Kinetics of Diethylene Glycol Formation from Bishydroxyethyl Terephthalate with Zinc Catalyst in the Preparation of Poly(ethylene terephthalate)

LEO-WANG CHEN, JONG-WU CHEN

Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan, Republic of China

ABSTRACT: To further discuss the effect of zinc catalyst on diethylene glycol (DEG) formation in the preparation of poly(ethylene terephthalate) (PET), this research focused on the kinetics of DEG formation during PET synthesis from purified bishydroxyethyl terephthalate (BHET) monomer with zinc catalyst. The rate expression of DEG formation from purified BHET monomer and zinc catalyst is described. It was found that the activation energy of BHET with zinc catalyst in DEG formation during PET synthesis is lower than that of BHET without the addition of catalyst. Moreover, a comparison of zinc catalyst in DEG formation with antimony catalyst at the same concentrations showed that the reaction rate of BHET with zinc catalyst in DEG formation is greater than that of BHET with antimony catalyst. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 1229–1234, 2000

Key words: DEG; PET; BHET; zinc; catalyst; kinetics

INTRODUCTION

Poly(ethylene terephthalate) (PET) is manufactured commercially either by the direct esterification of ethylene glycol (EG) and terephthalic acid or by the transesterification method in which dimethyl terephthalate is reacted with EG, usually in the presence of a catalyst.

Metal catalysts are used to accelerate PET synthesis, but they also promote certain undesirable side reactions. Such reactions include, in particular, the formation of diethylene glycol (DEG). The formation of DEG is an important side reaction in preparing PET.[1–4] The amount of DEG in PET molecules influences many important properties of the polymer; for instance, temperature, light stability, and melting point, which decreases by about 5°C for each percent increase in DEG concentration.[5]

In comparison with other catalysts, zinc acetate catalyst is used relatively widely in the polymerization and glycolysis reactions.[6] Moreover, the zinc salt was found to produce more ether bonds than either lead (II) or manganese (II) acetate catalysts.[7] Therefore, it is critical to study DEG formation during the preparation of PET in the presence of zinc acetate catalyst more deeply.

The kinetics of DEG formation during the preparation of PET from purified bishydroxyethyl terephthalate (BHET) monomer without the addition of catalyst and with the addition of proton catalyst were reported by Chen and Chen.[8,9] However, information concerning the kinetics of the etherification reaction of purified BHET monomer with the addition of zinc catalyst is scarce. To understand the effect of zinc catalyst on DEG formation during the preparation of PET in more depth, it is critical to study the kinetics of DEG formation during the preparation of PET from purified BHET monomer in the presence of zinc catalyst. This work is based on the interpre-

tation of experimental data to establish the rate of DEG formation.

EXPERIMENTAL

Materials

Zinc acetate used for catalyst was reagent grade; phenol, 1,1,2,2-tetrachloroethane used for the measurement of viscosity was reagent grade; benzyl alcohol (internal standard), 1- propanol, DEG, and potassium hydroxide used for the measurement of DEG were reagent grade. All of these chemicals were used without further purification. The BHET oligomer with a number average molecular weight ($\bar{M}_n$) range of 1750–1800 (measured by Gel Permeation Chromatography (GPC)) was obtained from the Industrial Technology Research Institute, Taiwan. The BHET oligomer was purified to monomer for the studies of the kinetics of DEG formation.

The Synthesis of PET (Glass Reactor)

Apparatus for the Study of the Kinetics of DEG Formation from BHET Monomer

Polycondensation of purified BHET monomer was performed in a reactor made of glass. The reactor was heated using a heating mantle and reaction temperature was controlled by a PID temperature controller.

Procedure

First, the BHET monomer was purified via the following process.[10] Fixed amounts of BHET oligomer, EG, and zinc acetate catalyst were charged to a four-necked flask, which was fitted with a stirrer, reflux condenser, nitrogen inlet, and thermometer. The reactor was heated in an oil bath. The glycolysis reaction was allowed to proceed for 8 h at a temperature of 190°C. This process was reported by Lin and Baliga.[11] The product of BHET oligomer glycolysis was agitated vigorously with water to dissolve unreacted EG and catalyst, while most of the glycolyzed products were precipitated out. After filtration, distilled water was added and brought to boiling point. The boiling solution was quickly filtered to separate BHET oligomer (n > 1) from the monomer. The mother liquid was cooled to 5°C, and crystals of BHET monomer were recovered by filtration. The monomer crystals were then vac-

uum dried in an oven at 70°C for 24 h. The monomer obtained was melted at a temperature range of 109–110°C.

