CHAPTER IV
# RESULTS AND DISCUSSION

The objective of this research was to synthesize polyphosphates and polyphosphonates, possessing flame retarding properties, with highest possible weight average molecular weight ($\overline{M}_w$). These synthesized compounds were investigated for their structures, and thermal properties such as glass transition temperature (T_g), degradation temperature (T_d), and percent char yield. In addition, limiting oxygen index (LOI) was determined and used as a preliminary indicating factors for flame retarding properties of the synthesized polymers. Correlations between polymer structures, thermal properties, and/or percent phosphorus versus polymer flammability have been made.

4.1 Polyphosphonates and polyphosphates

The preparation of a series of polyphosphonates (**16a-16e**) or polyphosphates (**19a-19e, 20a-20e**) was carried out by means of solution polycondensation reaction of appropriate bisphenols with phenylphosphonic dichloride (PPDC) or an appropriate *p*-substituted-phenylphosphorodichloridate in the presence of an acid acceptor under nitrogen atmosphere at reflux. This synthetic method was generally used to synthesize polyphosphonates and polyphosphates since this method is not complicated and gives products in moderate to high $\overline{M}_w$. The general equations are shown in Scheme 4.1

This solution polycondensation is known to be reversible and it generates hydrochloric acid as a by product, so the use of an acid acceptor is necessary. In this case triethylamine was selected as an acid acceptor. In addition, this reaction is moisture sensitive, therefore, the reactions were carried out in an anhydrous medium under a nitrogen atmosphere. Among several methods used in this work, it was found that method B was the best one (*vide infra*).

16

17, X = CH₃
18, X = Br

19, X = Br
20, X = CH₃

a, Ar =

b, Ar =

c, Ar =

d, Ar =

e, Ar =
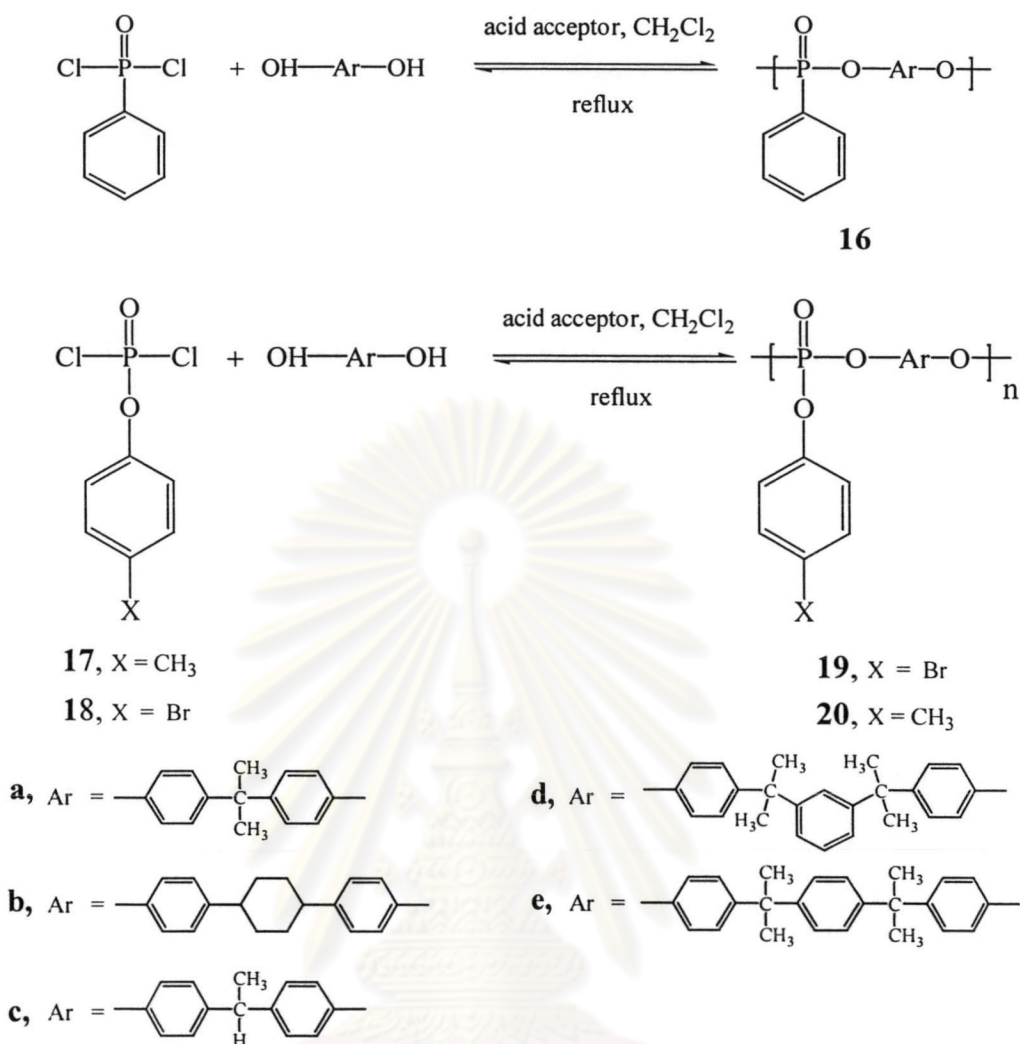
Scheme 4.1 The synthesis of target polyphosphonates and polyphosphates

