

## Solvent-free synthesis of poly (phenylene ether) (PPE) in supercritical carbon dioxide (scCO<sub>2</sub>)

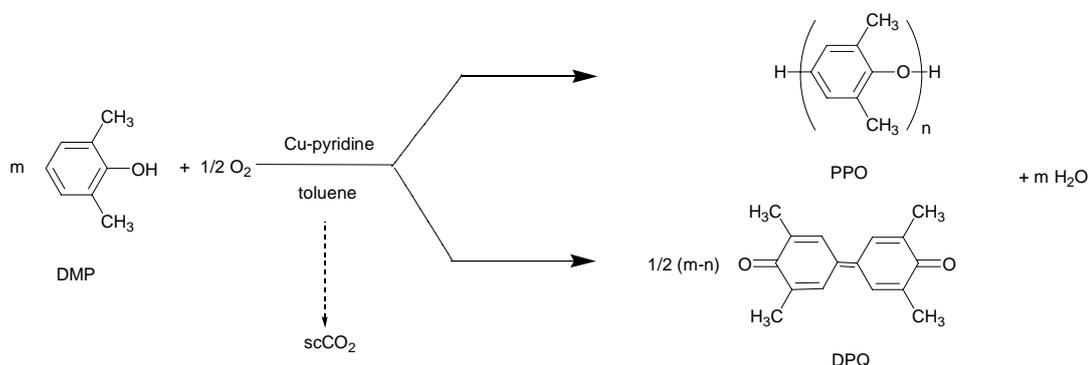
Ai Yamasaki, Yuta Sugiyama, Hideto Mikami, Masaru Watanabe, Yoshiyuki Sato,  
Richard Smith, Jr., Hiroshi Inomata  
Research Center of Supercritical Fluid Technology, Tohoku University  
Aoba, Aramaki 6-6-11-404, Aoba-ku, Sendai 980-8579, JAPAN  
Correspondence: inomata@scf.che.tohoku.ac.jp

### ABSTRACT

The synthesis of poly (phenylene ether) (PPE) has been carried out in supercritical carbon dioxide (scCO<sub>2</sub>) at 40 °C and 15 MPa with a one-step polymerization. Maximum yield and weight-average molecular weight (Mw) of the synthesized PPE were ca. 70 % and 1.1 10<sup>4</sup>, respectively. Two-step polymerizations at 55 °C, 22 MPa or 70 °C, 30 MPa for 8 h after synthesis at 40 °C, 15 MPa for 20 h, gave yields and Mw of up to ca. 80 % and 1.9x10<sup>4</sup>, respectively. A small amount of diphenoquinone (DPQ) was found in both one-step (1.4 %) and two-step (ca.1.7 %) polymerizations. The synthesized PPE was found to have similar glass transition temperature (T<sub>g</sub>, 200 °C) to that of commercial one. In the synthesis, scCO<sub>2</sub> seemed to function not only as a reaction solvent but also as a plasticizer for the PPE polymer.

### 1 INTRODUCTION

Poly (phenylene ether) (PPE) is one of the most widely-used engineering plastics due to its excellent heat-and water-resistance and mechanical properties. PPE was discovered in 1959 by Hay et al.[1] and has been synthesized via the oxidative coupling of 2,6-dimethylphenol (DMP) as catalyzed by copper-amine complex in toluene under ambient conditions and at O<sub>2</sub>/N<sub>2</sub> atmosphere. In the polymerization, PPE is formed by C-O coupling of DMP while diphenoquinone (DPQ), a by-product is formed by C-C coupling. Formation of the by-product DPQ is favored at higher temperatures.[2] H<sub>2</sub>O is also another intrinsic by-product from both C-C and C-O couplings.[3] Formation of DPQ is undesirable because DPQ is visibly colorful and it degrades the heat-resistant properties of the polymer. For separating the product polymer from the reaction solutions, methanol