The purified BHET monomer and zinc acetate catalyst were placed in the reactor and a slow stream of nitrogen gas was bubbled through the melt for a period of 2 h, and the system pressure was then reduced to 3mmHg. Polycondensation was continued for 3 h with simultaneous removal of EG and other volatile compounds by distillation. A sample of the polymer was removed every hour from the reactor. During sampling, the polymer was quenched in chilled water.

Characterization

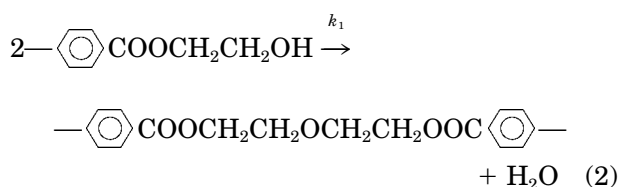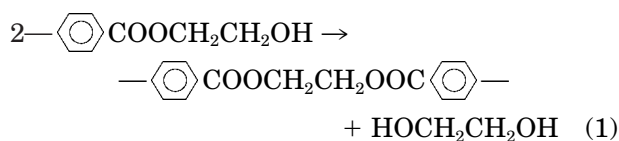#### Determination of the Intrinsic Viscosity

The intrinsic viscosity of PET was measured in a solvent mixture of phenol and 1,1,2,2-tetrachloroethane (6:4 w/w) at 30°C using a Ubblohde viscometer.

Determination of DEG Content

PET was depolymerized by saponification with potassium hydroxide in 1-propanol under reflux. Following neutralization with hydrochloride acid in 1-propanol and removal of precipitate, the liberated DEG was measured by gas chromatography (GC-FID). The method is referred to in the literature.[12,13] Benzyl alcohol was used as the internal standard. The GC column used was a Stabiwax-DA capillary column and analysis was made at 140–200°C with 20 cc/min of nitrogen as carrier gas.

RESULTS AND DISCUSSION

The Kinetics of Purified BHET Monomer with Zinc Catalyst

$$2-\bigcirc COOCH_2CH_2OH \rightarrow$$
$$-\bigcirc COOCH_2CH_2OOC\bigcirc -$$
$$+ HOCH_2CH_2OH \quad (1)$$

$$2-\bigcirc COOCH_2CH_2OH \xrightarrow{k_1}$$
$$-\bigcirc COOCH_2CH_2OCH_2CH_2OOC\bigcirc -$$
$$+ H_2O \quad (2)$$

In addition to undergoing polymerization, the purified BHET monomer also underwent the DEG formation reaction. The rate equation of DEG formation is:

$$\frac{d[\text{DEG}]}{dt} = k_1[\text{HET}]^2 \qquad (3)$$

$$[\text{HET}] = \frac{1000\rho}{(192\bar{P} + 62)} \qquad (4)$$

Equation (3) is a simplified kinetic equation which assumes that the reverse reaction (2) and the contribution to DEG formation from EG formed in reaction (1) are negligible.[8] Where $\bar{P}$ = the degree of polymerization; ρ = sample density; [HET] = the concentration of 2-hydroxyethyl terephthalate terminal groups (—⟨◯⟩COOCH$_2$CH$_2$OH). As stated in literature,[14] the relationship between $[\eta]$ and $\bar{P}$ is:

$$[\eta] = 7.55 \times 10^{-4} \times (192 \times \bar{P} + 62)^{0.685} \quad (5)$$

$[\eta]$ is intrinsic viscosity, $\bar{P}$ is derived from eq. (5) through the measurement of $[\eta]$ during sampling. Thus, the value of [HET] at each interval can be derived using eq. (4).

