

CHAPTER III EXPERIMENTAL

3.1 Chemicals

The weight of all chemicals was determined on a Mettler AE200 electrical balance. All solvents used in this research were purified prior to use by standard methods. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. Dichloromethane (CH_2Cl_2) was distilled from calcium hydride (CaH_2).

Phosphorus oxychloride, *p*-cresol, *p*-bromophenol and triethylamine (NEt_3) were obtained from Fluka. Phenylphosphonic dichloride (PPDC) was also obtained from Fluka and distilled under vacuum before use. The following compounds, 4,4'-isopropylidenediphenol (bisphenol A), 4,4'-ethylidenebisphenol (bisphenol E), 4,4'-(1,3-phenylenediisopropylidene)bisphenol (bisphenol P-1,3), 4,4'-(1,4-phenylenediisopropylidene)bisphenol (bisphenol P-1,4), 4,4'-cyclohexylidenebisphenol (bisphenol C), were purchased from Aldrich Chemical company. Tetrahydrofuran and dichloromethane were purchased from Lab-Scan. Nitrogen gas was attained from TGIT.

3.2 Measurements

Glass transition temperatures (T_g) were measured with Netzsch DSC 200 differential scanning calorimeter with heating rate of $10\text{ }^\circ\text{C}/\text{min}$, under nitrogen. Thermogravimatic datas were obtained on Netzsch TGA 409 C thermogravimatic analyzer with heating rate of $10\text{ }^\circ\text{C}/\text{min}$, under air. Elemental analyses of the polymers were also conducted on a Perkin Elmer PE 2400 Series II. Limiting oxygen indices were determined according to D-2863 ASTM standard.¹³

3.3 Spectroscopy

Characterization of product structures were performed by infrared (IR) spectroscopy. FTIR spectra were registered on a Nicolet Impact 410 fourier transform infrared spectrometer and nuclear magnetic resonance (NMR), proton (^1H) and carbon (^{13}C), spectra were recorded on a Bruker ACF 200 spectrometer operating at 200

MHz (^1H) and 50 MHz (^{13}C). Phosphorus (^{31}P) NMR spectra were recorded on Jeol JNM A-500 spectrometer operating at 202.48 MHz at the Scientific and Technology Research Equipment Center, Chulalongkorn University. All spectra were performed in deuterated chloroform (CDCl_3) with tetramethylsilane (TMS) as an internal reference. Chemical shifts (δ) are reported in parts per million (ppm) relative to TMS for ^1H and ^{13}C spectra in contrast to ^{31}P spectra relative to phosphoric acid as an external standard. Coupling constants (J) are proton-proton and proton-phosphorus and are reported in hertz (Hz).

3.4 Determination of the weight average molecular weight (\overline{M}_w)

The weight average molecular weight (\overline{M}_w) was determined by gel permeation chromatography (GPC; Waters-150 CV Millipore). The polymer (15 mg) was dissolved in tetrahydrofuran (THF) 5 mL and filtered through a membrane filter (45 micron). An aliquot of the solution was injected into the Polymer Lab[®] columns (300 mm \times 7.5 mm, PL gel 10 μm MIXED-B; 2 columns) with THF as the mobile phase. Polystyrene (5,460-1,290,000 D) was used as a standard. The calibration curve was shown in Figure 3.1. The detector was a differential refractometer (refractive index-detector). The sample GPC chromatogram was shown in Figure 3.2. The \overline{M}_w of polymers were reported in Dalton (D) relative to polystyrene standard having the same size.

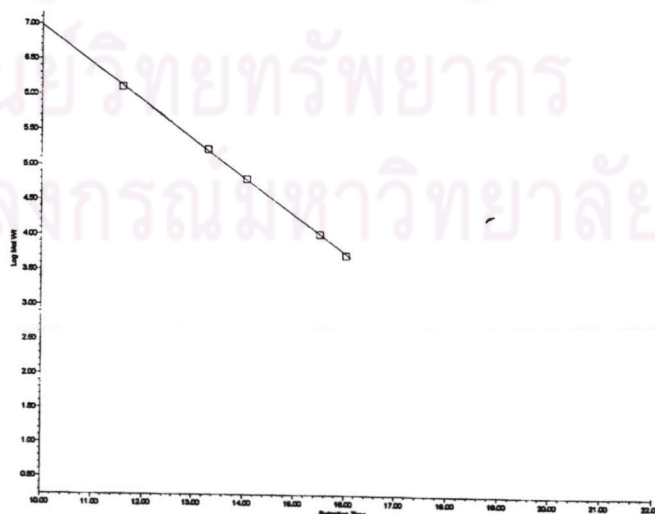


Figure 3.1 The calibration curve of polystyrene as a standard

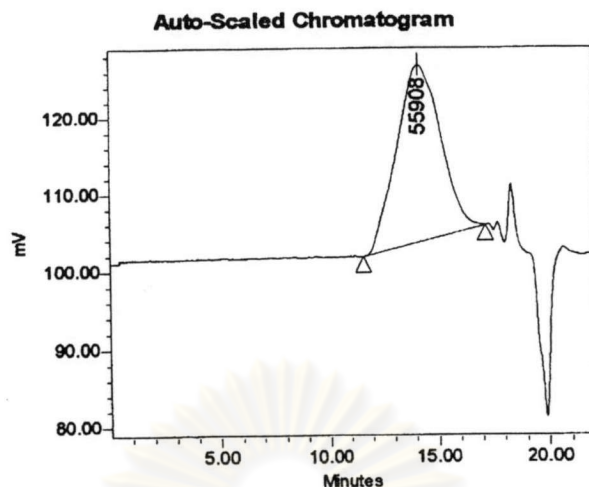
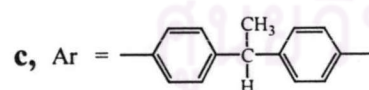
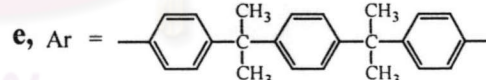
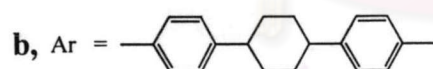
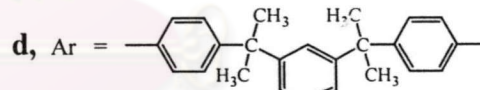
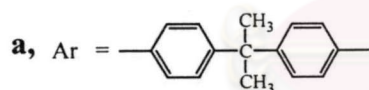
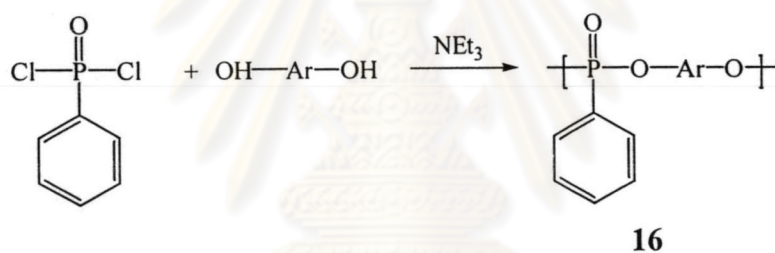


Figure 3.2 The GPC chromatogram of polyphosphate 20c

3.5 General procedures for the preparation of polyphosphonate esters.



Solution polycondensation: method A

A solution of selected aromatic diol in dry tetrahydrofuran (THF) was placed in a flask cooled in an ice bath. Triethylamine was added to the flask. The solution of phenylphosphonic dichloride (PPDC) was added dropwise under vigorous stirring. The reaction mixture was allowed to warm up to room temperature and was subsequently heated at reflux. The polymer was dissolved in THF. It was separated remove to triethylamine salt by filtration. The polymer was precipitated with methanol and dried *in vacuo*.

