

2-2-2. Synthesis of EBDEP

A mixture of $\text{BrCH}_2\text{CH}_2\text{Br}$ (18.8 g), triethyl phosphite (49.8 g) and $(\text{CH}_3)_4\text{NI}$ (0.35 g) was stirred at 160 °C for 6 h, $\text{CH}_3\text{CH}_2\text{Br}$ (19.8 g) and DEEP (18.5 g) were collected, respectively, under reduced pressure. The resulting product was distilled from 117 °C to 119 °C under vacuum (0.8 KPa) to give a colorless liquid product in 70.2% yield. $^1\text{H NMR}$ (CDCl_3 , 400 MHz), δ : 1.32(s, 12H, $J=6.9$ Hz), 1.72(s, 4H, $J=18.1$ Hz), 4.12(s, 8H, $J=7.2$ Hz); ESI-MS, m/z : 88.16, 154.89, 172.85, 190.92, 200.91, 18.90, 246.88, 275.10, 284.94, 303.21; FT-IR (KBr, cm^{-1}): 3524, 2979, 2909, 1447, 1168~1272, 1040, 971, 796.

2-2-3. Synthesis of MBDMP

An oven-dried four-necked round-bottomed flask was charged with BrCH_2Br (17.4 g), trimethyl phosphite (37.2 g) and $(\text{CH}_3)_4\text{NI}$ (0.25 g). The mixture was stirred at 115 °C for 6 h with reflux. Then the unreacted trimethyl phosphite was removed under reduced pressure. MBDMP was given as a slightly yellow liquid product in 36.5% yield without any dealing with. $^1\text{H NMR}$ (CDCl_3 , 400 MHz), δ : 1.32(s, 12H, $J=6.9$ Hz), 1.72(s, 4H, $J=18.1$ Hz), 4.12(s, 8H, $J=7.2$ Hz); ESI-MS, m/z : 110.73, 140.91, 170.67, 200.96, 218.34, 232.87. FT-IR (KBr, cm^{-1}): 3472, 2956, 2860, 1458, 1177~1238, 1046, 914.

2-2-4. Synthesis of MBDEP

A mixture of BrCH_2Br (17.4 g), triethyl phosphite (49.8 g) and $(\text{CH}_3)_4\text{NI}$ (0.35 g) was stirred between 135~165 °C for 14 h, The unreacted triethyl phosphite was removed under reduced pressure. MBDEP was dried under vacuum to give as a colorless liquid product in 30.3% yield. $^1\text{H NMR}$ (CDCl_3 , 400 MHz), δ : 1.28(s, 12H, $J=6.9$ Hz), 1.67(s, 2H, $J=17.9$ Hz), 4.10(s, 8H, $J=6.9$ Hz); ESI-MS, m/z : 90.07, 174.80, 212.71, 292.64, 274.91, 259.90, 310.58; FT-IR (KBr, cm^{-1}): 3538, 2983, 2896, 1375, 1159~1253, 1038, 954.

3. Results and Discussion

Four reactions were all catalyzed by small amount of $(\text{CH}_3)_4\text{NI}$ and refluxed for some time. The products were hygroscopic colorless viscous clear liquid and stable in air. Some of their properties were investigated and the results are shown in Table 1. Byproducts $\text{CH}_3\text{CH}_2\text{Br}$, CH_3Br , DMMP and DEEP were recovered under vacuum. It was found that only 30.3% and 36.5% yield of methylene bis(diethyl Phosphonate) (MBDEP) and methylene bis(dimethyl phosphonate) (MBDMP) were obtained through the reaction of BrCH_2Br with triethyl phosphite and trimethyl phosphite, respectively. However, 70.2% and 90.9% yield of 1,2-ethylene bis(diethyl phosphonate) (EBDEP) and 1,2-ethylene bis(dimethyl phosphonate) (EBDMP) were

Table 1. Performance of polyphosphorates

Performance	EBDMP	EBDEP	MBDMP	MBDEP
Color(Pt-Co)	100	100	100	100
P content / %	25.17	20.45	26.33	21.09
Acid value/mgKOH·g	<0.3	<0.3	<0.3	<0.3

obtained with the $\text{BrCH}_2\text{CH}_2\text{Br}$ in place of BrCH_2Br . The reason may be larger space steric hindrance of BrCH_2Br than $\text{BrCH}_2\text{CH}_2\text{Br}$. In comparison, 1,2-ethylene bis(dimethyl phosphonate) (EBDMP) could be obtained with the best result.

