

Synthesis of Polysulfide by Phase Transfer-Catalyzed Terpolymerization of Dibenzoylmethane, Carbon Disulfide, and α,α -Dichloro-*p*-xylene

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Aliphatic polysulfide was synthesized by polyaddition reaction of nonconjugated diolefin and dithiol using radical initiators¹ or by solution polymerization of disalt of dithiol with dibromoalkane in the anhydrous conditions.² More recently, Suh *et al.*³ successfully prepared polysulfide by terpolymerization of malononitrile, carbon disulfide and α,α -dichloro-*p*-xylene in the presence of phase transfer-catalyst. However, the reaction was accompanied with a side-reaction occurring from hydrolysis of cyano groups in malononitrile by base, which led to low yield of polymer. In order to overcome the problem, a proper active methylene compound should be employed.

Active methylene compound is a good nucleophile to react well with carbon disulfide in the presence of bases. Several researchers have synthesized various dithiolate over phase transfer-catalyst with proper active methylene compounds.^{4,5} D'Amico *et al.*⁶ synthesized a dithiol derivative by reacting malononitrile with carbon disulfide and subsequently with alkyl halide.

In this study, several active methylene compounds such as acetylacetone, benzoylacetone, dibenzoylmethane and benzyl cyanide were investigated as potential reactants for the more efficient synthesis of polysulfide. To obtain the basic information on reactivity of the compounds for the polymerization, a model reaction of each active methylene compound with carbon disulfide and benzyl chloride was carried out. A proper active methylene compound was chosen on the basis of yield of the model reaction. A reactant showing a higher yield in the model reaction is expected to produce a higher molecular weight polymer with more regular structure. Phase transfer catalyzed polymerization was carried out with a selected active methylene compound, carbon sulfide and α,α -dichloro-*p*-xylene using benzyltriethylammonium chloride (BTEAC) as a catalyst. Effects of polymerization conditions on the yield and the molecular weight of the terpolymer were investigated.

Experimental

Materials. α,α -Dichloro-*p*-xylene from Aldrich Chemical Co. was recrystallized from benzene. Carbon disulfide from Osaka Chemical Co. and acetylacetone from Junsei Chemical Co. were purified by distillation. Benzyl chloride from Junsei Chemical Co. was used as received. Benzoylacetone from Janssen Chemical and dibenzoylmethane from Aldrich Chemical Co. were recrystallized from methanol. Benzyl cyanide from Janssen Chemical Co. was distilled under reduced pressure. Benzyltriethylammonium chloride (BTEAC) was prepared by the reaction of benzyl chloride and triethylamine from Osaka Chemical Co. and the sub-

sequent recrystallization from benzene. Tetramethylammonium chloride (TMAC) from Fluka Co., tetraethylammonium chloride (TEAC) from Tokyo Kasei and tetrabutylammonium chloride (TBAC) from Fluka Co. were purified by precipitation in acetone, ethylether and ethylether-respectively. Methyltridecyl ammonium chloride (MTDAC) from Aldrich Chemical Co. was used as received. 18-crown-6-ether(18-C-6) from Aldrich Chemical Co. was recrystallized from acetonitrile.⁷ All solvents were purified by distillation prior to use.

Characterization. Chemical structures of model compounds and polysulfide were analyzed by ¹H NMR spectrometer (60 MHz, JNM-PMX 60), IR spectrometer (Perkin Elmer 1430), and elemental analyzer (Perkin Elmer, 204C elemental analyzer). Inherent viscosity of polysulfide was measured by Cannon-Fenske viscometer at 30 °C using polymer solution in DMF with concentration of 0.5 g/dL. The thermal transition behaviors of polysulfide were examined by differential scanning calorimetry (Dupont DSC 700) and thermogravimetric analyzer (Dupont TGA 100). All thermograms were obtained under nitrogen atmosphere at the heating rate of 10 °C/min.

Synthesis of 1,1-Dibenzylmercapto-2,2-diacetyl-ethylene (DMDAE). Acetylacetone (1.5 mL, 15 mmol), carbon disulfide (3.5 mL, 60 mmol) and benzyl chloride (6.9 mL, 60 mmol) dissolved in 8 mL of chloroform were added to 100 mL of flask equipped with a stirrer and condenser. Catalyst solution was prepared by dissolving 3.41 g of benzyltriethylammonium chloride in 8 mL of 10% NaOH aqueous solution. The catalyst solution (15 mmol) was added to the reactant system and then the mixture was heated at 60 °C for 6 hours. After neutralizing the reaction mixture with 0.1 M of HCl and washing the organic layer with distilled water several times to remove the residual catalyst, the organic layer was precipitated into 50 mL of ethanol. 2.1 g (39% yield) of white solid was obtained after recrystallization from ethanol. mp 120 °C. ¹H NMR (CDCl₃) δ 2.1 (s, 6H, CH₃-C=O), 4.1 (s, 4H, CH₂-S), 7.3 (s, 10H, phenyl). IR (KBr, cm⁻¹) 1680 (C=O). Elemental analysis (%) C 66.82 (calcd. 67.37), H 5.70 (calcd. 5.66).