**Fig.1** Over reaction scheme for the oxidative coupling of DMP to PPE and DPQ..

is used to precipitate PPE from toluene solution and to rinse the residues from PPE polymer in the commercial process.[4] Methanol/toluene mixtures are subjected to distillation to separate these solvents for recycle use. Water is additionally used to separate methanol from toluene for their recycle use. Thus the present PPE production process requires many solvents and their separations operations, which leads to an increase in the process cost/time and also increases the probability of product contamination. Green sustainable processes are expected to reduce or minimize use of organic solvents. Saito et al. has studied the PPE synthesis with a surfactant in alkaline aqueous solutions that is the one of the environmental friendly solvents.[5] PPE synthesis in a non-toxic and inexpensive supercritical CO<sub>2</sub> (scCO<sub>2</sub>, T<sub>c</sub>: 31.1 °C, P<sub>c</sub>: 7.38 MPa) is alternative environmental friendly process, which can reduce the consumption of organic solvent as shown in Fig.1.

A process that uses CO<sub>2</sub> as the main solvent can meet the goals of green sustainable process and greatly simplify the product separation by de-pressurization.[6] Further, CO<sub>2</sub> might be used to remove residual solvent and monomer from the final product. These simplified processes reduce consumption of organic solvents and lowers energy consumption. CO<sub>2</sub> is also miscible with O<sub>2</sub> and can control the O<sub>2</sub> partial pressure, which consequently leads to safe process operation and reduces the danger of explosion. As a result, PPE synthesis in scCO<sub>2</sub> has economical and safety advantages.

PPE synthesis in scCO<sub>2</sub> with or without surfactants has been reported by DeSimone et al. in 1996.[7] The authors found that it is difficult to synthesize a high molecular weight PPE in scCO<sub>2</sub> without surfactants due to the precipitation of the high molecular weight PPE. Surfactants are supposed to be essential to dissolve/disperse the polymer particles in scCO<sub>2</sub> phase for continuing the polymerization to obtain a higher molecular weight polymer.[7,8] On this point, however, there have been reports for other polymers in which the polymerization might proceed even in a precipitated polymer phase that has been plasticized to exhibit due to polymer chain mobility.[9] Shi et al. reported the solid-state polymerization of poly (bisphenol A carbonate) facilitated by scCO<sub>2</sub>. [10] In their study, scCO<sub>2</sub> played both roles as a reaction solvent and plasticizer for the polymer. This suggests the possibility for synthesizing high molecular weight PPE polymers in scCO<sub>2</sub> with no surfactants via polymer phase polymerization after polymer precipitation.

In this work, we have made an attempt to synthesize a high molecular weight PPE in scCO<sub>2</sub> without using any surfactants. Firstly, the reactions were carried out at 40 °C and 15 MPa to study the reaction time dependence of polymer yield and weight-average molecular weight (M<sub>w</sub>) and to understand the polymerization behavior of PPE. Secondly, the reaction was carried out at 40 °C and 15 MPa for 20 h same as the above and then successively the reaction was carried out at 55 °C or 70 °C as a second reaction temperature for 8 h under constant CO<sub>2</sub> density with the expectation of continuing the polymerization in polymer phase even though the precipitation of growing polymer chains probably takes place in reaction phase. Comparison with results at different second reaction temperatures allowed us to discuss the reaction temperature dependence of the polymer yield and M<sub>w</sub> and to study conditions for synthesizing higher molecular weight PPE in scCO<sub>2</sub>. We also compare the two-step polymerization with the one-step polymerization.

## 2 EXPERIMENTAL

### 2.1 Materials

The 2,6-dimethylphenol (DMP, 99<sup>+</sup> %, Wako Chemical), CuBr (99.9 %, Wako Chemical), and pyridine (99.9 %, Wako Chemical) were used as received. High purity CO<sub>2</sub> (99.995 %, Nihon Sanso) and O<sub>2</sub> (99.9 %, Nihon Sanso) were filtered (5 μm) and dried with anhydrous calcium sulfate.

