

## A Methanesulfonic Acid/Sulfuric Acid-Based Route for Easily-Controllable Chloromethylation of Poly(ether ether ketone)

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**ABSTRACT:** A mixed methanesulfonic acid/sulfuric acid solvent based chloromethylation of poly(ether ether ketone) (PEEK) is described. Methanesulfonic acid is the solvent, sulfuric acid is the catalyst, and chloromethyl octyl ether (CMOE) is the chloromethylating reagent. <sup>1</sup>H-NMR spectra confirmed the successful synthesis of chloromethylated PEEK (CMPEEK). The effects of polymer concentration, catalyst/polymer ratio, and reaction temperature on the rate of PEEK chloromethylation were investigated. In order to minimize crosslinking, the PEEK concentration must be kept very low (< 2%). The reaction rate increases with increased catalyst/polymer ratio and reaction temperature. The activation energy of PEEK chloromethylation is 30.9 kJ mol<sup>-1</sup>. The extent of reaction for the new route is more easily controllable as compared with the previous sulfuric acid based route. The reaction rate constant at 25°C for the new route is 1.29 h<sup>-1</sup> which is lower than that for chloromethylation by concentrated sulfuric acid at -10°C (rate constant 1.88 h<sup>-1</sup>). As a result, the degree of chloromethylation of CMPEEK can be easily controlled at room temperature using this mixed solvent. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41404.

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### INTRODUCTION

Chloromethylated polymers are useful intermediates that can easily react with tertiary-amine or tertiary-phosphine to synthesize the polymers with functional groups, such as quaternary-ammonium,<sup>1-3</sup> quaternary-phosphonium,<sup>4-6</sup> imidazolium,<sup>7-10</sup> and guanidinium.<sup>11-13</sup> These functionalized polymers have been widely applied for fuel cells,<sup>14-16</sup> electro dialysis,<sup>17</sup> gas separations,<sup>18</sup> and phase-transfer catalysis.<sup>19</sup>

Chloromethylated polymers have typically been synthesized by the chloromethylation reaction of high-performance commercial engineering polymers, such as polystyrene,<sup>20</sup> polysulfone,<sup>2,7</sup> poly(aryl ether sulfone),<sup>21</sup> and polyetherimide,<sup>22,23</sup> with chloromethyl alkyl ethers as chloromethylating reagents. The reactions are carried out in chlorinated hydrocarbon solvents, with Lewis acid catalysts.

Poly(ether ether ketone) (PEEK) is an important engineering polymer with high thermal stability, good chemical resistance, and excellent mechanical properties. Unfortunately, PEEK is nearly insoluble in organic solvents including chlorinated hydrocarbons, which has prevented chloromethylation of PEEK by the typical chlorinated hydrocarbon/Lewis acid route.<sup>24</sup> By

using sulfuric acid as both solvent and catalyst, PEEK was chloromethylated successfully.<sup>25</sup> However, the chloromethylation reaction by the sulfuric acid based route is fast, making it hard to control the degree of chloromethylation (DC), even at sub-ambient reaction temperatures of -10°C. Another chloromethylation route was reported in which PEEK was first partially sulfonated with sulfuric acid to improve the solubility and then chloromethylated with 1-methyl-2-pyrrolidone (NMP) as solvent. However, the sulfonic acid groups introduced into the polymers can change the polymer's properties.<sup>26,27</sup> Therefore, an alternative route for controllable chloromethylation of PEEK at a moderate reaction temperature was sought.

In this study, a mixed solvent of methanesulfonic acid and sulfuric acid is developed to carry out the chloromethylation of PEEK at a moderate reaction temperature. Methanesulfonic acid (CH<sub>3</sub>SO<sub>3</sub>H) is used as the solvent, sulfuric acid is the catalyst, and chloromethyl octyl ether (CMOE) is the chloromethylating reagent. The effects of polymer concentration, catalyst/polymer ratio, and reaction temperature on the rate of reaction were investigated. The mixed methanesulfonic acid/sulfuric acid solvent based route is compared to the sulfuric acid based one.

