

# Biphasic Polycondensation of 4-Bromo-2,6-dimethylphenol Using Silica Gel as a Promoter

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Poly(2,6-dimethyl-1,4-phenylene ether) (PPE) was successfully prepared by the biphasic polymerization of 4-bromo-2,6-dimethylphenol (BDMP) with the use of silica gel as a promoter at 20 °C under air. Silica gel was hydrolyzed with alkaline to afford water-soluble siloxane oligomers, which acted as an effective phase transfer agent for the biphasic polymerization of BDMP. The pure PPE was easily separated from the siloxane oligomers by the ordinal reprecipitation process, and the oligomers were reassembled into silica gel by the condensation of silanol groups in an acidic medium. The morphologies of the reassembled silica gel are worm-like and spherical with wormholes in it.

KEY WORDS: Poly(2,6-dimethyl-1,4-phenylene ether) / 2,6-Dimethylphenol / Phase Transfer Catalyst / Biphasic Polymerization / Silica Gel / Siloxane / Alkaline Hydrolysis /

Organic-aqueous interfacial synthesis is an attractive alternative to conventional homogeneous synthesis.<sup>1</sup> By using a phase transfer catalyst (PTC) to transfer the substrates from an inorganic phase into an organic one, interfacial synthesis permits convenient recovery of the catalyst and reaction product. At the same time, the ability of the PTC to take up the substrates and confine them in the interfacial region makes it possible to promote the desired reaction faster and more selectively than in homogeneous processes. Thus, many PTC-promoted polymerizations have been developed, where much milder conditions and much more rapid polymerization were realized.<sup>2</sup> Generally speaking, biphasic polymerization proceeds by the use of cationic or nonionic PTCs such as ammonium and phosphonium salts or crown ethers, which are commercially available oil-derived materials. Silica gel, industrially prepared from silicon dioxide, is most commonly encountered in our everyday life as a desiccant, and in the laboratory as the stationary phase in chromatography. Silicone-based PTC has been developed and commercialized, in which hydrophilic side chains such as oxyethylene units, derived from oil, are introduced onto a polysiloxane backbone.<sup>3</sup> It is known that silica gel can be alkaline hydrolyzed, resulting in alkali metal silicates, whose solution contains a variety of anionic silicate species in dynamic equilibrium.<sup>4</sup> In the presence of an organic base such as tetrapropylammonium salt, the silicate anion forms several specific silicate cages, *i.e.*, a curved hydrophobic SiO<sub>2</sub> surface encompasses the organic molecule with all hydroxyl groups of the silicate pointing outward.<sup>5</sup> Thus, a bifunctional interface with an outer hydrophilic and an inner hydrophobic surface is created.

Poly(2,6-dimethyl-1,4-phenylene ether) (PPE) is a well-known engineering plastic that can be catalytically prepared from 2,6-dimethylphenol with oxygen *via* an oxidative coupling polycondensation.<sup>6</sup> This polymer is usually used in a

modified form, *e.g.*, a blend of PPE with polyamide, polyolefin, or polystyrene, in order to decrease its processing temperature.<sup>7</sup> PPE is also available by the PTC polycondensation of 2,6-dimethylphenol<sup>8</sup> or 4-bromo-2,6-dimethylphenol (BDMP)<sup>9</sup> with and without copper catalyst, but all of these are the result of utilizing an oil-derived PTC.

We expect that if silica gel was added into an alkali metal BDMP solution in water/organic medium, the organic molecule would form inside the silica cages, followed by consecutive coupling to give PPE. We here report the first non-oil-derived PTC polymerization, the polycondensation of BDMP with silica gel as a PTC.

## EXPERIMENTAL

### Reagents

Silica gel (Wako gel C300: grain size 45–75 μm, 100–200 mesh) was purchased from Wako Pure Chemicals and used as received. All other reagents and solvents were used as received.

