Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Syntheses of Key Monomers for Advanced Polymer Materials Using Cyclodextrin as Catalyst

Hidefumi Hirai

To cite this Article Hirai, Hidefumi(1994) 'Syntheses of Key Monomers for Advanced Polymer Materials Using Cyclodextrin as Catalyst', Journal of Macromolecular Science, Part A, 31: 11, 1491 — 1500

To link to this Article: DOI: 10.1080/10601329408545864

URL: http://dx.doi.org/10.1080/10601329408545864

J.M.S.—PURE APPL. CHEM., A31(11), pp. 1491–1500 (1994)

SYNTHESES OF KEY MONOMERS FOR ADVANCED POLYMER MATERIALS USING CYCLODEXTRIN AS CATALYST

HIDEFUMI HIRAI

Department of Industrial Chemistry
Faculty of Engineering
Science University of Tokyo
Kagurazaka, 1–3, Shinjuku-ku, Tokyo 162, Japan

ABSTRACT

Terephthalic acid was synthesized by the carboxylation of benzoic acid with carbon tetrachloride in aqueous sodium hydroxide solution in the presence of cyclodextrin (CyD) and copper powder as catalyst. By the use of β-CyD at the initial molar ratio to benzoic acid of 0.5, the carboxylation at 60°C for 7 hours produced terephthalic acid in 75 mol% yield with 87% selectivity. The selective synthesis of 4,4′-biphenyldicarboxylic acid in 70 mol% yield was achieved by the carboxylation of 4-biphenylcarboxylic acid with carbon tetrachloride in the presence of β-Cyd under similar conditions. The carboxylation of 2-naphthalene carboxylic acid with carbon tetrachloride using β-Cyd under similar conditions produced 2,6-naphthalenedicarboxylic acid in 67 mol% yield with 84% selectivity. When α-CyD and γ-CyD were used in place of β-Cyd, both the yields and the selectivities of the dicarboxylic acids were markedly small. In the absence of CyD, carboxylation did not proceed. Inclusion complex formations between β-Cyd and aromatic monocarboxylic acids were indicated by the ^{1}H chemical shifts of the β-Cyd. The reaction mechanism was discussed on the basis of inclusion complex formation.

INTRODUCTION

Aromatic dicarboxylic acids are a key monomer for the syntheses of high performance polymers and liquid-crystalline compounds.

Terephthalic acid (TPA) is widely used as an essential monomer, not only for a conventional polyester, namely poly(ethylene terephthalate), but also for high performance polymers such as poly(*p*-phenylene terephthalamide), poly[(terephthalic acid)-*alt*-(*p*-phenylene diamine; 3,4′-diaminodiphenylether)], poly(*p*-phenylene benzobisthiazol), etc.

4,4′-Biphenyldicarboxylic acid (4,4′-BPDA) is an effective monomer for poly[(ethylene glycol)-*alt*-4,4′-biphenyldicarboxylic acid; terephthalic acid)], which has mechanical and thermal properties superior to those of poly(ethylene terephthalate) [1].

2,6-Naphthalenedicarboxylic acid (2,6-NDA) is a versatile intermediate for the syntheses of high performance polymers [2] and liquid-crystalline compounds [3]. For example, poly(ethylene 2,6-naphthoate) surpasses poly(ethylene terephthalate) in mechanical properties, thermostability and gas-barrier ability of films [4, 5].

TPA, 4,4′-BPDA and 2,6-NDA are conventionally synthesized by the oxidation of the corresponding dialkyl aromatic compounds, *p*-xylene, 4,4′-dimethylbiphenyl, and 2,6-dimethylnaphthalene, respectively [6]. However, the production of these dimethyl isomers from the petro- and a coal-chemical industry is limited, and the alkylation of aromatic compound is not selective enough to yield the regiospecific dimethyl isomers. Recently, 2,6-NDA was produced by oxidation of 2-alkyl-6-acylnaphthalene [7].

Alpha-, β-, and γ-cyclodextrins (α-Cyd, β-Cyd, and γ-Cyd) are cyclic oligomers of 6, 7, and 8 glucose units, respectively, and they form inclusion complexes with aromatic compounds in aqueous solution [8].