It can be seen from the FT-IR spectrum of EBDMP, EBDEP, MBDMP and MBDEP that they all exhibit three characteristic peaks; for instance, at near 1200 cm^{-1} , which are due to P=O double ring. Additional band at near 1040 cm^{-1} is due to P-O-C groups. Moreover, important peaks between 1375 and 1467 cm^{-1} assigned to the P-C linkage are observed [12-16]. Moreover, they all have methyl bands.

The TGA traces of them provide information about their thermal stability [17-22] and char residue [23-26]. Fig. 2 shows TGA curves of specimens that were evaluated in nitrogen atmosphere. Clearly, the TGA results show differences among the products with different groups. It is well known that DMMP and DEEP undergo sharp degradation at low temperature; at the same time, the char residue is only 0.09% at 92 °C and 0.56% at 130 °C, respectively. Whereas, EBDMP exhibits a greatly different degradation behavior corresponding to very low mass loss rates (15.9% at 92 °C) and 6.2% char residue at 350 °C. Similarly, EBDEP exhibits relatively at group and weight loss is 57.6% at 150 °C. Considering the char residue at 350 °C, however, the EBDEP yielded as high as 8.0% char residues, revealing a higher thermal stability at high temperature. The samples of MBDEP and MBDMP revealed slightly lower char residues of 1.6% and 1.0%, respectively. It can be seen that biposphonates possess more excellent thermal stability and higher char residue than DMMP because two P-C covalent linkages are more stable than single P-C covalent linkage. At the same time, EBDEP is superior to EBDMP due to the strength of P-C covalent linkage.

The results reveal that the groups introduced in the backbone can influence the thermal stability of the biposphonates [27,28]. It seems that the contained P-C linkage in the backbone is more ther-

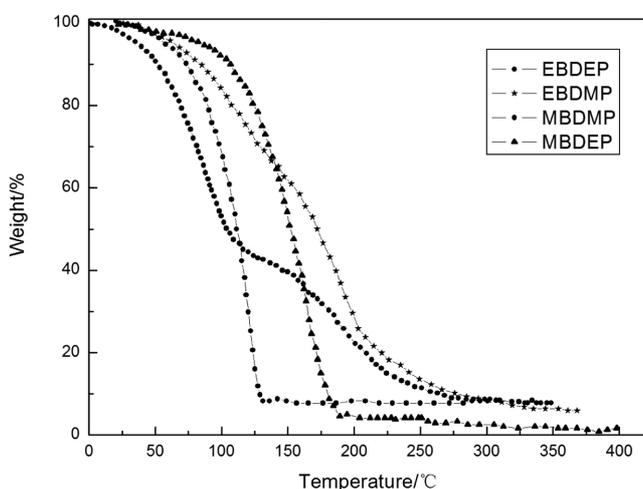


Fig. 2. TGA for EBDMP EBDEP MBDMP and MBDEP.

Table 2. Influence of EBDEP to polyurethane soft foam

Mass fraction of EBDEP/%	P content/%	LOI/%	UL94
5	0.99	20.3	V-2
8	1.26	23.6	V-2
10	1.57	25.5	V-0
13	2.02	27.2	V-0
15	2.37	26.5	V-0
18	2.82	26.0	V-0



(1) Before burn After burn (2) Before burn After burn

Fig. 3. Char images of (1) soft foam (no EBDEP) and (2) soft foam dealing with EBDEP.

mally stable in the high temperature region than that containing P-O-C linkage only. The first decomposition is explained by the break of P-O-C [29] bonds of methyl phosphonic chain; then with the increase of temperature, there is a loss of P-C band. Because the char yield in nitrogen has been correlated to the flame retardancy, these biphosphonates are expected to possess high flame-retardant properties. The high char yield can decrease the production of combustible gases, limit the exothermicity of the pyrolysis reactions, and inhibit the thermal conductivity of the burning materials. The application of EBDEP in polyurethane soft foam was studied and the results illustrated its excellent flame-proofing properties (Table 2). It is obvious that the LOI increased gradually with the increasing weight of EBDEP in polyurethane soft foam. And polyurethane soft foam containing 10% EBDEP reached the requirement of re-retardancy (UL 94: V-0; LOI: 25.5). The soft foam gave off black dense smoke during combustion; however, no obvious phenomena of burning were observed after dealing with EBDEP (Fig. 3).