### Polymerization

**Method A.** Into a sample vial containing a magnetic stir bar were placed sodium hydroxide (1.6 g, 40 mmol), BDMP (0.38 g, 1.9 mmol), and distilled water (5 mL). The solution was vigorously stirred under air until the monomer was completely dissolved. Silica gel (0.0038 g, 1 wt % to the monomer) was added, and the mixture was stirred at 20 °C for 0.5 h under air. Toluene (5 mL) was then added, and the polymerization was kept for 12 h at this temperature. The resulting viscous emulsion was poured into methanol (50 mL) containing concentrated hydrogen chloride (1 mL) to precipitate the polymer. The precipitate was collected and washed with methanol, water, 1 N hydrogen chloride solution in water, and methanol. It was then dried, dissolved in chloroform, and

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reprecipitated in methanol (50 mL) containing concentrated hydrogen chloride (1 mL) through filter paper to give a white fibrous polymer (0.17 g, 76% yield).

**Method B.** Into a sample vial containing a magnetic stir bar were placed sodium hydroxide (1.6 g, 40 mmol), BDMP (0.38 g, 1.9 mmol), and distilled water (5 mL). The solution was vigorously stirred under air until the monomer was completely dissolved. Toluene (5 mL) and silica gel (0.0038 g, 1 wt% to the monomer) were added consecutively, and the mixture was stirred at 20 °C for 12 h under air. The other protocols were the same as in Method A. A white fibrous polymer was obtained (0.18 g, 79% yield).

### Reassembly of Silica Gel

Typical procedures were as follows. After the polymerization using silica gel (0.38 g, 100 wt %) in method B, concentrated hydrogen chloride was added into the polymerization solution until the pH of the solution become almost 1. The heterogeneous mixture was stirred for 12 h, and then poured into methanol. The precipitate was collected, washed with methanol, water, 1 N hydrogen chloride solution in water, methanol, and dried. The resulting solid was dissolved in chloroform, and filtered to remove PPE. The solid on the filter was carefully washed with chloroform, and dried *in vacuo* to give a white solid (0.32 g, 83% yield).

### Oligomerization of BDM for NMR Measurements

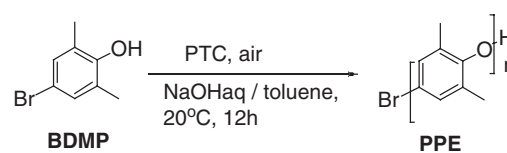
To characterize the polymer chain ends, a relatively low molecular weight polymer was prepared in 1 h by method B. The corresponding polymer was obtained as a white powder (73% yield,  $M_n = 5,300$ ,  $M_w/M_n = 1.8$ ).

### Polymerization of BDMP by Reassembled Silica Gel

The reassembled silica gel was used instead of the commercially available silica gel (Wako gel C300) for the polymerization of BDMP by method B. A white fibrous polymer was obtained (86% yield,  $M_n = 72,700$ ,  $M_w/M_n = 2.4$ ).

### Measurements

$^1\text{H}$  NMR spectra were recorded on a Bruker AC400 NMR spectrometer. Deuterated chloroform was used as the solvent for  $^1\text{H}$  NMR measurements with tetramethylsilane as an internal standard. Number-average and weight-average molecular weights ( $M_n$  and  $M_w$ ) were estimated by gel permeation chromatography (GPC) with a Tosoh HLC 8120 GPC system with polystyrene gel columns (TSKgel) calibrated by polystyrene standard samples at 40 °C in chloroform. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed with a Seiko TG/DTA320 and a Shimadzu DSC190 at a heating rate of 10 °C/min under nitrogen, respectively. Scanning electron micrographs were collected on a Hitachi S-2300 at 15 kV accelerating voltage.  $\text{N}_2$  adsorption-desorption isotherms were measured by SA-3100 systems, and pore-size distributions were determined by the Barrett-Joyner-Halenda (BJH) method.



Scheme 1.

