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Synthesis and characterization of new organosoluble polyaspartimides containing phosphorus

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Abstract

Novel polyaspartimides were successfully synthesized via Michael addition reactions involving phosphorus-containing diamines and bismaleimides as monomers and using *p*-toluenesulfonic acid and *N*-*N*-dimethylacetamide as a catalyst and a solvent, respectively. The yields of the polymerization and the molecular weights and inherent viscosities of the polymers increased with the increasing monomers' concentrations, with an upper limit of 0.92 mol/l. All of the obtained polymers were soluble in organic solvents and showed high glass transition temperatures of 227–256 °C, good thermal stability of 360–427 °C, high char yields of 53–64% in nitrogen and 25–46% in air at 700 °C. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Bismaleimide (BMI) is one of the important high performance thermosetting polymers for applications in advanced composites, electronics, and aerospace. The maleic double bonds in BMIs can undergo facile thermal addition polymerization to result in highly crosslinked and brittle polyimides [1,2]. On the other hand, Michael addition of primary or secondary diamines to BMIs was also usually used to effect chain extension prior to thermal curing [3–5], to reduce the polymers' crosslinking density and brittleness. Moreover, with proper feeding ratios of the reactants, using nucleophilic difunctional reagents and BMIs can form linear, high-molecular-weight polyimides [6]. Diamines have particularly been used in the above-mentioned reactions to prepare linear polyaspartimides [7–10]. As it has been reported, these polybismaleimides and polyaspartimides have shown more facile properties in processing than condensation polyimides [9].

In contrast to polyimides' excellent thermal, mechanical, and electrical properties, their low solubility and poor processibility limit their extensive application. Therefore, many efforts were done to prepare organosoluble polyimides [11–14]. The same defect of poor solubility was also countered with high-molecular-weight polyaspartimides. For improving the flaw of polyaspartimides, Liaw et al. [10] incorporated flexible units and bulky substituents into polyaspartimides, to improve the polymers' organosolubility. However, diamines with complex synthesis routes were involved in the report to increase the difficulty in scaling production. In our previous study [15], a phosphorus-containing bismaleimide, 3,3′-bis(maleimidophenyl)-phenylphosphine oxide (BMPPPO), was prepared to show good organosolubility, low melting point, and high thermal stability. Other reports also indicated that incorporating polar and bulky phosphorus-containing groups into polymers could significantly improve their solubility [16–18]. Therefore, utilizing phosphorus-containig diamines and bismaleimide, it is of interest to prepare phosphorus-containing polyaspartimides with excellent processing properties.

2. Experimental

2.1. Materials

9,10-Dihydro-oxa-10-phosphaphenanthrene-10-oxide (DOPO, I) from ADD APT Chemicals AG, The Netherlands, was recrystallized from tetrahydrofuran prior to use.

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4,4′-Diaminobenzophenone (DABP, from Aldrich Co.) was used as received. 4,4′-Bismaleimidodiphenylmethane (BMDM), bis(3-ethyl-5-methyl-4-maleimidophenyl)methane (BEMM), and 4,4′-diaminodiphenylmethane (DDM) from TCI Co. were used as received. *p*-Toluenesulfonic acid (*p*-TSA) from TCI Co. was used as a catalyst for Michael addition reaction. *N*-*N*-Dimethylacetamide (DMAc) from Aldrich Co. was refluxed with BaO and was distilled out prior to use. 3,3′-Bis(maleimidophenyl)phenylphosphine oxide (BMPPPO) was synthesized from triphenylphosphine oxide according to the method elsewhere reported [15].

