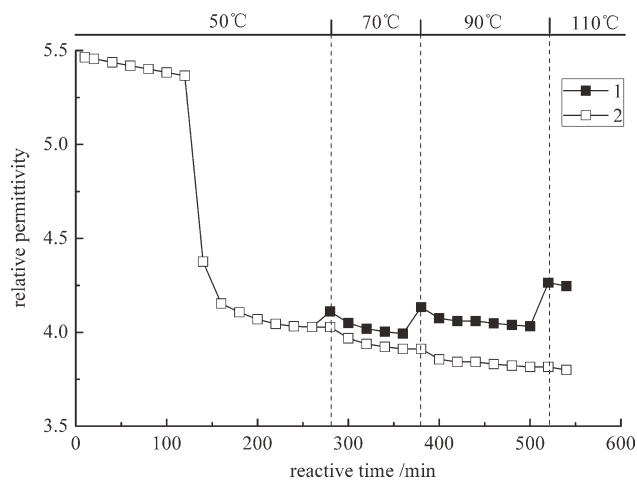
First, 40 mg of AIBN was dissolved in 20 mL of MMA in a hermetic glass bottle. Then, the prepolymerization reaction took place at 85°C for 30 min until the conversion of reaction system reached a certain value. The cooled prepolymer was then put into a polymerization container, as shown in Figure 3, and maintained at the following heating stages: 50°C for some time and 70°C for 2 h, 90°C for 2 h, and 110°C for 1 h. Meanwhile, TR-10C type electric bridge was used to measure the permittivity  $\epsilon_r$  of reaction system. Therefore, the permittivity as the function of reactive time was recorded.

For comparison, NAR-2T type Abbe's refractometer was used to measure the refractive index of polymerization system during the polymerization process. Considering the volume shrinkage (about 21%) of reaction system, the aluminum electrodes ( $\Phi = 30$  mm) in polymerization container should be inundated within liquid reactants.

Experimentally, relative permittivity of both MMA and PMMA at reactive temperature of 50°C should first be measured as  $\epsilon_{r1}$  and  $\epsilon_{r2}$ , respectively. Then, the measured  $\epsilon_r$  varying with reactive time  $t$  can be transformed into  $X_2$  varying with  $t$  from eq.



**Figure 4** The relative permittivity of MMA and PMMA (at 23°C).



**Figure 5** Variation of permittivity with increasing reactive time (30 kHz): (1) measurement and (2) correction.

(14), which represents the polymerization process of MMA.

## RESULTS AND DISCUSSION

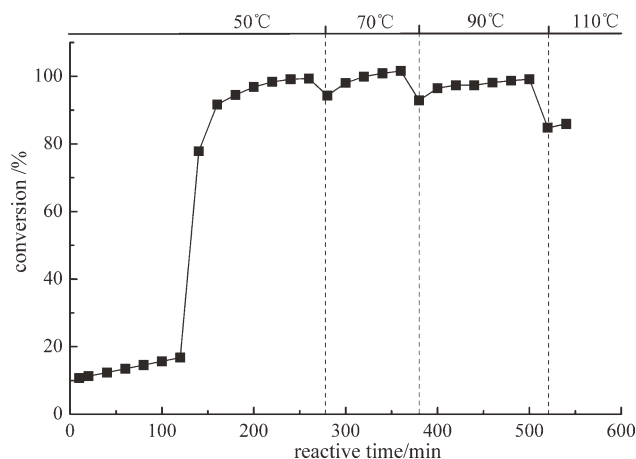
### Verification of dielectric method

The permittivities of both MMA and PMMA measured at same temperature are shown in Figure 4. It shows that the permittivity of MMA is much higher than that of PMMA in the frequency range from 3 to 100 kHz. This indicates that the permittivity  $\epsilon_r$  of polymerization reaction system should decrease from the initial permittivity  $\epsilon_{r1}$  of MMA to the final permittivity  $\epsilon_{r2}$  of PMMA as the polymerization progresses. Therefore, it is possible to describe the conversion rate from liquid monomers to solid polymers by measuring the changes of permittivity  $\epsilon_r$  of the polymerization reaction system.