Table I. Biphasic polymerization of BDMP<sup>a</sup>

Run	Silica gel /wt % <sup>b</sup>	TBAHS /wt % <sup>b</sup>	NaOH /equiv <sup>c</sup>	Yield /%	$M_n^d$	$M_w/M_n^d$
1	0	0	20	12	2,700	1.5
2	0	20	20	24	20,200	2.3
3	20	0	20	74	92,800	4.4
4	1	0	20	79	79,700	3.7
5	0.5	0	20	90	85,100	7.0
6	1	0	15	59	22,700	2.8

<sup>a</sup>Polymerization conditions: BDMP 1.9 mmol,  $\text{H}_2\text{O}$  5 mL, toluene 5 mL, at 20 °C for 12 h under air. Method B was applied. <sup>b</sup>Weight % to BDMP. <sup>c</sup>Equivalent to OH group of BDMP. <sup>d</sup>Determined by GPC ( $\text{CHCl}_3$ , PSt standards).

## RESULTS AND DISCUSSION

As described in the Introduction, silica gel is easily decomposed in alkaline solution to give water-soluble siloxane oligomers, which can be reassembled into silica gel by adjusting the pH of the solution. To confirm whether silica gel functions as a PTC, the biphasic polymerization of BDMP was performed with and without silica gel under air (Table I). When the polymerization was conducted in toluene/alkaline biphasic solution without silica gel, only oligomeric products were obtained in poor yield (Run 1). A typical oil-derived PTC, tetrabutylammonium hydrogen sulfate (TBAHS), gave a polymer in 24% yield (Run 2). In contrast, the addition of the same amounts of silica gel gave a polymer with a higher molecular weight in good yield (Run 3). These results clearly suggested that silica gel, a non-oil derived material, acts as a powerful PTC under these conditions. In addition, only 0.5 wt % silica gel was found to effectively promote the polymerization of BDMP (Run 5). The concentration of the alkaline solution affected the rate of the biphasic polymerization of BDMP, which is generally observed in this type of reaction.<sup>8b</sup>

Silica gel is transformed into various types of water-soluble siloxane oligomers, whose structures are dynamically interconverted with each other especially in the presence of organic molecules.<sup>5</sup> Thus, determining the conditions for the alkaline hydrolysis of silica gel is important for the subsequent biphasic polymerization of BDMP. We examined two methods of hydrolysis for the polymerization. In Method A, silica gel is hydrolyzed in an alkaline medium by itself. In Method B, silica gel is added into a toluene/alkaline biphasic solution, so that the silica gel is alkaline hydrolyzed at the interface. In this case, silica gel is transformed into water-soluble siloxane oligomers, which can include toluene as a guest molecule.

**Table II.** Biphasic polymerization of BDMP by using silica gel as PTC<sup>a</sup>

Run	Method <sup>b</sup>	Silica gel /wt % <sup>c</sup>	Yield /%	$M_n^d$	$M_w/M_n^d$
1	A	1	76	50,700	3.1
2	A	20	76	70,100	4.3
3	A	50	37	76,200	8.8
4	A	80	29	15,300	1.9
5	A	100	43	32,700	3.3
6	B	1	79	79,700	3.7
7	B	20	74	98,800	4.4
8	B	50	84	112,600	5.4
9	B	80	84	84,400	7.7
10	B	100	86	63,600	4.9

<sup>a</sup>Polymerization conditions: BDMP 1.9 mmol, H<sub>2</sub>O 5 mL, toluene 5 mL, at 20 °C for 12 h under air. <sup>b</sup>Method A: Silica gel was added into the BDMP solution in NaOH (aq.) After stirring the solution for 15 min, toluene was added. Method B: Silica gel was added into the biphasic solution of BDMP in NaOH (aq.) and toluene. <sup>c</sup>Weight % to BDMP. <sup>d</sup>Determined by GPC (CHCl<sub>3</sub>, PSt standards).

Table II summarizes the results of the polymerization. In Method A, high molecular weight polymers were obtained in good yield when the polymerization was conducted with less than 20 wt % of silica gel as a PTC (Runs 1 and 2). However, when using larger amounts of silica gel, both the yields and molecular weights of the polymer decreased (Runs 3, 4, and 5). In contrast, these were clearly improved in Method B (Runs 6 to 10). These results indicated that the water-soluble siloxane oligomers obtained in Method B were favorable for the biphasic polymerization of BDMP. The siloxane oligomers containing toluene as guest molecules might favorably encapsulate BDMP and its oligomers.