## EXPERIMENTAL

## Materials

PEEK (VESTAKEEP® 4000P) powder was generously provided by Evonik Degussa (China) Co. CMOE was synthesized according to the Ref.<sup>20</sup>. Dichloromethane, *n*-octanol, polyoxymethylene, calcium chloride anhydrous, hydrochloric acid (37–38%), sodium chloride, sulfuric acid, ethanol, and NMP were commercially obtained and used as received without further purification. All the used chemicals in the experiments were analytical grade.

## Mixed Methanesulfonic Acid/Sulfuric Acid Solvent for CMPEEK Synthesis

About 0.5 g PEEK was added to methanesulfonic acid at room temperature and continuously stirred until the PEEK was completely dissolved. The temperature was adjusted to a certain one, followed by addition of sulfuric acid and CMOE. The reaction mixture was stirred for a certain time at which time the reaction solution was quenched in ice water, precipitating the CMPEEK. The precipitated polymer was washed with deionized water until neutral and then dried under vacuum at room temperature. The polymer product was further purified by dissolution in NMP, precipitated by adding ethanol, completely washed with ethanol, and finally dried under vacuum at room temperature. The synthetic process is summarized in Figure 1.

## Synthesis of CMPEEK Using Sulfuric Acid Solvent

CMPEEK was synthesized with sulfuric acid serving as both the solvent and the catalyst as described previously.<sup>25</sup> About 0.5 g PEEK was added to concentrated sulfuric acid at 0°C with stirring. After complete dissolution the temperature of the solution was adjusted to a certain one and CMOE added. The reaction solution was stirred for a certain time and then the reaction was quenched in ice water. The precipitated polymer product, CMPEEK, was washed with deionized water until neutral and then dried under vacuum at room temperature. The polymer product was further purified by dissolution in NMP, precipitated by quenching with ethanol, completely washed with ethanol, and finally dried under vacuum at room temperature.

## Characterizations

<sup>1</sup>H-NMR spectroscopy was used to confirm the chemical structure of chloromethylated PEEK, and also to determine the DC. <sup>1</sup>H-NMR spectra of PEEK and CMPEEKs were recorded by a Varian Unity Inova 400 spectrometer at a resonance frequency of 399.73 MHz. About 2 wt % CMPEEK solutions were obtained by directly dissolving CMPEEK into DMSO-*d*<sub>6</sub>. Tetramethylsilane (TMS) was used as the internal standard in all cases. A Thermogravimetric analysis (TGA) analyzer (Mettler Toledo TGA/SDTA851<sup>c</sup>) was used to test the thermal stability of the PEEK and CMPEEK. About 5–10 mg samples were heated from 100 to 700°C at a heating rate of 10°C min<sup>-1</sup> under a nitrogen atmosphere (N<sub>2</sub> flow rate: 80 mL min<sup>-1</sup>). The samples were dried for 24 h at 50°C in vacuum to remove moisture prior to the test. For the mechanical test, the CMPEEK film was prepared. CMPEEK was completely dissolved in NMP at room temperature, followed by casting the solution onto a glass plate. After dried at 80°C for 48 h, its film was peeled off from the glass plate when all the NMP solvent was evaporated. The mechanical property of

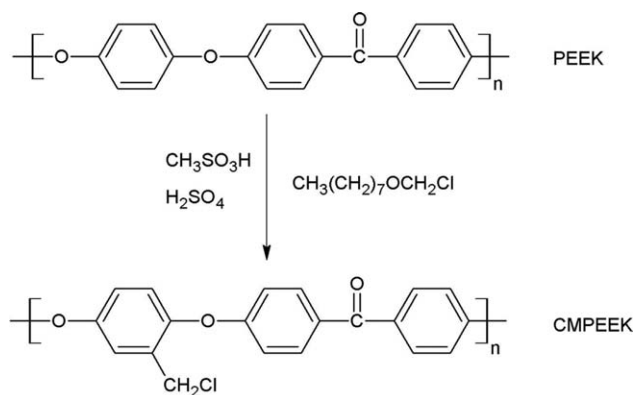


Figure 1. Synthesis of CMPEEK.

the CMPEEK film was tested with a SANS mechanical analyzer in an air atmosphere at room temperature with the cross-head speed of 5 mm min<sup>-1</sup>. Dumbbell-shaped membrane samples were tailored following the international standard ISO 527. Tensile strength and tensile strain at break were recorded.