## 2.2 One-step polymerization

Figure 2 shows schematically the experimental apparatus for PPE synthesis in scCO<sub>2</sub> solvent. The reaction was performed in a reactor whose volume was 32 mL (ϕ 30x 45 L).

In typical experiments, DMP(0.66 M) and CuBr(0.0135 M) were loaded into the reactor. After purging the reactor with CO<sub>2</sub>, O<sub>2</sub> was added to be 0.58 M in the reactor. Then, the reactor was immersed in a water bath and the temperature of the reactor reached the reaction temperature (40 or 70 °C) within a few minutes. CO<sub>2</sub> was pumped continuously up to 15 or 33 MPa by a plunger pump, when CO<sub>2</sub> was heated through a preheating coil before entering the reactor.

During the CO<sub>2</sub> feeding at about 13 or 25 MPa, 0.05 ml (0.79 M) of pyridine was added to the reactor by changing the flow path with a rotary injection valve. Pyridine injection was assumed to initiate the reaction. The reaction was carried out continuously for the desired reaction times without sampling during the reaction and then the sample was taken and analyzed after terminating the reaction by cooling and depressurization. Each data point represents a separate experiment.

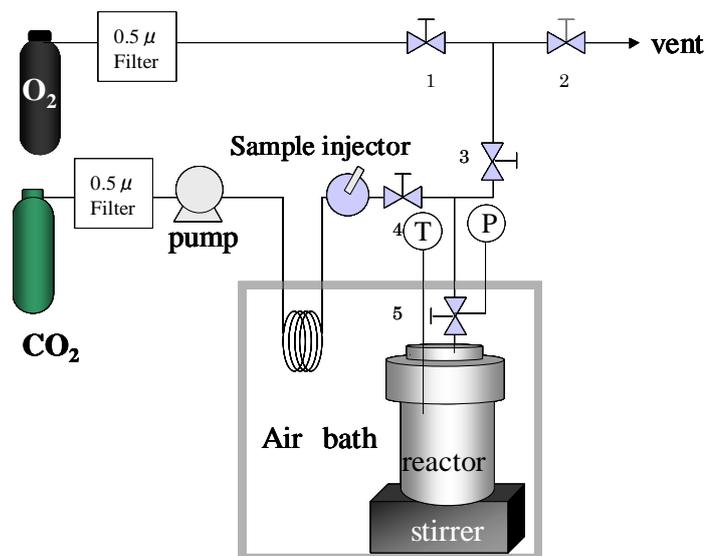


Fig. 2 Experimental Apparatus of PPE synthesis in scCO<sub>2</sub>.

## 2.3 Two-step polymerization

Two-step polymerizations were carried out initially at the same conditions as one-step polymerization and then followed by heating the reactor from 40 °C to 55 °C or 70 °C under isochoric condition. Reactions were quenched by cooling the reactor and then venting CO<sub>2</sub> to the atmosphere.