The term diethylene glycol (DEG) is generally applied to the dimer of glycol molecules. The ether bond structure (—CH$_2$CH$_2$OCH$_2$CH$_2$—) also appears in the main chain of PET. This structure is also usually referred to as DEG. It is assumed that the reactivity of functional groups does not depend on the polymer chain length. DEG content in the final product is obtained through the depolymerization of the sample. During sampling, it was found that the amount of DEG discovered in the trap device (containing mostly EG, H$_2$O, and oligomer) was even smaller than that in the sample under the operating conditions, and therefore could be ignored. Hornof[15] found that DEG is not likely to be immediately removed from the reaction by distillation because of its rather high boiling point (245°C). The volume of DEG in the sample was assumed to be negligible because DEG content in the sample was minutely small. Therefore, the concentration of DEG could be expressed as the following equation:

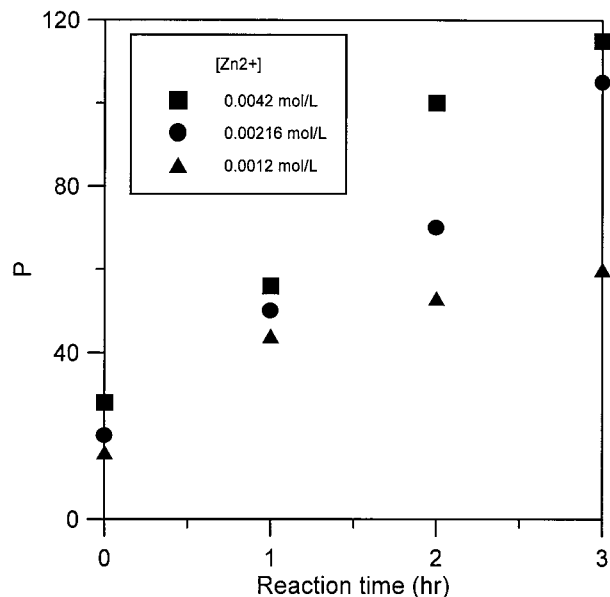$$[\text{DEG}] = \frac{(\text{DEG wt. }\%/M_{\text{DEG}})}{100} \times \rho \times 1000 \quad (6)$$

Figure 1 The relationship between the degree of polymerization and reaction time at three different zinc concentrations: 4.2×10^{-3}, 2.16×10^{-3}, 1.2×10^{-3} mol/L.

Effect of the Concentration of Zinc Catalyst

The influence of different concentrations of zinc catalyst on DEG formation in PET synthesis at the same temperature (270°C) was examined in this work.

Figure 1 shows the relationship between $\bar{P}$ and reaction time t at every interval and at three different zinc concentrations. Figure 2 shows the concentration of DEG at every interval and at three different zinc concentrations. The values of [DEG] shown in Figure 2 give the incremental amount of [DEG], that is, the total amount of [DEG] at a certain time minus the amount of [DEG] at the base time. The value of $d[\text{DEG}]/dt$ is derived from the differential of each point on the fitting curve in Figure 2. The fitting curve is obtained by using the standard error deviation method on each point in Figure 2. The values of $[\text{HET}]^2$ are obtained from eq. (4). The plot indicated by eq. (3) is presented in Figure 3 and the slope obtained gives the value of reaction rate constant k_1. The values of k_1 derived at three different concentrations at the same temperature (270°C) are shown in Figure 4 and summarized in Table I. The reaction rate constant is linearly dependent on catalyst concentration and can be expressed in the following equation:

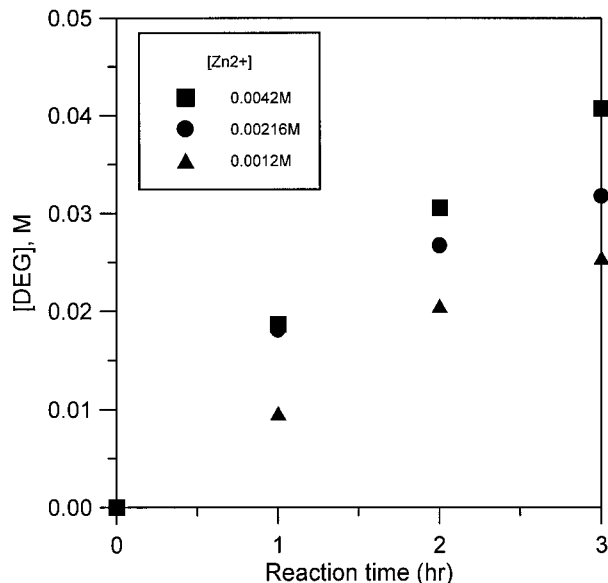$$\frac{d[\text{DEG}]}{dt} = (k_1'[\text{Zn}^{2+}] + k_{10})[\text{HET}]^2$$

Figure 2 The relationship between DEG concentration and reaction time at three different zinc concentrations: 4.2×10^{-3}, 2.16×10^{-3}, 1.2×10^{-3} mol/L.