Synthesis of 1,1-Dibenzylmercapto-2-acetyl-2-benzoyl-ethylene (DMABE). Reaction was carried out using benzoylacetone (2.54 g, 15 mmol) as a active methylene compound with the same method as employed in the synthesis of DMDAE. After recrystallization from ethanol, 3.9 g (62% yield) of yellow solid was obtained. mp 120 °C. ¹H NMR (CDCl₃) δ 2.1 (s, 3H, CH₃-C=O), 4.0 (s, 2H, CH₂-S), 4.1 (s, 2H, CH₂-S), 7-8 (m, 15H, phenyl). IR (KBr, cm⁻¹) 1650 (C=O of benzoyl group), 1660 (C=O of acetyl group). Elemental analysis (%) C 71.34 (calcd. 71.73),

H 5.31 (calcd. 5.30).

Synthesis of 1,1-Dibenzylmercapto-2,2-dibenzoylethylene (DMDBE). Using dibenzoylmethane (1.5 mL, 15 mmol) was used as a active methylene compound, DMDBE was prepared with the same method as described above. After purification, 4.6 g (63% yield) of light yellow solid was obtained. mp 156 °C. ¹H NMR (CDCl₃) δ 4.0 (s, 4H, CH₂-S), 7-8 (m, 20H, phenyl). IR (KBr, cm⁻¹) 1630 (C=C), 1660 (C=O). Elemental analysis (%) C 74.60 (calcd. 74.96), H 5.05 (calcd. 5.04).

Synthesis of 1,1-Dibenzylmercapto-2-cyano-2-phenylethylene (DMCPE). Benzyl cyanide (1.7 mL, 15 mmol) was used as a active methylene compound and the reaction was carried out with the same conditions as described above. However, neutralization was done with saturated sodium bicarbonate solution in order to prevent the hydrolysis of cyano group. After removing solvent and unreacted chemicals from the organic layer by distillation under reduced pressure, 4.58 g of oily material was obtained. The crude product mixture was purified by column chromatography and finally 0.936 g (16% yield) of DMCPE was obtained. The chromatography column (diameter 25 mm) was filled with 50 g of Kieselgel 60 (Art 7731, Merk) and developing medium was the mixed solvent of benzene and hexane (50:50 vol%). ¹H NMR (CDCl₃) δ 3.7 (s, 2H, CH₂-S), 4.2 (s, 2H, CH₂-S), 7.3, 7.5 (d, 15H, phenyl). IR (NaCl liquid cell, cm⁻¹) 2250 (CN). Elemental analysis (%) C 73.11 (calcd. 73.90), H 5.14 (calcd. 5.13), N 4.04 (calcd. 3.85).

Synthesis of Polysulfide. Dibenzoylmethane (1.68 g, 7.5 mmol), carbon disulfide (3.6 mL, 30 mmol), and α,α-dichloro-*p*-xylene (1.31 g, 7.5 mmol) were dissolved in 8 mL of chloroform. And 8 mL of 10% NaOH aqueous solution containing phase-transfer catalyst (1.61 g, 7.5 mmol) was added. The mixture was heated at 70 °C for 6 hours. After neutralizing and drying the organic phase, the reaction product was purified by precipitation in methanol. mp 156 °C. ¹H NMR (CDCl₃) δ 3.8 (s, 4H, CH₂-S), 6.8-7.8 (m, 14H, phenyl). IR (KBr, cm⁻¹) 1650 (broad, overlapped peak of C=C and C=O). Elemental analysis (%) C 71.07 (calcd. 71.60), H 4.78 (calcd. 4.52).