4.2 *p*-Substituted phenylphosphorodichloridate

The preparation of selected *p*-substituted phenylphosphorodichloridate was performed utilizing the condensation reaction between phosphorus oxychloride ($O=PCl_3$) and an appropriate phenol under a nitrogen atmosphere and suitable reflux time. The general equation is shown in Scheme 4.2.

17, X = CH₃
18, X = Br
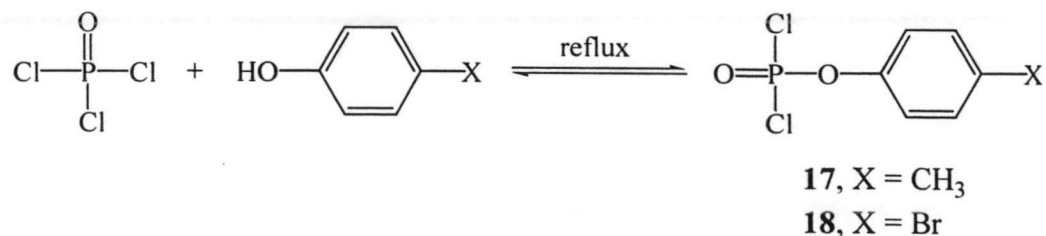
Scheme 4.2 The synthesis of *p*-substituted phenylphosphorodichloridate

In this case the amount of phosphorus oxychloride was used in 3 folds higher than that of a selected phenol because this reaction is known to be reversible. The usual method is to drive the equation to the right by using excess amounts of phosphorus oxychloride. Phosphorus oxychloride was then removed by distillation several times under reduced pressure.

In this work, five polyphosphonates (**16a-16e**), ten polyphosphates (**19a-19e**, **20a-20e**) and two *p*-substituted phenylphosphorodichloridates (**17**, **18**) were synthesized.

4.3 Spectroscopic data of polyphosphates and polyphosphonates

In general, IR spectra of all the polymers were similar except in the absorption region of the moiety derived from bisphenols. The strong absorption around 1180 and 960 cm^{-1} corresponds to P-O-C (aromatic) stretching. The absorption around 1300 cm^{-1} is due to P=O stretching and the characteristic aromatic C-H stretches around 3060 cm^{-1}. Olefinic C=C ring stretching bands at 1600 and 1460 cm^{-1} were seen for all polymers. This is characteristic for phosphate ester compounds.

^{1}H-NMR spectral data of all the polymers are summarized in Table 4.1; aromatic protons of the main chain and the pendent phenyl groups resonating in the region of 7.0 to 8.0 ppm appear as broad multiplets. Coupling of proton to proton and proton to phosphorus were also detected, $^3J_{HP}$ = 13.7-14.0 Hz, $^3J_{HH}$ = 6.6-7.3 Hz.

^{13}C-NMR spectra of the polymers show the resonance corresponding to all the carbons of the given polymer structures. The carbon signals of methyl groups appear around 20 and 30 ppm, methylene groups of cyclohexane appear around 22 to 45 ppm, methine groups appear around 43 ppm, quaternary carbons appear around 43 ppm and peaks of aromatic carbons show in the region of 119 to 149 ppm. Carbon-phosphorus couplings were detected, $^1J_{CP}$ = 10.3-10.4 Hz, $^2J_{CP}$ = 5.4-7.7 Hz, $^3J_{CP}$ = 4.3-4.9 Hz.