Where k'_1 is the reaction rate constant in the synthesis of PET with the addition of zinc catalyst. The concentration of zinc is not included in the rate constant k'_1. k_{10} is the reaction rate constant in the synthesis of PET without the addition of zinc catalyst.
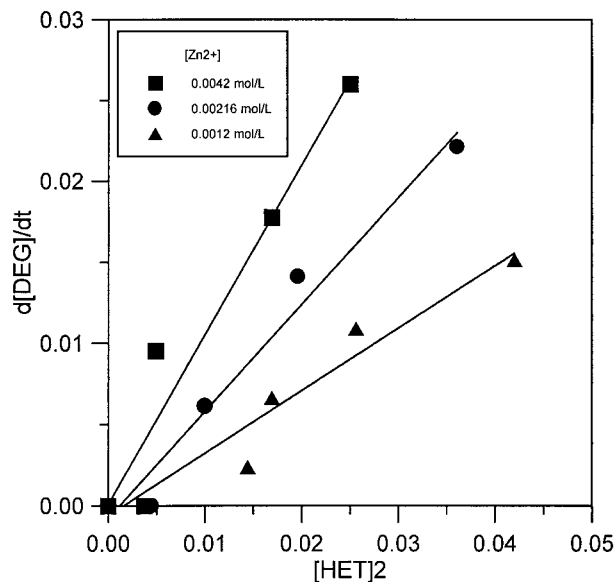

Figure 3 The plot according to eq. (3) for various concentrations of zinc with BHET (270°C). The slope gives k_1.
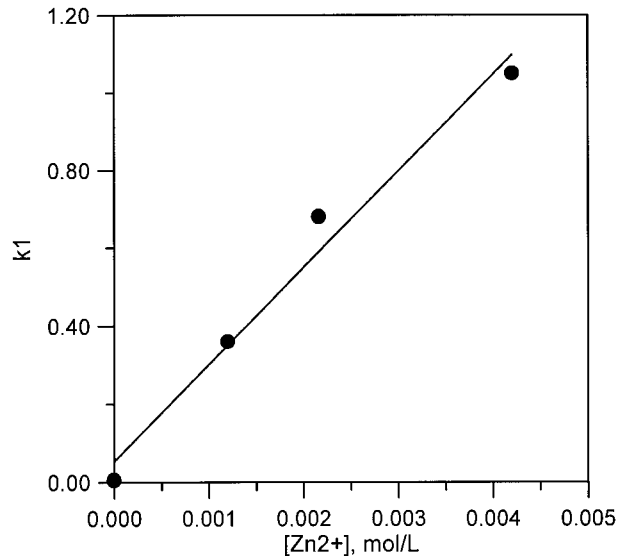

Figure 4 The relationship between the reaction rate constant k_1 and the concentration of zinc.

Effect of Reaction Temperatures

The influence of different reaction temperatures on DEG formation with the same zinc catalyst concentration (2.16×10^{-3} mol/L) in PET synthesis was examined in this work.

Figure 5 shows the relationship between $\bar{P}$ and reaction time t at every interval and at four different temperatures (270, 280, 285, and 290°C). Figure 6 shows the concentration of DEG at every interval and at the four different temperatures. The values of [DEG] shown in Figure 6 represent the incremental amount of [DEG], that is, the total amount of [DEG] at a certain time minus the amount of [DEG] at the base time. The value of $d[DEG]/dt$ is derived from the differential of each point on the fitting curve in Figure 6. The fitting curve is obtained by using the standard error deviation method on each point in Figure 6. The values of $[HET]^2$ are obtained from eq. (4). The plot indicated by eq. (3) is presented in Figure 7

Table I Effect of Zinc Concentration on DEG Formation at the Same Temperature (270°C)