## RESULTS AND DISCUSSION

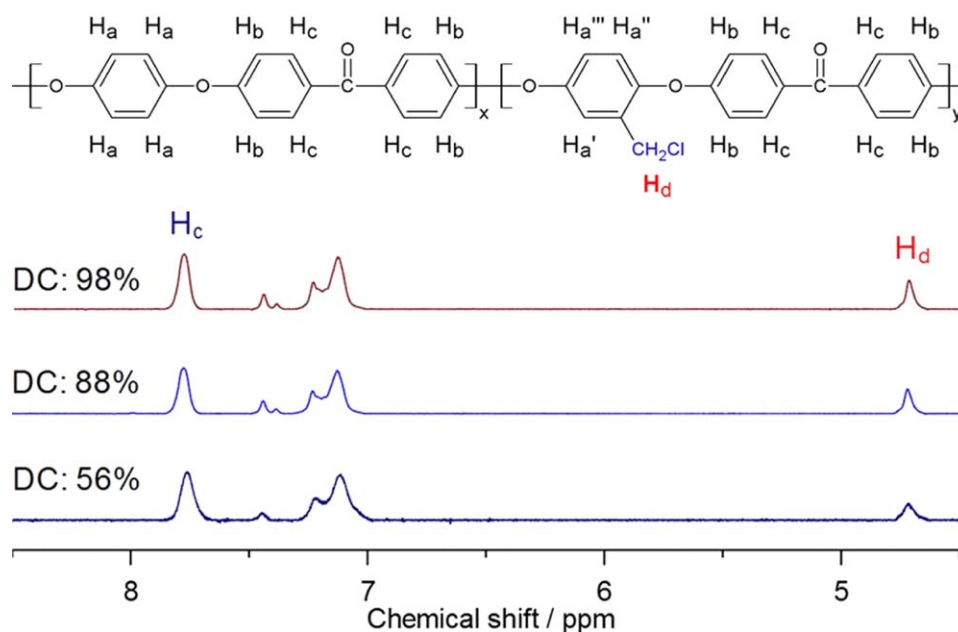
## Characteristics

<sup>1</sup>H-NMR spectra of PEEK and CMPEEKs are presented in Figure 2. In the <sup>1</sup>H-NMR spectrum of pristine PEEK, H<sub>a</sub> and H<sub>b</sub> appear at about 7.0–7.3 ppm, while H<sub>c</sub> has a greater chemical shift (7.8 ppm), due to lower electron-density. After chloromethylation, a new peak, H<sub>d</sub> is seen at 4.7 ppm, characteristic of —CH<sub>2</sub>Cl. This peak is identical to the proton chemical shift of chloromethyl group in CMPEEK described in our previous work.<sup>25</sup> The DC of CMPEEK was calculated from the area under the <sup>1</sup>H peaks as defined in our previous work.<sup>25</sup>

The TGA curves of PEEK and CMPEEK with DC of 56% are shown in Figure 3. The onset decomposition temperature is lower for CMPEEK than for PEEK. It is because the chloromethyl group side-chain has a lower decomposition temperature than the PEEK main-chain. The mechanical properties of CMPEEKs are listed in Table I. For all the tested CMPEEKs, the tensile strengths are above 40 MPa and the tensile strains are above 30%. Such good mechanical properties suggest that no serious degradation side reaction of PEEK main-chain occurs during the chloromethylation. Based on TGA and mechanical test results, the CMPEEK has enough thermal and mechanical stability.

## The Effects of Polymer Concentration and Catalyst/Polymer Ratio on the Chloromethylation Reaction Rate

The degrees of chloromethylation of CMPEEK are listed in Table II. In methanesulfonic acid solvent, the extent of reaction increased with increasing polymer concentration (*C*<sub>PEEK</sub>), and the rate of PEEK chloromethylation increased as a function of *C*<sub>PEEK</sub>. The opposite trend of the chloromethylation reaction rate was observed in sulfuric acid solvent; the DC of CMPEEK decreased with increasing *C*<sub>PEEK</sub>. We suggest that catalyst/polymer ratio is reduced with increasing *C*<sub>PEEK</sub> in sulfuric acid solvent. Gelation was identified by a large increase in solution viscosity of the stirred reaction solution. The reaction solution gelled when *C*<sub>PEEK</sub> was greater than 1.81 wt % in mixed