Each ^{31}P NMR spectrum of all of these polymers shows only one signal, corresponding to the P in the repeating unit. Phosphorus signals of polyphosphonates appear around 12.4 to 12.5 ppm and phosphorus signals of polyphosphates show in the region of 16.4 to 16.8 ppm. The substitution on the phenyl ring of polyphosphates does not cause any significant change in the ^{31}P chemical shifts values, presumably because of fact that the substitution being more than five bonds away from the phosphorus atom.[24]

Table 4.1 ^{1}H-NMR spectral data of polymers

Polymer	Chemical shift values (ppm)			
	CH$_3$ (methyl group)	C$_6$H$_{10}$ (cyclohexane)	CH (methine group)	Aromatic
16a	1.5	-	-	7.0-8.0
16b	-	1.4, 2.1	-	6.9-7.9
16c	1.5	-	4.0	6.9-7.9
16d	1.5	-	-	6.9-7.9
16e	1.6	-	-	7.0-8.0
19a	1.6	-	-	7.0-7.4
19b	-	1.4, 2.1	-	7.0-7.4
19c	1.5	-	4.0	7.0-7.4
19d	1.6	-	-	6.9-7.4
19e	1.6	-	-	7.0-7.4
20a	1.6, 2.2	-	-	7.0-7.2
20b	2.2	1.4, 2.1	-	7.0-7.2
20c	1.5, 2.2	-	4.0	7.0-7.2
20d	1.6, 2.3	-	-	6.9-7.2
20e	1.6, 2.2	-	-	7.0-7.2

4.4 Factors affecting $\overline{M}_W$ of polyphosphonates and polyphosphates

In general the factors which affect the $\overline{M}_W$ of synthetic polymers include method of polymerization, ratio of the monomers, concentration of the monomers, volume of acid acceptor, and reflux time. Thus, effects of these factors were studied to find an optimized condition to achieve high molecular weight polyphosphonates and polyphosphates.

4.4.1 Effect of monomer concentration.

In order to determine the effect of monomer concentration, solutions of monomers with varying amounts of solvent were used in the polymerization. Methods A and B were used and the results were summarized in Table 4.2

Table 4.2 The $\overline{M}_w$ of polyphosphonates as a function of solvent volumes in solution polycondensation methods A and B.

Method	Bisphenol	Bisphenol solution		PPDC solution		$\overline{M}_w$ (D)
		Bisphenol (mol)	solvent (mL)	PPDC (mol)	Solvent (mL)	
A	Bisphenol P-1,4[a]	0.01	15	0.01	3	5,035
		0.01	40	0.01	10	3,190
		0.01	20	0.01	10	7,183
		0.01	50	0.01	20	2,388
B	Bisphenol P-1,4[b]	0.01	30	0.01	10	11,906
		0.01	20	0.01	5	12,325
		0.01	55	0.01	15	7,090
	Bisphenol A[c]	0.02	25	0.02	10	13,407
		0.02	25	0.02	5	14,797
	Bisphenol E[b]	0.01	30	0.01	10	8,476
		0.01	20	0.01	5	15,275

All reactions were refluxed for 6 h. [a] NEt_3 = 0.02 mol; [b] NEt_3 = 0.03 mol; [c] NEt_3 = 0.06 mol.

From Table 4.2, it was clearly seen that the $\overline{M}_w$ of polyphosphonates increased when the volume of solvent used decreased. It is obvious that the probability of reaction increases when the concentration of reactant increases.

4.4.2 Effect of monomer ratio.

The effect of ratio of monomers used in polymerization to $\overline{M}_w$ of the polyphosphonates was examined by using varying ratios between amount of the starting bisphenols and PPDC in solution polycondensation methods A and B, shown in Table 4.3

Table 4.3 The result of $\overline{M}_w$ of polyphosphonate where the ratio of monomers were varied.