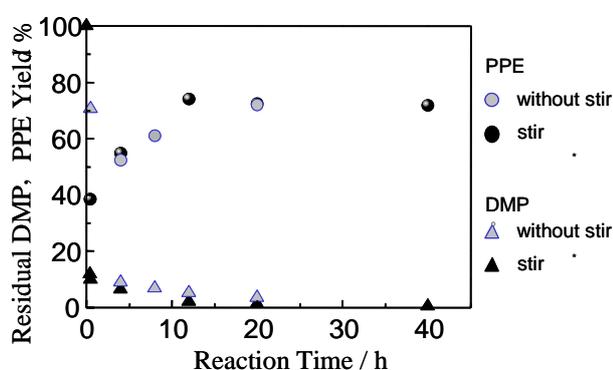
## 2.3 Analysis

Polymer products were dissolved in toluene/methanol solution (13/2 v/v) including a small amount of HCl aqueous solution. HCl was used to ensure reaction termination in the toluene/methanol solution. A small portion of this solution was used to determine the DPQ yield with UV/Vis spectrophotometer (JASCO; U-best V-570) at 421 nm. The PPE was collected by precipitating in excess amount of methanol and the polymer yield was determined with gravimetric analyses after drying. The molecular structure of the products was determined with the <sup>1</sup>H-NMR (Bruker; DRX500) with CDCl<sub>3</sub> solution. All synthesized polymers were identified as PPE. The weight-average molecular weight (M<sub>w</sub>) and the polydispersity index (PDI) were determined with a gel permeation chromatography (GPC) equipped with a refractive index (RI) detector. Columns used were HT406M, two KF803L, and KF801 (Shodex). Tetrahydrofuran (THF) was used as a mobile phase with a flow rate of 1 mL/min at 40 °C. Polystyrene standards were used for calibration. Differential scanning calorimetry (DSC, TA Instruments; DSC2910) was used to determine the T<sub>g</sub> under N<sub>2</sub> atmosphere at a heating or cooling rate of 10 °C /min.

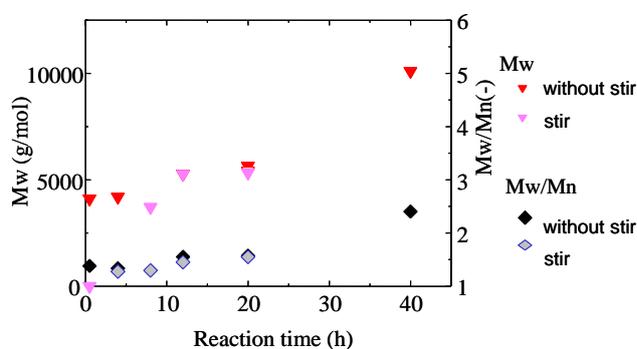
### 3 RESULTS AND DISCUSSION

#### 3.1 One-step polymerization

Figure 3 shows the reaction time dependence of polymer yield and monomer residual. The polymer yield increased up to ca. 70 % at 12 h while the monomer was rapidly consumed in a short time. Fluctuations observed might be attributed to experimental errors in the analysis method. Figure 4 shows the dependence of Mw on reaction time. The Mw increased gradually and stayed around  $M_w = 6.0 \times 10^3$  during 10~20 h, and then increased again to attain the value of ca.  $1.1 \times 10^4$  after 40 h while the PPE yield was almost constant around 70 %. The PDI of the PPE product was 1.5 – 2.5 which was found for all experiments. The PDI of  $scCO_2$  synthesized PPE was found to be comparable to that of synthesized PPE in organic solvents.[3] However, the polymer yield might have some small influence on GPC measurement.

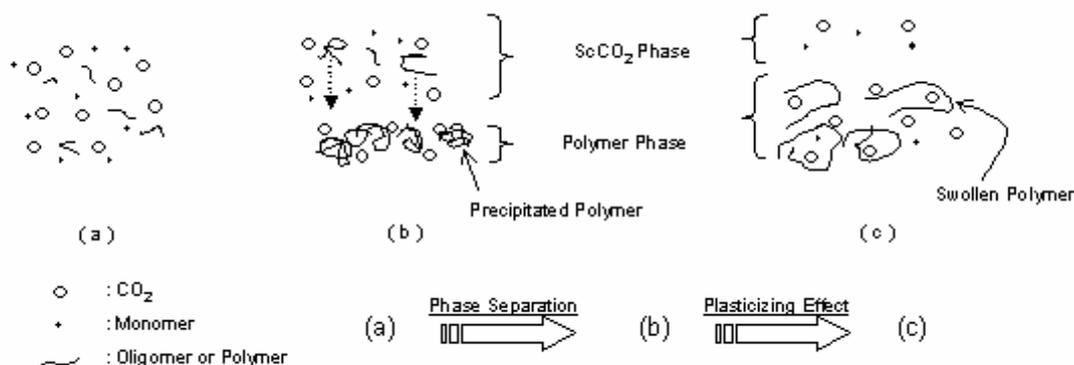


**Fig. 3** The reaction time dependence of residual DMP and PPE yields. (40C, 17MPa,  $[CuBr]=0.0135M$ , DMP:CuBr:Py =49:1:59)