2.2. Synthesis of phosphorus-containing diamine monomer of m-2DOPO-2NH$_2$

9,10-Dihydro-oxa-10-phosphaphenanthrene-10-oxide (DOPO, 32 g, 0.15 mol) and 4,4′-diaminobenzophenone (DABP, 5.35 g, 0.025 mol) were mixed together in a 250 ml round-bottom flask. The mixture was heated to 180 °C and stirred for 3 h. The reaction mixture then became thick. After being cooled to 100 °C, toluene (150 ml) was added into the flask. The precipitant was filtered and washed with toluene. The obtained solid was then recrystallized from THF to give while powder product (yield 75%; mp, 324–325 °C). MS m/z (M$^+$) calcd for $C_{37}H_{28}O_4N_2P_2$, 626.; found, 626. IR (KBr, cm^{-1}): 1186 and 930 (P–O–Ph), 1210 (P=O), 1583 (P–Ph), 3249, 3351, 3419, and 3471 (–NH$_2$). ^{1}H NMR (300 MHz, DMSO-d$_6$, ppm): 4.86 (b, 4H); 5.77 (s, 1H); 5.82–5.95 (m, 3H); 6.63–6.87 (m, 5H); 7.05–7.13 (m, 3H); 7.25–7.30 (m, 2H); 7.54 (m, 2H); 7.65–7.70 (m, 3H); 7.76–7.79 (m, 1H); 7.91–7.93 (m, 2H); 8.17(s, 1H); 8.63 (s, 1H). ^{31}P NMR (300 MHz, DMSO-d$_6$, ppm): 30.12 and 31.78. $C_{37}H_{28}O_4N_2P_2$ (626) Cacl. (%) C 70.93 H 4.47 N 4.47 P 9.90 Found (%) C 70.80 H 4.41 N 4.50 P 10.01.

2.3. Synthesis of polyaspartimides (PAS-II-1)

Polyaspartimides were prepared from diamine and bismaleimides via a Michael addition reaction. The general procedure in this study was performed as follows. A 50 ml three-necked flask was used to equip with a magnetic stirrer, a reflux condenser, a thermometer, and nitrogen inlet. 1.5 g (2.40 mmol) of *m*-2DOPO-2NH$_2$ and 10 ml of DMAc were added into the flask. The mixture was stirred. While *m*-2DOPO-2NH$_2$ completely dissolved, 0.86 g (2.40 mmol) of bismaleimide BMDM and 0.1 g of *p*-TSA were added into the flask. The reaction mixture was then stirred at 100 °C for 96 h. The reaction solution was poured into excess ethanol with vigorous stirring and the polymer was precipitated out from the non-solvent. The precipitate was filtered out, washed with hot ethanol for three times. After being dried under vacuum at 70 °C for 24 h the product was obtained with a yield of 91%.

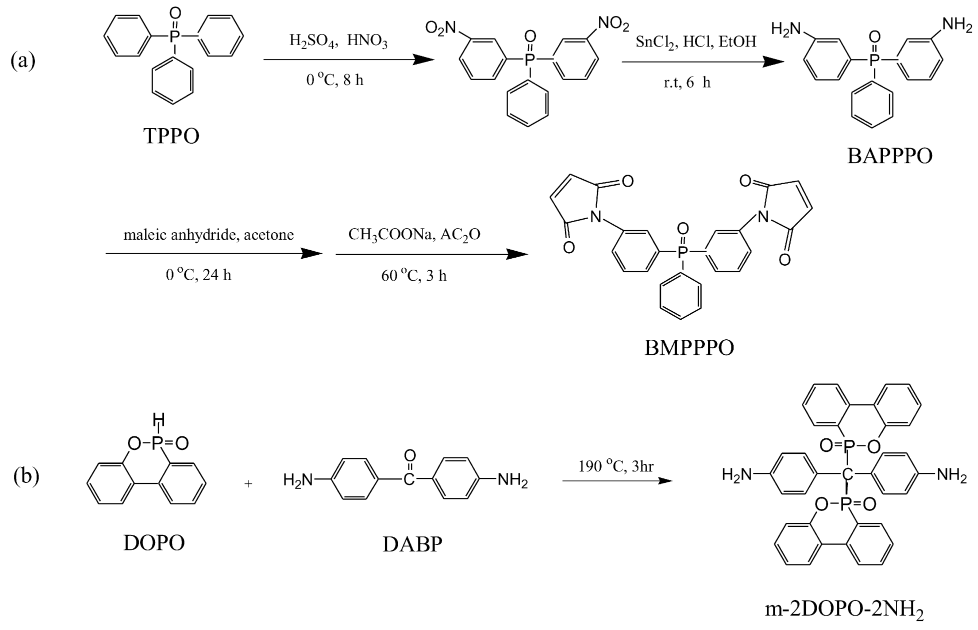
2.4. Instrumental analysis and measurements