Method	Bisphenol	Bisphenol solution		PPDC solution		Ratio of	$\overline{M}_w$
		Bisphenol (mol)	Solvent (mL)	PPDC (mol)	Solvent (mL)	BIS P-1,4/ PPDC	(D)
A	Bisphenol P-1,4[a]	0.010	20	0.010	10	50/50	4,938
		0.008	20	0.012	10	40/60	4,810
		0.012	20	0.080	10	60/40	3,922
		0.060	20	0.014	10	30/70	3,644
		0.014	20	0.006	10	70/30	3,439
B	Bisphenol P-1,4[b]	0.010	30	0.010	10	50/50	11,906
		0.009	30	0.011	10	45/55	8,733
	Bisphenol A[c]	0.022	25	0.022	10	50/50	13,407
		0.022	25	0.028	10	44/56	8,855

[a] NEt_3 was used in a slight excess ; [b] NEt_3 = 0.03 mol; [c] NEt_3 = 0.06 mol. All reactions were reflux for 6 h.

From Table 4.3, it can be seen that the $\overline{M}_w$ of polyphosphonate product depends on the ratio of amount of monomer reactants. When the monomer ratio of 1:1 was used, highest $\overline{M}_w$ of polyphosphonate was achieved. This is because the reaction is a step-reaction polymerization, the esterification reaction occurs anywhere in the monomer matrix where two monomer molecules collide. Once the ester has formed (with loss of a water molecule), both ends of the newly formed dimer, can react further by virtue of its still-reactive hydroxyl and carboxyl groups. The net effect is that monomer molecule are consumed rapidly without any concomitant large increase in molecular weight. Therefore, using the 1:1 ratio of monomers led to complete polymerization and highest $\overline{M}_w$ of polymer were obtained.

4.4.3 Effect of reflux time.

Initially, in most reactions products with relatively low molecular weight were obtained. A series of reactions carried out at different periods of reflux time in order to find an optimum reflux period were examined and the results are summarized in Table 4.4.

Table 4.4 The $\overline{M}_W$ of polyphosphonate obtained by using different reflux time.

| Method | Bisphenol | Bisphenol solution | | PPDC solution | | Reflux time (h) | $\overline{M}_W$ (D) |
		Bisphenol (mol)	Solvent (mL)	PPDC (mol)	Solvent (mL)		
A	Bisphenol	0.01	40	0.01	10	6	3,190
	P-1,4[a]	0.01	40	0.01	10	24	2,981
B	Bisphenol	0.01	30	0.01	10	1	11,906
	P-1,4[a]	0.01	30	0.01	10	12	6,015
	Bisphenol	0.02	25	0.02	10	1	13,407
	A[b]	0.02	25	0.02	10	6	12,155
	Bisphenol	0.01	20	0.01	5	1	10,556
	E[a]	0.01	20	0.01	5	5	10,962

[a] NEt_3 = 0.03 mol; [b] NEt_3 = 0.06 mol

One might predict that increasing reflux time would result in a more complete reaction, hence, higher molecular weight. Apparently, no significant change in the molecular weight of the polyphosphonates was detected. In some cases, a long period of reflux resulted in even a lower $\overline{M}_W$. It can be seen that only 1 h of reflux time is adequate for such a polymerization as long as an appropriate amount of triethylamine is added.

As discussed so far, solution polycondensation method B, where dichloromethane was used as a solvent, yield the best results. Dichloromethane is less hygroscopic than tetrahydrofuran, therefore, the reaction mixture would remain anhydrous for a longer period of time. The best conditions, thus far, leading to highest $\overline{M}_W$ polyphosphonates include using 0.01 mol of bisphenol in 20 mL CH_2Cl_2, 0.01 mol of PPDC in 5 mL CH_2Cl_2, 0.03 mol NEt_3, and an hour of reflux time.

Representative data for best results obtained in the synthesis of each polyphosphonates are illustrated in Table 4.5.

Table 4.5 The best results on $\overline{M}_W$ of polyphosphonates synthesized by using optimized condition.

Polyphosphonate	$\overline{M}_W$ (D)	Polydispersity
16a	14,346	2.07
16b	6,648	2.45
16c	15,275	1.63
16d	31,269	1.79
16e	11,906	3.32

1 h for reflux time for each reaction. [a]0.8 M of bisphenol A in CH_2Cl_2, 4.4 M of PPDC in CH_2Cl_2, 0.055 mol NEt_3; [b] 0.5 M of bisphenol in CH_2Cl_2, 2 M of PPDC in CH_2Cl_2, 0.03 mol NEt_3.

