

Simple synthesis of Biphosphonates with Excellent Flameproofing Properties

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Abstract – Four excellent halogen-free biphosphonate flame retardants (EBDMP, EBDEP, MBDMP, MBDEP) were synthesized through polycondensation and Arbuzov rearrangement reactions without using any solvents. The products were characterized by ESI-MS, FT-IR and ¹H NMR. The application of EBDEP in polyurethane soft foam was studied and the results illustrated its excellent flame-proofing properties

Key words: Flame Retardants, Biphosphonates, Synthesize, Polycondensation

1. Introduction

Phosphonates [1-3] have been hot research targets owing to their obvious advantages, such as good thermal stability and chemical stability, excellent waterproofing and solvent resistance. And phosphonates [4-6] were proposed to have potential for flame retardancy to polymers due to their thermal stability. Such as, diethyl ethyl phosphonate (DEEP) and dimethyl methylphosphonate (DMMP) can be used as good flame retardants for polyurethane. Unfortunately, single phosphonates show a degree of incompatibility with polymers, which causes many difficulties for applications. Research shows that biphosphonates [7-9] enhance compatibility with polymers. However, some methylene biphosphonates [10] have been studied following low yield, releasing dangerous gases or use of expensive catalyst, etc.

So, (CH₃)₄Ni was used to catalyze four biphosphonates (Fig. 1) as additive-type flame retardants. Their structures were characterized by ESI-MS, ¹H NMR, FT-IR. According to the thermogravimetric analysis (TGA) of these biphosphonates and single phosphonates (DEEP Supported by the Jiangsu Natural Science Foundation of China (BK2011369) and Priority Academic Program Development of Jiangsu Higher Education Institutions and DMMP), results showed that biphosphonates had better thermal stability and higher char residue, two important measures of low flammability materials. These flame retardants were synthesized through polycondensation and Arbuzov rearrangement reactions [11] (Scheme 1).

2. Experimental

2-1. Materials

All raw materials (AR) used in synthesis, including trimethyl phosphite, (CH₃)₄Ni, BrCH₂CH₂Br triethyl phosphite, and BrCH₂Br were received from Chemical Company, China.

2-2. Physico-chemical characterization

¹H NMR spectra were recorded with a Varian XL-400 spectrometer (chemical shifts are downfield from TMS), using hot deuterated CDCl₃ as solvent. The thermogravimetric analyses (TGA) were performed using a Perkin Elmer TGA 7 apparatus in N₂ (gas flow: 40 mL/min) at 10 °C/min heating rate, from 20 °C to 600 °C. IR spectra were recorded in KBr disks on a Bomem MB154S FT-IR spectrometer. Mass spectra were taken on an Agilent LC-MS 1100 series instrument in the electrospray ionization (positive ESI) mode.

2-2-1. Synthesis of EBDMP

18.8 g BrCH₂CH₂Br and 37.2 g trimethyl phosphite were charged into a four-necked flask with a catalyst of (CH₃)₄Ni (0.25 g), then the mixture was magnetically stirred in an oil bath at 150 °C for 4 h. CH₃Br (12.1 g) and DMMP (125.5g) were collected at different temperature under reduced pressure. The resulting product was evaporated from 106 °C to 108 °C under vacuum (0.8 KPa) to give as a colorless liquid product in 90.9% yield. ¹H NMR(CDCl₃, 400 MHz), δ: 1.38(s, 4H, J=15.0 Hz), 3.64(s, 12H); ESI-MS, m/z: 92.99, 110.99, 126.99, 136.99, 214.97, 246.93; FT-IR (KBr, cm⁻¹): 3491, 2954, 2852, 1467, 1187~1261, 1049, 962, 734.

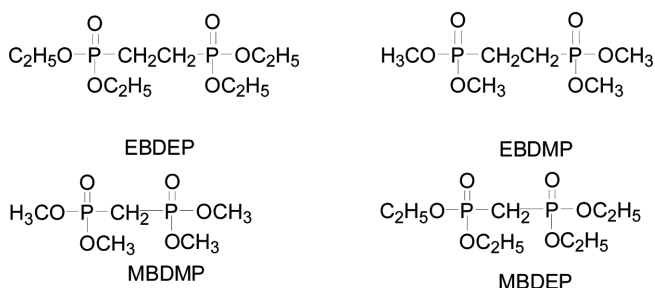
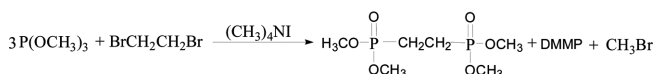


Fig. 1. Structures of biphosphonates.



Scheme 1. Synthesis of EBDMP.

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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. ^1H 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, 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 ask 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. ^1H 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, 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. ^1H 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, 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 phosphnate) (MBDMP) were obtained through the reaction of BrCH_2Br with triethyl phosphite and trimethyl phosphate, 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

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 statum 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-

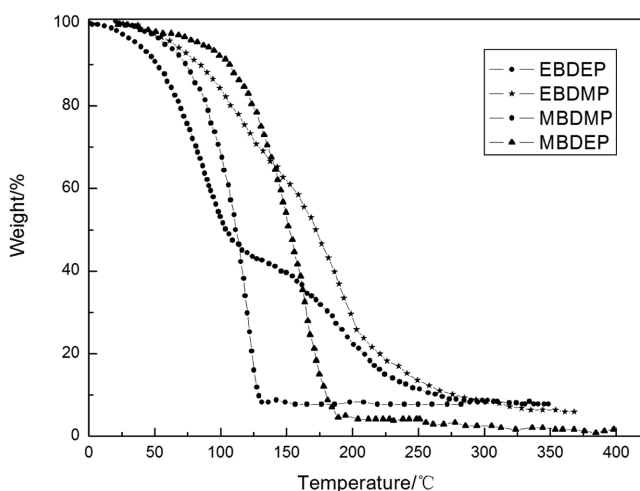


Fig. 2. TGA for EBDMP EBDEP MBDMP and MBDEP.

Table 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

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.

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