Results and Discussion

Synthesis of Model Compounds. Model compounds, DMDAE, DMABE, DMDBE and DMCPE were prepared from the reactions of acetylacetone, benzoyl acetone, dibenzoylmethane and benzyl cyanide with carbon disulfide and benzyl chloride, respectively. ¹H NMR spectrum of DMDAE shows three singlet peaks at 7.3 ppm, 4.1 ppm and 2.1 ppm, which correspond to phenyl ring, methylene and methyl protons, respectively. In IR spectrum of DMDAE, the strong peak attributed to the carbonyl group appears at 1680 cm⁻¹. And the experimental results of elemental analysis coincide with calculated values quite well. The characterization results of the other model compounds are given in experimental section. These results indicate that model compounds were prepared successfully. DMCPE prepared by using benzyl cyanide as a active methylene compound shows lowest yield, which is attributed to side reactions such as a hydrolysis of the cyano group. And, DMDBE is produced with highest yield. So, it is thought

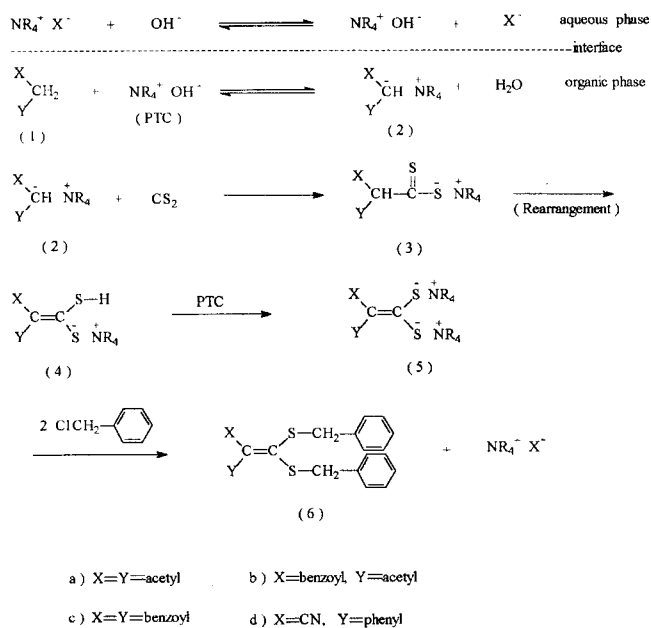


Figure 1. Reaction mechanism of model reactions.

that dibenzoylmethane is a most efficient active methylene compound in this model reaction.

A proposed reaction mechanism for this reaction is shown in Figure 1: since carbon disulfide is the stronger electrophile than benzyl chloride against the carboanion, active methylene compound selectively reacts with carbon disulfide to be dithiocarboxylic salt. By tautomerization, the salt is transformed into enolmercaptane, which leads to enedithiolate by the reaction with the base.^{8,9} The enedithiolate finally reacts with benzyl chloride, which results in model compound having enedisulfide unit.¹⁰

Synthesis of Polysulfide. Dibenzoylmethane was chosen as a monomer for terpolymerization based on the results of the model reaction. The reaction for the synthesis of polysulfide having enethiol unit is shown in Figure 2.

¹H NMR spectrum of polysulfide shows the singlet peak at 3.8 ppm and multiplet peaks in the range of 6.8 to 7.8 ppm, due to methylene and phenylene protons, respectively. Both transitions are shifted by the amount of 0.2 ppm compared with those of DMDBE. Polysulfide exhibits broad IR absorption band at 1650 cm⁻¹, which is considered as the overlapped peak of C=O and C=C bonds. And the chemical composition of polysulfide was confirmed by

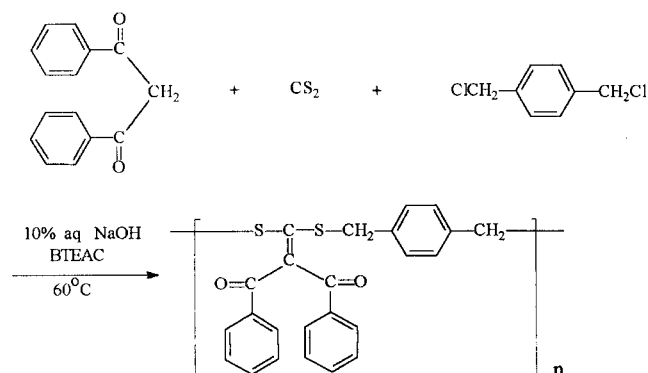


Figure 2. Synthesis of polysulfide having enedithiol moiety.

Table 1. Effects of phase transfer catalyst type on synthesis of polysulfide

PTC ^a	Yield (%)	η_{inh}^b
TMAC	17	0.052
TEAC	70	0.072
TBAC	75	0.093
BTEAC	82	0.110
MTDAC	86	0.093
18-C-6	49	0.042

^a Polymerization are carried out in 8 mL of chloroform, 8 mL of 10% NaOH at 70 °C for 6 hrs. ^b measured in DMF at 30 °C.

elemental analysis. The found values of C and H were 71.07% and 4.75%, which coincide with calculated values of 71.60% and 4.52%, respectively.