Infrared spectra (FT-IR) were obtained from a Perkin Elmer 2000 FT-IR. ^{31}P NMR spectra were recorded with a Bruker MSL-300 (300 MHz) NMR spectrometer with DMSO-d$_6$ as a solvent. The phosphorus contents of the synthesized resins were determined via phosphorus elemental analysis by a Micro Digestion Apparatus with a spectrophotometer. The inherent viscosities of the polymers were measured with using an Ubbelohde viscometer. Differential scanning calorimetry (DSC) thermograms were recorded with a thermal analysis (TA) DSC-2900 at a heating rate of 10 °C/min under nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed by a TA TGA-2950 thermogravimetric analyzer at a heating rate of 10 °C/min under nitrogen or air atmosphere.

3. Results and discussion

3.1. Preparation of monomers and polyaspartimides

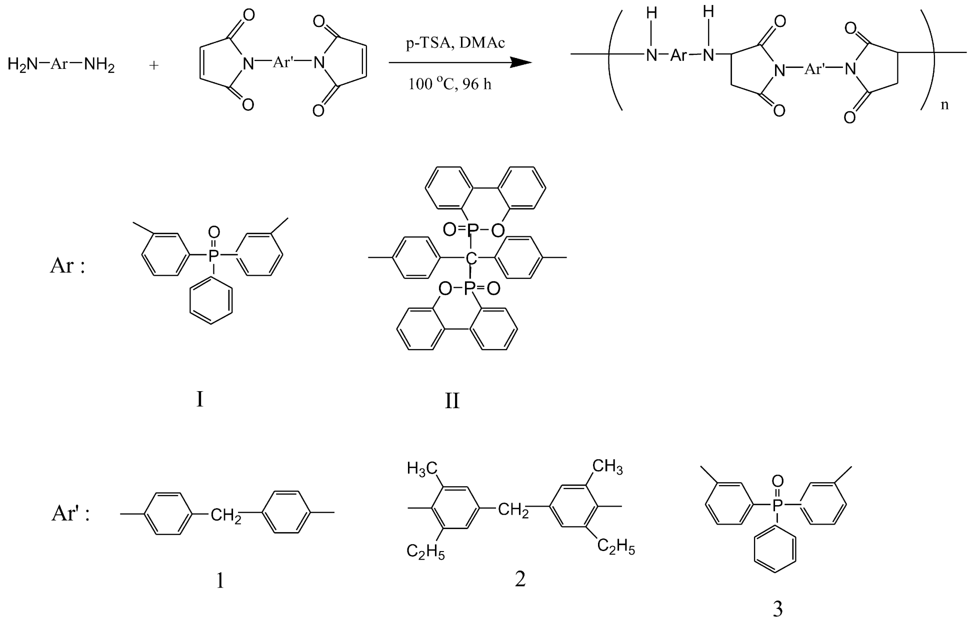
Phosphorus-containing monomers for synthesizing polyaspartimides were prepared according to the routes shown in Scheme 1 [15]. All of the monomers were characterized with FT-IR, ^{1}H and ^{31}P NMR, and elemental analysis to confirm their chemical structures. Polyaspartimides were prepared with reacting diamine monomers with bismaleimides via Michael addition reaction (Scheme 2). According to the literatures [7–10], the polymerization was usually performed with *o*-cresol as a solvent. However, *o*-cresol is highly toxic. Therefore, another solvent *N*,*N*-dimethylacetamide (DMAc) was utilized instead of *o*-cresol in this study. The success in replacement of the polymerization system's solvent was demonstrated with the high inherent viscosity and high yields of the obtained polyaspartimides. Moreover, Liaw et al. [10] reported that the molecular weights and the yields of the obtained polyaspartimides tended to increase with increasing monomer concentrations of the polymerization systems. The similar result was also observed in the present study (Table 1). While a high monomer concentration of 0.92 mol l^{-1} was utilized, the reaction solution became very viscous and began to gel. The gel product could not be dissolved in excess DMAc, to reveal that an upper-limited concentration was valid for obtaining high molecular weight PAS-I-1. The same gel phenomenon was also observed at Liaw's experiments [10]. However, the gel could be dissolved with adding excess *o*-cresol, since unsymmetrical bismaleimide BEMM was used in Liaw's study to result in polymers with high organosolubility. To examine this point of view, BAPPPO was polymerized with BEMM (PAS-I-2). Gel was observed while high monomer concentration of 1.10 mol l^{-1} was applied to the polymerization, and the gel can be dissolved with adding excess DMAc solvent.



