



Synthesis and Thermal Properties of Two Novel P-N Compounds

SHANSHAN WEI, LIGONG CHEN and YANG LI*

School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, P.R. China

*Corresponding author: Tel/Fax: +86 22 27406314; E-mail: liyang777@tju.edu.cn

Received: 6 May 2014;

Accepted: 22 July 2014;

Published online: 30 March 2015;

AJC-17067

Two novel P-N compounds were synthesized through a two-step reaction including the synthesis of 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane-2-oxide (M) and its reaction with 2,2,6,6-tetramethylpiperidine-4-amine and N-butyl-2,2,6,6-tetramethylpiperidine-4-amine. The structures were confirmed by NMR (^1H , ^{13}C , ^{31}P), FT-IR and MS. Their thermal properties were also evaluated by thermogravimetric analysis (TGA). The TG curves showed that the two compounds have residues of 4.9 and 1.1 wt % at 600 °C and the temperature of maximum weight loss rate (T_{max}) was 292 and 255 °C, respectively.

Keywords: Synthesis, P-N compounds, Flame retardants, Thermal properties, T_{max} .

INTRODUCTION

As well known, polymers have been widely employed in the daily life of human beings because of their advantages such as enough strength, corrosion resistance and good insulation. However, the flammable, aging characters limit their uses in many areas.

Intensive studies have been done to improve the properties of polymers¹⁻⁴. Fortunately, various additives doped in these polymers are successfully developed.

Flame retardants (FRs) and light stabilizers (LSs) are two important classes of polymer additives which are very helpful in retarding the degradation processes^{5,6}. The mono intumescent flame retardant (IFR) containing P-N in the molecular was the new generation of the flame retardants as the low smoke emission and toxic gases produced during burning, anti-dripping property and the synergistic effect between P and N⁷.

It is usually composed of three parts: the carbon agent, the acid agent and the blowing agent⁸⁻¹⁰. Some intumescent flame retardants were synthesized through 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane-2-oxide (M)¹¹⁻¹³. It provided both carbon agent and acid agent for the flame retardants. 2,2,6,6-Tetramethylpiperidine-4-amine and its derivatives consist of a class of efficient hindered amine light stabilizers (HALSs) due to their ability to remain an active participant in the Denisov cycle, forming and reforming the nitroxyl radical intermediate¹⁴⁻¹⁶. It was reported that the hindered amines could perform as the flame retardants^{17,18}. 2,2,6,6-Tetramethylpiperidine-amine has an unhindered nitrogen atom which could serve as the blowing agent of the flame retardant. However, there

were few reports about connecting the two parts in one molecule. Therefore, we designed two novel P-N compounds *i.e.*, 5,5-dimethyl-2-[(2,2,6,6-tetramethylpiperidin-4-yl)amino]-1,3,2-dioxaphosphorinane-2-oxide (A) and 2-[butyl(2,2,6,6-tetramethylpiperidin-4-yl)amino]-5,5-dimethyl-1,3,2-dioxaphosphorinane-2-oxide (B) (Fig. 1).

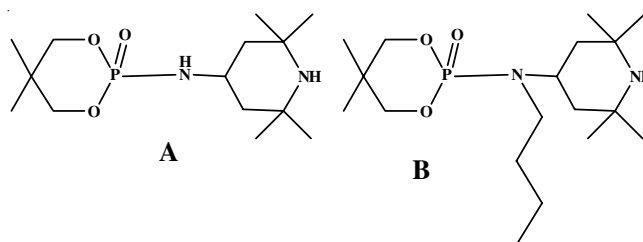


Fig. 1. Structure of compound A and B

The aim of this work was to synthesize the designed compounds which contained the 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane-2-oxide (M) and 2,2,6,6-tetramethylpiperidine-amine or its derivatives in the same molecule. Their thermal properties were studied using the thermogravimetric analysis. Further studies on the dual-function additives are in progress.