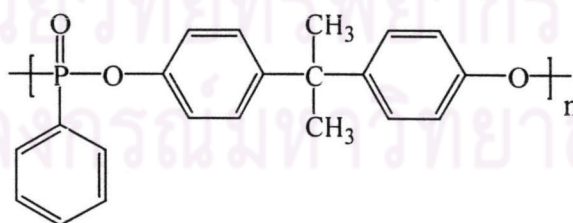
Solution polycondensation: method B

A flask was charged with a solution of a selected bisphenol in dry dichloromethane and triethylamine. A solution of phenylphosphonic dichloride in dichloromethane was slowly added to the flask with rapid stirring. After all of the solution was added, the reaction mixture was refluxed for 1 h. The polymer solution was cooled to room temperature, washed with dilute hydrochloric acid (HCl), and distilled water until the aqueous phase was neutral to litmus paper. The polymer was precipitated by methanol. The precipitate was collected by filtration and dried under vacuum.

Solution polycondensation: method C

A flask equipped with a magnetic bar, an addition funnel and a reflux-condensor was charged with aromatic diol, dichloromethane and triethylamine and subjected to vigorous stirring at 0 °C. Then a solution of phenylphosphonic dichloride in dichloromethane was slowly added to the flask. The reaction mixture was allowed to warm to room temperature and was subsequently refluxed for 4 h. The polymer solution was washed with dilute hydrochloric acid and distilled water until the aqueous phase was neutral to litmus paper. The solution was filtered. The polymer was precipitated with methanol and the precipitate was collected by filtration and dried *in vacuo*.

Preparation of poly(bisphenol A-phenylphosphonate) (16a)

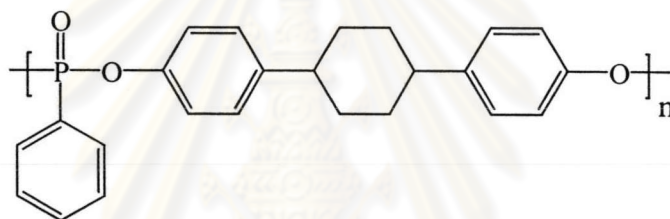


16a

The synthesis of polymer **16a** by solution polycondensation method A resulted in the polymer with low weight average molecular weight (\overline{M}_w) (lower than 5,000 D). Therefore, the solution polycondensation method B was selected as an alternative. Bisphenol A (5.00 g, 21.9 mmol) was reacted with phenylphosphonic dichloride (4.93

g, 21.9 mmol) in the presence of triethylamine (7.7 mL, 55.0 mmol) in dichloromethane (30 mL) for 1 h. Polymer **16a** was obtained as a white solid (5.09 g, 52%) with \overline{M}_w of 14,346 D. $^1\text{H-NMR}$ (200 MHz, CDCl_3) δ 1.54 (s, 6 H, CH_3), 7.03-7.08 (m, 8 H, Ar), 7.43-7.52 (m, 3 H, ArP), 7.91 (dd, $^3J_{\text{HP}} = 13.71$ Hz, $^3J_{\text{HH}} = 7.33$ Hz, 2 H, ArP); $^{31}\text{P-NMR}$ (202.48 MHz, CDCl_3 , $\{^1\text{H}\}$) δ 12.55; $^{13}\text{C-NMR}$ (50 MHz, CDCl_3 , $\{^1\text{H}\}$) δ 30.87 (CH_3), 42.25 (CCH_3), 119.99 (d, $^3J_{\text{CP}} = 4.6$ Hz), 128.07, 128.49, 128.86 (d, $^2J_{\text{CP}} = 5.4$ Hz), 132.24 (d, $^1J_{\text{CP}} = 10.4$ Hz), 133.21 (d, $J_{\text{CP}} = 3.2$ Hz), 147.15, 148.23 (d, $^2J_{\text{CP}} = 7.6$ Hz); IR (KBr)/ cm^{-1} ; 3050, 2964, 1602, 1504, 1438, 1385, 1284 (P=O), 1164 (POAr), 948 (POAr).

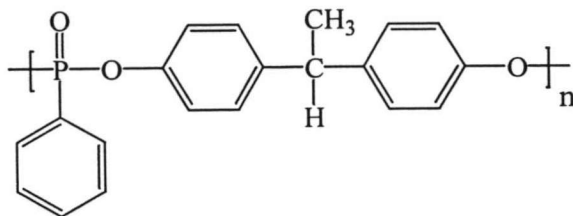
Preparation of poly(bisphenol C-phenylphosphonate) (**16b**)



16b

Preparation of polymer **16b** by solution polycondensation methods A and C gave low \overline{M}_w ($< 7,000$ D). Therefore, polymer **16b** was obtained from solution polycondensation method B instead. Bisphenol C (5.37 g, 20.0 mmol) was reacted with phenylphosphonic dichloride (3.90 g, 20.0 mmol) in the presence of triethylamine (6.5 mL, 46.0 mmol) in dichloromethane (25 mL) for 1 h. Polymer **16b** was obtained as a white solid (4.99 g, 52%) with \overline{M}_w of 8,481 D. $^1\text{H-NMR}$ (200 MHz, CDCl_3) δ 1.42 (s, 6 H, C_6H_{10}), 2.11 (s, 4 H, C_6H_{10}), 6.97-7.10 (m, 8 H, Ar), 7.41-7.47 (m, 3 H, ArP), 7.89 (dd, $^3J_{\text{HP}} = 14.02$ Hz, $^3J_{\text{HH}} = 6.86$ Hz, 2 H, ArP); $^{31}\text{P-NMR}$ (202.48 MHz, CDCl_3 , $\{^1\text{H}\}$) δ 12.44; $^{13}\text{C-NMR}$ (50 MHz, CDCl_3 , $\{^1\text{H}\}$) δ 22.71, 26.22, 37.22, 45.51, 120.18 (d, $^3J_{\text{CP}} = 4.4$ Hz), 128.00, 128.45, 128.79, 132.19, (d, $^1J_{\text{CP}} = 10.4$ Hz), 133.20 (d, $^3J_{\text{CP}} = 2.8$ Hz), 145.12, 147.99 (d, $^2J_{\text{CP}} = 7.6$ Hz); IR (KBr)/ cm^{-1} ; 3058, 2935, 1600, 1504, 1469, 1454, 1273 (P=O), 1132 (POAr), 953 (POAr).