The synthesized polymers were soluble in polar solvents such as DMSO, THF, DMF, pyridine, chloroform, and nitrobenzene. From thermogravimetric analysis, it was found that the polymer was decomposed in the range of 280 °C and 310 °C, resulting in weight loss of 60%. But no more weight loss was observed up to 500 °C.

Effects of Reaction Conditions on Polymerization.

Chloroform, dichloromethane, benzene and nitrobenzene were organic solvents used in this two-phase reaction. Yield and inherent viscosity of polymer were higher in chloroform. Effects of type of the phase-transfer catalysts on the reaction are shown in Table 1. The quarternary ammonium salts give the better results than crown ether. Also, it was observed that molecular weight and yield of polymer increases as the bulkiness of alkyl substituent in quaternary ammonium salt increases. The $R_4N^+OH^-$ produced *via* the reaction of the quaternary ammonium salt with alkali in the water phase shows higher lipophilicity as the alkyl substituent become bulkier. The easier shift of the catalyst with bulky alkyl group into the organic phase leads to higher molecular weight polymer with high yield.

As shown in Table 2, the yield increases continuously as the concentration of NaOH varies from 1 to 30%. However, the inherent viscosity shows maximum at 10% NaOH solution and then decreases with the amount of base. This may be due to the substitution reaction of chlorine of α,α -dichloro-*p*-xylene with hydroxyl ion, which consequently suppresses the increase of molecular weight of product.

The effects of catalyst concentration on the reaction are shown in Table 3. It can be seen that there is a maximum in yield at catalyst concentration of 7.5 mmole but molecular weight of the polymer was increased with the increasing amount of catalyst.

Table 2. Effects of NaOH concentration on synthesis of polysulfide

NaOH conc. (%) ^a	Yield (%)	η_{inh}^b
1	3	0.031
5	55	0.060
10	82	0.081
20	92	0.050
30	98	0.050

^a Polymerization are carried out in 8 mL of chloroform at 60 °C for 6 hrs. ^b measured in DMF at 30 °C.

Table 3. Effects of BTEAC concentration on synthesis of polysulfide

Amount of catalyst	Yield (%)	η_{inh}^b
0	28	0.010
3.75	71	0.054
7.50	82	0.081
11.25	78	0.086
15.00	72	0.093
18.75	68	0.094

^a Polymerization are carried out in 8 mL of chloroform, 8 mL of 10% NaOH at 60 °C for 6 hrs. ^b measured in DMF at 30 °C.

Table 4. Effects of reaction time on synthesis of polysulfide

Polymerization time	Yield (%)	η_{inh}^b
3	75	0.067
6	82	0.081
9	84	0.083
12	85	0.087
15	85	0.089
24	85	0.091
48	85	0.094

^a Polymerization are carried out in 8 mL of chloroform, 8 mL of 10% NaOH, and 7.5 mmol of BTEAC at 60 °C. ^b measured in DMF at 30 °C.

Table 5. Effects of reaction temperature on synthesis of polysulfide

Polymerization Temperature (°C) ^a	Yield (%)	η_{inh}^b
40	71	0.038
50	78	0.062
60	82	0.081
70	82	0.110
80	82	0.080
90	83	0.078

^a Polymerization are carried out in 8 mL of chloroform, 8 mL of 10% NaOH, and 7.5 mmol of BTEAC for 6 hours. ^b measured in DMF at 30 °C.

Table 4 shows the effects of reaction time on the polymerization reaction. The molecular weight increased initially with increasing reaction time, but it became slow down after 6 hours. And the yield increased initially and then became almost same after 9 hours.

In Table 5, it can be seen that inherent viscosity shows maximum at 70 °C, whereas yield increased with temperature initially and then reached almost constant value at over 60 °C.

Conclusions

Four model compounds were prepared from the reactions of different active methylene compounds such as acetylacetone, benzoylacetone, dibenzoylmethane and benyl cyanide with carbon disulfide and benzyl chloride. Structures of the products were identified as 1,1-dibenzylmercapto-2,2-diacetylene (DMDAE), 1,1-dibenzylmercapto-2-acetyl-2-benzoylene (DMABE), 1,1-dibenzylmercapto-2,2-dibenzoylene (DMDBE), and 1,1-dibenzylmercapto-2-

cyano-2-phenylethylene respectively (DMCPE). The proposed reaction mechanism was confirmed.