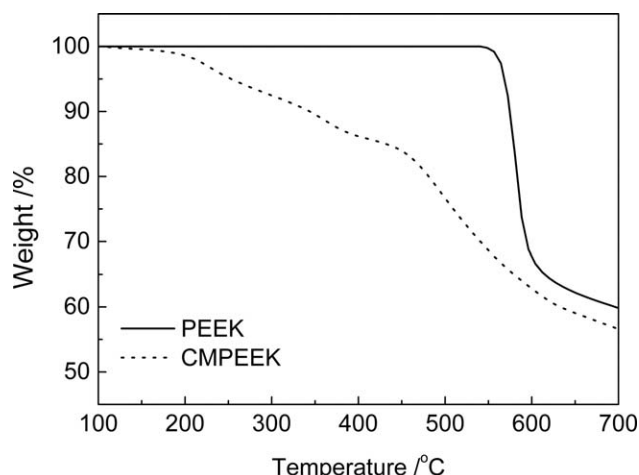


**Figure 2.**  $^1\text{H-NMR}$  of PEEK and CMPEEKs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

methanesulfonic acid/sulfuric acid solvent and greater than 1.43 wt % in sulfuric acid solvent. Gelation is believed to be the result of crosslinking between a chloromethyl group and an unsubstituted bisphenol ring of another macromolecular chain via Friedel–Crafts alkylation,<sup>28</sup> as shown in Figure 4. PEEK has

bisphenol rings, in which two powerful electron-donating ether groups endow it with high electron-density. It leads not only to high chloromethylation activity, but also to high Friedel–Crafts alkylation activity, since both reactions are electrophilic substitution reactions. Therefore, low  $C_{\text{PEEK}}$  is required to increase the distance between polymer chains to reduce the probability of the crosslinking reaction between a chloromethyl group and unsubstituted bisphenol rings.

During the chloromethylation of PEEK, CMOE was in large excess (the ratio of CMOE to PEEK was 18.) The CMOE



**Figure 3.** The TGA curves of PEEK and CMPEEK.

**Table I.** The Mechanical Properties of CMPEEKs

Polymer	Tensile strength/MPa	Tensile strain/%
CMPEEK 50%	48	37
CMPEEK 78%	42	31
CMPEEK 98%	45	32

CMPEEK xx%, where xx% is DC of CMPEEK.

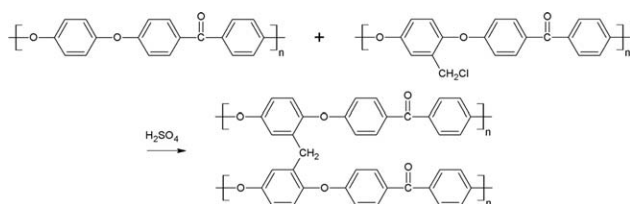
**Table II.** The Effect of Polymer Concentration on DC for Both Routes

$C_{\text{PEEK}}^a$ (wt/vol %)	Sulfuric acid based route <sup>b</sup>		Methanesulfonic acid/sulfuric acid based route <sup>c</sup>	
	Sulfuric acid/PEEK (mL g <sup>-1</sup> )	DC	Methanesulfonic acid/PEEK (mL g <sup>-1</sup> )	DC
1.00	80	0.84	–	–
1.11	70	0.79	–	–
1.25	60	0.70	40	0.37
1.43	50	Gel	30	0.44
1.67	–	–	20	0.50
1.81	–	–	15	Gel

<sup>a</sup>  $C_{\text{PEEK}}$ , concentration of PEEK, wt/vol %, defined as the concentration of PEEK in the reaction solution.

<sup>b</sup> Reaction temperature is  $-10^\circ\text{C}$ , reaction time is 15 min, the concentration of sulfuric acid is 95.5%, and the mole ratio of CMOE and PEEK is 18 to 1.

<sup>c</sup> Reaction temperature is  $25^\circ\text{C}$ , the reaction time is 1 h, the concentration of sulfuric acid is 95.5%, the mole ratio of CMOE to PEEK is 18 to 1, and the sulfuric acid/PEEK ratio is 20 mL g<sup>-1</sup>.



