

아드만탄 기반의 새로운 설폰네이트 폴리카보네이트 난연제 성능 연구

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Performance of a Novel Sulfonate Flame Retardant Based on Adamantane for Polycarbonate

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Abstract: A novel sulfonate flame retardant, 1,3,5,7-tetrakis(phenyl-4-sodium sulfonate)adamantane (FR-A), was successfully synthesized from 1-bromoadamantane in sequential four-step reactions involving Fiedel-Crafts phenylation, sulfonation, hydrolysis, and neutralization. The success of synthesis was confirmed by FTIR spectra, ¹H NMR spectra, elemental analyses and mass spectra. The effect of FR-A on the flame retardancy of polycarbonate (PC) has been studied. Limiting oxygen index (LOI) and thermogravimetric analysis (TGA) showed that this novel sulfonate flame retardant had effective flame retardancy on polycarbonate (PC). With a small amount (0.08 wt%) of FR-A, the flame retardancy of PC was improved obviously, which got to UL 94 V-0 rating. TGA and DTA curves demonstrated that the additive raised the degradation rate of PC by promoting the quick formation of an insulating carbon layer on the surface, and confirmed that the flame retardant mechanism of PC/FR-A system was similar to potassium diphenylsulfone sulfonate (KSS).

Keywords: 1,3,5,7-tetrakis(phenyl-4-sodium sulfonate)adamantane (FR-A), polycarbonate, flame retardant, thermal degradation rate.

Introduction

Polycarbonate (PC) is an engineering plastic that is widely used in many fields such as automobile, electrical and electronic devices, construction, aerospace industry, machinery, and textile. It is a self-extinguishing, highly flame retardant plastic and by itself shows a V-2 rating in the UL 94 test due to relatively high tendency to charring.¹ The oxygen index can vary from 21 to 24 depending on polymer molecular weight and branching, and that of typical virgin bisphenol-A polycarbonate is about 25. Therefore, PC needs flame retardant agents to enhance combustion resistance, but some additives require in general high loading levels (up to 15-20%) in order to perform a fire protective action on the substrate.² And

research has been diverted to the flame retardants free of bromine and chlorine together with environmental considerations, such as sulfur-, silicone-, or phosphorous-based flame retardants.³⁻⁸ Among them sulfonate salts such as potassium perfluorobutane sulfonate, are found particularly effective in flame retardancy of PC even at very low loading.^{9,10} As a kind of flame retardant additive for PC, sulfonate flame retardant have significant ability to reduce the generation of smoke, heat and toxic carbon monoxide gas during PC combustion.^{11,12} This has stimulated the interest in synthesis of new sulfonate flame retardants.

1,3,5,7-tetrakis(phenyl-4-sodium sulfonate)adamantine (FR-A), which was based on adamantane that had four phenyl groups and four sulfo group, has not been studied so far. As a sulfonate salt, FR-A was expected to be compatible with PC as a new attractive flame retardant. This paper reports the experimental results of FR-A on flame retardancy.

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Experimental

Materials. Commercial graded adamantane was offered by Zhangjiagang Xikai Chemical Co., Ltd. Butyl bromide was supplied by Aladdin (China Republic). Other agents were supplied by Guangzhou Chemical Reagent Factory. All agents were used as received. PC (by BAYER, Makrolon 2805) was used as received and no attempt was made to analyze, so that may be part of the commercial formulation.

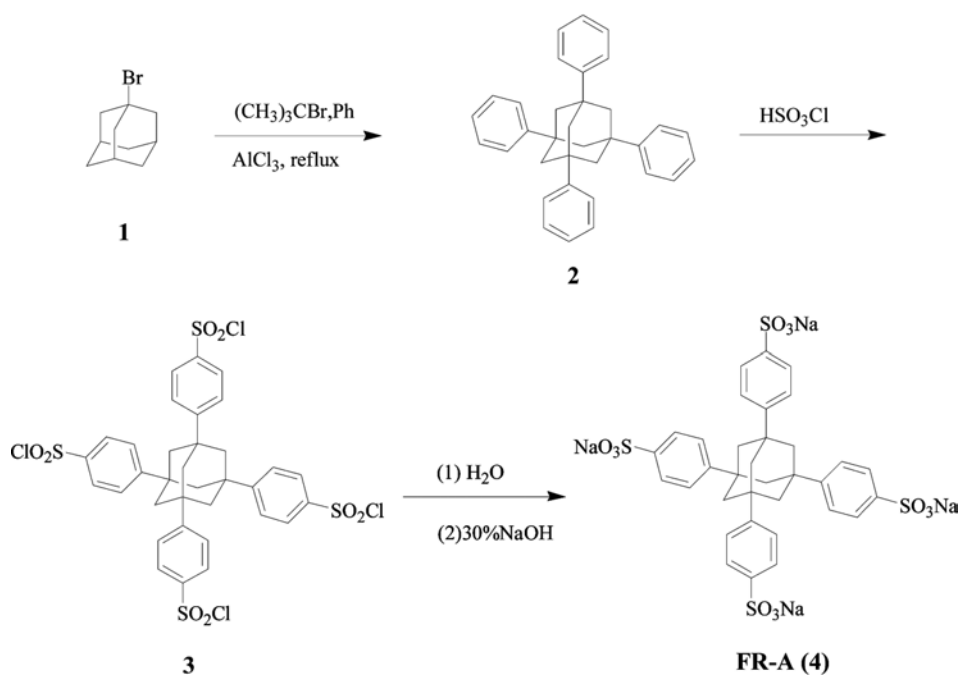
Synthesis. FR-A was synthesized in three steps starting from 1-bromoadamantane by Friedel-Crafts phenylation reaction with benzene followed by sulphonation reaction with chlorosulfonic acid and subsequent hydrolysis of sulfonyl chloride group to sulfonic acid group and neutralization of sulfonic acid group to its sodium salt according to the reaction sequence described in Scheme 1.