EXPERIMENTAL

Reagents and solvents were obtained from commercial suppliers. 2,2,6,6-Tetramethyl-piperidine-4-amine and N-butyl-2,2,6,6-tetramethylpiperidine-4-amine were kindly supplied from Tiangang Specialty Chemicals Co., Beijing, China. Anhydrous dichloromethane and acetonitrile were

distilled from calcium hydride and phosphorus pentoxide, respectively. Melting points were measured on a YRT-3 Melting Point Tester without correction. The IR spectra were recorded with KBr pellets on a Bruker-Tensor 27 spectrometer. The NMR spectra (^1H , ^{13}C and ^{31}P) were recorded on a Bruker-400 MHz NMR spectrometer. Compounds were dissolved in CDCl_3 or MeOD and chemical shifts were referenced to TMS (^1H and ^{13}C NMR) and 85 % H_3PO_4 (^{31}P NMR). MS were recorded on an LCQ Advanced MAX mass spectrometer. The thermal properties were measured with a STA 409 PC thermogravimetric (TG) analyzer at a scanning rate of $10\text{ }^\circ\text{C}/\text{min}$ under high purity N_2 , from room temperature to $600\text{ }^\circ\text{C}$. The weights of the samples were kept within 9-12 mg.

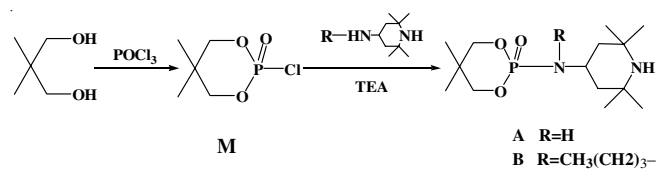
Synthesis of 2-chloro-5,5-dimethyl[1,3,2]dioxaphosphorinane 2-oxide (M)^{11,21}: A solution of phosphorus oxychloride (1.53 g, 0.01 mol) in 20 mL of dichloromethane was added dropwise over a period of 20 min from a dropping funnel to a stirred solution of 2,2-dimethyl-1,3-propanediol (0.52 g, 5 mmol) in 50 mL of dichloromethane at reflux. Continuous dry nitrogen purge under mild suction was used to remove the hydrogen chloride evolved in the reaction. After the addition, the reaction mixture was stirred at refluxing for 4 h. The progress of the reaction was monitored by TLC. The residue was washed with petroleum ether ($60\text{--}90\text{ }^\circ\text{C}$, 3 mL \times 100 mL) and then dried under vacuum at 0.1 MPa for 4 h at $70\text{ }^\circ\text{C}$ to give a white solid (1.82 g). Yield: 98.6 %, m.p. $99.1\text{--}100\text{ }^\circ\text{C}$ (lit.: $94\text{--}96\text{ }^\circ\text{C}$ ¹¹). IR (KBr, ν_{max} , cm^{-1}): 2976, 2947, 1473, 1304, 1053, 1005, 983, 922, 786, 548^{11,12}. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 0.94 (3H, s), 1.35 (1H, s), 3.98-4.08 (2H, dd, $J = 12\text{ Hz}$, $J = 28\text{ Hz}$), 4.25-4.28 (2H, d, $J = 12\text{ Hz}$). ^{31}P NMR (125 MHz, CDCl_3) δ (ppm): -2.66 ¹¹.