**Figure 4.** The crosslinking of CMPEEK and PEEK.

concentration is nearly constant through the course of reaction. The sulfuric acid concentration is also constant through the course of reaction, though the catalyst/polymer ratio can be adjusted by changing the sulfuric acid/polymer ratio in the reaction mixture. In each synthesis run, only the PEEK concentration changes as a function of time. The rate of chloromethanation was assumed to be first order in PEEK concentration with a first order rate constant  $k$ . The concentration of PEEK decays exponentially with time [eq. (1), where  $C_{\text{PEEK}0}$  is the initial concentration of PEEK]. The first order rate constant can be obtained from the slope of a graph of  $\ln(1/(1 - \text{DC}))$  vs. time [eq. (2)].

$$C_{\text{PEEK}} = C_{\text{PEEK}0} \cdot \exp(-kt) \quad (1)$$

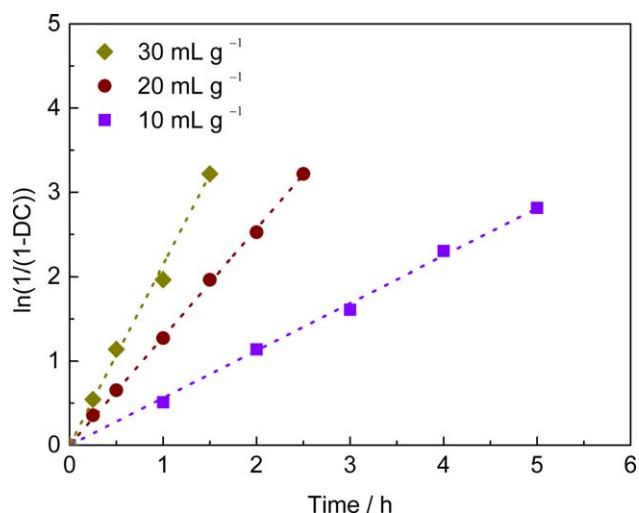
$$\ln(1/(1 - \text{DC})) = kt \quad (2)$$

The curves of  $\ln(1/(1 - \text{DC}))$  vs.  $t$  at different sulfuric acid/PEEK ratios for methanesulfonic acid solvent are shown in Figure 5. The data are consistent with first order reaction kinetics. The rate constant,  $k$ , increased with sulfuric acid/PEEK ratio. The first order rate constants are summarized in Table III. The first order rate constant increased with sulfuric acid/PEEK ratio consistent with catalytic activity of sulfuric acid.

When sulfuric acid was employed as the solvent and catalyst, the catalyst/polymer ratio was regulated by varying the concentration of sulfuric acid with constant  $C_{\text{PEEK}}$ . The solubility of PEEK in sulfuric acid of lower than 92.8% concentration was insufficient to fully dissolve the PEEK. The effect of the concentration of sulfuric acid on the chloromethylation of PEEK was investigated for sulfuric acid of over 92.8%. The rate of reaction was fit to first order reaction kinetics and the data for  $\ln(1/(1 - \text{DC}))$  vs.  $t$  are shown in Figure 6. The first order rate constants,  $k$ , for sulfuric acid concentrations of 92.8%, 94.0%, and 95.5% are summarized in Table III. The rate constant increases rapidly with the concentration of sulfuric acid, e.g., a slight increase of 2.7% in the strength of sulfuric acid causes a 300% change in the reaction rate.

**Table III.** First Order Rate Constants for Chloromethanation Reaction

Solvent	Reaction temperature (°C)	Sulfuric acid/PEEK (mL g <sup>-1</sup> )	Concentration of sulfuric acid (%)	First order rate constant (h <sup>-1</sup> )
Methanesulfonic acid	25	10	95.5	0.56
Methanesulfonic acid	25	20	95.5	1.29
Methanesulfonic acid	25	30	95.5	2.12
Sulfuric acid	-10	60	92.8	1.88
Sulfuric acid	-10	60	94.0	4.10
Sulfuric acid	-10	60	95.5	5.33