Synthesis of 1,3,5,7-Tetraphenyladamantane(2) According to Literature^{13,14}: A solution of 1-bromoadamantane (**1**) (5.0 g, 23 mmol) and butyl bromide (6.5 g, 0.05 mol) in benzene (50 mL) was added aluminum chloride (0.5 g); the mixture was inserted into a preheated oil bath and heated under vigorous reflux for 1 h. A lot of solid formed in the reaction. The mixture was poured into ice water, ether was added, and the insoluble off-white solid was collected. The poor solubility of 1,3,5,7-tetraphenyladamantane (**2**) allows for purification by washing with CHCl_3 in a Soxhlet extractor for 24 h. The

desired product (7.2 g, 16 mmol, yield: 70%) was insoluble in chloroform and the melting point of more than 300 °C. Mass spectrum: M^+ , $m/e=440.25$ (strong); IR (KBr) ν : 3028, 2925, 2851, 1960, 1891, 1814, 1754, 1678, 1603, 1594, 1491, 1445, 1360, 1080, 1028, 760, 748, 700 cm^{-1} . Anal. calcd for $\text{C}_{34}\text{H}_{32}$: C 92.68, H 7.32; Found C 92.80, H 7.33.

Synthesis of 1,3,5,7-Tetra(phenyl-4-sulfonyl chloride)adamantane (3): A 100 mL round-bottle, flask was charged with 20 mL of chlorosulfonic acid and cooled to 0 °C. After 20 min, solid 1,3,5,7-tetraphenyladamantane (**2**) (2.0 g, 4.51 mmol) was added slowly. The flask was stoppered, and the mixture was stirred. After 1.6 h, the mixture was dumped into 30 g of ice. The white solid was filtered and dried to give 1,3,5,7-tetra(phenyl-4-sulfonyl chloride)adamantane (**3**) (2.0 g, 2.43 mmol, yield: 57%). ^1H NMR (CD_3CN , 400 MHz): δ 2.250(s, 12H), 7.706, 7.775, 7.906, 8.095(AA¹BB¹, 16H). ^{13}C -NMR 41.113(CH_2), 45.802(C-PhSO₂Cl), 128.185, 128.314, 142.808, 158.401 (PhSO₂Cl). IR(KBr): ν 2928, 2855, 1631, 1592, 1370, 1175, 1128, 1007, 918, 586 cm^{-1} . Anal. Calcd for $\text{C}_{34}\text{H}_{28}\text{Cl}_4\text{O}_8\text{S}_4$: C 48.93, H 3.38, Cl 16.99, O 15.34, S 15.37; Found C 48.90, H 3.40, Cl 16.95, O 15.35, S 15.39.

Synthesis of 1,3,5,7-Tetrakis(phenyl-4-sodium sulfonate)adamantane (FR-A): A 100 mL round-bottom flask was charged with solid 1,3,5,7-tetra(phenyl-4-sulfonyl chloride)adamantane (**3**) (2.0 g, 2.43 mmol) and 40 mL of CH_2Cl_2 , then 20 mL of water was added into the mixture slowly at 0 °C for



Scheme 1. Synthesis of 1,3,5,7-tetrakis(phenyl-4-sodium sulfonate)adamantane (FR-A).