4. Conclusions

Four biphosphonates have been synthesized through polycondensation and Arbuzov rearrangement reactions. The biphosphonates have several advantages: (1) they are high molecular polymer, halogen-free, and show superior thermal stability and high char residue in the presence of P-C covalent linkage. (2) They can be green synthesized without dangerous chemical products. (3) Compared to the commercial flame retardant compound used for polyurethane, i.e., DMMP and DEEP, the adducts of biphosphonates, and especially of EBDEP, show a better behavior in flame retardant. Finally, the molecular weights of the synthesized adducts are higher than that of DMMP and DEEP, which will avoid migration of the FRs towards the surface of the polyurethane.

Acknowledgment

A project funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions and Jiangsu Natural Science Foundation of China (BK2011369).

References

- Lassiaz, S., Galarneau, A., Trens, P., Labarre, D., Mutin, H. and Brunel, D., "Organo-Lined Alumina Surface from Covalent Attachment of Alkylphosphonate Chains in Aqueous Solution," *New J. Chem.*, **34**, 1424 (2010).
- Vasiljević, J., Hadžić, S., Jerman I., Černe L., Tomšič, B., Medved, J., Godec, M., Orel, B. and Simončič, B., "Study of Flame-retardant Finishing of Cellulose Fibres: Organic-inorganic Hybrid Versus Conventional Organophosphonate," *Polym. Degrad. Stabi.*, 2013, doi/10.1016/.
- Lin, H.-J., Liu, S.-R., Han, L.-J., Wang, X.-M., Bian, Y.-J., Dong, L.-S., "Effect of a Phosphorus-containing Oligomer on Flame-retardant, Rheological and Mechanical Properties of Poly (lactic acid)," *Polym. Degrad. Stabi.*, **98**(7), 1389-1396(2013).
- Köhler, J., Keul, H. and Möller, M., "Post-polymerization Functionalization of Linear Polyglycidol with Diethyl Vinylphosphonate," *Chem. Commun.*, **47**, 8148-8150(2011).
- Evano, G., Tadiparthi, K. and Couty, F., "Copper-mediated Cross-coupling of 1,1-dibromo-1-alkenes with Dialkyl Phosphites: a Convenient Synthesis of 1-alkenylphosphonates," *Chem. Commun.*, **47**(1), 179-181(2011).
- Murugavel, R. and Singh, M. P., "One, two, and Three Methylene Phosphonic Acid Groups (-CH₂PO₃H₂) on a Mesitylene Ring: Synthesis, Characterization and Aspects of Supramolecular Aggregation," *New J. Chem.*, **34**(9), 1846-1854(2010).
- Bourbigot, S. and Duquesne, S., "Fire Retardant Polymers: Recent Developments and Opportunities," *J. Mater. Chem.*, **17**, 2283-2300(2007).
- Bourbigot, S. and Fontaine, G., "Flame Retardancy of Polyacrylate: An Overview," *Polym. Chem.*, **1**, 1413-1422(2010).
- Lim, H. and Chang, J. Y., "Thermally Stable and Flame Retardant Low Dielectric Polymers Based on Cyclotriphosphazenes," *J. Mater. Chem.*, **20**, 749-754(2010).
- Wu, M. S., Chen, R. Y. and Huang, Y., "Progress in Synthesis of Bisphosphonic(ate) Analogues," *Chin. J. Org. Chem.*, **24**(5), 485-497(2004).
- Jansa, P., Holý, A., Dračinský, M., Baszczyński, O., Česnek, M. and Janeba, Z., "Efficient and 'green' Microwave-assisted Synthesis of Haloalkylphosphonates via the Michaelis-Arbuzov Reaction," *Green Chem.*, **13**, 882-888(2011).
- Masuda, K., Sakiyama, N., Tanaka, R., Noguchi, K. and Tanaka, K., "Rhodium-Catalyzed Enantioselective Cyclizations of γ -Alkynylaldehydes with Acyl Phosphonates: Ligand- and Substituent-Controlled C-P or C-H Bond Cleavage," *J. Am. Chem. Soc.*, **133**(18), 6918-6921(2011).
- Zhuang, R. Q., Xu, J. and Cai, Z. S., "Copper-Catalyzed C-P Bond Construction via Direct Coupling of Phenylboronic Acids with H-Phosphonate Diesters," *Org. Lett.*, **13**(8), 2110-2113(2011).
- Ashkenazi, N., Segall, Y. and Chen, R., "The Mechanism of Nucleo-