**Fig. 4** The reaction time dependence of molecular weight and Mw/Mn. (40C, 17MPa,  $[CuBr]=0.0135M$ , DMP:CuBr:Py =49:1:59)

Considering the above results, we assumed the following reaction mechanism. The reaction is initially assumed to proceed in the  $scCO_2$  phase homogeneously (Fig. 5-a), because the amount of



**Fig.5** The illustration of the reaction progress.

DMP and pyridine used in this study were far below their saturated solubility into  $scCO_2$  and thus DMP and pyridine will not occur phase separation. The polymer yield and Mw were increased with the reaction time via probably a step growth mechanism in the early stage of polymerization. The

plateau region in the plot of  $M_w$  against reaction time could result from phase separation via precipitation of PPE polymers after some progress in polymerization. Since the monomer could play as a co-solvent and its concentration decreased with the reaction progress, the solvent power of  $scCO_2$  phase would be expected to decrease with reaction time. The polymer chains probably initiated polymer chain growth in the  $scCO_2$  phase until they reached a critical polymer chain size where the polymers begin to precipitate from the solutions and finally form a polymer phase (Fig. 5-b). On the other hand, the remaining monomer in the  $scCO_2$  could produce new polymer chains of lower molecular weight PPE. Consequently, it is possible for the average molecular weight to be constant or to decrease with time. When the reaction was continued even after the polymer phase separation (20 h ~ 40 h), the  $M_w$  increased gradually again towards a  $M_w$  maximum because of polymer chain propagation. This secondary increase in  $M_w$  after 20 h might be due to solid-state polymerization. This would be difficult to quantify since there could be partitioning of the monomer, catalyst and oxygen between  $scCO_2$  and polymer phases once the reaction conditions became heterogeneous. However, it might be noted that the reaction can proceed even in the polymer phase because polymer phases can be plasticized and swollen with  $CO_2$ . [11] This is shown in Fig. 5-c.

Shi et al. have studied the solid-state polymerization of poly (bisphenol-A carbonate) (PC) in  $scCO_2$  or in  $N_2$  [10]. They found that the plasticizing effect of  $scCO_2$  in PC facilitated the condensate (phenol) removal and the reaction between the polymer chains. Generally, solid-state polymerization is a method to obtain high molecular weight polymers and should be carried out at the temperature between glass transition temperature ( $T_g$ ) and melting temperature ( $T_m$ ) to have enough polymer chain mobility for reaction. [11] The reaction temperature of 40 °C used in this work, was lower than the glass transition temperature of PPE. However, an unmistakable increase in  $M_w$  was observed in our experiments. The increase in  $M_w$  can be attributed to the probable  $CO_2$  plasticizing, suggesting the possibility that the precipitated polymer phase was already in a swollen state. This would allow the polymer chain mobility for further reaction for monomer-polymer or polymer-polymer. The results in this work are supported by the previous reports that PPE becomes plasticized effectively by dissolved  $CO_2$  [12] because it has fairly large free volume particularly in comparison with other polymers such as poly (styrene) (PS) and PC. [13]