Recently, carboxylations of benzoic acid [9] and 2-naphthalenecarboxylic acid [10] with carbon tetrachloride have been found to occur in aqueous sodium hydroxide solution under mild conditions by the use of cyclodextrin and copper powder as catalyst.

In the present study, selective syntheses of TPA, 4,4′-BPDA, and 2,6-NDA were carried out by the carboxylation of benzoic acid, 4-biphenylcarboxylic acid (4-BPA), and 2-naphthalene carboxylic acid (2-NCA), respectively, with carbon tetrachloride in aqueous sodium hydroxide in the presence of CyD and copper powder as catalyst. The role of CyD in the reaction was also investigated.

EXPERIMENTAL

Materials

Alpha- and γ-CyD were of guaranteed grade from Tokyo Chemical Industry Co. and Nakarai Tesque Inc., respectively. Beta-CyD was of reagent grade from Tokyo Chemical Industry Co.

Two kinds of copper powder were used: copper powder I (Kanto Chemical Industry Co., extra pure grade; average particle diameter of 125 μm) and copper powder II (Aldrich Chemical Co., 99%, for organic synthesis; average particle diameter of 1 μm).

Benzoic acid and TPA were of guaranteed grade from Kanto Chemical Co. 4-BPA and 4,4′-BPDA were of reagent grade and of guaranteed grade, respectively, from Tokyo Chemical Industry Co. 2-NCA was of guaranteed grade from Nakarai Tesque Inc. 2,6-NDA was of reagent grade from Aldrich Chemical Co.

Carboxylation

The following procedures are representative. Three millimoles of the aromatic monocarboxylic acid, 0.8 mmol (0.05 g) of the copper powder, and 3.0 mmol of β-Cyd were added to 30 mL of 30 wt% aqueous sodium hydroxide solution. The reaction was started by the addition of 8.5 mmol carbon tetrachloride and was continued at 60°C for 7 hours with magnetic stirring under nitrogen. Then the residual carbon tetrachloride was removed by evaporation under reduced pressure. The cooled reaction mixture was neutralized with hydrochloric acid. Product analysis on the resulting mixture was made by high performance liquid chromatography (HPLC). The products were identified by comparison with authentic samples (HPLC, MS, and IR). The main products were isolated and confirmed to be the target dicarboxylic acids, respectively, by ^{1}H NMR and IR. The yields of the products were based on the starting amount of the monocarboxylic acid. The selecitivity of the target dicarboxylic acid was based on the total amount of carboxylated products.

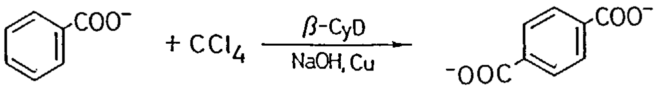
Measurement

^{1}H-NMR spectra were recorded on a JEOL GX-400 spectrometer, with the chemical shift δ from tetramethylsilane as 0 ppm.

RESULT AND DISCUSSION

Synthesis of Terephthalic Acid

The carboxylation of benzoic acid with carbon tetrachloride proceeded in aqueous sodium hydroxide solution in the presence of β-Cyd and copper powder under mild conditions.



(1)

As shown in Fig. 1, the yield of TPA (*p*-carboxylate product) increase with an increasing amount of β-Cyd and reaches a maximum (31 mol% with 95% selectivity) at an initial molar ratio of β-Cyd to benzoic acid of 0.5 in the presence of copper powder I and a yield of isophthalic acid (*m*-carboxylated product) of 1.8 mol%. Formation of phthalic acid (*o*-carboxylated product) is not observed.

In the absence of β-Cyd, however, carboxylation did not occur. When ethanol/30 wt% NaOH aq (volume ratio = 2:1) was used instead of 30 wt% NaOH aq, carboxylation occurred without β-Cyd but gave only isophthalic acid in 1.1 mol%