Scheme 1. The synthesis routes to prepare phosphorus-containing monomers.

3.2. Characterization of polymers

Table 2 shows the polymerization results and characterization data of the synthesized polyaspartimides. The polymerization was taken with a monomer concentration of 0.76 mol l^{-1} at 100 °C for 96 h. All of the polymers were obtained with high yields over 90% with moderate inherent viscosities of 0.48–0.58 dl g^{-1}. The number average molecular weight of the polymers measured with GPC were in the range of 14,600–19,500 with polydispersity indexes of about 2.8–3.0. The performance of Michael addition reaction was demonstrated using FT-IR analysis. The absence of the band at about 666 and 3110 cm^{-1} demonstrate the consumption of C=C double bonds in maleimide rings after polymerization. The observation of the absorption peaks from C=O stretching of the imido group (1711–1717 cm^{-1}) and N–H group (1629–1634 cm^{-1}) further confirmed the performance of the addition reaction [10]. Moreover, other absorption peaks of P=O, P–Ph, P–O–Ph, and $-CH_3$ groups were also observed (Table 2) for the



Scheme 2. Preparation of phosphorus-containing polyaspartimides.

Table 1
The polymerization of BAPPPO with BMDM at various monomer concentrations

Run no.[a]	Monomer concentration (mol l^{-1})	Yield (%)	η_{inh} (dl g^{-1})[b]	$\bar{M}_n \times 10^{-4}$[c]	Polymerization conditions
1	0.92	97	–	–	Gel
2	0.76	93	0.58	1.91	Homogeneous
3	0.48	87	0.38	0.98	Homogeneous
4	0.36	82	0.31	0.70	Homogeneous

[a] The polymerization was taken place in DMAc for 96 h.
[b] Inherent viscosity measured at a concentration of 0.5 g dl^{-1} in DMAc at 30 °C.
[c] Number average molecular weight determined from GPC with DMF as a solvent and polystyrene as a standard.

Table 2
Synthesis and characterization data of polyaspartimides

Polymers[a]	Yield (%)	η_{inh} (dl g^{-1})[b]	$M_n \times 10^{-4}$[c]	IR spectra (cm^{-1})						^{31}P NMR chemical shift (ppm)	
				N–H	C=O	P=O	P–Ph	P–O–Ph	CH_3	DOPO[d]	TPPO[e]
PAS-I-1	92	0.58	1.95	1632	1715	1181	1437	–	–	–	26.9
PAS-I-2	93	0.52	2.14	1629	1711	1188	1438	–	–	–	26.6
PAS-I-3	95	0.50	1.46	1632	1717	1178	1423	–	2969	–	25.3, 26.4
PAS-II-1	91	0.52	1.91	1632	1715	1204	1584	927	–	31.5	–
PAS-II-2	91	0.48	1.58	1634	1714	1204	1485	923	–	31.3	–
PAS-II-3	93	0.49	1.66	1634	1715	1203, 1186	1584, 1428	925	2967	31.4	25.8

[a] The polymerization was taken place in DMAc with monomer concentrations of 0.76 mol l^{-1} for 96 h.
[b] Inherent viscosity measured at a concentration of 0.5 g dl^{-1} in DMAc at 30 °C.
[c] Number average molecular weight determined from GPC with DMF as a solvent and polystyrene as a standard.
[d] Peak derived from phosphorus in cyclic DOPO structure.
[e] Peak derived from phosphorus in triphenylphosphine oxide structure.