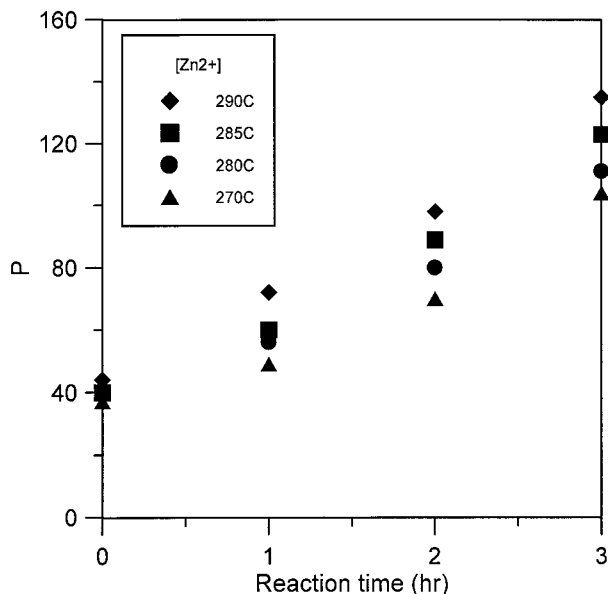| [Zn^{2+}], mol/L	k_1
0	0.00524[a]
1.20×10^{-3}	0.35
2.16×10^{-3}	0.66
4.20×10^{-3}	1.05

[a] Reference 8.

Figure 5 The relationship between the degree of polymerization and reaction time at four different temperatures: 270, 280, 285, and 290°C.

and the slope obtained gives the value of reaction rate constant k_1. The values of k_1 are derived at four different temperatures and expressed in Table II. Thus, the value of k'_1 can be derived from eq. (7).

According to the Arrhenius equation, the reaction rate constant could be used to derive the
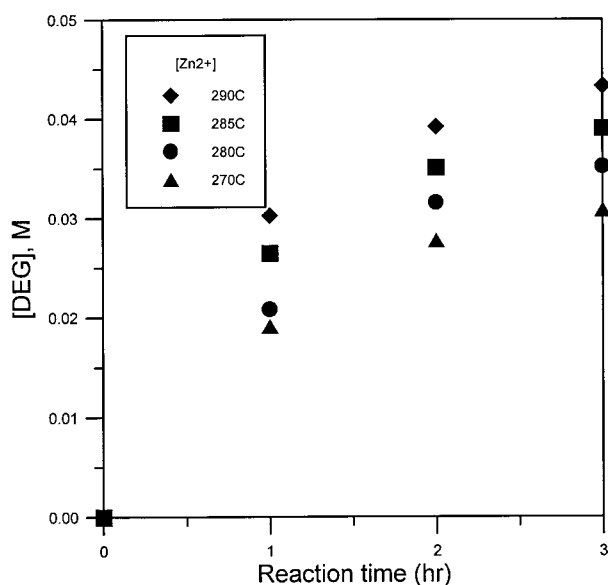

Figure 6 The relationship between DEG concentration and reaction time at four different temperatures: 270, 280, 285, and 290°C.
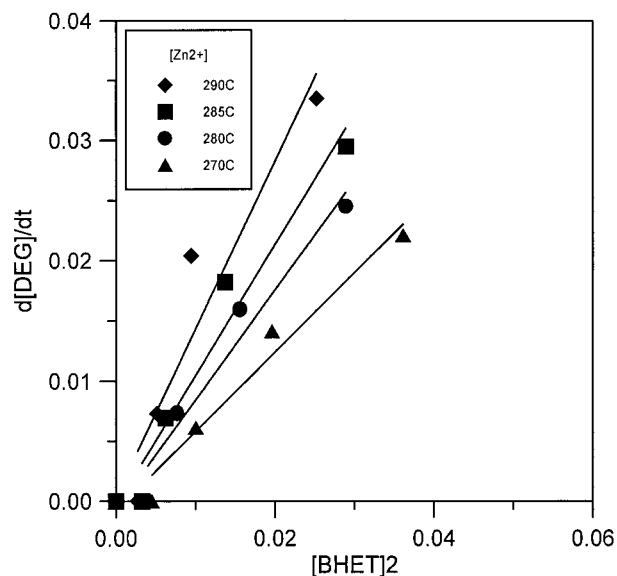

Figure 7 The plot according to eq. (3) for various temperatures at the same zinc concentration (2.16 $\times 10^{-3}$ mol/L). The slope gives k_1.

activation energy and pre-exponential factor. $\ell n k'_1$ is plotted against $1/T$. The slope obtained from the diagram gives the activation energy of DEG formation:

Activation energy $E = 88,265$ J/mol

Pre-exponential factor $A = 9.7 \times 10^{10}$

Therefore, the rate constant of DEG formation from BHET with zinc acetate catalyst is:

$$k'_1 = 9.7 \times 10^{10} \times e^{(-88,265/RT)} \qquad (8)$$

Table II Effect of Temperature on DEG Formation at the same Zinc Concentration (2.16 $\times 10^{-3}$ mol/L)