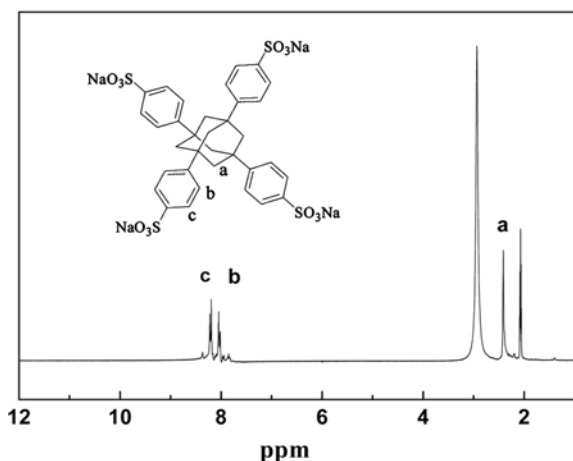


Figure 1. ^1H NMR spectra of FR-A.

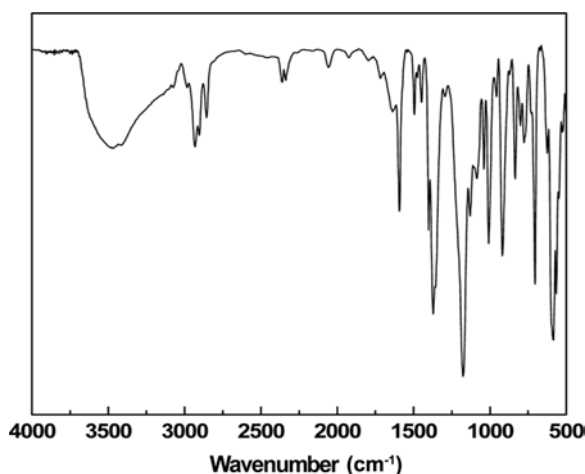


Figure 2. FTIR spectrum of FR-A.

48 h, a white precipitate formed gradually and was filtered. Then the precipitate was neutralized by 2 mol/L NaOH and a pH=8 had been achieved. The water was evaporated and the sample dried at 50 °C under vacuum. The yield of the salt (FR-A) was 50%, and the melting point of FR-A was more than 300 °C. Figure 1 shows the ^1H NMR spectra of FR-A, ^1H NMR (CD_3CN , 400 MHz): δ 2.385(s, 12H, ) , 8.378, 8.172, 8.019, 7.906 (AA¹BB¹, 16H, ) . Figure 2 shows the FTIR spectrum of FR-A, IR (KBr): ν 3090-3020, 2929, 2855, 1175, 1128, 1007, 748, 726, 586 cm^{-1} . Anal. Calcd for $\text{C}_{34}\text{H}_{28}\text{Na}_4\text{O}_{12}\text{S}_4$: C 48.11, H 3.32, O 22.62, S 15.11; Found C 48.09, H 3.31, O 22.64, S 15.12.

Samples. The PCs were mixed with 0.05, 0.08, 0.10, and 0.15 wt% of fine dried FR-A powders by tumbling the ingredients in a tumbler. The resulting mixtures were melt-kneaded and extruded into pellets using a TE-34 twin-screw extruder at

cylinder temperature of 230-250 °C and a screw speed of 24 r/min. The resulting pellets were dried and then injection-molded at an injection temperature of 230-250 °C in CJ110E Plastic Moulding Machine into test pieces for measurement of flame retardant properties.

Measurements. LOI (ATLAS Company, UK) measurements were performed according to ASTM D2863-91 method. Flame retardancy was examined in accordance with UL 94. The sample bars with 3.0 mm thickness were made by injection molding. TGA and differential scanning calorimeter (DSC) spectra were performed on a differential scanning calorimetry (SDT2960, TA Company, USA) under flowing nitrogen at a heating rate of 10 °C/min.

Results and Discussion

Flame Retardancy of FR-A on PC. The flame retardancy of PC containing different proportion of FR-A was investigated. The type of the PC/FR-A flame was distinctive as compared with that of neat-PC. The LOI of PC composition as a function of FR-A amounts is shown in Table 1. A quite small amount of FR-A caused a sensible increment in LOI of the PC. The LOI attained the value of 26.4% when FR-A went up to 0.15 wt% (based on the weight of PC). And during the measurement heavy black smoke became poor. The flame retardancy is effective. From Table 2, it was known that the sample at 0.08 wt% for 3.0 mm thickness was measured to achieve UL 94 V-0 rating, and also its self-extinguishes time was reduced to below 6 s. Compared with current efficient and commercial used sulphonate flame retardant for PC, about 0.06-0.1 wt% of PPFBS (potassium perfluorobutane sulfonate¹⁵) or 0.05-0.2 wt% of KSS (potassium diphenylsulfone sulfonate¹⁶) can get to UL 94 V-0 rating. It can be found that the novel sulfonate flame retardant was similar to KSS and PPFBS via UL 94 test. Moreover, the ability to resist the flame ignition and to restrain the excessive smoke was efficiently enhanced during combustion. All of these showed that FR-A had quite effective

Table 1. Flame Retardancy of PC/FR-A System with Different Contents

Samples (A^a %)	0	0.05	0.08	0.10	0.15
LOI/%	21	23.5	24.3	25.5	26.4
UL-94 Rating (3 mm)	F	V-1	V-0	V-0	V-0
Self-extinguishes/s	Burnout	24	6	5	5
Dripping	Yes	No	NO	NO	NO

^aThe number indicates the content of FR-A added to the PC.

performance of flame retardancy on PC.