resulted polymers to confirm their chemical structures. ^{31}P NMR spectra (Fig. 1) of the polymers give another evidence to the occurrence of Michael addition reaction and the chemical structure of the polymers. The peak at about $\delta = 31.4$ ppm was assigned to be from phosphorus in the cyclic DOPO group, and the peak at about $\delta = 25.8$ ppm was assigned to be from phosphorus in the triphenylphosphine oxide group. Moreover, the chemical shifts of the phosphorous compounds before and after reactions showed considerable changes. Taking PAS-II-3 as an example, the phosphorus chemical shift from DOPO changed from $\delta = 30.1/31.8$ to $\delta = 31.4$ ppm and the phosphorus chemical shift from triphenylphosphine oxide structure changed from $\delta = 28.5$ ppm [15] to $\delta = 25.8$ ppm. This change in chemical shifts of ^{31}P NMR spectra also provides additional support to the occurrence of the Michael addition reaction between diamines and bismaleimides.

The solubility of the phosphorus-containing polyaspartimides in various solvents was examined and the results were shown in Table 3. It is noteworthy that at room temperature most of the polymers were soluble in high polar solvents such as *N*,*N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidinone (NMP), dimethylsulfoxide (DMSO), and DMAc. Moreover, while an unsymmetrical bismaleimide BEMM was utilized, the resulted polymers (PAS-I-2 and PAS-II-2) were soluble in chloroform, dichloromethane, and tetrahydrofuran, to exhibit the greatest solubility among the polymers. From results shown in Table 3, the enhancement of the solubility on polyaspartimides by the incorporation of phosphorus groups into the polymer structure was obvious, since a phosphorus-free polyaspartimide composed of DDM and BMDM showed poor solubility in the test solvents. When polymerized with *m*-2DOPO-2NH$_2$, the phosphorus-containing BMPPPO based polyaspartimide (PAS-II-3) showed better solubility than that of the phosphorus-free BMDM based polymer (PAS-II-1). The approaches to

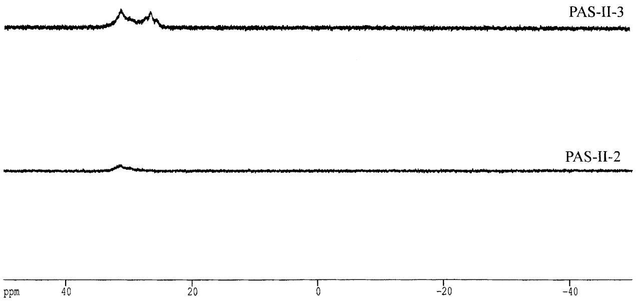


Fig. 1. ^{31}P NMR spectra of polyaspartimides (a)PAS-II-2 and (b)PAS-II-3.

Table 3
Solubility of the synthesized polyaspartimides (◎ soluble at room temperature; ○ soluble at 70 °C; △ partially soluble at 70 °C; × insoluble at 70 °C; number average molecular weight determined from GPC with DMF as a solvent and polystyrene as a standard)

Polymers	Solvent[a]								
	Acetone	MEK	Chloroform	Dichloromethane	THF	DMSO	DMAc	DMF	NMP
DDM-BMDM	×	×	×	×	×	×	×	△	△
PAS-I-1	×	×	×	×	×	◎	◎	◎	◎
PAS-I-2	△	△	◎	◎	◎	◎	◎	◎	◎
PAS-I-3	×	×	×	×	×	◎	◎	◎	◎
PAS-II-1	×	×	×	×	×	△	△	◎	◎
PAS-II-2	○	○	◎	◎	◎	◎	◎	◎	◎
PAS-II-3	×	×	×	×	×	◎	◎	◎	◎

[a] Abbreviations: MEK, methylethylketone; THF, tetrahydrofuran; DMSO, dimethylsulfoxide; DMF, *N*,*N*-dimethylformamide; NMP, *N*-methyl-2-pyrrolidinone.

improve polymers' solubility have been reported [10–18] with the efforts of attaching polar groups, bulky pendent groups, and alicyclic groups onto the polymers as well as of using unsymmetrical monomers and non-coplanar monomers. Therefore, introducing triphenylphosphine oxide group into polyaspartimides would bring high polar and bulky pendent groups into the polymers. Using *m*-2DOPO-2NH$_2$ as a monomer to prepare polyaspartimides would bring high polar group, bulky pendants, and non-coplanar effects to the polymers to improve their solubility. However, which of the two is superior in solubility enhancement is not clear from the results of this study.