In Method B, there is no significant difference in the molecular weights of the resulting polymer. This value, however, gradually increased to 112,600, and decreased after that. This might be due to the effect of the size and number of micelles in the solution. Therefore, in the polymerization with 50 wt % silica gel, the size and number of the micelles created from the resulting siloxane oligomers should be the best for the fast propagation of PPE.

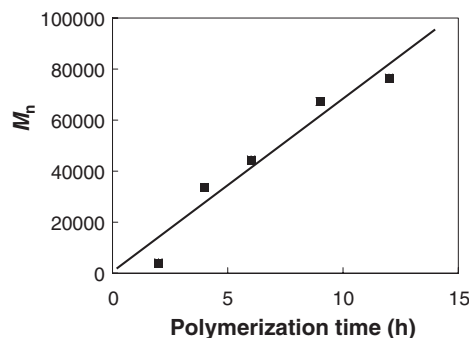
To understand the polymerization behavior in more detail, the number-average molecular weights ( $M_n$ ) of the polymer were plotted against the polymerization time as shown in Figure 1. The polymerization was performed by Method B. The polymerization mixture became an emulsion after more than about 6 h. A waxy mixture resulted after 12 h which made it difficult to isolate the product polymer. Therefore, the polymerization time was set to be 12 h in this experiment.

The  $M_n$  linearly increased with polymerization time. Theoretically, the degree of the polymerization  $X_n$  is expressed as

$$X_n = C_0kt + 1$$

where  $C_0$ ,  $k$ , and  $t$  are initial concentration of the monomer, rate constant of the polymerization, and polymerization time, respectively. Therefore, the rate constant  $k$  was estimated to be 0.0425 s<sup>-1</sup> from the slope in Figure 1.