When the monomer conversion of MMA reached around 85%, extending reactive time could no longer accelerate reaction. Higher temperatures were required to promote polymerization reaction.<sup>8</sup>

The dependence of permittivity of reaction system on the reaction time is shown in Figure 5, in which Curve 1 shows an initial slow fall immediately followed by a rapid decrease and final slight reduction in the first stage at 50°C. The rapid decrease represents the gel effect and the autoacceleration process. Permittivity fluctuates as temperature increases in the later stages. Temperature change in the different stages results in the drop of the conversion of MMA as shown in Figure 6. This could not correctly describe the real polymerization process. Therefore, it is important to eliminate the influence of the temperature variation on the permittivity as a function of reactive time.

Given that the temperature upgrade accomplishes within 20 min, which is much less than the maintaining time (2 h), and the permittivity fluctuation is



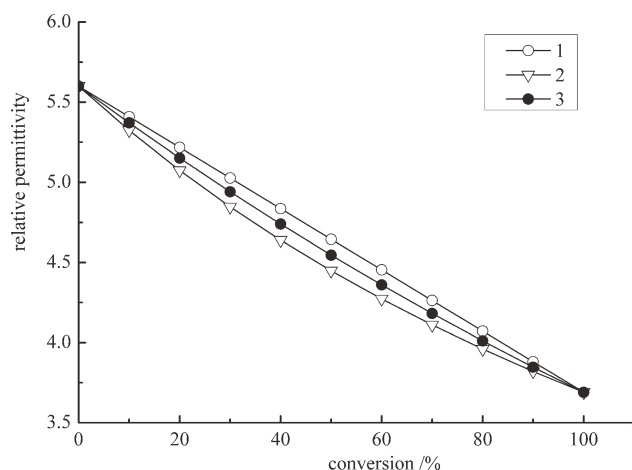
**Figure 6** Variation of MMA conversion with reactive time.

caused by temperature variation, which is much less than that caused by change of all the reactive conditions, a further calculation method is proposed to achieve normalization of relative permittivities between two different temperatures.

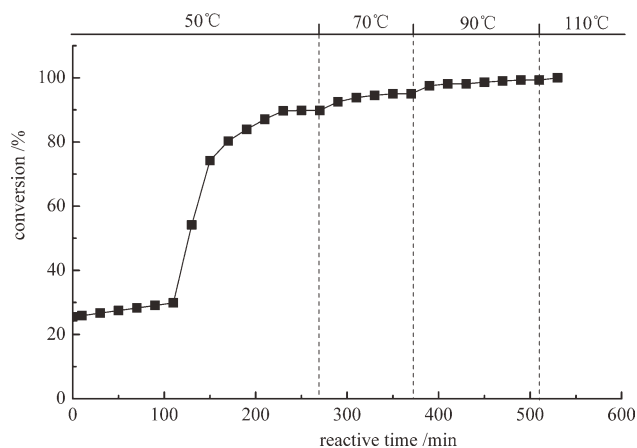
#### Normalization of permittivity at different temperatures

It is assumed that (1) the conversion of MMA stays constant when temperature increases from 50 to 70°C in 20 min and (2) the conversion at the end of each stage is almost changeless. Therefore, Curve 1 in Figure 5 could be smoothed as the permittivity remains the same immediately before and after temperature upgrade.

First, the close similarity of three dielectric models, that is, uniform mixing, parallel, and series, as shown in Figure 7, indicates that uniform mixing model could approximately be described as parallel one in eq. (6). Therefore, the permittivity of mixture



**Figure 7** The comparison of three dielectric models: (1) parallel; (2) series; and (3) uniform mixing.



**Figure 8** Variation of conversion with reactive time calculated from corrected data in Figure 5.

could be in linear superposition of permittivity of both MMA and PMMA.