3.3. Thermal properties of phosphorus-containing polyaspartimides

Table 4 shows the thermal properties of the phosphorus-containing polyaspartimides evaluated with DSC and TGA. All of the polymers exhibited high T_gs over 220 °C. Especially, it is noteworthy that PAS-II-1 showed a high T_g of 256 °C. The high T_g of PAS-II-1 should be attributed from the bulky side group of DOPO, which inhibited the polymer backbones' free rotation. The polymer PAS-II-3 containing triphenylphosphine oxide group in the main chain exhibited lower T_g than did polymer PAS-II-1. The pendent phenyl group in PAS-I-3 might reduce the polymer's rigidity, therefore, to lower its T_g [19]. The same result was also observed for PAS-I-3, which contains high content of pendent phenyl group and exhibits the lowest T_g among the polymers.

Thermal gravimetric analysis on the polymers reveals more information about the polymers thermal properties. The obtained polyaspartimides exhibited certain thermal stability (determined as the temperature of 1% weight loss) at temperatures of about 270 and 310 °C for PAS-I and PAS-II series polymers, respectively. The thermal stability of the phosphorus-containing polyaspartimides was poor than that of other phosphorus-free polyaspartimides and polyimides. The relatively poor thermal stability of the phosphorus-containing polyaspartimides should be derived from the phosphorus groups decomposing at low temperatures. The decomposition of phosphorus groups results in weight loss at low temperature region. A two-stage weight loss pattern was observed (Fig. 2) [20]. On the other hand, polymers containing DOPO groups (PAS-II series) were more thermally stable than the polyaspartimides with triphenylphosphine oxide groups. It has been recognized that the cyclic DOPO group was more thermally stable than other phosphorus groups. And, some of the

Table 4
Thermal properties of the synthesized polyaspartimides

Polymers	T_g (°C)[a]	Thermal stability (°C)[b]		Decomposition temperature (°C)[c]		Char yield at 700 °C		Char yield at 800 °C	
		In N$_2$	In air	In N$_2$	In air	In N$_2$	In air	In N$_2$	In air
PAS-I-1	239	286	262	412	407	64	25	60	9
PAS-I-2	235	277	274	427	418	61	25	59	9
PAS-I-3	227	270	277	394	393	61	35	59	22
PAS-II-1	256	309	306	360	363	53	37	50	9
PAS-II-2	248	317	310	376	378	49	39	47	12
PAS-II-3	245	308	298	367	365	61	46	58	24

[a] Data measured from DSC at a heating rate of 10 °C/min.

[b] Determined at 1% weight loss by TGA at a heating rate of 10 °C/min.

[c] Determined at 10% weight loss by TGA at a heating rate of 10 °C/min.

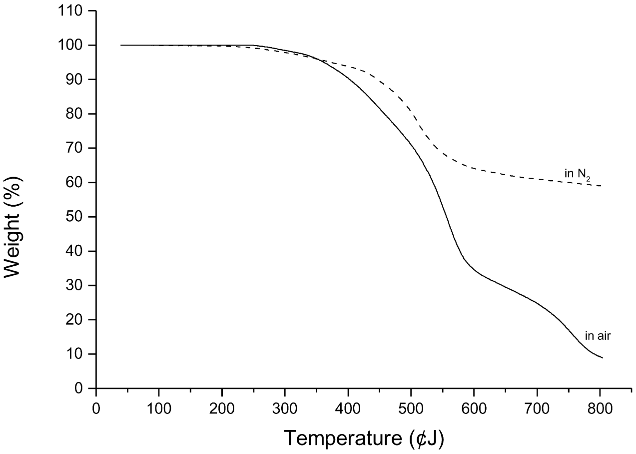


Fig. 2. TGA thermograms of PAS-I-2.

reported polymers containing DOPO showed thermal stability at temperatures higher than 300 °C [21–24], which is coincident with the thermally stable temperatures of the PAS-II series polyaspartimides.