Synthesis of 5,5-dimethyl-2-[(2,2,6,6-tetramethylpiperidin-4-yl)amino][1,3,2]dioxaphosphinane-2-oxide (A): A mixture of 2,2,6,6-tetramethylpiperidine-4-amine (1.71 g, 0.011 mol) and triethylamine (1.30 g, 0.012 mol) dissolved in acetonitrile (100 mL) under dry N_2 were placed into a four-necked 250 mL flask equipped with a magnet stirrer, a thermometer, a reflux condenser and a dropping funnel. The intermediate **M** (1.85 g, 0.01 mol) in acetonitrile (50 mL) was added dropwise over a period of 1.5 h when the mixture was heated to reflux. After the addition, the reaction mixture was kept refluxing for 7 h, monitored by TLC. The filtrate obtained from filtering was evaporated under reduced pressure (0.1 MPa). The residue was dissolved in dichloromethane and washed with distilled water to give the crude product. The solid was further purified by recrystallization from methanol and water. After dried under vacuum at 0.1 MPa at room temperature for overnight, the white solid (**A**) was obtained (2.41 g). Yield: 79.2 %, m.p. $129.2\text{--}130.1\text{ }^\circ\text{C}$. IR (KBr, ν_{max} , cm^{-1}): 3532, 3237, 2967, 1588, 1462, 1391, 1231, 1059, 1013, 827, 630, 486. ^1H NMR (400 MHz, MeOD) δ (ppm): 1.02 (3H, s), 1.16 (3H, s), 1.49 (6H, s), 1.51 (6H, s), 1.55-1.61 (2H, t, $J = 12\text{ Hz}$), 2.07-2.12 (2H, dd, $J = 4\text{ Hz}$, $J = 12\text{ Hz}$), 3.58-3.62 (1H, m), 3.96-4.03 (2H, dd, $J = 12\text{ Hz}$, $J = 16\text{ Hz}$), 4.15-4.19 (2H, m). ^{13}C NMR (100 MHz, MeOD) δ (ppm): 76.6, 76.5, 57.4, 43.3, 43.2, 42.2, 31.6, 31.5, 29.2, 23.8, 20.2, 19.7. ^{31}P NMR (125 MHz, MeOD) δ (ppm): 5.0. MS (ESI) m/z : calcd. for $\text{C}_{14}\text{H}_{29}\text{N}_2\text{O}_3\text{P}$ 305.19 (positive ion), found 305.20 (positive ion).

2-[Butyl-(2,2,6,6-tetramethylpiperidin-4-yl)amino]-5,5-dimethyl[1,3,2]dioxaphosphinane-2-oxide (B): White solid. Yield: 81.7 %, m.p. $130.5\text{--}131.1\text{ }^\circ\text{C}$. IR (KBr, ν_{max} , cm^{-1}): 3293, 2960, 1470, 1375, 1361, 1251, 1230, 1208, 1053, 1008, 817, 627, 509, 487. ^1H NMR (400 MHz, MeOD) δ (ppm): 0.89 (3H, s), 0.93-0.97 (3H, t, $J = 8\text{ Hz}$), 1.18 (6H, s), 1.24 (6H, s), 1.29-1.35 (2H, m), 1.31 (3H, s), 1.45-1.51 (2H, m), 1.53-1.61 (2H, m), 1.63-1.67 (2H, dd, $J = 4\text{ Hz}$, $J = 12\text{ Hz}$), 2.99-3.07 (2H, m), 3.77-3.94 (3H, m), 4.29-4.32 (2H, d, $J = 12\text{ Hz}$). ^{13}C NMR (100 MHz, MeOD) δ (ppm): 77.4, 76.8, 76.0, 75.9, 51.5, 49.8, 44.1, 42.9, 42.8, 35.0, 34.4, 31.8, 31.7, 28.4, 22.4, 20.8, 20.2, 13.8. ^{31}P NMR (125 MHz, MeOD) δ (ppm): -8.9 . MS (ESI) m/z : calcd. for $\text{C}_{18}\text{H}_{37}\text{N}_2\text{O}_3\text{P}$ 361.25 (positive ion), found 361.26 (positive ion).

RESULTS AND DISCUSSION

The designed compounds were synthesized through a two-steps reaction. The synthetic route was shown in **Scheme-I**.



Scheme-I: Synthetic route of compound **A** and **B**

The intermediate **M** was prepared by the cyclization of phosphorus oxychloride and 2,2-dimethyl-1,3-propanediol at a high yield (98.6 %) and then reacted with 2,2,6,6-tetramethylpiperidine-amine and *N*-butyl-2,2,6,6-tetramethylpiperidine-4-amine in acetonitrile using triethylamine as the acid binding agent. The target compounds were obtained in yields of 79.2 and 81.7 %, respectively.