New polysulfide synthesized by terpolymerization of dibenzoylmethane, carbon disulfide, and α,α' -dichloro-*p*-xylene in the presence of benzyltriethylammonium chloride as a phase transfer catalyst shows reasonably higher yield and molecular weight than that obtained in previous report.³

The optimum reaction conditions for the terpolymerization were found to be 7.5 mmol of phase transfer-catalyst (quaternary ammonium salt type), 10% of NaOH solution, 60 °C-70 °C of reaction temperature, and 6 hours of reaction time in chloroform. Among the reaction variables, concentration of base and reaction temperature were considered to be the most important ones.

References

1. Marvel, C. S.; Aldrich, P. H. *J. Amer. Chem. Soc.* **1950**, *72*, 1978
2. Marvel, C. S.; Kotch, A. *J. Amer. Chem. Soc.* **1951**, *73*, 481.
3. Suh, D. H.; Won, J. C.; Kim, D. K. *J. Polym. Sci.: Part C: Polym. Lett.* **1988**, *26*, 83.
4. Starks, C. M. *J. Amer. Chem. Soc.* **1971**, *93*, 195.
5. Brandstrom, A.; Junggren, U. *Tetrahedron* **1974**, *30*, 93. **1974**, *30*, 93.
6. D'Amico, J. J.; Ruminski, P. G.; Suda, L. A.; Freeman, J. J.; Dahl, W. E. *Phosphorous and Sulfur* **1985**, *21*, 307.
7. Perrin, D. D.; Armarego, W. L. F., In *Purification of Laboratory Chemicals*; Pergamon Press: 3rd Ed., 1988, 285.
8. Larsson, F. C. V.; Lawesson, S. O. *Tetrahedron* **1972**, *28*, 5341.
9. Dalgaard, L.; Anderson, H. K.; Lawesson, S. O. *Tetrahedron* **1972**, *29*, 2077.
10. Dalgaard, L.; Lawesson, S. O. *Tetrahedron* **1972**, *28*, 2051.

Photolysis of Chlorobenzene in Aqueous Solution

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As the environmental pollution caused by halogenated aromatic compounds increased, these materials have been the hot subject of investigation in recent years.¹⁻³ Among the halogenated aromatic compounds, chlorobenzene is the simplest, best-utilized chloroaromatic compound. Chlorobenzene is a colorless, volatile liquid with an aromatic almond-like odor under standard environmental conditions. It is used primarily as a solvent (e.g. resins, dyes, rubbers, pesticides, and perfumes), a degreasing agent, and a chemical intermediate. Because chlorobenzene enters the environment from industrial and municipal discharge, it can be concentrated in the tissues and internal organs of fishes, animals and humans and it can pose significant human health hazards to large populations by its possible toxicity and carcinogenicity. Since the potential hazards of chlorobenzene on human health had been reported,⁴ considerably large number of investigations concerning photochemical behavior, transformation routes and accumulation in environment were carried out.⁵⁻¹¹ It is therefore important to investigate the photochemical reaction of chlorobenzene, because the waste water containing chloroaromatic pollutants could be purified or some organic compounds could be also synthesized by photochemical reaction.

Most of the photochemical behavior of chlorobenzene was investigated only in organic solvents such as cyclohexane,⁵ isopropanol⁶ and methanol.^{7,8} Sometimes methanol/water⁹ or acetonitrile/water mixtures^{10,11} were used, but photochemical studies on aqueous chlorobenzene solution have not been

studied so extensively because of its low solubility in water (510 mg/L at 25 °C).¹² Tissot *et al.* reported that photolysis of chlorobenzene in water-acetonitrile gives phenol via the shorted-lived (30 ns) triplet state and they proposed a mechanism involving photohydrolysis from the triplet state.¹³ It is important to measure the quantum yield, assess the effects of aerated and degassed solvent in order to clarify the reaction mechanism. The purpose of this study is to elucidate the mechanism concerning the photolysis reaction of aqueous chlorobenzene based on the products analysis.

Experimental

Reagents and General. Chlorobenzene, dichloromethane and methanol (Aldrich Chemical Co., 99.9% A.C.S HPLC grade) were used as commercial compounds without further purification. All other chemicals were reagent grade and used as received. Irradiations were carried out at 25±0.1 °C using low pressure Hg lamp (Osram HNS 10W/U OFR). Low pressure Hg lamp is classified into two types depending on the method of its emitting wavelength; ozone generating lamp and ozone-free lamp.¹⁴ The ozone-free lamp used in this study emits only 253.7 nm UV light, but on the other hand ozone generating lamp emits two monochromatic lights of 184.9 and 253.7 nm. The irradiation vessel was of cylindrical shape fitted with a magnetic stirrer and a waterbath circulator maintained the solution temperature at 25±0.1 °C. The intensity of the 253.7 nm light was