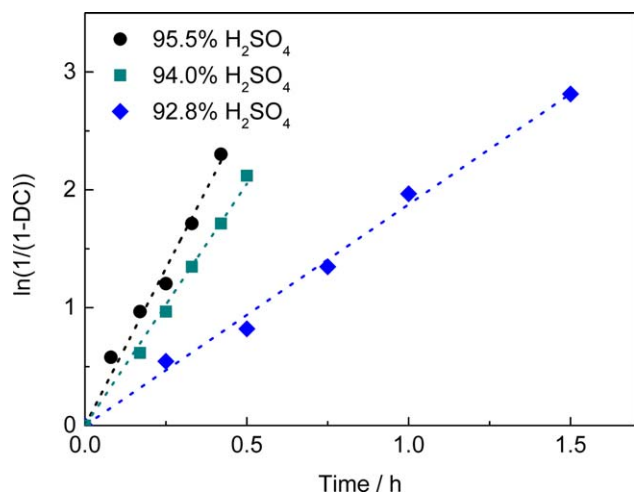
**Figure 5.** Kinetics curves at different sulfuric acid/polymer ratios for methanesulfonic acid/sulfuric acid based route ( $C_{\text{PEEK}}$  is 1.67 wt/vol %, the concentration of sulfuric acid is 95.5%, and the mole ratio of CMOE to PEEK is 18 to 1). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

### The Effects of Reaction Temperature

Figure 7 shows DC of CMPEEK as a function of time at different temperatures for chloromethylation in methanesulfonic acid/sulfuric acid based route. DC of CMPEEK increases moderately with reaction time even at 25°C, indicating that DC of CMPEEK could be easily controlled at room temperature. Figure 8 shows DC of CMPEEK as a function of the chloromethylation time at different temperatures in sulfuric acid based route. DC of CMPEEK increases too rapidly with reaction time at room temperature to control, e.g. at 20°C, the DC is 0.90 after only 20 min. Therefore, sub-ambient reaction temperatures, e.g. -10°C, are required for reasonable control of DC of CMPEEK.

The pseudo-first order rate constants for chloromethanation at different temperatures were calculated from the data shown in Figures 7 and 8. The activation energy for chloromethanation in methanesulfonic acid and sulfuric acid solvents were found in Arrhenius plots of the rate constants, shown in Figure 9. At the same temperature, the rate constant in the methanesulfonic acid solvent is much less than the rate constant in sulfuric acid solvent. However, the activation energy for chloromethanation are nearly the same in both solvents;  $\Delta E_a = 30.9 \text{ kJ mol}^{-1}$  in



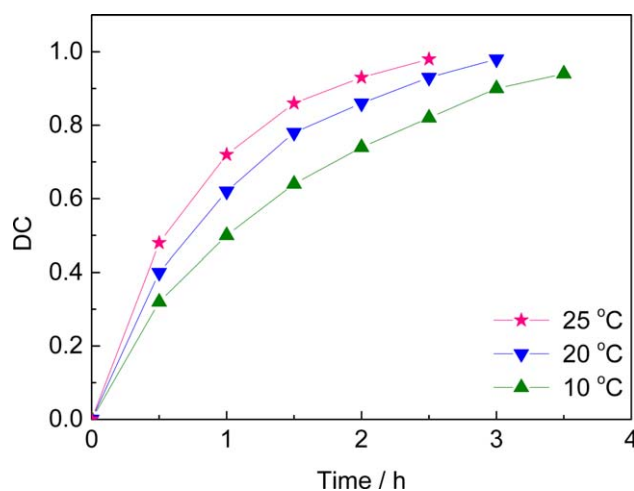


**Figure 6.** Kinetics curves for sulfuric acid based route (Reaction temperature is  $-10^{\circ}\text{C}$ ,  $C_{\text{PEEK}}$  is 1.25 wt/vol %, and the mole ratio of CMOE to PEEK is 18 to 1). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

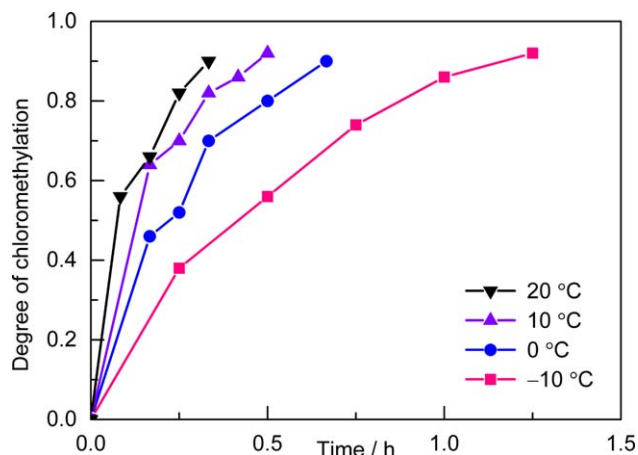
methanesulfonic acid and  $\Delta E_a = 32.3 \text{ kJ mol}^{-1}$  in sulfuric acid solvent. These results suggest that there is a solvent effect for dissolution of the PEEK, but the catalytic reaction is the same in the different solvents.