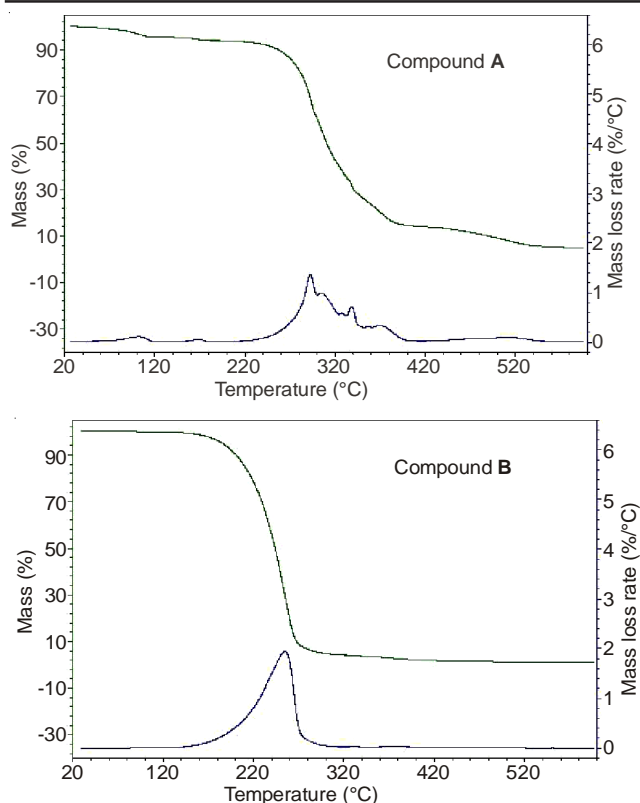
The recorded TG curves of compounds **A** and **B** were presented in Fig. 2. The analysis showed that the initial degradation of **A** was at about $200\text{ }^\circ\text{C}$ and it had a residual mass of about 5 % at $600\text{ }^\circ\text{C}$. The temperature of maximum weight loss rate (T_{max}) was $292\text{ }^\circ\text{C}$ with the rate of 1.36 wt %/ $^\circ\text{C}$. Between 200 and $327\text{ }^\circ\text{C}$, a rapid degradation was observed which might be related to the chain breakage of the P-O-C¹³. During this temperature range, about 56 % mass loss was noted. There was a major mass loss peak ($272\text{ }^\circ\text{C}$) and a minor one ($306\text{ }^\circ\text{C}$). Between 327 and $416\text{ }^\circ\text{C}$, a multistep decomposition was found with the 24 % weight loss which might be associated with the char formation^{13,19}.

Compared with **A**, the compound **B** showed a one-step degradation. The highest mass-loss rate was 1.95 wt %/ $^\circ\text{C}$ at $254.8\text{ }^\circ\text{C}$ (T_{max} of **B**) and the residue at $600\text{ }^\circ\text{C}$ was 1.1 wt %.

The important data of the TGA was shown in Table-1. It was clear that both **A** and **B** met the condition that the initial decomposition temperature of additives lower than that of the polymers^{19,20}. At the same time, both **A** and **B** had low residues at high temperature ($600\text{ }^\circ\text{C}$). Therefore, further studies were necessary on improving the char-forming efficiency of compounds **A** and **B**.