Figure 2 depicts a) the <sup>1</sup>H NMR spectrum of the PPE

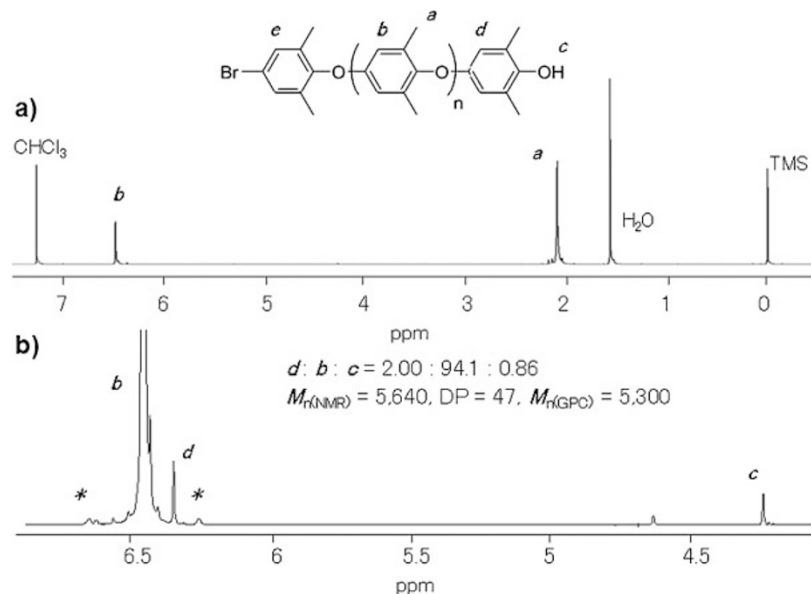


**Figure 1.**  $M_n$  vs. polymerization time by the use of 1 wt % of silica gel as a PTC (Run 6, Table II).

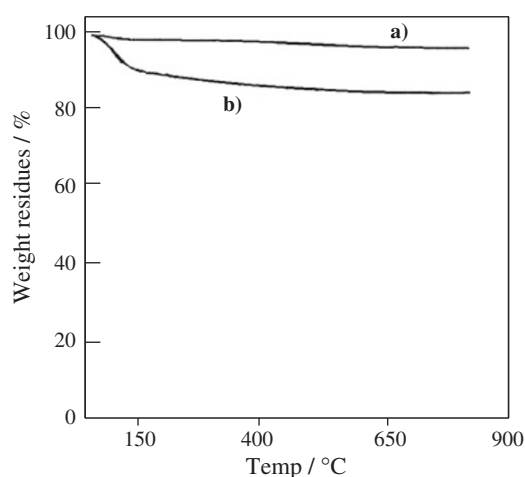
prepared in Method B, and b) the expanded aromatic region. Two typical signals are observed at 2.08 and 6.47 ppm, which are assigned to the methyl and aromatic protons (*a* and *b*), respectively. In the expanded spectrum, terminal aromatic protons *d* of the PPE are observed at 6.36 ppm. Hydroxyl protons in the polymer-chain-end are also observed at 4.24 ppm, which was broadened by the addition of deuterium oxide into this solution, indicating the active hydrogens. The integration ratio of *d* and *c* is 2.00:0.86, which is close to the theoretical values of 2:1. From the integration ratio of the signals of the polymer-chain-end to the polymer backbone, the molecular weight of the polymer was calculated to be  $M_{n(\text{NMR})} = 5,640$ ; thus  $X_n = 47$ . This is in good agreement with the molecular weight estimated by GPC measurements ( $M_n = 5,300$ ). The TGA and DSC analysis of the prepared PPE were performed under nitrogen, in which 5 wt % loss temperature ( $T_{d5}$ ) and glass transition temperature ( $T_g$ ) were 435 and 220 °C, respectively, which were in good agreement with the values of the commercially available PPE ( $T_{d5} = 430$  °C,  $T_g = 215$  °C). These results also support the satisfactory formation of pure PPE.

Water-soluble siloxane oligomers were reassembled into silica gel after the polymerization by adjusting the pH of the solution. Figure 3 depicts the TGA profiles of a) the originally used silica gel (Wako gel C300) and b) reassembled silica gel under nitrogen. In the original silica gel, 7% weight-loss was observed after heating to 800 °C, which could be attributed to absorbed water. In the reassembled silica gel under the same heating conditions, 16% weight-loss was observed. This could be both absorbed water and the water produced by condensation between silanol functions. No organic residues were found in the elemental analysis of the reassembled silica gel.<sup>10</sup> It is noticeable that no significant weight-loss was observed at more than 150 °C, suggesting that the reassembled silica gel has no organic parts.

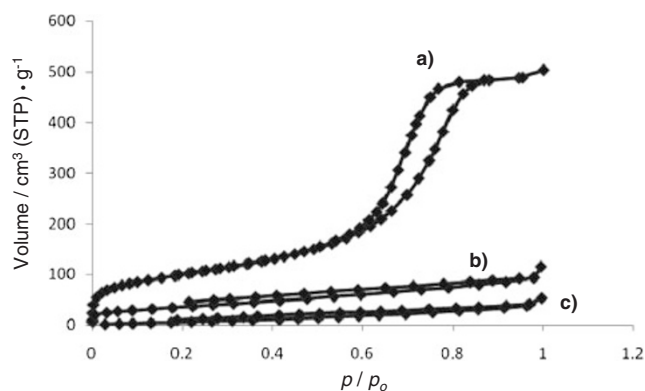
To investigate the reassembled silica gel in more detail, nitrogen absorption-desorption experiments were performed. Figures 4 and 5 represent the profiles and pore diameter distributions. Table III summarizes the BET surface areas and pore diameters of the various silica gels obtained from Figures 4 and 5. Originally used silica gel has a BET surface area of 353 m<sup>2</sup>/g and pore diameter of 7.63 nm. In contrast, the