It can be seen that for each polyphosphonate except for the polymer **16b**, $\overline{M}_W$ higher than 10,000 D was obtained when current best conditions were employed. Since the concentration of monomer has been shown to give more effect on the polycondensation than other factors, an adjustment to fine-tune the conditions for polycondensation of **16b** was carried out in an attempt to obtain **16b** with molecular weight higher than 10,000 D. Representative data are shown in Table 4.6.

Table 4.6 The result of $\overline{M}_W$ of polyphosphonate **16b** as a function of monomer concentration.[a]

Bisphenol C solution		PPDC solution		NEt_3 (mol)	$\overline{M}_W$ (D)
Bisphenol C (mol)	CH_2Cl_2 (mL)	PPDC (mol)	CH_2Cl_2 (mL)		
0.01	20	0.01	5	0.030	6,648
0.02	20	0.02	5	0.046	8,481

[a] 1 h of reflux time.

As shown, the best $\overline{M}_W$ of polymer **16b** obtain still falls short of 10,000 D. An alternative method by Liaw, D.J.[7] was utilized in an attempt to improve the $\overline{M}_W$

of **16b**. Thus polybisphenol C / PPDC was synthesized by solution polycondensation method C. Polymers **16c** and **16e** were also synthesized by method C for comparison in order to validate the method itself (Table 4.7).

Table 4.7 The result of $\overline{M}_W$ of polyphosphonate synthesized by solution polycondensation method C.[a]

Bisphenol	Bisphenol solution		PPDC solution		NEt₃ (mol)	$\overline{M}_W$ (D)
	Bisphenol (mol)	CH₂Cl₂ (mL)	PPDC (mol)	CH₂Cl₂ (mL)		
Bisphenol E	0.01	25	0.01	5	0.030	7,761
Bisphenol p-1,4	0.02	25	0.02	5	0.057	7,205
Bisphenol C	0.02	30	0.02	10	0.046	6,646

[a] 4 h of reflux time.

Clearly, solution polycondensation method B proves far more superior than method C. Unfortunately, higher $\overline{M}_W$ of **16b** could not be obtained even when method B was employed in the synthesis. Further attempts had not been made and polymer **16b** with $\overline{M}_W$ of 8,481 D was used as a sample to investigate its thermal properties. Table 4.8 summarizes the $\overline{M}_W$ of synthesized polyphosphonates of which batch was investigated for thermal properties and flammability.

Table 4.8 The highest $\overline{M}_W$ of each synthesized polyphosphonates.

Polyphosphonate	$\overline{M}_W$ (D)	Polydispersity
16a	14,346	2.07
16b	8,481	2.09
16c	15,275	1.63
16d	31,269	1.79
16e	11,906	3.32

Thus far, in the process of optimization, it was found that the best condition for synthesis of polyphosphonates was using solution polycondensation method B, 0.01 mol bisphenol in 20 mL CH₂Cl₂, 0.01 mol PPDC in 5 mL CH₂Cl₂, 0.03 mol NEt₃

and an hour of reflux time. Therefore, a series of polyphosphates were synthesized from selected bisphenols with appropriated *p*-substituted phenylphosphoro-dichloridate by solution polycondensation method B using the optimized condition of polyphosphonates (Table 4.9).

Table 4.9 The highest $\overline{M}_w$ of each synthesized polyphosphates

Polyphosphophate	$\overline{M}_w$ (D)	Polydispersity
19a	9,332	1.69
19b	14,892	1.56
19c	16,390	2.21
19d	63,357	1.85
19e	9,295	2.45
20a	19,386	1.74
20b	12,895	1.63
20c	94,817	3.32
20d	24,408	1.71
20e	14,204	2.03