Conclusion

Two P-N compounds were synthesized successfully with yields of 79.2 and 81.7 %, respectively. Their chemical structures

Fig. 2. TG curves of compounds A and B in N₂ atmosphereTABLE-1
TGA DATA OF COMPOUND A AND B^a

Sample	T _{-10%} (°C) ^b	T _{-50%} (°C) ^c	T _{max} (°C) ^d	Residue (wt %) At 600 °C
A	257	311	292	5.0
B	200	244	255	1.1

^aErrors ± 0.5 wt %, ± 1 °C. ^bT-10 % temperature at which the weight loss of the sample was 10 %. ^cT-50 % temperature at which the weight loss of the sample was 50 %. ^dT_{max} temperature of maximum weight loss rate of the sample.

were characterized by ¹H NMR, ¹³C NMR, ³¹P NMR, IR and MS. The thermal properties were investigated by TGA. The

TG curves showed the residue at 600 °C of compound A and B was 5.0 and 1.1 wt %, respectively. The temperature of maximum weight loss rate (T_{max}) was 292 °C with the rate of 1.36 wt%/°C (A) and 254.8 °C with the rate of 1.95 wt%/°C (B). The residues of both A and B at high temperature (600 °C) were low. Further researches on the properties and modifying the compounds were required.

REFERENCES

1. Y. Halpern, D.M. Mott and R.H. Niswander, *Ind. Eng. Chem. Prod. Res. Dev.*, **23**, 233 (1984).
2. M. Minagawa, *Polym. Degrad. Stab.*, **25**, 121 (1989).
3. W. Yang, R.K.K. Yuen, Y. Hu, H.D. Lu and L. Song, *Ind. Eng. Chem. Res.*, **50**, 11975 (2011).
4. D.J. Kind and T.R. Hull, *Polym. Degrad. Stab.*, **97**, 201 (2012).
5. H. Horacek and S. Pieh, *Polym. Int.*, **49**, 1106 (2000).
6. M.R.L. Paine, P.J. Barker and S.J. Blanksby, *Analyst*, **136**, 904 (2011).
7. C.H. Ke, J. Li, K.Y. Fang, Q.L. Zhu, J. Zhu, Q. Yan and Y.Z. Wang, *Polym. Degrad. Stab.*, **95**, 763 (2010).
8. P. Lv, Z.Z. Wang, K.L. Hu and W.C. Fan, *Polym. Degrad. Stab.*, **90**, 523 (2005).
9. F. Xie, Y.Z. Wang, B. Yang and Y. Liu, *Macromol. Mater. Eng.*, **291**, 247 (2006).
10. G. Camino, L. Costa and L. Trossarelli, *Polym. Degrad. Stab.*, **6**, 243 (1984).
11. W.Y. Xing, L. Song, P. Lv, G.X. Jie, X. Wang, X.Q. Lv and Y. Hu, *Mater. Chem. Phys.*, **123**, 481 (2010).
12. S.Q. Zhang, B. Li, M. Lin, Q.F. Li, S.L. Gao and W. Yi, *J. Appl. Polym. Sci.*, **122**, 3430 (2011).
13. L.G. Lu, X. Wang, S.S. Yang, X.L. Dong, K. Tang and H.J. Yu, *Acta Chim. Sin.*, **70**, 190 (2012).
14. E.T. Denisov, *Polym. Degrad. Stab.*, **34**, 325 (1991).
15. J.L. Hodgson and M.L. Coote, *Macromolecules*, **43**, 4573 (2010).
16. J.L. Hodgson, L.B. Roskop, M.S. Gordon, C.Y. Lin and M.L. Coote, *J. Phys. Chem. A*, **114**, 10458 (2010).
17. Th. Schmutz, E. Kramer, H. Zweifel and G. Dörner, *J. Elastom. Plast.*, **30**, 55 (1998).
18. D. Zhu, D.Y. Gui and J.P. Liu, *Henan Chem. Ind.*, **22**, 14 (2005).
19. H.Y. Ma, L.F. Tong, Z. Xu, Z. Fang, Y. Jin and F. Lu, *Polym. Degrad. Stab.*, **92**, 720 (2007).
20. V. Sarannya, P. Sivasamy, N.D. Mathan, T. Rajkumar, D. Ponraju and C.T. Vijayakumar, *J. Therm. Anal. Calorim.*, **102**, 1071 (2010).
21. W. Ten Hoeve and H. Wynberg, *J. Org. Chem.*, **50**, 4508 (1985).