### 3.2 Two-step polymerization

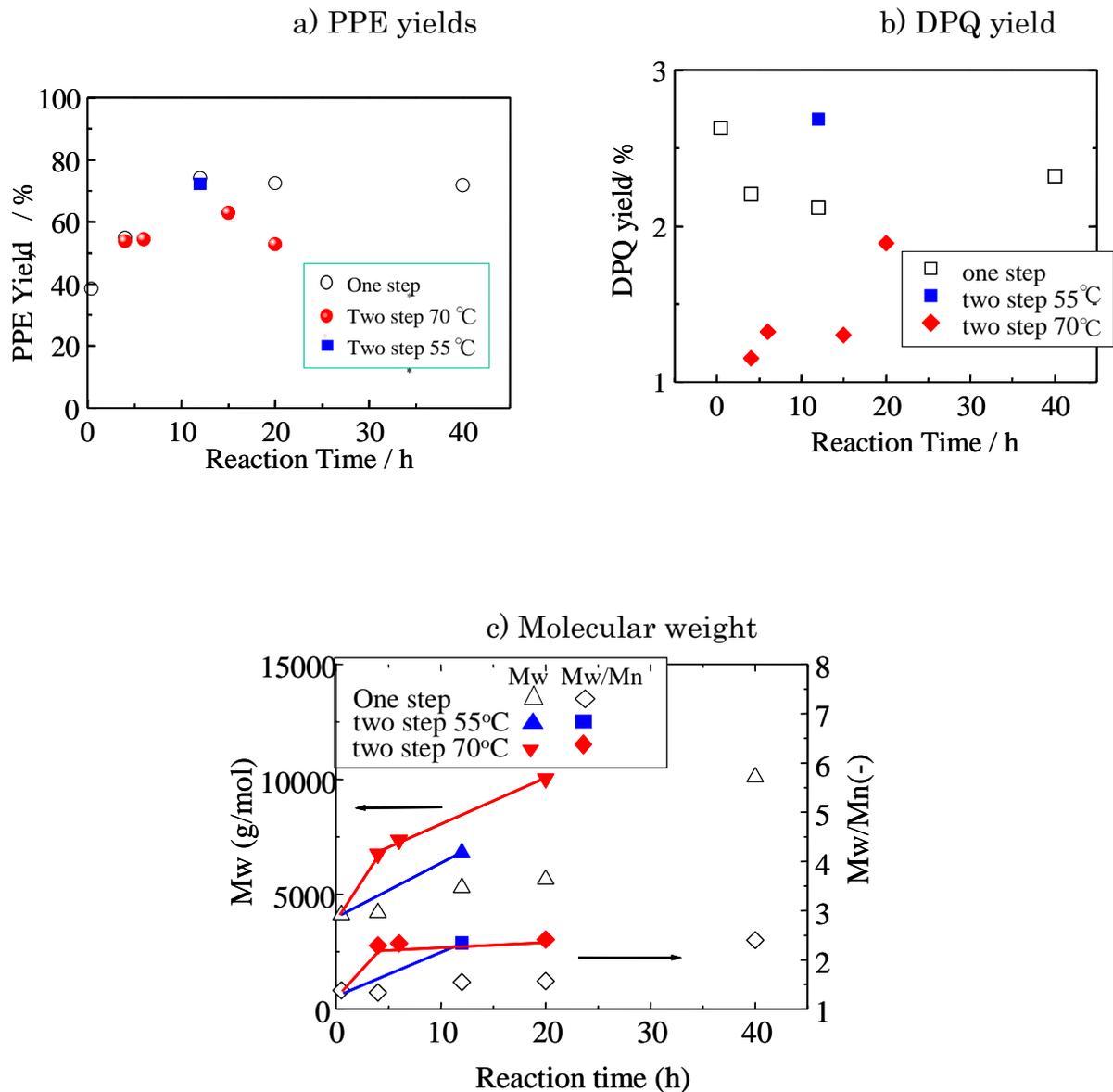
To obtain more evidence for the above mechanism, two-step polymerizations were performed in which the reaction temperature was raised from 40 °C to 55 °C or 70 °C at the reaction time of 0.5 h under constant  $CO_2$  density. This heating brought about an increase in pressure in accordance with the  $CO_2$  thermal expansion; namely from 15 MPa to 22 MPa (55 °C) or from 15 MPa to 30 MPa (70 °C).