Second, the permittivity of MMA and PMMA at 70°C could be normalized to that at 50°C by the ratio  $k$  of permittivity at such two temperatures, where  $k_1 = (\epsilon_{r1})_{70^\circ\text{C}}/(\epsilon_{r1})_{50^\circ\text{C}}$ ,  $k_2 = (\epsilon_{r2})_{70^\circ\text{C}}/(\epsilon_{r2})_{50^\circ\text{C}}$ .

The permittivity of mixture at 50°C could thus be calculated by the following equation:

$$(\epsilon_r)_{50^\circ\text{C}} = X_1(\epsilon_{r1})_{70^\circ\text{C}}/k_1 + X_2(\epsilon_{r2})_{70^\circ\text{C}}/k_2 \quad (17)$$

Finally, the above normalization method could be used at the temperatures of 90 and 110°C, respectively, and the corrected data of relative permittivity is obtained as shown in Curve 2 of Figure 5.

According to eq. (14), the final curve of conversion of MMA with reaction time was obtained in Figure 8. It shows that the gel effect would appear at about 2 h while conversion of prepolymerization is about 24% and reactive temperature remains at 50°C.

#### Comparison between dielectric measurement and Abbe's method

The conversion measured by dielectric measurement and Abbe's refractometer is compared in Table I. The results show a very good agreement between each other in the early and late stages of polymerization reaction. However, in the mid-stage (autoacceleration process), results obtained by Abbe's refractometer method is much larger than that by dielectric method. Actually, Abbe's refractometer method is not a real-time measurement; it always takes several minutes and lags behind dielectric method. The difference between Abbe's refractometer method and dielectric method in early and late stages is not obvious while reactive rate is lower; however, it becomes larger when reaction proceeds into autoacceleration period and reactive rate is much higher. Generally, the data measured by Abbe's refractometer method are larger than that by dielectric method.

**TABLE I**  
Conversion (%) with Two Methods

Reactive time (min)	Dielectric measurement	Abbe's refractometer	Relative error (%)
0	21.3	21.4	0.5
20	21.8	21.9	0.5
40	22.6	22.7	0.4
120	26.3	26.9	2.2
160	28.2	29.3	3.8
200	81.3	84.2	3.4
280	88.2	89.1	1
360	93.5	93.8	0.3
420	95.4	95.7	0.3

### Analysis of influencing factors on reaction

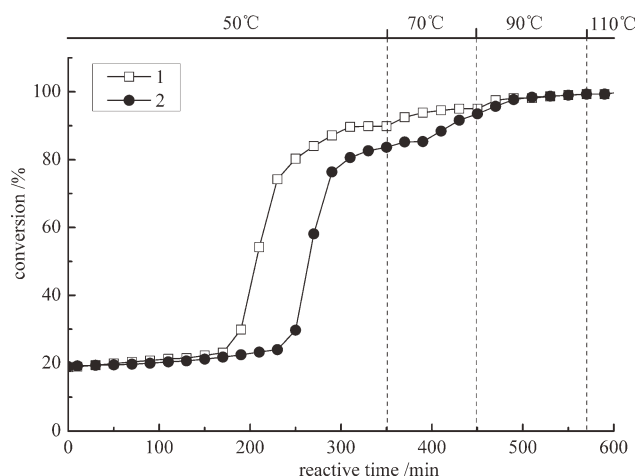
Dielectric measurement method could be used to investigate the influence of reactive temperature, reactive time, conversion of prepolymerization, and oxygen environment on polymerization process.