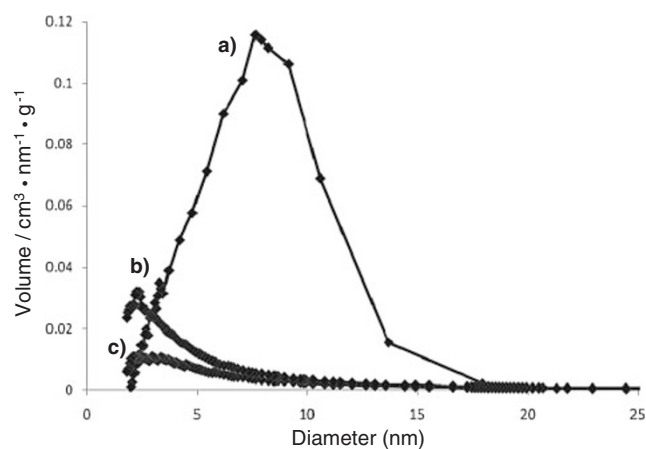
**Figure 2.** a) <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 20 °C) of PPE prepared by the biphasic polymerization of BDMP and b) the expanded spectrum. Signals marked with \* are spinning side bands.



**Figure 3.** TGA profiles of a) original and b) reassembled silica gels under nitrogen.



**Figure 4.** N<sub>2</sub> gas adsorption-desorption isotherms of (a) original silica gel (Wako gel C300), (b) reassembled silica gel (run 8 in Table II), and (c) reassembled silica gel (run 10 in Table II).



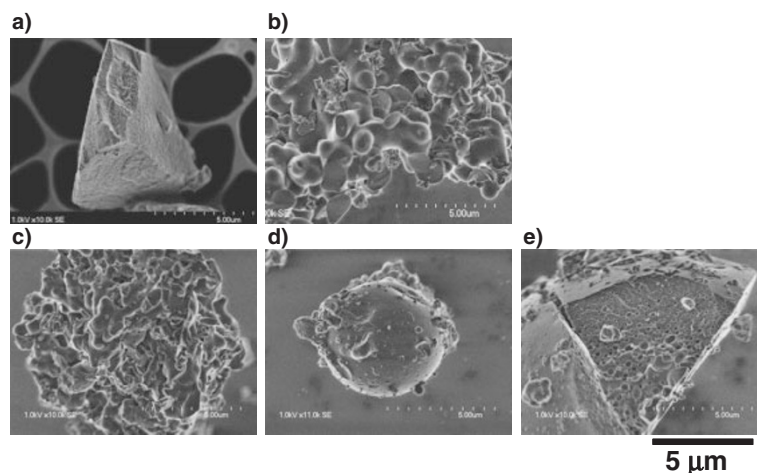
**Figure 5.** The pore size distribution of (a) original silica gel (Wako gel C300), (b) reassembled silica gel (run 8 in Table II), and (c) reassembled silica gel (run 10 in Table II). Pore size distribution was calculated using BJH analysis.

**Table III.** BET surface areas and pore diameters of original and reassembled silica gels

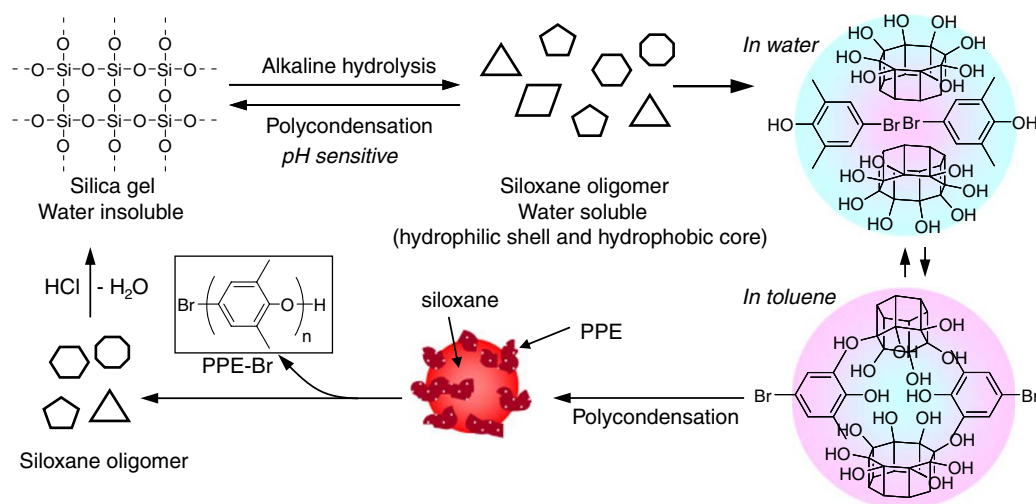
Run	Silica gel	BET surface /m <sup>2</sup> ·g <sup>-1</sup>	Pore diameter /nm
1	Original <sup>a</sup>	353	7.63
2	Reassembled <sub>50</sub> <sup>b</sup>	39.0	2.43
3	Reassembled <sub>100</sub> <sup>c</sup>	126	2.23