4.5 Determination of thermal properties of polyphosphonates and polyphosphates

In this research, thermal properties of all synthetic polymers were investigated to study a relationship between their structure and their thermal properties. The thermal behavior of all polymers was evaluated by of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA results of polyphosphates and polyphosphonates are summarized in Table 4.10. A representative thermogram of a polyphosphonate with a 10 °C min^{-1} heating rate in nitrogen is shown in Figure 4.1. The degradation of all polymers occurs as a two-step process. This phenomenon was also found by Kishore *et. al.*[19] The first step was reported as the formation of various phenols and phosphates with some amount of char remaining, which subsequently carbonizes in the second step.
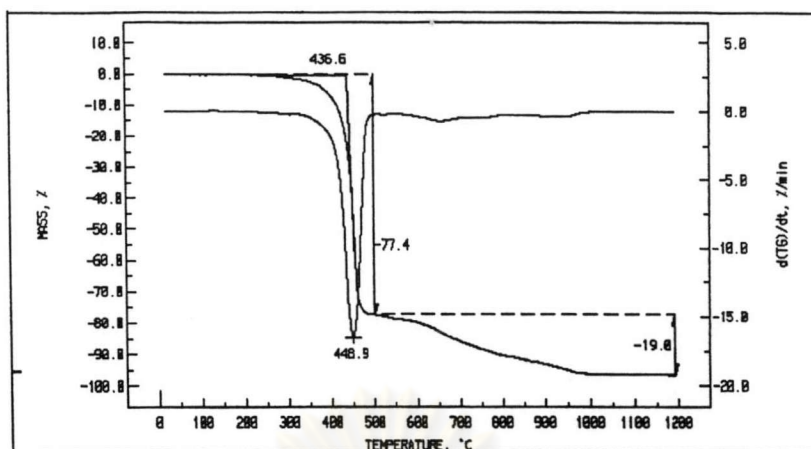
Figure 4.1 Thermogravimatric trace of polyphosphate **20b** in air.

Table 4.10 Thermal properties of synthetic polyphosphates and polyphosphonates

Polymer	$T_d{}^a$ (^{o}C)	Percent char yield (700°C)	$T_g{}^b$ (^{o}C)
polyphosphonate **16a**	476.0	22	99.0
polyphosphonate **16b**	466.8	13	120.2
polyphosphonate **16c**	484.5	35	94.4
polyphosphonate **16d**	482.2	18	84.9
polyphosphonate **16e**	465.2	15	113.7
polyphosphate **19a**	448.8	18	72.3
polyphosphate **19b**	445.4	12	85.4
polyphosphate **19c**	462.9	26	66.2
polyphosphate **19d**	466.4	13	64.9
polyphosphate **19e**	447.7	16	85.6
polyphosphate **20a**	470.0	22	61.1
polyphosphate **20b**	448 9	13	76.3
polyphosphate **20c**	494.4	24	55.4
polyphosphate **20d**	469.4	17	54.9
polyphosphate **20e**	436.7	13	80.4

^{a}TGA conducted at a heating rate of 10 ^{o}C min^{-1} in air

^{b}DSC analysis conducted at a heating rate of 10 ^{o}C min^{-1} in nitrogen

From the data in Table 4.10, the polyphosphates and polyphosphonates exhibited residual masses of 13% and 30% at 700 ^{o}C in air. The comparison of T_d values (^{o}C) and % char at 700 ^{o}C of all polymers was made by plotting T_d values (^{o}C) and % char at 700 ^{o}C of each synthesized polymer as shown in Figure 4.2.
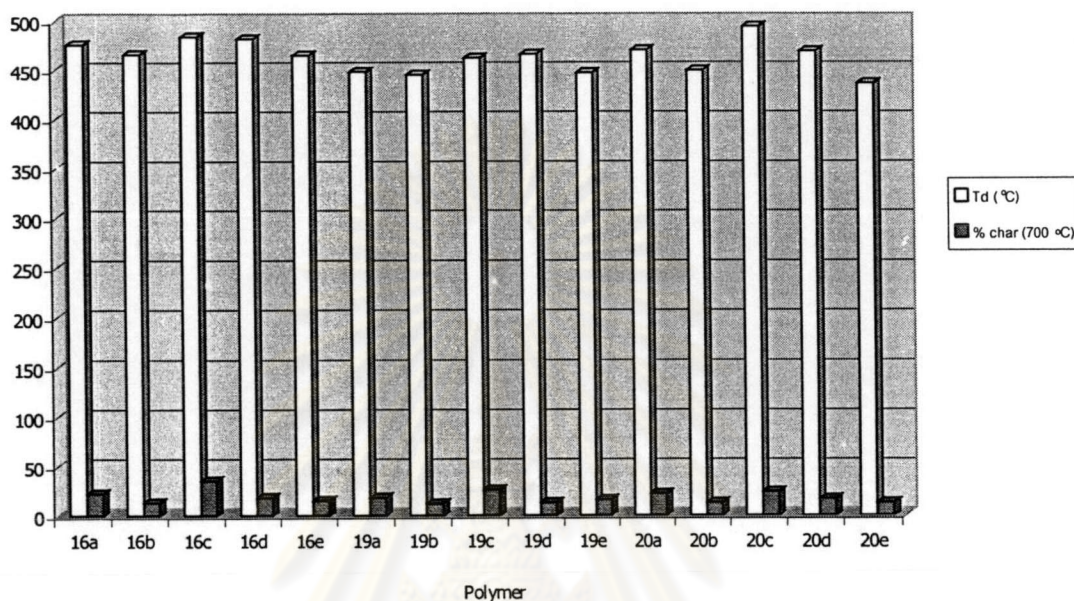
Figure 4.2 The comparison T_d and % char yield of polyphosphonates and polyphosphates.