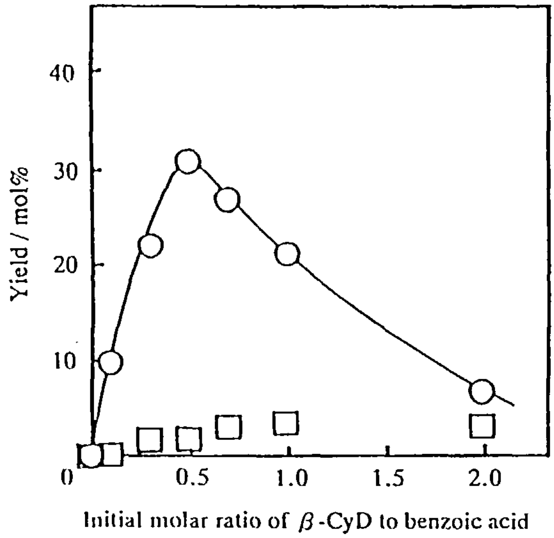


FIG. 1. Plots of yields of terephthalic acid (O) and of isophthalic acid (□) vs the initial molar ratio of β-CyD to benzoic acid. Conditions: 30 wt% NaOH aq, 30 mL; Cu powder I, 0.8 mmol; benzoic acid, 3.0 mmol; CCl_4, 9.5 mmol; 60°C, 7 hours.

yield. When α-Cyd and γ-Cyd were used in place of β-Cyd, the reactions produced only isophthalic acid in 0.2 mol% yield and only TPA in 0.3 mol% yield, respectively.

Figure 2 shows plots of the yields of TPA and isophthalic acid vs the initial molar ratio of carbon tetrachloride to benzoic acid in the carboxylation of benzoic acid using β-Cyd at an initial molar ratio of 0.5 in the presence of copper powder I and of copper powder II. In the case of copper powder I, the yield of TPA has a maximum value (47 mol% with 92% selectivity) at an initial molar ratio of carbon tetrachloride to benzoic acid of 10, where the yield of isophthalic acid was 4.2 mol%. When copper powder II is used instead of copper powder I, the yield of TPA increases remarkably and has a maximum (74 mol% with 84% selectivity) at an initial molar ratio of carbon tetrachloride to benzoic acid of 50, where the yield of isophthalic acid is 14 mol%.

The effect of the amount of copper powder II on the yields of TPA and isophthalic acid in the carboxylation of benzoic acid with β-Cyd at a molar ratio of 0.5 was investigated by using carbon tetrachloride at a molar ratio of 50. The yield of TPA is maximum (75 mol% with 87% selectivity) at an initial molar ratio of copper powder II to benzoic acid of 0.18, where the yield of isophthalic acid is 11 mol%.

Synthesis of 4,4′-Biphenyldicarboxylic Acid

The selective carboxylation of 4-BPA with carbon tetrachloride occurred under the similar mild conditions.

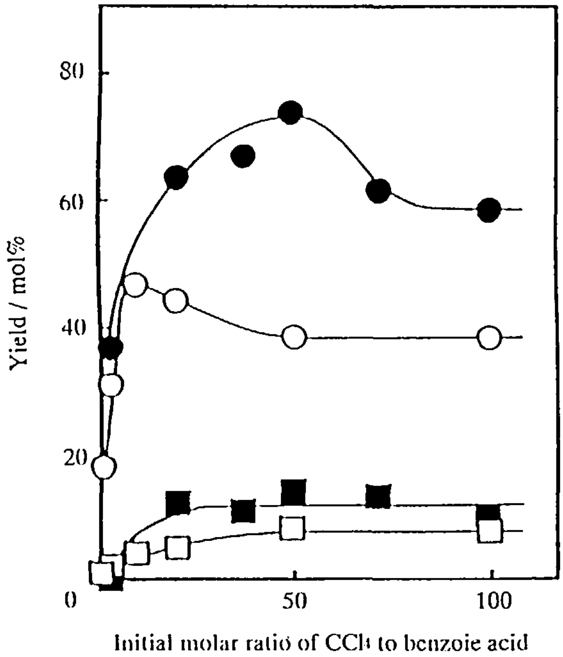
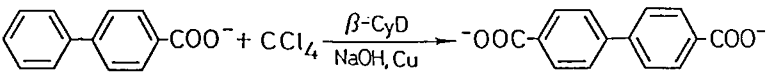


FIG. 2. Plots of yields of terephthalic acid (○, ●) and of isophthalic acid (□, ■) vs the initial molar ratio of CCl_4 to benzoic acid: Cu powder I (○, □), Cu powder II (●, ■). Conditions: 30 wt% NaOH aq, 30 mL; Cu powder, 0.8 mmol; benzoic acid, 3.0 mmol; β-CyD, 1.5 mmol; 60°C, 7 hours.