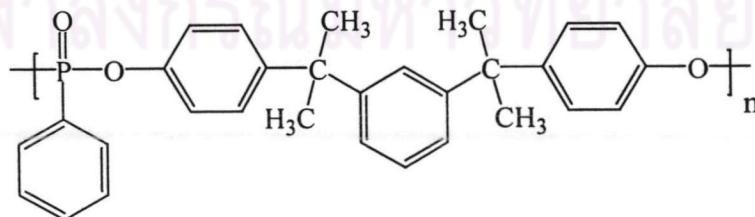
Preparation of poly(bisphenol E-phenylphosphonate) (16c)



16c

Preparation of polymer **16c** by solution polycondensation methods A and C gave low \overline{M}_w ($< 7,000$ D). Therefore, polymer **16c** was obtained from solution polycondensation method B instead. Bisphenol E (2.14 g, 0.01 mol) was reacted with phenylphosphonic dichloride (1.95 g, 0.01 mol) in the presence of triethylamine (4.2 mL, 0.03 mol) in dichloromethane (25 mL) for 1 h. Polymer **16c** was obtained as a white solid (2.56 g, 63%) with \overline{M}_w of 15,275 D. $^1\text{H-NMR}$ (200 MHz, CDCl_3) δ 1.48 (d, $^3J_{\text{HH}} = 7.19$ Hz, 3 H, CH_3), 3.99 (q, $^3J_{\text{HH}} = 7.11$ Hz, 1 H, CH), 6.98-7.06 (m, 8 H, Ar), 7.42-7.55 (m, 3 H, ArP), 7.90 (dd, $^3J_{\text{HP}} = 13.96$ Hz, $^3J_{\text{HH}} = 6.76$ Hz, 2 H, ArP); $^{31}\text{P-NMR}$ (202.48 MHz, CDCl_3 , $\{^1\text{H}\}$) δ 12.53; $^{13}\text{C-NMR}$ (50 MHz, CDCl_3 , $\{^1\text{H}\}$) δ 22.00 (CH_3), 43.41 (CHCH_3), 120.48 (d, $^3J_{\text{CP}} = 4.4$ Hz), 128.30 (d, $J_{\text{CP}} = 2.5$ Hz), 128.54, 128.82, 132.26 (d, $^1J_{\text{CP}} = 10.3$ Hz), 133.28 (d, $J_{\text{CP}} = 2.9$ Hz), 142.90, 148.58 (d, $^2J_{\text{CP}} = 7.6$ Hz); IR (KBr)/ cm^{-1} : 3058, 2965, 2873, 1601, 1504, 1454, 1375, 1282 (P=O), 1162 (POAr), 952 (POAr).

Preparation of poly(bisphenol P-1,3-phenylphosphonate) (16d)

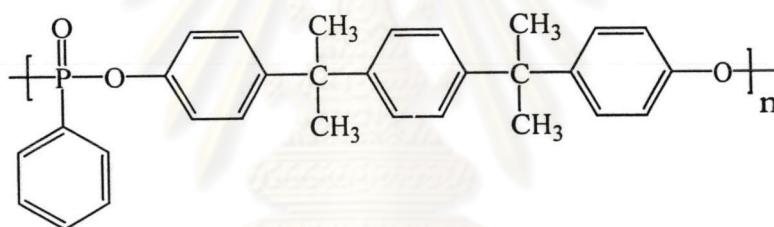


16d

Preparation of polymer **16d** by solution polycondensation method A resulted in low \overline{M}_w ($< 5,000$ D). Therefore, polymer **16d** was obtained from solution

polycondensation method B instead. Bisphenol P-1,3 (3.47 g, 0.01 mol) was reacted with phenylphosphonic dichloride (1.95 g, 0.01 mol) in the presence of triethylamine (4.2 mL, 0.03 mol) in dichloromethane (25 mL) for 1 h. Polymer **16d** was obtained as a white solid (2.97 g, 59%) with \overline{M}_w of 31,269 D. $^1\text{H-NMR}$ (200 MHz, CDCl_3) δ 1.52 (s, 12 H, CH_3), 6.88-7.03 (m, 12 H, Ar), 7.41-7.53 (m, 3 H, ArP), 7.92 (dd, $^3J_{\text{HP}} = 13.95$ Hz, $^3J_{\text{HH}} = 6.68$ Hz, 2 H, ArP); $^{31}\text{P-NMR}$ (202.48 MHz, CDCl_3 , $\{^1\text{H}\}$) δ 12.50; $^{13}\text{C-NMR}$ (50 MHz, CDCl_3 , $\{^1\text{H}\}$) δ 30.85 (CH_3), 42.72 (CCH_3), 119.98 (d, $^3J_{\text{CP}} = 4.6$ Hz), 124.37, 124.87, 127.67, 128.12, 128.52, 128.88 (d, $J_{\text{CP}} = 4.8$ Hz), 132.31 (d, $^1J_{\text{CP}} = 10.3$ Hz), 133.23 (d, $J_{\text{CP}} = 3$ Hz), 147.65 (d, $J_{\text{CP}} = 1.3$ Hz), 148.15 (d, $^2J_{\text{CP}} = 7.5$ Hz), 149.88; IR (KBr)/ cm^{-1} ; 3058, 2965, 1600, 1504, 1438, 1384, 1276 (P=O), 1168 (POAr), 925 (POAr).

Preparation of poly(bisphenol P-1,4-phenylphosphonate) (**16e**)



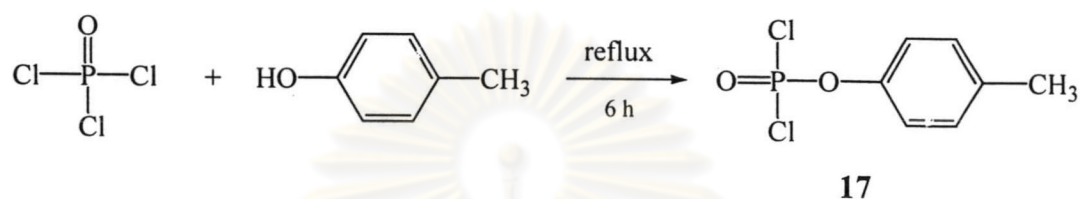
16e

Preparation of polymer **16e** by solution polycondensation method A resulted in low \overline{M}_w ($< 7,500$ D). Therefore, the solution polycondensation method B was selected as an alternative. Bisphenol P-1,4 (3.47 g, 0.01 mol) was reacted with phenylphosphonic dichloride (1.95 g, 0.01 mol) in the presence of triethylamine (4.2 mL, 0.03 mol) in dichloromethane (25 mL) for 1 h. Polymer **16e** was obtained as a white solid (2.80 g, 52%) with \overline{M}_w of 10,347 D. $^1\text{H-NMR}$ (200 MHz, CDCl_3) δ 1.63 (s, 12 H, CH_3), 7.08-7.20 (m, 12 H, Ar), 7.45-7.53 (m, 3 H, ArP), 7.99 (dd, $^3J_{\text{HP}} = 13.9$ Hz, $^3J_{\text{HH}} = 6.8$ Hz, 2 H, ArP); $^{31}\text{P-NMR}$ (202.48 MHz, CDCl_3 , $\{^1\text{H}\}$) δ 12.46; $^{13}\text{C-NMR}$ (50 MHz, CDCl_3 , $\{^1\text{H}\}$) δ 30.89 (CH_3), 42.22 (CCH_3), 120.02 (d, $^3J_{\text{CP}} = 4.6$ Hz), 126.38, 128.18, 128.55, 128.96 (d, $J_{\text{CP}} = 9.5$ Hz), 132.28 (d, $^1J_{\text{CP}} = 10.4$ Hz), 133.25 (d, $J_{\text{CP}} = 3.0$ Hz), 147.53, 147.60 (d, $J_{\text{CP}} = 1.2$ Hz), 148.20 (d, $^2J_{\text{CP}} = 7.7$ Hz);

IR (KBr)/cm⁻¹; 3057, 2963, 1635, 1603, 1506, 1440, 1385, 1278 (P=O), 1126 (POAr), 926 (POAr).