From Figure 4.2, polymers **16c, 19c, 20c** containing high %P, showed higher thermal degradation temperatures and higher % char yields at 700 ^{o}C than the other polymers in the same group. Polymers **19a-19e**, containing bromine atoms, had a low thermal degradation temperatures. This result may be explained by the fact that hydrogen bromide gas is easily evolved from bromine-containing polymers during the thermal degradation process.[25]

In Table 4.10, the polyphosphates and polyphosphonates had glass transition temperatures between 80 and 114 ^{o}C. The comparison of T_g values of polyphosphonates and polyphosphates is as shown in Figure 4.3.
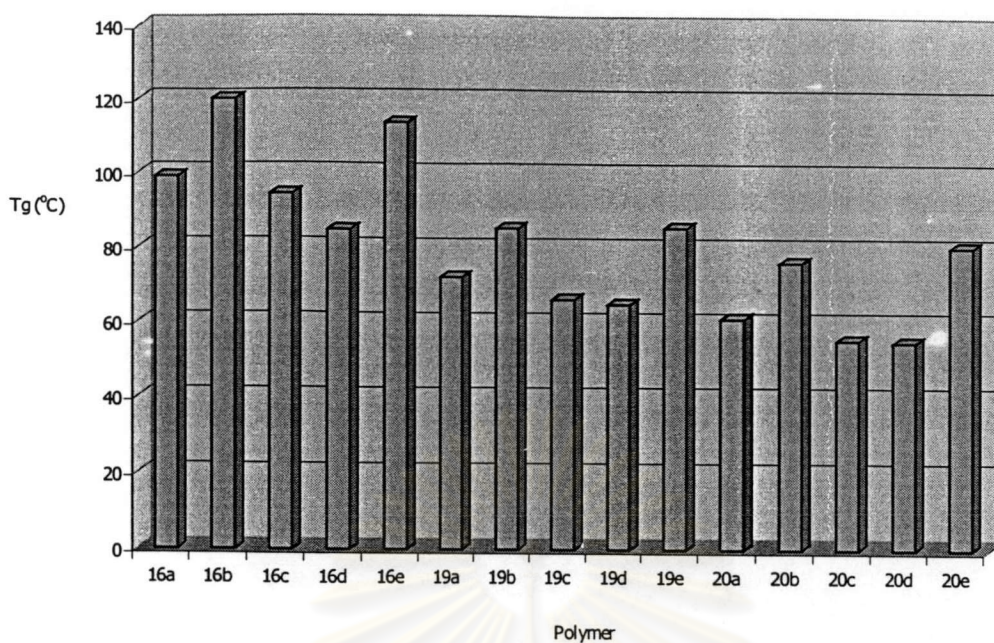
Figure 4.3 The comparision T_g (°C) of polyphosphonates and polyphosphates

From Figure 4.3, polymer **16b**, **16e**, **19b**, **19e**, **20b**, **20e** showed higher glass transition temperatures than other polymers in the same group. In addition, as a whole, T_g values of polyphosphate group are higher than those of the polyphosphonate group. It is suggestive that a decrease in chain flexibility, i.e., higher rigidity, would result in an increased glass transition temperature. In addition, a comparison between T_g values of polyphosphates synthesized from *p*-methyl phenylphosphorodichloridate and *p*-bromophenylphosphorodichloridate shows that the former gave lower T_g values than that of the latter. The rationale is based on a suggestion that bromine substitution on aromatic rings results in an increase in steric hindrance which help decreasing chain flexibility.