(2)

The yield of 4,4′-BPDA increases with an increasing amount of β-Cyd in the presence of copper powder I and reaches a maximum (25 mol%) at an initial molar ratio of β-Cyd to 4-BPA of 1.0, as shown in Fig. 3.

In the absence of β-Cyd, however, carboxylation did not occur. When α-Cyd and γ-Cyd were used in place of β-Cyd, no carboxylation products were detected.

Figure 4 shows plots of the yields of 4,4′-BPA vs the initial molar ratio of copper powder to 4-BPA. Copper powder II has a larger catalytic activity than copper powder I, particularly at an initial molar ratio smaller than 1.0.

Thus, selective synthesis of 4,4′-BPDA is achieved by using copper powder II at a molar ratio of 0.5, β-Cyd at a molar ratio of 1.0, and carbon tetrachloride at a molar ratio of 40, resulting in a 70 mol% yield of 4,4′-BPDA with 29% recovery of 4-BPA.

Synthesis of 2,6-Naphthalenedicarboxylic Acid

2-NCA underwent carboxylation with carbon tetrachloride under similar conditions.

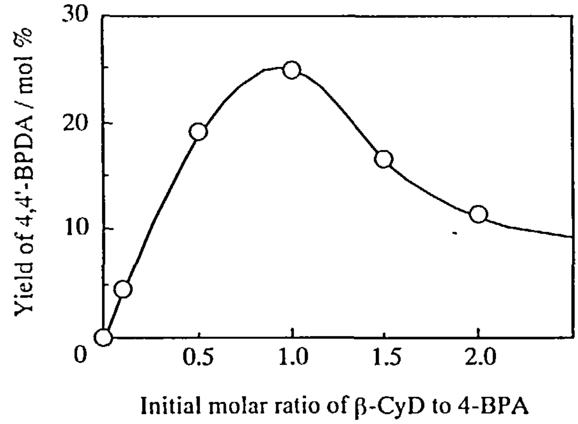
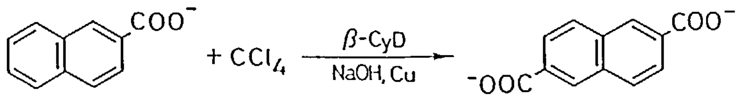


FIG. 3. Plot of yield of 4,4′-biphenyldicarboxylic acid (4,4′-BPDA) vs the initial molar ratio of β-CyD to 4-biphenylcarboxylic acid (4-BPA). Conditions: 30 wt% NaOH aq, 30 mL; Cu powder I, 0.8 mmol; CCl_4, 9.6 mmol; 60°C, 7 hours.



(3)

As shown in Fig. 5, the yield of 2,6-NDA increases with an increasing amount of β-Cyd in the presence of copper powder I, and reaches a maximum (39 mol% with 78% selectivity) at an initial mole ratio of β-Cyd to 2-NCA of 1,0, where 2,7-naphthalenedicarboxylic acid (2,7-NDA) and 1,6-naphthadicarboxylic acid (1,6-NDA) are 9.1 an 1.7 mol%, respectively.

When ethanol/30 wt% NaOH aq (volume ratio = 3:1) was used instead of 30

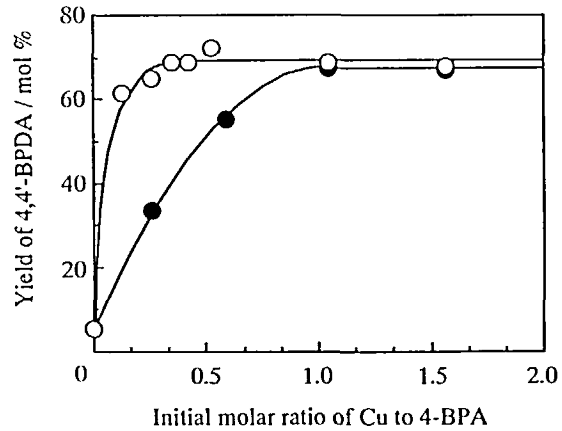


FIG. 4. Plots of yield of 4,4′-biphenyldicarboxylic acid (4,4′-BPDA) vs the initial molar ratio of Cu powder to 4-biphenylcarboxylic acid (4-BPA): Cu powder I (●), Cu powder II (○). Conditions: 30 wt% NaOH aq, 30 mL; 4-BPA, 3 mmol; β-CyD, 3 mmol; CCl_4, 120 mmol; 60°C, 7 hours.