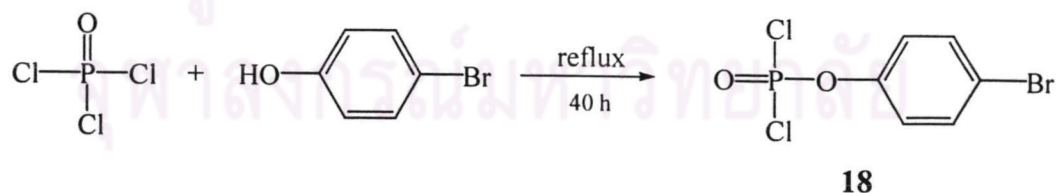
3.6 The synthesis of polyphosphate esters

Preparation of *p*-methylphenylphosphorodichloridate (17)



Compound **17** was prepared by refluxing a mixture of *p*-methylphenol (25.00 g, 0.23 mol) and phosphorus oxychloride (105.80 g, 0.69 mol) for 6 h followed by distillation under reduced pressure; bp 83-85 °C, 0.1 atm. The compound was obtained as a colorless liquid (40.17 g, 78%). ¹H-NMR (200 MHz, CDCl₃) δ 2.31 (d, ⁴J_{HP} = 1.82 Hz, 3 H, CH₃) 7.15-7.19 (m, 4 H, Ar); ³¹P-NMR (202.48 MHz, CDCl₃, {¹H}) δ 4.56; ¹³C-NMR (50 MHz, CDCl₃, {¹H}) δ 20.81 (d, J_{CP} = 1.4 Hz, CH₃), 120.24 (d, ³J_{CP} = 5.0 Hz), 130.71 (d, J_{CP} = 2.5 Hz), 137.09 (d, ⁴J_{CP} = 2.8 Hz), 147.62 (d, ²J_{CP} = 12.2 Hz); IR (NaCl)/cm⁻¹; 3037, 2929, 1650, 1598, 1504, 1454, 1382, 1309 (P=O), 1160 (POAr), 953 (POAr).

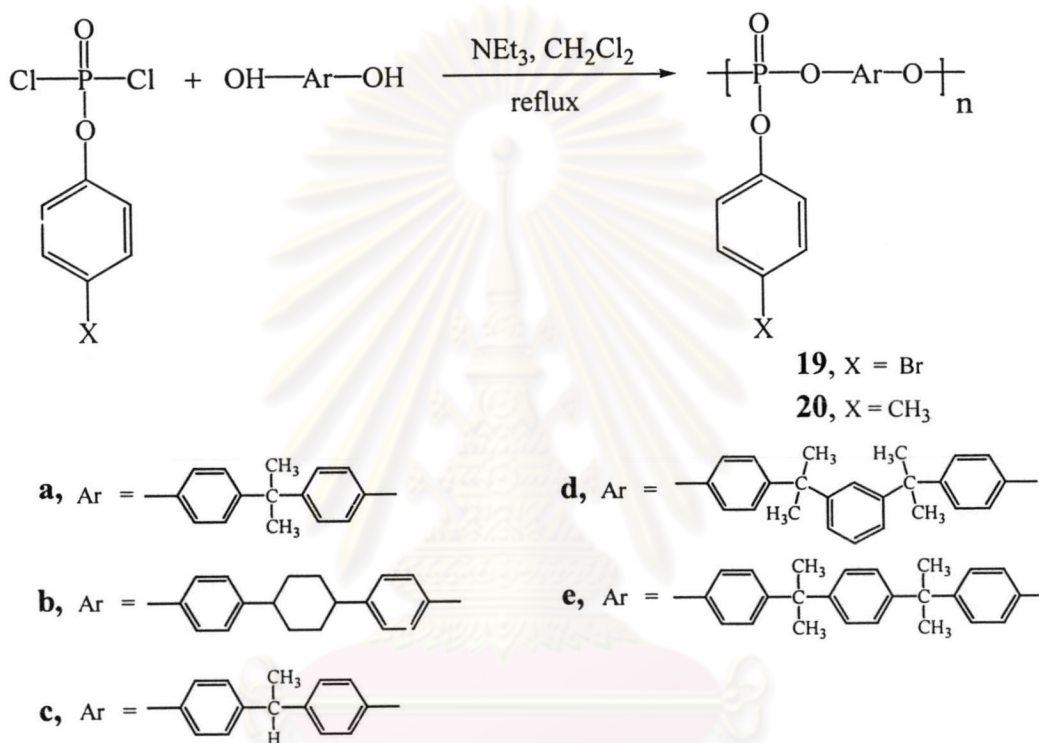
Preparation of *p*-bromophenylphosphorodichloridate (18)



Compound **18** was prepared by refluxing a mixture of *p*-bromophenol (20.00 g, 0.12 mol) and phosphorus oxychloride (85.0 g, 0.55 mol) for 40 h followed by distillation under reduced pressure; bp 120-122 °C, 0.1 atm. The compound was obtained as colorless liquid (26.60 g, 79%). ¹H-NMR (200 MHz, CDCl₃) δ 7.13-7.18 (dt, ³J_{HH} = 8.36 Hz, ⁴J_{HP} = 1.95 Hz, ⁴J_{HH} = 1.22 Hz, 2 H, Ar), 7.48-7.53 (dd, ³J_{HH} =

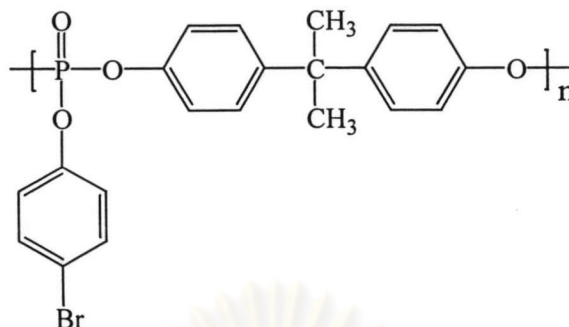
8.96 Hz, $^4J_{\text{HH}} = 1.15$ Hz, 2 H, Ar); ^{31}P -NMR (202.48 MHz, CDCl_3 , { ^1H }) δ 4.17; ^{13}C -NMR (50 MHz, CDCl_3 , { ^1H }) δ 120.54 (d, $^4J_{\text{CP}} = 3.5$ Hz), 122.37 (d, $^3J_{\text{CP}} = 5.5$ Hz), 133.37 (d, $J_{\text{CP}} = 2.0$ Hz), 148.58 (d, $^2J_{\text{CP}} = 11.1$ Hz); IR (NaCl)/ cm^{-1} ; 3095, 1650, 1579, 1481, 1305 (P=O), 1162 (POAr), 946 (POAr).