Figure 6 shows the experimental results of PPE synthesis in  $scCO_2$  via one-step and two-step polymerizations. As shown in Fig.6(a), the polymer yields are generally same for both methods, showing 70 % at times longer than 12 h. Slight decrease in PPE yield observed for two-step reaction may be due to the occurrence of gelation of polymer chains. Whereas the amount of DPQ, by-product of PPE polymerization, was significantly decreased for two-step reaction compared with that for one-step reaction as shown in Fig.6(b). Although it is very difficult to rationalize this DPQ behavior, it would be possible to estimate that the DPQ was captured in PPE polymers during propagation. According to Viersen et al. [14], the DPQ reaction is possibly inhibited for two-step polymerizations, because the reactant species are mostly oligomers/polymers. This is another possible explanation of DPQ behavior. Consequently, it seems that two-step polymerizations allow high molecular weight PPE synthesis and minimize the amount of DPQ formed.

Figure 6 (c) shows the comparison of  $M_w$  time evolutions for two-step and one-step reactions. It is clearly seen that the rapid increase in  $M_w$  was observed for two-step reaction, especially for

higher temperature two-step reaction at 70 °C. The data indicated that the Mw did increase significantly up to ca.  $1.1 \times 10^4$  at 20 h for the two-step polymerization. The PDI for two-step reaction is always higher than that for one-step reaction, but the values do not exceed 2.5 although the reaction was supposed to proceed both in scCO<sub>2</sub> phase and polymer phase.

It should be noted that the two-step polymerization was effective to obtain higher molecular weight PPE efficiently via scCO<sub>2</sub> phase polymerization as expected from the discussion of the one-step polymerization. Although the mechanism cannot be explored in detail in this work, the polymer yield and Mw increase shown in Fig.6 can be explained in terms of phase separation and does provide evidence for our proposed polymerization mechanism.



**Fig. 6** The reaction time dependence of total PPE (PPE + gel PPE), DPQ yield and Mw, Mw/Mn with one step and two step polymerization.

The polymer yield and Mw increase after increasing reaction temperature can also be explained by the polymerization in polymer phase after polymer precipitation, which is strongly dependent on the

plasticizing effect of CO<sub>2</sub> dissolved into the polymer phase[10,11]. Higher temperatures tend to increase the polymer chain mobility in polymer phase swollen with scCO<sub>2</sub>. Therefore when there is enough oxygen and catalyst in the polymer phase, polymer chains can be transformed into longer polymer chains via collision or so-called propagation reactions. This phenomenon could lead to the increase in Mw. It has been demonstrated that it is effective to raise the second reaction temperature to obtain higher molecular weight PPE.

The T<sub>g</sub> of the PPE synthesized with two-step polymerization (ca. 200 °C) was found to be comparable with commercial PPE. Thus we could demonstrate the advantage of controlling reaction temperature profile. From the two-step polymerization results, scCO<sub>2</sub> seems act as a reaction solvent and also as a plasticizer for PPE polymers. In the future, we hope to study the phase distribution of selected species between scCO<sub>2</sub> and polymer phases, and investigate the plasticizing effect of scCO<sub>2</sub> in more detail to better understanding the polymerization kinetics.

#### 4 CONCLUSIONS

We have synthesized relatively high molecular weight PPE in scCO<sub>2</sub> via a two-step polymerization method. The synthesized PPE had similar thermal properties to commercial PPE. Polymer chain growth probably initiated in the scCO<sub>2</sub> phase until a critical polymer chain size was reached. Once the polymer precipitated, scCO<sub>2</sub> probably acted as plasticizer for the polymer and also monomer transport through the swollen phase. This plasticizing effect allowed higher Mw PPE to be synthesized. The use of scCO<sub>2</sub> as PPE reaction solvent could allow a new green production process to be developed.

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