- philic Displacements at Phosphorus in Chloro-Substituted Methylphosphonate Esters: PO vs PC Bond Cleavage: A DFT Study" *J. Org. Chem.*, **75**(6), 1917-1926(2010).
15. Rueping, M., Zhu, S. Q. and Koenigs, R. M., "Photoredox Catalyzed C-P Bond Forming Reactions-visible Light Mediated Oxidative Phosphonylations of Amines;" *Chem. Commun.*, **47**(30), 8679-8681(2011).
 16. Negrell-Guirao, C., Boutevin, B., David, G., Fruchier, A., Sonnier, R. and Lopez-Cuesta, J., "Synthesis of Polyphosphorinanes Part II. Preparation, Characterization and Thermal Properties of Novel Flame Retardants;" *Polym. Chem.*, **2**, 236-243(2011).
 17. Song, P. A., Xu, L. H., Guo, Z. H., Zhang, Y. and Fang, Z. P., "Flame-retardant-wrapped Carbon Nanotubes for Simultaneously Improving the Flame Retardancy and Mechanical Properties of Polypropylene;" *J. Mater. Chem.*, **18**, 5083-5091(2008).
 18. Song, P. A., Liu, H., Shen, Y., Du, B. X., Fang, Z. P. and Wu, Y., "Fabrication of Dendrimer-like Fullerene (C₆₀)-decorated Oligomeric Intumescent Flame Retardant for Reducing the Thermal Oxidation and Flammability of Polypropylene Nanocomposites;" *J. Mater. Chem.*, **19**, 1305-1313(2009).
 19. Zhuo, D. X., Gu, A. J., Liang G. Z., Hu, J. T., Yuan, L. and Chen, X. X., "Flame Retardancy Materials Based on a Novel Fully End-capped Hyperbranched Polysiloxane and Bismaleimide/diallyl-bisphenol A Resin with Simultaneously Improved Integrated Performance;" *J. Mater. Chem.*, **21**, 6584-6594(2011).
 20. Brebu, M. and Sakata, Y., "Novel Debromination Method for Flame-retardant High Impact Polystyrene (HIPS-Br) by Ammonia Treatment;" *Green Chem.*, **8**, 984-987(2006).
 21. Bhaskar, T., Hosokawa, A., Muto, A., Tsukahara, Y., Yamauchi, T. and Wada, Y. J., "Enhanced Debromination of Brominated Flame Retardant Plastics Under Microwave Irradiation;" *Green Chem.*, **10**, 739-742(2008).
 22. Mosurkal, R., Kirby, R. and Muller, W. S., "Simple Green Synthesis of Polyborosiloxanes as Environmentally-safe, Non-halogenated Flame Retardant Polymers;" *Green Chem.*, **13**, 659-665(2011).
 23. Song, P. A., Zhao, L. P., Cao, Z. H. and Fang, Z. P., "Polypropylene Nanocomposites Based on C₆₀-decorated Carbon Nanotubes: Thermal Properties, Flammability, and Mechanical Properties;" *J. Mater. Chem.*, **21**, 7782-7788(2011).
 24. Wilkie, C. A., Chigwada, G. and Gilman, Sr. J. W., "High-throughput Techniques for the Evaluation of Fire Retardancy;" *J. Mater. Chem.*, **16**, 2023-2030(2006).
 25. Shi, Y. M. and Li, L. J., "Chemically Modified Graphene: Flame Retardant or Fuel for Combustion?;" *J. Mater. Chem.*, **21**, 3277-3279(2011).
 26. Ranganathan, T., Cossette, P. and Emrick, T., "Halogen-free, Low Flammability Polyurethanes Derived from Deoxybenzoin-based Monomers;" *J. Mater. Chem.*, **20**, 3681-3687(2010).
 27. Urbanczyk, L., Bourbigot, S., Calberg, C., Detrembleur, C., Jérôme, C., Boschini F. and Alexandre, M., "Preparation of Fire-resistant Poly(styrene-co-acrylonitrile) Foams Using Supercritical CO₂ Technology;" *J. Mater. Chem.*, **20**, 1567-1576(2010).
 28. Tai, Q. L., Hu, Y., Yuen, R. K. K., Song, L. and Lu, H. D., "Synthesis, Structure-property Relationships of Polyphosphoramides with High Char Residues;" *J. Mater. Chem.*, **21**, 6621-6627(2011).
 29. Liu, Y. L., Hsiue, G. H., Chiu, Y. S., Jeng, R. J. and Perng, L. H., "Phosphorus-containing Epoxy for Flame Retardant. I. Synthesis, Thermal, and Flame-retardant Properties;" *J. Appl. Polym. Sci.*, **61**, 613-621(1996).