General procedure for the preparation of polyphosphate esters.



A flask was charged with a solution of a selected bisphenol in dry dichloromethane and triethylamine. A solution of *p*-substituted phenylphosphorodichloridate in dichloromethane was slowly added to the flask with rapid stirring. After all of the solution was added, the reaction mixture was refluxed for 1 h. The polymer solution was cooled to room temperature, washed with dilute hydrochloric acid and distilled water until the aqueous phase was neutral to litmus paper. The polymer was precipitated by methanol. The precipitate was collected by filtration and dried *in vacuo*.

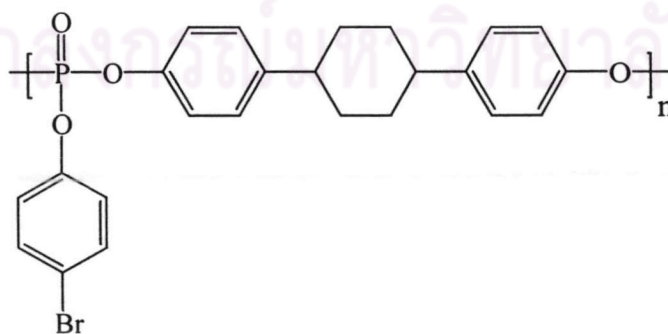
Preparation of poly(bisphenol A-*p*-bromophenylphosphate) (19a)



19a

Polymer **19a** was prepared by solution polycondensation method B. Bisphenol A (5.00 g, 21.9 mmol) was reacted with *p*-bromophenylphosphorodichloridate (**18**) (6.34 g, 21.9 mmol) in the presence of triethylamine (7.7 mL, 55.0 mmol) in dichloromethane (25 mL) for 1 h. Polymer **19a** was obtained as a white solid (5.12 g, 46%) with \overline{M}_w of 9,332 D. $^1\text{H-NMR}$ (200 MHz, CDCl_3) δ 1.60 (s, 6 H, CH_3), 7.06-7.24 (m, 10 H, Ar, ArOP), 7.41 (d, $^3J_{\text{HH}} = 8.72$ Hz, 2 H, ArOP); $^{31}\text{P-NMR}$ (202.48 MHz, CDCl_3 , $\{^1\text{H}\}$) δ -16.87; $^{13}\text{C-NMR}$ (50 MHz, CDCl_3 , $\{^1\text{H}\}$) δ 30.87 (CH_3), 42.39 (CCH_3), 119.46 (d, $^3J_{\text{CP}} = 4.2$ Hz), 121.94 (d, $^3J_{\text{CP}} = 4.9$ Hz), 122.12, 128.22 (d, $J_{\text{CP}} = 3.7$ Hz), 132.92 (d, $J_{\text{CP}} = 5.2$ Hz), 147.77, 148.23 (d, $^2J_{\text{CP}} = 7.3$ Hz), 149.49 (d, $^2J_{\text{CP}} = 7.4$ Hz); IR (KBr)/ cm^{-1} : 3057, 2965, 1643, 1604, 1504, 1481, 1403, 1384, 1315 (P=O), 1164 (POAr), 964 (POAr).

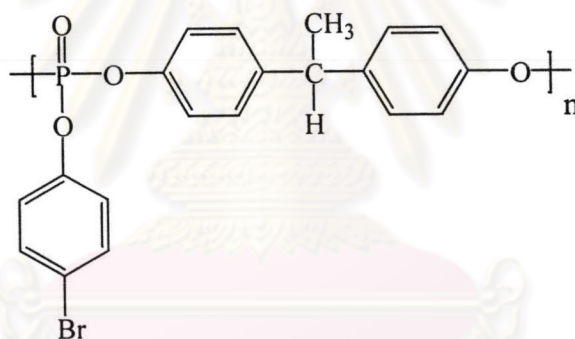
Preparation of poly(bisphenol C-*p*-bromophenylphosphate) (19b)



19b

Polymer **19b** was prepared by solution polycondensation method B. Bisphenol C (5.37 g, 0.02 mol) was reacted with *p*-bromophenylphosphorodichloridate (**18**) (5.80 g, 0.02 mol) in the presence of triethylamine (7.0 mL, 0.05 mol) in dichloromethane (25 mL) for 1 h. Polymer **19b** was obtained as a white solid (7.76 g, 70%) with \overline{M}_w of 14,892 D. $^1\text{H-NMR}$ (200 MHz, CDCl_3) δ 1.46 (s, 6 H, C_6H_{10}), 2.16 (s, 4 H, C_6H_{10}), 7.02-7.91 (m, 10 H, Ar, ArOP), 7.38 (d, $^3J_{\text{HH}} = 8.56$ Hz, 2 H, ArOP); $^{31}\text{P-NMR}$ (202.48 MHz, CDCl_3 , $\{^1\text{H}\}$) δ -16.95; $^{13}\text{C-NMR}$ (50 MHz, CDCl_3 , $\{^1\text{H}\}$) δ 22.73, 26.18, 37.20, 45.59 (C_6H_{10}), 118.63(d, $J_{\text{CP}} = 1.4$ Hz), 119.75 (d, $^3J_{\text{CP}} = 4.9$ Hz), 121.96 (d, $^3J_{\text{CP}} = 5.3$ Hz), 128.86, 132.86, 145.76, 147.98 (d, $^2J_{\text{CP}} = 7.3$ Hz), 149.48 (d, $^2J_{\text{CP}} = 7.5$ Hz); IR (KBr)/ cm^{-1} ; 3062, 2933, 1644, 1603, 1504, 1481, 1454, 1311 (P=O), 1160 (POAr), 965 (POAr).

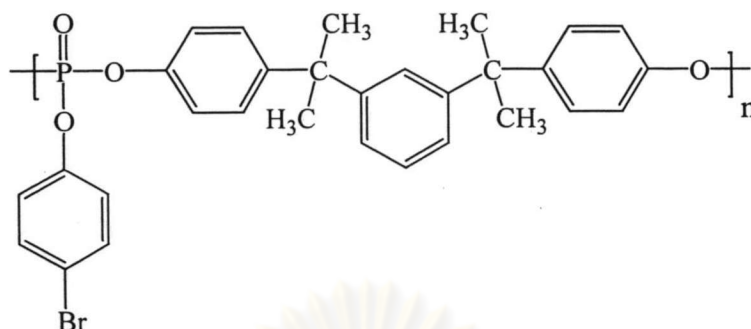
Preparation of poly(bisphenol E-*p*-bromophenylphosphate) (**19c**)