In spite that the phosphorus-containing groups decomposed at low temperature region, the dramatic weight loss, which resulted from the decomposition of the entire polymer matrix, was not observed to be closely followed by the first weight loss for the phosphorus-containing polyaspartimides (Fig. 2). This behavior leads to the polymers exhibiting their 10% weight loss temperature (T_{d10}, defined as the polymer's decomposition temperature) at relatively high temperature region (360–427 °C). The high T_{d10} of the phosphorus-containing polyaspartimides are comparable with those of the reported phosphorus-free polyaspartimides (395–421 °C) [10]. On the other hand, PAS-I series polymers exhibit higher T_{d10} temperatures than PAS-II series polymers do. This result implied that PAS-I polymers' weight loss rate was slower than that of PAS-II polymers (Fig. 3). While a phosphorus-containing polymer is heated, a crosslinking carbonization occurred during its decomposition process [25]. This carbonization results in phosphorus-rich char to retardate further thermal degradation. PAS-I polymers decompose at low temperature and gain time to generate thermally stable char in the heating process, consequently, to exhibit relatively low weight lose rate. The low weight loss rates of PAS-I series polymers also results in high char formation under nitrogen atmosphere.

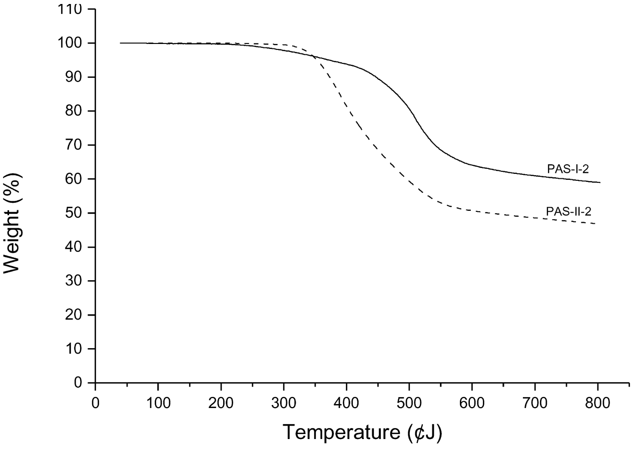


Fig. 3. TGA thermograms of PAS-I-2 and PAS-II-2 in nitrogen.

However, the TGA thermograms of the polymers under nitrogen and air were very different. When heated in nitrogen (Fig. 2), only small amount of weight loss (about 3 wt%) was observed at temperatures between 600 and 800 °C. However, weight loss rate suddenly increased at temperatures higher than 700 °C when polymers heated in air. The weight loss observed only in air environment should be conducted with oxygen, and has been described as oxidation weight loss [20,25]. This oxidation makes char to lose its weight at high temperature region. Therefore, the char formation in air is much less than that in nitrogen. In addition, PAS-II series polymers showed high char yields under air atmosphere than the PAS-I series polymers. The result is just opposite to the data exhibited in nitrogen atmosphere. As previously mentioned, the phosphorus groups decomposed at low temperature region to form phosphorus-rich char. Since the phosphorus-rich char is relatively thermally stable and anti-oxidant, high phosphorus contents of the polymers (PAS-II series) would give high char yields at high temperatures under air. Therefore, it is reasonable that PAS-I-3 and PAS-II-3 exhibit highest char yields among the polymers, since they contain the highest phosphorus contents.

4. Conclusions

The phosphorus-containing polyaspartimides from Michael addition reactions of reacting phosphorus-containing dimaines and bismaleimides were successfully obtained. The polymers were characterized to be organosoluble, to show high glass transition temperatures and good thermal stability. The variation in weight loss patterns of the polymers were correlated to the affection of phosphorus, to result in retarded weight loss rate and high char yields.

Acknowledgements

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