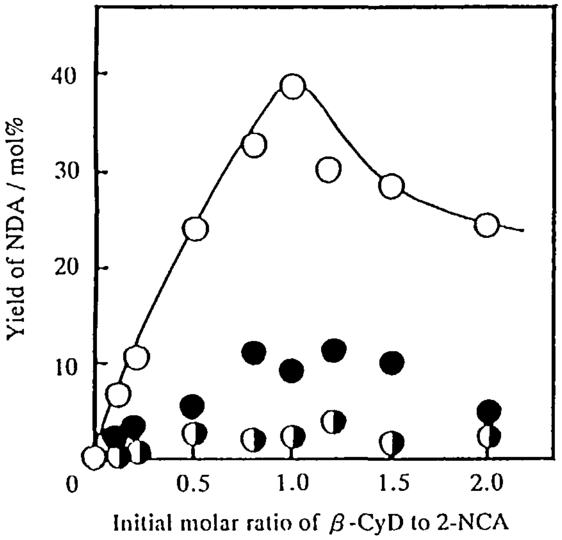


FIG. 5. Plots of the yields of naphthalenedicarboxylic acids (NDA) vs the initial molar ratio of β-CyD to 2-naphthalenecarboxylic acid (2-NCA): 2,6-NDA (O), 2,7-NDA (●), 1,6-NDA (O). Conditions: 30 wt% NaOH aq, 30 mL; Cu powder I, 0.8 mmol; 2-NCA, 3.0 mmol; CCl_4, 8.5 mmol; 60°C, 7 hours.

wt% NaOH aq without β-Cyd, the yields of 2,6-NDA, 2,7-NDA, and 1,6-NDA were 0.7, 1.1, and 0.1 mol%, respectively. When γ-Cyd was used in place of β-Cyd, the yields of 2,6-NDA, 2,7-NDA, and 1,6-NDA were 0.5, 0.7, and 0.2 mol%, respectively. When α-Cyd was used instead of β-Cyd, the reactions did not proceed.

Figure 6 shows the relationship between the yields of naphthalenedicarboxylic acids and the amount of carbon tetrachloride in the case of copper powder II. The yield of 2,6-NDA has a maximum value (58 mol% with 83% selectivity) at an initial mole ratio of carbon tetrachloride to 2-NCA of 5.0, where the yields of 2,7-NDA and 1,6-NDA are 10 and 2.5 mol%, respectively.

The optimum account of β-Cyd needed was investigated under the following conditions: The initial mole ratio of carbon tetrachloride to 2-NCA was 5.0 and that of copper powder II to 2-NCA was 0.1. At an initial mole ratio of β-Cyd to 2-NCA of 2.0, the yield of 2,6-NDA went up to 61 mol% with 85% selectivity.

The efficient addition of carbon tetrachloride was attempted. The reaction was started with the addition of 0.06 mL (0.62 mmol) of carbon tetrachloride to the aqueous sodium hydroxide solution containing 3 mmol 2-NCA, 6.0 mmol β-Cyd, and 0.3 mmol copper powder II. It was continued for 8 hours by adding 0.06 mL carbon tetrachloride to the reaction mixture every 15 minutes. The resulting yields of 2,6-NDA, 2,7-NDA, and 1,6-NDA were 67, 10, and 2.4 mol%, respectively, where the selectivity of 2,6-NDA was 84%.

Inclusion Complex Formation

The inclusion formation constants of the α-Cyd–carbon tetrachloride complex and of the γ-Cyd–carbon tetrachloride complex were much smaller than that of the β-Cyd–carbon tetrachloride complex [11].