19c

Polymer **19c** was prepared by solution polycondensation method B. Bisphenol E (4.28 g, 0.02 mol) was reacted with *p*-bromophenylphosphorodichloridate (**18**) (5.80 g, 0.02 mol) in the presence of triethylamine (7.0 mL, 0.05 mol) in dichloromethane (25 mL) for 1 h. Polymer **19c** was obtained as a white solid (4.60 g, 46%) with \overline{M}_w of 16,390 D. $^1\text{H-NMR}$ (200 MHz, CDCl_3) δ 1.55 (d, $^3J_{\text{HH}} = 7.1$ Hz, 3 H, CH_3), 4.08 (q, $^3J_{\text{HH}} = 7.3$ Hz, 1 H, CH), 7.05-7.15 (m, 10 H, Ar, ArOP), 7.40 (d, $^3J_{\text{HH}} = 8.8$ Hz, 2 H, ArOP); $^{31}\text{P-NMR}$ (202.48 MHz, CDCl_3 , $\{^1\text{H}\}$) δ -16.91; $^{13}\text{C-NMR}$ (50 MHz, CDCl_3 , $\{^1\text{H}\}$) δ 21.97(CH_3), 43.45 (CH CH_3), 118.64, 119.97 (d, $^3J_{\text{CP}} = 4.5$ Hz), 121.93 (d, $^3J_{\text{CP}} = 4.8$ Hz), 128.97, 132.86, 143.44, 148.56 (d, $^2J_{\text{CP}} = 7.3$ Hz), 149.47 (d, $^2J_{\text{CP}} = 7.2$ Hz); IR (KBr)/ cm^{-1} ; 3066, 2965, 2873, 1646, 1604, 1504, 1481, 1376, 1313 (P=O), 1160 (POAr), 975 (POAr).

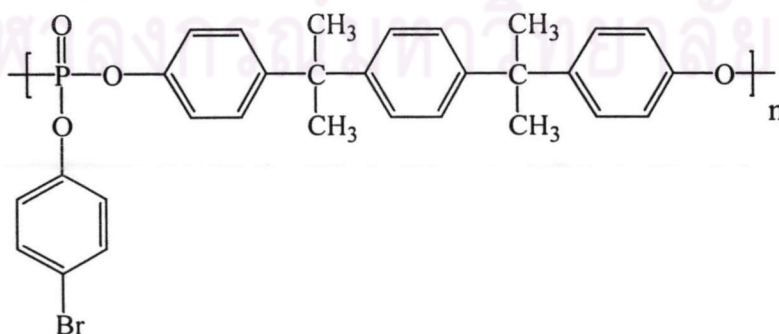
Preparation of poly(bisphenol P-1,3-*p*-bromophenylphosphate) (19d)



19d

Polymer **19d** was prepared by solution polycondensation method B. Bisphenol P-1,3 (6.93 g, 0.02 mol) was reacted with *p*-bromophenylphosphorodichloridate (**18**) (5.80 g, 0.02 mol) in the presence of triethylamine (7.0 mL, 0.05 mol) in dichloromethane (25 mL) for 1 h. Polymer **19d** was obtained as a white solid (8.90 g, 70%) with \overline{M}_w of 63,357 D. $^1\text{H-NMR}$ (200 MHz, CDCl_3) δ 1.57 (s, 12 H, CH_3), 6.91-7.11 (m, 14 H, Ar, ArOP), 7.39 (d, $^3J_{\text{HH}} = 8.7$ Hz, 2 H, ArOP); $^{31}\text{P-NMR}$ (202.48 MHz, CDCl_3 , $\{^1\text{H}\}$) δ -16.80; $^{13}\text{C-NMR}$ (50 MHz, CDCl_3 , $\{^1\text{H}\}$) δ 30.85 (CH_3), 42.79 (CCH_3), 118.57 (d, $J_{\text{CP}} = 1.9$ Hz), 119.41 (d, $^3J_{\text{CP}} = 4.8$ Hz), 121.96 (d, $^3J_{\text{CP}} = 4.9$ Hz), 124.49, 124.70, 127.74, 128.26, 132.84, 148.11 (d, $^2J_{\text{CP}} = 7.5$ Hz), 148.33 (d, $J_{\text{CP}} = 1.7$ Hz), 149.56 (d, $^2J_{\text{CP}} = 7.2$ Hz), 149.75; IR (KBr)/ cm^{-1} : 3060, 2965, 1646, 1600, 1504, 1384, 1315 (P=O), 1164 (POAr), 984 (POAr).

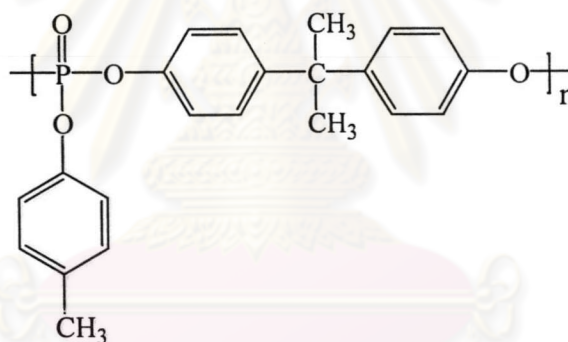
Preparation of poly(bisphenol P-1,4-*p*-bromophenylphosphate) (19e)



19e

Polymer **19e** was prepared by solution polycondensation method B. Bisphenol P-1,4 (6.93 g, 0.02 mol) was reacted with *p*-bromophenylphosphorodichloridate (**18**) (5.80 g, 0.02 mol) in the presence of triethylamine (7.0 mL, 0.05 mol) in dichloromethane (25 mL) for 1 h. Polymer **19e** was obtained as a white solid (6.71 g, 53%) with \overline{M}_w of 9,295 D. $^1\text{H-NMR}$ (200 MHz, CDCl_3) δ 1.60 (s, 12 H, CH_3), 7.05-7.19 (m, 14 H, Ar, ArOP), 7.40 (d, $^3J_{\text{HH}} = 8.7$ Hz, 2 H. ArOP); $^{31}\text{P-NMR}$ (202.48 MHz, CDCl_3 , $\{^1\text{H}\}$) δ -16.91; $^{13}\text{C-NMR}$ (50 MHz, CDCl_3 , $\{^1\text{H}\}$) δ 30.84 (CH_3), 42.28 (CCH_3), 118.61 (d, $J_{\text{CP}} = 1.4$ Hz), 119.44 (d, $^3J_{\text{CP}} = 4.8$ Hz), 122.00 (d, $^3J_{\text{CP}} = 4.8$ Hz), 126.17, 126.31 (d, $J_{\text{CP}} = 5.2$ Hz), 128.33, 132.85, 148.09 (d, $^2J_{\text{CP}} = 7.6$ Hz), 148.32 (d, $J_{\text{CP}} = 1.1$ Hz), 149.48 (d, $^2J_{\text{CP}} = 7.2$ Hz); IR (KBr)/ cm^{-1} ; 3047, 2965, 1641, 1602, 1504, 1384, 1315 (P=O), 1164 (POAr), 963 (POAr).