<sup>a</sup>Originally used silica gel (Wako gel C300). <sup>b</sup>Reassembled silica gel used for the polymerization of BDMP (Run 8, Table II). <sup>c</sup>Reassembled silica gel used for the polymerization of BDMP (Run 10, Table II).

reassembled silica gels have less BET surface areas of 39 to 126 m<sup>2</sup>/g and smaller pore diameters of 2.2 to 2.4 nm. These results suggested that the silica gel was first decomposed into siloxane oligomers, which functioned as a PTC for the polymerization of BDMP.



**Figure 6.** Scanning micrographic images of a) original silica gel, b) reassembled silica gel obtained in the polymerization of run 8 in Table II, and c)–e) reassembled silica gel obtained in the polymerization of run 10 in Table II.



**Figure 7.** Plausible mechanism for the biphasic polymerization of BDMP with silica gel.

Figure 6 depicts the scanning micrographic (SEM) images of a) original silica gel, b) reassembled silica gel obtained in the polymerization of run 8 in Table II (50 wt% silica gel was used), and c)–e) reassembled silica gel obtained in the polymerization of run 10 in Table II (100 wt% silica gel was used). The typical grain size of the original silica gel was about 5 μm as shown in Figure 6a, and the reassembled silica gels have smaller grain sizes. The reassembled silica gel obtained after the polymerization of BDMP (50 wt% silica gel) took similar worm-like forms (Figure 6b), but there were two types of morphologies in the reassembled silica gel (100 wt% silica gel); one is worm-like forms as seen in Figure 6c, and the other one is sphere-like structures (Figure 6d and 6e). Spherical silica gel has a smooth surface (Figure 6d), but inside of the sphere there are many wormhole structures (Figure 6e). The size of the pore is around 150 nm, and the distribution is large. Because of this, no significant capillary concentration phenomena are observed in Figure 4b and 4c. Thus we cannot conclude if there are penetrated pores inside the sphere.

In order to know the durability of the catalyst, the silica gel reassembled after the polymerization of run 10 in Table II was reused for the polymerization under the same conditions as run 6 in Table II. As a result, a polymer with  $M_n$  of 72,700 ( $M_w/M_n = 2.4$ ) was obtained in 86% yield, indicating that the reassembled silica has a similar ability to catalyze the polymerization of BDMP.

Figure 7 depicts a plausible mechanism of this polymerization. First, the silica gel is decomposed with alkaline solution to give water-soluble siloxane oligomers. Because these siloxane oligomers have hydrophobic cores, the monomer is absorbed in the structure, and the polymerization takes place in such concentrated conditions. Thus, the biphasic polymerization of BDMP efficiently proceeds under mild conditions, giving high molecular weight PPE with corresponding structures. The siloxane oligomers can be reacted with each other by changing the pH to give reassembled silica gel, which was easily separated from the PPE by filtration.

## SUMMARY

We have demonstrated the first biphasic polymerization of BDMP promoted by silica gel, a non-oil derived material. High molecular weight PPE was easily obtained at ambient temperature under air. The kinetics of the polymerization obeyed theoretical equations generally observed in condensation polymerizations. The resultant PPE was carefully characterized to be the pure PPE free from silicon atoms. The reassembled silica gel has no contamination from PPE, and the morphology was unique, *e.g.*, worm-like and spheres containing wormholes, which were observed in SEM measurements. The reassembled silica gel also functioned as a PTC for the polymerization of BDMP with similar activity of the commercially available silica gel.

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