Temperature (°C)	k_1	$k_1{}^{a}$
270	0.68	0.11
280	0.94	0.13
285	1.10	0.16
290	1.38	0.24

[a] The reaction rate constants of the purified BHET monomer and antimony catalyst are provided for the purpose of comparison. Please see reference 16.

where R is the gas constant, 8.314 $\mathrm{Jgmol^{-1}K^{-1}}$. The rate constant of DEG formation from BHET without the addition of catalyst is:

$$k_{10} = 8 \times 10^{10} \times e^{(-137,140/RT)} \qquad (9)$$

where R is the gas constant, 8.314 $\mathrm{Jgmol^{-1}K^{-1}}$. The process to derive the value of k_{10} was previously reported by Chen and Chen.[8] It was found that the reaction rate constant of BHET monomer with zinc catalyst in DEG formation was greater than that of BHET monomer without the addition of catalyst, and the activation energy of k_{10} is significantly larger than that of k'_1. From the standpoint of kinetics, zinc acetate has a catalytic effect on the polycondensation reaction. In addition, it promotes a further increase in the rate of DEG formation.

Comparison of the Activity of Zinc Catalyst with that of Antimony Catalyst in DEG Formation During PET Synthesis

According to Table II, which lists a comparison of the reaction rate constants of zinc catalyst in DEG formation with those of antimony catalyst at the same concentrations, the reaction rate constant of purified BHET monomer with zinc catalyst in DEG formation is greater than that of purified BHET monomer with antimony catalyst. The study of antimony catalyst activity in DEG formation was published previously.[16] Therefore, the activity of zinc catalyst is greater than that of antimony catalyst in DEG formation during PET synthesis.

CONCLUSIONS

The effects of catalyst concentration on DEG formation were discussed and it was found that the reaction rate constant is linearly dependent on catalyst concentration and can be expressed in the following equation:

$$(d[\mathrm{DEG}]/dt) = (k'_1[Zn^{2+}] + k_{10})[\mathrm{HET}]^2$$

The rate constant of DEG formation from purified BHET monomer with zinc acetate catalyst is:

$$k'_1 = 9.7 \times 10^{10} \times e^{(-88,265/RT)}$$

It was found that the activation energy of purified BHET monomer with zinc catalyst in DEG formation is lower than that of purified BHET monomer without the addition of catalyst. As far as the kinetics is concerned, zinc acetate has a catalytic effect on the polycondensation reaction. In addition, it promotes a further increase in the rate of DEG formation. Moreover, it was found that the activity of zinc catalyst is greater than that of antimony catalyst in DEG formation during PET synthesis.

REFERENCES

1. Buxbaum, L. H. Die Angew Chem 1968, 80, 225.
2. Buxbaum, L. H. Die Angew Chem Int Ed 1968, 7, 182.
3. Janssen, R.; Ruysschaert, H.; Vroom, R. Makromol Chem 1964, 77, 153.
4. Zimmermann, H.; Kim, N. T. Polym Eng Sci 1980, 20, 680.
5. Benoin, J. M.; Choi, K. Y. Macromol Chem Phys 1989, C29, 55.
6. Tomita, K. Polymer 1973, 14, 50.
7. Hornof, V. J Macromol Sci, Chem 1981, A15, 503.
8. Chen, J. W.; Chen, L. W. J Polym Sci, Polym Chem Ed 1998, 36, 3073.
9. Chen, L. W.; Chen, J. W. J Appl Polym Sci, to appear.
10. Baliga, S.; Wong, T. J Polym Sci, Polym Chem Ed 1989, 27, 2027.
11. Lin, C. C.; Baliga, S. J Appl Polym Sci 1986, 31, 2483.
12. Kirby, J. R.; Baldwin, A. J.; Heidner, R. H. Anal Chem 1965, 37, 1306.
13. Tindall, G. W.; Perry, R. L.; Little, J. L.; Spangh, A. T. Anal Chem 1991, 63, 1251.
14. Kamatani, H.; Konagaya, S.; Nakamura, Y. Polym J 1980, 12, 125.
15. Hornof, V. J Macromol Sci, Chem 1981, A15, 503.
16. Chen, J. W.; Chen, L. W. J Polym Sci, Polym Chem Ed 1999, 37, 1797.