#### Reactive temperature

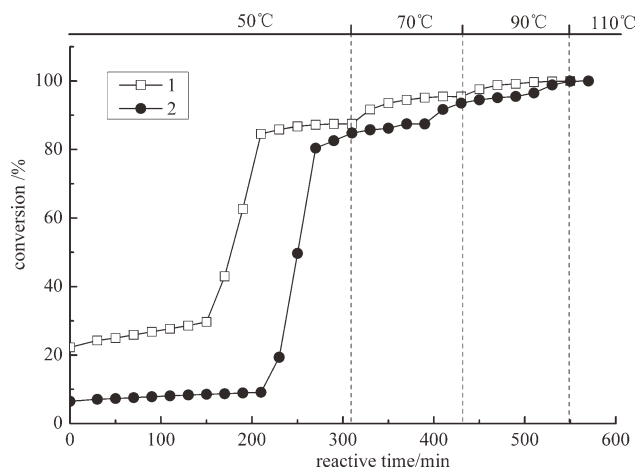
The curves of the conversion of MMA with reactive time at different reactive temperatures are shown in Figure 9. The increase in reaction temperature can enhance reactive rate and reduce reactive time; however, it is more difficult to control autoacceleration process during polymerization. Dielectric measurement method could be used to determine when the temperature needs to be changed and make autoacceleration process occurring at a stage of a lower temperature and avoid explosive polymerization.

#### Conversion of prepolymerization

Higher conversion of prepolymerization can shorten reactive time; however, it is more difficult to control the prepolymerization process. Figure 10 shows that the higher the conversion, the earlier the autoaccelera-



**Figure 9** Effect of temperature on conversion (at 30 kHz): (1) 50°C and (2) 45°C.

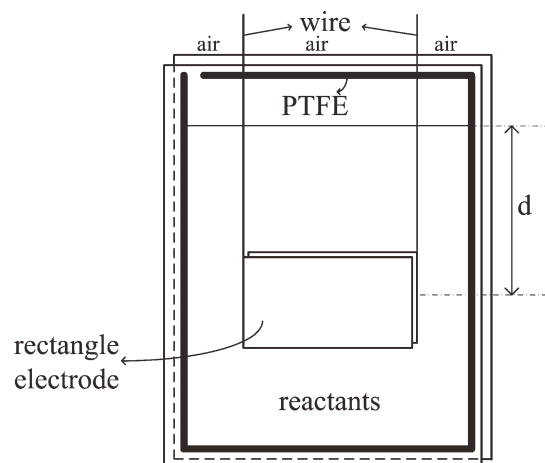


**Figure 10** Effect of prepolymerization conversion of on reaction: (1) 21% conversion of prepolymerization and (2) 7% conversion of prepolymerization.

tion process occurs. Therefore, an appropriate conversion of prepolymerization is essential to experiments.

#### Oxygen environment

To study the influence of oxygen environment on reaction, the round electrode of polymerization measuring system showed in Figure 3 was changed into rectangle electrode (3 cm × 0.5 cm) as shown in Figure 11. Because reactants only contacted air in one direction, one-dimensional influence of oxygen could be studied by increasing the depth ( $d$ ) of electrodes within liquid reactants and described by the time ( $t$ ) that gel effect appeared at 50°C. The results in Table II show that oxygen is a polymerization inhibitor at 50°C when the depth is less than 0.25 cm. Consequently, vacuum treatment with prepolymer should be undertaken to avoid direct contact with air. It is also essential to exhaust the air in the polymerization container into which the prepolymer is poured.



**Figure 11** Two-rectangle electrode system.

TABLE II  
The Time Gel Effect Appeared at Different Depth

<i>d</i> (cm)	0.25	0.5	1	2	3	4	5
<i>t</i> (h)	>10	4.1	4.3	4.2	4.3	4.2	4.2

### CONCLUSIONS

Based on the two-phase dielectric model, it was proved that the dielectric measurement method is feasible for studying and monitoring the polymerization process of MMA, especially for determining the start of gel effect. Results measured by dielectric measurement method showed good agreement with data obtained from Abbe's refractometer method. Correlation between dielectric behaviors and conversion of MMA had been established by the dielectric model of two-phase uniform mixing composites. Thus, the MMA conversion with time could be obtained. It was shown that the conversion of MMA was elevated with extension of the reactive time. Analysis of influence factors on polymerization progress indicated that the conversion

increased with the enhancement of temperature and the conversion of prepolymerization. It also showed that oxygen was a polymerization inhibitor at low temperature.

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