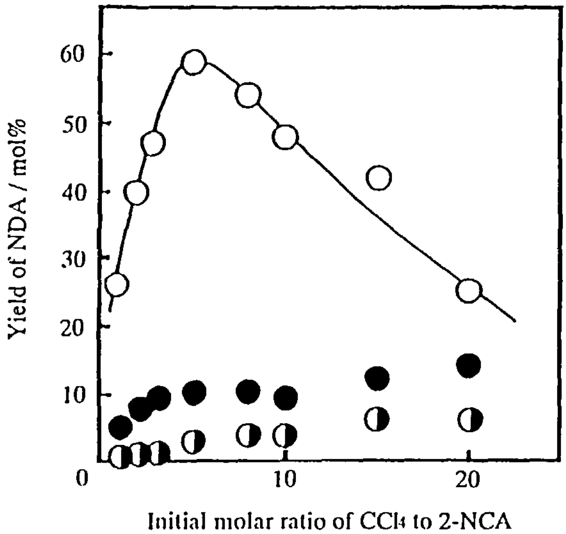
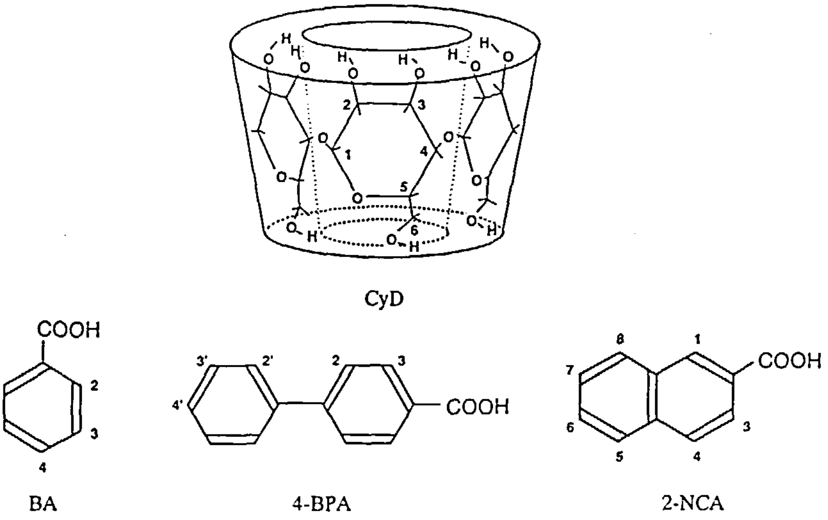


FIG. 6. Plots of the yields of naphthalenedicarboxylic acids (NDA) vs the initial molar ratio of CCl_4 to 2-naphthalene-carboxylic acid (2-NCA): 2,6-NDA (○), 2,7-NDA (●), 1,6-NDA (○). Conditions: 30 wt% NaOH aq, 30 mL; Cu powder II, 0.3 mmol; 2-NCA, 3.0 mmol; β-CyD, 3.0 mmol; 60°C, 7 hours.

The interaction between the aromatic monocarboxylic acid and β-Cyd was examined by ^{1}H NMR on a solution of β-Cyd (0.1 mol·L^{-1}) and the monocarboxylic acid (0.1 mol·L^{-1}) in 1 wt% NaOD in D_2O at 27°C.

As shown in Table 1, the chemical shifts of H-1, H-3, H-4, H-5, and H-6 of β-Cyd changed toward a higher magnetic field in the presence of benzoic acid. The



CyD

BA

4-BPA

2-NCA

FIG. 7. Positional numbers of cyclodextrin and aromatic carboxylic acids.

TABLE 1. Proton Chemical Shifts of β-Cyclodextrin (β-CyD) in the Absence (δ_0) and the Presence (δ) of Benzoic Acid (BA)[a] (see Fig. 7)

Protons of β-CyD	δ_0, ppm	δ, ppm	$\delta_0 - \delta$, ppm[b]
1	4.930	4.921	+0.009
2	3.489	3.492	−0.003
3	3.855	3.828	+0.027
4	3.415	3.412	+0.003
5	3.769	3.711	+0.058
6	3.809	3.782	+0.027

[a] β-CyD (0.1 mol·L^{-1}), BA(0.1 mol·L^{-1}), and NaOD (1 wt%) in D_2O at 27°C.

[b] + and − signs refer the high and low field shifts, respectively.