4.6 Determination of flame retarding property of synthesized polymers.

The study flame retarding property of synthetic polyphosphonates and polyphosphates was done by studying the relationship between limiting oxygen index (LOI) values as a function of the percentage of phosphorus (percent P) in the polymers. The data on LOI and percent P of the polymers are shown in Table 4.11. The LOI values of the polyphosphonates and polyphosphates generally fall in the range of 27 and 40. These polymers show higher LOI values and presumably a higher

degree of flame retardancy compared with commercial polypropylene (LOI =16) and polyethylene (LOI = 17).

Table 4.11 The LOI value and percent P of polyphosphonates and polyphosphates

Polyphosphophonate and Polyphosphates	LOI value	Percent P
polyphosphonate **16a**	28.0	8.86
polyphosphonate **16b**	-[a]	7.95
polyphosphonate **16c**	34.3	9.23
polyphosphonate **16d**	26.4	6.62
polyphosphonate **16e**	26.2	6.62
polyphosphate **19a**	32.9	6.97
polyphosphate **19b**	34.5	6.39
polyphosphate **19c**	40.8	7.19
polyphosphate **19d**	36.4	5.51
polyphosphate **19e**	37.1	5.51
polyphosphate **20a**	27.2	8.16
polyphosphate **20b**	30.4	7.38
polyphosphate **20c**	34.6	8.47
polyphosphate **20d**	33.2	6.22
polyphosphate **20e**	32.8	6.22

[a]Not characterized.

A plot of LOI values as a function of percent phosphorus of all polymers in each group is shown in Figure 4.4.
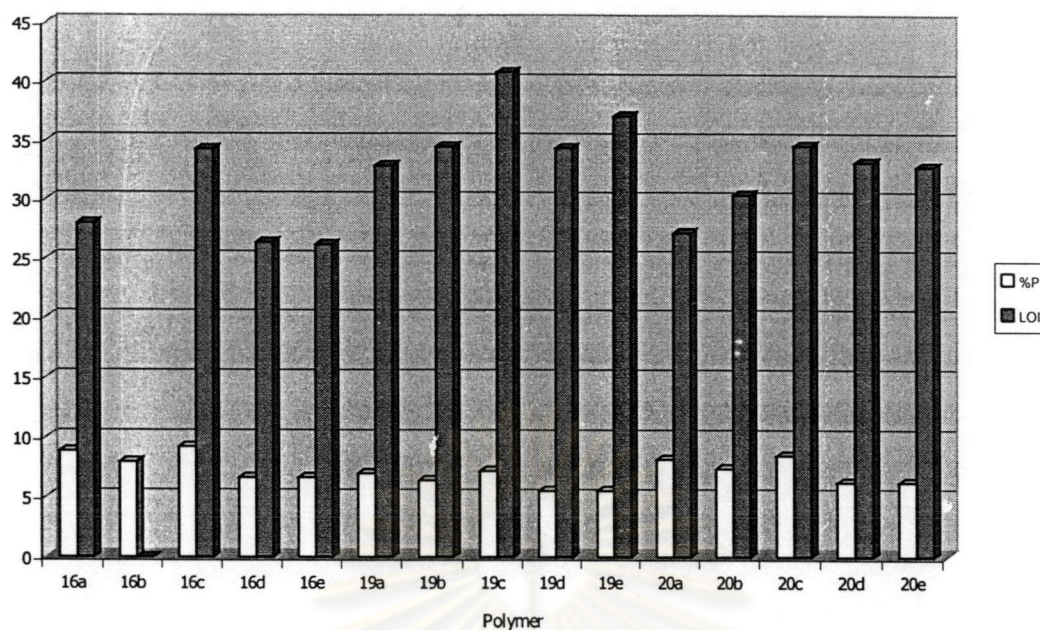
Figure 4.4 The comparison of LOI value of all synthetic polymers

As illustrated, the LOI values of polymers **16c**, **19c**, **20c** (each possessing highest phosphorus percentage) are highest within the same group (**16**, **19**, **20**). These results suggest a trend of a correlation between LOI and percent P values. The polymers containing high percent P, apparently, lead to high LOI values. In addition polymers **19a-19e** possess higher LOIs than other polymers (**16a-16e**, **20a-20e**). These results show that the flame retardancy of the polyphosphates is considerably increased by the introduction of bromine into the polyphosphates.[26]