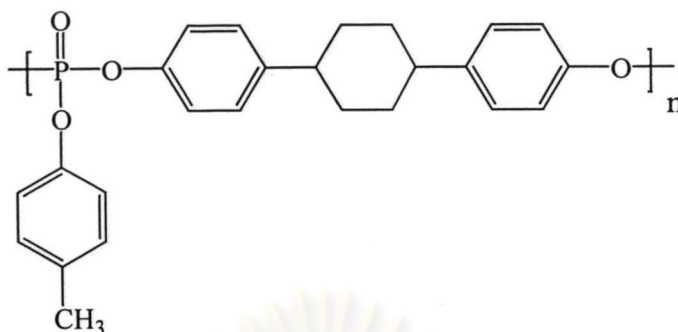
Preparation of poly(bisphenol A-*p*-methylphenylphosphate) (**20a**)



20a

Polymer **20a** was prepared by solution polycondensation method B. Bisphenol A (5.00 g, 21.9 mmol) was reacted with *p*-methylphenylphosphorodichloridate (**17**) (4.93 g, 21.9 mmol) in the presence of triethylamine (7.7 mL, 55.0 mmol) in dichloromethane (25 mL) for 1 h. Polymer **20a** was obtained as a white solid (5.16 g, 52%) with \overline{M}_w of 19,386 D. $^1\text{H-NMR}$ (200 MHz, CDCl_3) δ 1.59 (s, 6 H, CH_3), 2.27 (s, 3 H, CH_3Ar), 7.06-7.12 (m, 12 H, Ar, ArOP); $^{31}\text{P-NMR}$ (202.48 MHz, CDCl_3 , $\{^1\text{H}\}$) δ -16.45; $^{13}\text{C-NMR}$ (50 MHz, CDCl_3 , $\{^1\text{H}\}$) δ 20.70 (CH_3Ar), 30.92 (CH_3), 42.40 (CCH_3), 119.64 (d, $^3J_{\text{CP}} = 4.9$ Hz), 119.85 (d, $^3J_{\text{CP}} = 4.9$ Hz), 128.22, 130.31, 138.26 (d, $J_{\text{CP}} = 1.2$ Hz), 147.62 (d, $J_{\text{CP}} = 1.3$ Hz), 148.29 (d, $^2J_{\text{CP}} = 7.1$ Hz), 148.44 (d, $^2J_{\text{CP}} = 7.5$ Hz); IR (KBr)/ cm^{-1} ; 3039, 2965, 1649, 1604, 1504, 1384, 1315 (P=O), 1163 (POAr), 983 (POAr).

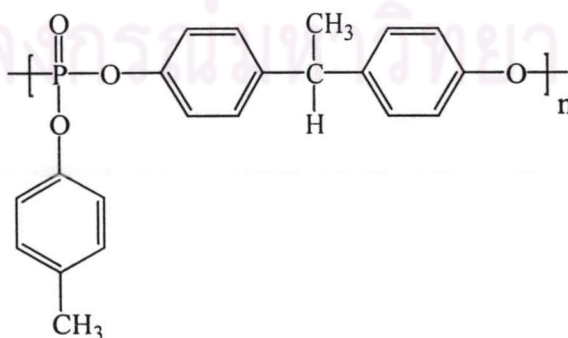
Preparation of poly(bisphenol C-*p*-methylphenylphosphate) (20b)



20b

Polymer **20b** was prepared by solution polycondensation method B. Bisphenol C (5.37 g, 0.02 mol) was reacted with *p*-methylphenylphosphorodichloridate (**17**) (4.5 g, 0.02 mol) in the presence of triethylamine (7.0 mL, 0.05 mol) in dichloromethane (25 mL) for 1 h. Polymer **20b** was obtained as a white solid (5.26 g, 63%) with \bar{M}_w of 12,895 D. $^1\text{H-NMR}$ (200 MHz, CDCl_3) δ 1.46 (s, 6 H, C_6H_{10}), 2.16 (s, 4 H, C_6H_{10}), 2.26 (s, 3 H, CH_3Ar), 7.00-7.18 (m, 12 H, Ar, ArOP); $^{31}\text{P-NMR}$ (202.48 MHz, CDCl_3 , $\{^1\text{H}\}$) δ -16.54; $^{13}\text{C-NMR}$ (50 MHz, CDCl_3 , $\{^1\text{H}\}$) δ 20.77 (CH_3Ar), 22.75, 26.23, 37.25, 45.60 (C_6H_{10}), 119.81 (d, $^3J_{\text{CP}} = 4.8$ Hz), 119.84 (d, $^3J_{\text{CP}} = 4.9$ Hz), 128.79, 130.29, 135.22 (d, $J_{\text{CP}} = 1.3$ Hz), 145.59, 148.17 (d, $^2J_{\text{CP}} = 7.5$ Hz), 148.28 (d, $^2J_{\text{CP}} = 7.5$ Hz); IR (KBr)/ cm^{-1} : 3064, 2935, 2890, 1643, 1604, 1504, 1454, 1475, 1382, 1315 (P=O), 1162 (POAr), 979 (POAr).

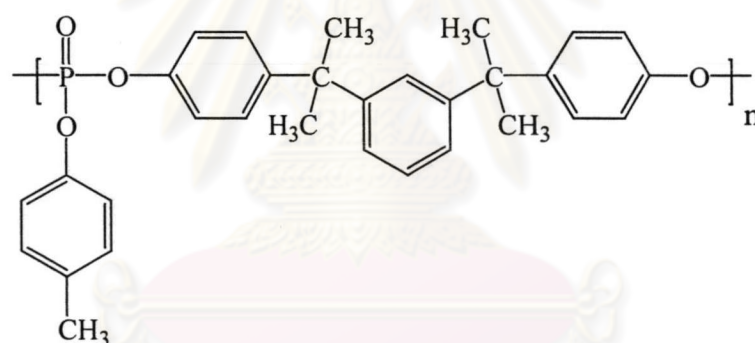
Preparation of poly(bisphenol E-*p*-methylphenylphosphate) (20c)



20c

Polymer **20c** was prepared by solution polycondensation method B. Bisphenol E (4.28 g, 0.02 mol) was reacted with *p*-methylphenylphosphorodichloridate (**17**) (4.5 g, 0.02 mol) in the presence of triethylamine (7.0 mL, 0.05 mol) in dichloromethane (25 mL) for 1 h. Polymer **20c** was obtained as a white solid (4.75 g, 54%) with \overline{M}_w of 94,817 D. $^1\text{H-NMR}$ (200 MHz, CDCl_3) δ 1.54 (d, $^3J_{\text{HH}} = 7.18$ Hz, 3 H, CH_3), 2.27 (s, 3 H, CH_3Ar), 4.07 (q, $^3J_{\text{HH}} = 7.30$ Hz, 1 H, CH), 7.05-7.15 (m, 12 H, Ar, ArOP); $^{31}\text{P-NMR}$ (202.48 MHz, CDCl_3 , $\{^1\text{H}\}$) δ -16.49; $^{13}\text{C-NMR}$ (50 MHz, CDCl_3 , $\{^1\text{H}\}$) δ 20.78 (CH_3Ar), 22.01 (CH_3), 43.46 (CHCH_3), 119.84 (d, $^3J_{\text{CP}} = 4.8$ Hz), 120.05 (d, $^3J_{\text{CP}} = 4.8$ Hz), 128.92, 130.31, 135.25 (d, $J_{\text{CP}} = 1.3$ Hz), 143.32 (d, $J_{\text{CP}} = 1.0$ Hz), 148.27 (d, $^2J_{\text{CP}} = 7.6$ Hz), 148.76 (d, $^2J_{\text{CP}} = 7.2$ Hz); IR (KBr)/ cm^{-1} ; 3066, 2965, 2873, 1646, 1608, 1521, 1454, 1384, 1321 (P=O), 1157 (POAr), 917 (POAr).