H-3 and H-5 atoms are directed toward the interior of the cavity of β-Cyd whereas the H-1, H-2, and H-4 atoms are located on the exterior [2]. Thus, the larger changes in the chemical shifts of H-3 and H-5 compared with those of H-1, H-2, and H-4 indicate the formation of an inclusion complex between β-Cyd and benzoic acid.

In the presence of 4-BPA, the chemical shifts of H-2, H-3, H-4, H-5, and H-6 of β-Cyd changed toward a higher magnetic field by $\Delta\delta$ = 0.02, 0.16, 0.02, 0.24, and 0.17, respectively. These values suggest that β-CyD includes 4-BPA.

In the presence of 2-NCA, the chemical shifts of all the protons of β-CyD changed toward a higher magnetic field by $\Delta\delta$ = H-1 (0.038), H-2 (0.032), H-3 (0.099), H-4 (0.026), H-5 (0.027), and H-6 (0.145). The larger changes in the chemical shifts of H-3 and H-5 indicate the inclusion of 2-NCA in β-Cyd.

Reaction Mechanism

The promotion of carboxylation by β-Cyd is probably attributable to inclusion complex formation. The solubilities of carbon tetrachloride and the aromatic monocarboxylic acids in the aqueous alkali in high concentration are increased by the formation of the β-Cyd–carbon tetrachloride complex and of the β-Cyd–monocarboxylic acid complex.

The aromatic monocarboxylic acid included in β-Cyd may be predominantly attacked at a specific position by the active species. The specific position is probably the entrance to the cavity of β-Cyd.

The active species formed from carbon tetrachloride, aqueous alkali, and copper powder was proposed to be a trichloromethyl cation [12]. The formation of active species is promoted by inclusion complex formation between β-Cyd and carbon tetrachloride. A considerable part of the active species is decomposed by reaction with hydroxide ion when the active species is formed too fast to react with the aromatic monocarboxylic acid.

CONCLUSION

The selective syntheses of terephthalic acid, 4,4′-biphenyldicarboxylic acid, and 2,6-naphthalenedicarboxylic acid have been achieved by carboxylations of benzoic acid, 4-biphenylcarboxylic acid, and 2-naphthalenecarboxylic acid, respectively, with carbon tetrachloride in aqueous alkali using β-cyclodextrin and copper powder as catalyst under mild conditions.

ACKNOWLEDGMENT

The work has been financially supported, in part, by a Grant-in-Aid for Scientific Research (No. 05555248) from the Ministry of Education, Science and Culture, Japan.

REFERENCES

[1] US Patent 4,082,731 (1978), Avtex Fibers Inc. (W. N. Knopka).

[2] A. Y. Billibin, A. V. Tenkovtsev, O. N. Piraner, E. E. Pashkovsky, and S. S. Skorokhodov, *Makromol. Chem.*, *186*, 1575 (1985).

[3] W. J. Jackson Jr., *Macromolecules*, *16*, 1027 (1983).

[4] H. Aoki, S. Shimotsuma, T. Asai, and M. Hosoi, *Proc. Jpn. Congr. Mater. Res.*, *17*, 217 (1974).

[5] D. Chen and H. G. Zachmann, *Polymer*, *32*, 1612 (1991).

[6] K. Weissermel and H.-J. Arpe, *Industrielle Organische Chemie, Bedeutende Vor- und Zwischen-produkte*, Verlag Chemie, Weinheim, Germany, 1976.

[7] European Patent 324342 (1989), Mitsubishi Gas Chemical Co. (T. Tanaka and M. Inari); *Chem. Abstr.*, *112*, 55279j (1990).

[8] M. L. Bender and M. Komiyama, *Cyclodextrin Chemistry*, Springer-Verlag, Berlin, 1978.

[9] H. Hirai and H. Mihori, *Chem. Lett.*, p. 1523 (1992).

[10] H. Hirai, H. Mihori, and R. Terakado, *Makromol. Chem.*, *Rapid Commun.*, *14*, 439 (1993).

[11] M. Nishimura, T. Deguchi, and I. Sanemasa, *Bull. Chem. Soc. Jpn.*, *62*, 3718 (1989).

[12] M. Komiyama and H. Hirai, *J. Am. Chem. Soc.*, *106*, 174 (1984).