## CONCLUSIONS

A new mixed methanesulfonic acid/sulfuric acid solvent based chloromethylation route was compared with sulfuric acid based chloromethylation. Methanesulfonic acid was the solvent, CMOE is the chloromethylating reagent, and sulfuric acid catalyzes the reaction.  $^1\text{H-NMR}$  spectra confirmed the successful synthesis of chloromethylated PEEK. The effects of polymer concentration, catalyst/polymer ratio, and reaction temperature on the chloromethylation of PEEK were investigated. The con-

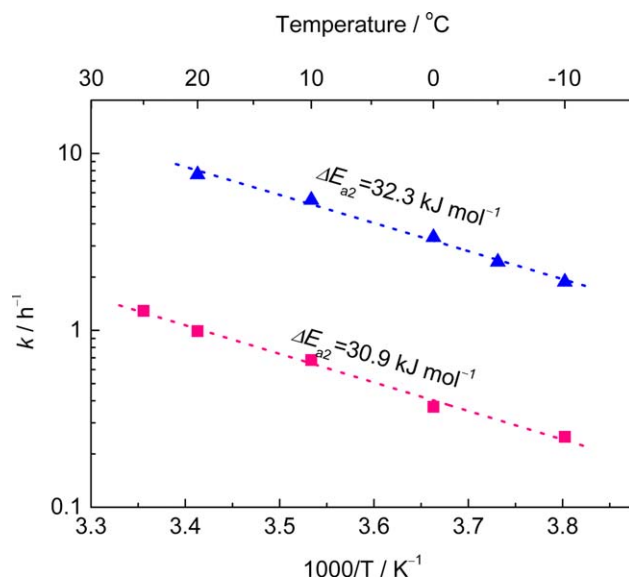


**Figure 7.** DC of CMPEEK as a function of chloromethylation time at different temperatures for methanesulfonic acid/sulfuric acid based route ( $C_{\text{PEEK}}$  is 1.67 wt/vol %, the concentration of sulfuric acid is 95.5%, and the mole ratio of CMOE to PEEK is 18 to 1). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 8.** DC of CMPEEK as a function of chloromethylation time at different temperatures for sulfuric acid based route ( $C_{\text{PEEK}}$  is 1.25 wt/vol %, the concentration of sulfuric acid is 92.8%, and the mole ratio of CMOE to PEEK is 18 to 1). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

centration of PEEK needs to very low for both routes to avoid gelation of the reaction mixture. The reaction rate constant,  $k$ , is much lower for the mixed methanesulfonic acid/sulfuric acid solvent than for the sulfuric acid solvent, e.g. the  $k$  at  $25^{\circ}\text{C}$  for the methanesulfonic acid/sulfuric acid based route ( $1.29 \text{ h}^{-1}$ ) is even lower than that at  $-10^{\circ}\text{C}$  for the sulfuric acid based route ( $1.88 \text{ h}^{-1}$ ). The DC of CMPEEK in the mixed methanesulfonic acid/sulfuric acid solvent can be easily controlled by varying the reaction time at room temperature, whereas sub-ambient temperatures are required for sulfuric acid solvent.



**Figure 9.** The effect of the reaction temperature on reaction rate constant ( $k$ ) (For methanesulfonic acid/sulfuric acid based route,  $C_{\text{PEEK}}$  is 1.67 wt/vol %, the concentration of sulfuric acid is 95.5%, and the mole ratio of CMOE to PEEK is 18 to 1; for sulfuric acid based route  $C_{\text{PEEK}}$  is 1.25 wt/vol %, the concentration of sulfuric acid is 92.8%, and the mole ratio of CMOE to PEEK is 18 to 1). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

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