Preparation of poly(bisphenol P-1,3-*p*-methylphenylphosphate) (**20d**)

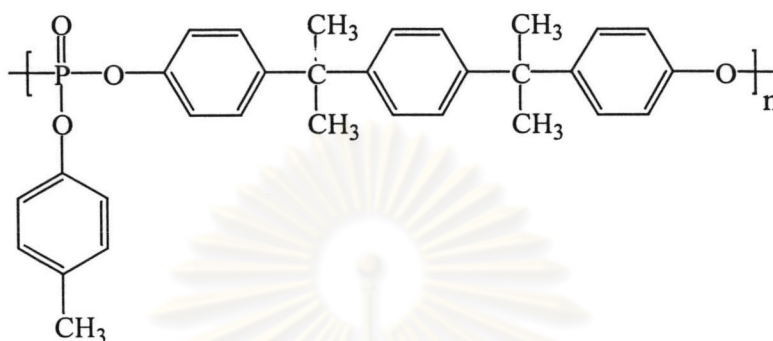


20d

Polymer **20d** was prepared by solution polycondensation method B. Bisphenol P-1,3 (3.47 g, 0.01 mol) was reacted with *p*-methylphenylphosphorodichloridate (**17**) (2.25 g, 0.01 mol) in the presence of triethylamine (4.2 mL, 0.03 mol) in dichloromethane (25 mL) for 1 h. Polymer **20d** was obtained as a white solid (3.93 g, 69%) with \overline{M}_w of 24,408 D. $^1\text{H-NMR}$ (200 MHz, CDCl_3) δ 1.57 (s, 12 H, CH_3), 2.27 (s, 3 H, CH_3Ar), 6.93 (d, $^3J_{\text{HH}} = 8.42$ Hz, 2 H, Ar CH_3), 7.03-7.16 (m, 14 H, Ar, ArOP); $^{31}\text{P-NMR}$ (202.48 MHz, CDCl_3 , $\{^1\text{H}\}$) δ -16.40; $^{13}\text{C-NMR}$ (50 MHz, CDCl_3 , $\{^1\text{H}\}$) δ 20.78 (CH_3Ar), 30.87 (CH_3), 42.79 (CCH_3), 119.50 (d, $^3J_{\text{CP}} = 4.6$ Hz), 119.86 (d, $^3J_{\text{CP}} = 4.7$ Hz), 124.49, 124.70, 127.71, 128.19, 130.28, 135.17, 148.09, 148.17 (d,

$^2J_{CP} = 7.8$ Hz), 148.33 (d, $^2J_{CP} = 7.3$ Hz), 149.83; IR (KBr)/ cm^{-1} ; 3068, 2965, 1649, 1602, 1506, 1450, 1385, 1315 (P=O), 1164 (POAr), 979 (POAr).

Preparation of poly(bisphenol p-1,4-p-methylphenylphosphate) (20e)



20e

Polymer **20e** was prepared by solution polycondensation method B. Bisphenol P-1,4 (3.47 g, 0.01 mol) was reacted with *p*-methylphenylphosphorodichloridate (**17**) (2.25 g, 0.01 mol) in the presence of triethylamine (4.2 mL, 0.03 mol) in dichloromethane (25 mL) for 1 h. Polymer **20e** was obtained as a white solid (3.21 g, 56%) with \overline{M}_w of 14,204 D. $^1\text{H-NMR}$ (200 MHz, CDCl_3) δ 1.60 (s, 12 H, CH_3), 2.27 (s, 3 H, CH_3Ar), 7.04-7.18 (m, 16 H, Ar, ArOP); $^{31}\text{P-NMR}$ (202.48 MHz, CDCl_3 , $\{^1\text{H}\}$) δ -16.42; $^{13}\text{C-NMR}$ (50 MHz, CDCl_3 , $\{^1\text{H}\}$) δ 20.83 (CH_3Ar), 30.88 (CH_3), 42.28 (CCH_3), 119.55 (d, $^3J_{CP} = 4.8$ Hz), 119.91 (d, $^3J_{CP} = 4.8$ Hz), 126.40, 128.27, 130.32, 135.21 (d, $J_{CP} = 1.3$ Hz), 147.51, 148.07, 148.17 (d, $^2J_{CP} = 7.5$ Hz), 148.32 (d, $^2J_{CP} = 7.1$ Hz); IR (KBr)/ cm^{-1} ; 3035, 2965, 1646, 1603, 1504, 1387, 1315 (P=O), 1164 (POAr), 968 (POAr).

3.7 General procedure for flammability determination (limiting oxygen index; LOI) of polyphosphonate and polyphosphate esters.

The specimen was prepared by dissolving 1.5-2.0 g of the polymer in 9 mL toluene. The polymer solution was poured into a mold (52 mm \times 140 mm \times 1 mm) and was left in air and vacuum to dryness.

In a flammability test,¹³ the specimen was clamped vertically approximately in the center of the column with the top of the specimen positioning at least 100 mm below the top of the open column. The initial concentration of oxygen was selected

based on prior experience with similar materials. The initial set point for LOI value was 25 (The reported LOI value of poly(bisphenol A-phenylphosphonate) was 28).⁹ The initial concentration of oxygen was purged through the column for at least 1 minute. The entire top of the specimen was ignited with the ignition lamp until the specimen was well lit and then the ignition flame was removed. If the flame at the specimen extinguished, the amount of input oxygen would have to be increased by a 0.3 increment. The method was repeated until the specimen continued to burn for at least 100 mm long. The percentage of oxygen purged into the apparatus was then taken as the LOI.

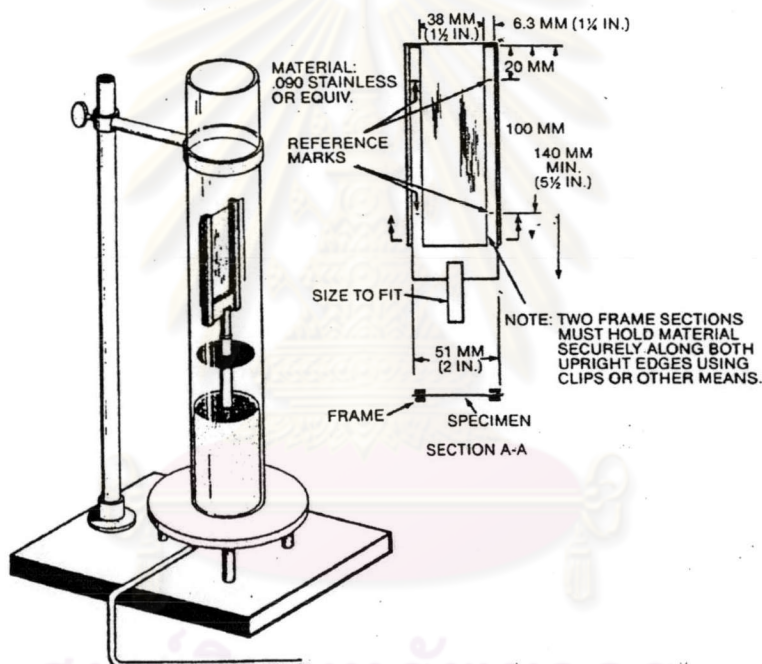


Figure 3.3 Apparatus for limiting oxygen index (LOI) determination