Thermogravimetric Analysis. TGA was used to investigate the degradation in terms of mass loss and thermal degradation of PC compositions. The TGA and DTG curves for

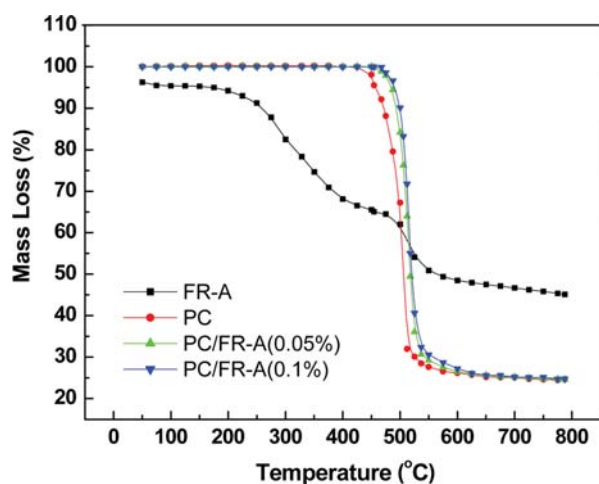


Figure 3. TGA of FR-A, PC, PC/FR-A(0.05%), and PC/FR-A(0.1%) at a heating rate of 10 °C/min in N₂.

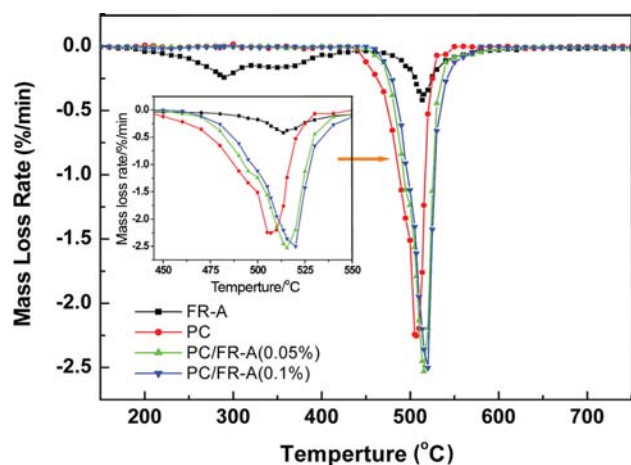


Figure 4. DTG of FR-A, PC, PC/FR-A(0.05%), and PC/FR-A(0.1%) at a heating rate of 10 °C/min in N₂.

FR-A, PC and PC/FR-A were depicted in Figures 3 and 4.

The major degradation of FR-A were from 231.1 to 321.3 °C and from 425.2 to 558.1 °C going with nearly 50% of the total mass loss, and the peak rates were at 289.7 and 513.6 °C. For neat PC, one-step degradation was apparently observed at 441.67-546.7 °C with about 68% mass loss, and the peak of maximum mass loss rate was taken at 506.9 °C. As to the PC containing 0.05% FR-A, the major mass loss occurred at 454.6-538.4 °C with 69% char formation at 600 °C. And the maximum mass loss rate occurred at 513.1 °C. It was observed that the initial temperature of mass loss increases and the peak temperature of maximum mass loss rate decreased. For the PC/FR-A (0.1%), the degradation was at 467.4-529.7 °C having 71% mass lost, and the temperature of the peak rate was at 520.3 °C. It was evident that the peak temperature and the original temperature have changed to go ahead with an increase as FR-A amount increases. The peak temperature was from 506.9 to 520.3 °C, and no difference in residues between PC and PC/FR-A (0.05 and 0.1 wt% by weight) in DTG curves. The results were summarized in Table 2. From Table 2, it was known that a small amount of FR-A had done give rise to remarkable influences, for example, considerable increase in LOI by almost 5 units and dramatic suppression of dripping. Then it was observed that the initial temperature of mass loss and the peak temperature of maximum mass loss rate of FR-A were higher than KSS and PPFBS, indicated that the PC/FR-A (0.1%) had a better thermal stability. However, the LOI of PC/FR-A (0.1%) can not compare favourably with PC/KSS and PC/PPFBS.

DSC spectra provide changes of temperatures of the material in pyrolysis process and the changes of heat releasing. Figures 5 and 6 show DSC curves of PC with 0.05 and 0.1% of FR-A. And it was observed that at the end of the test, neat PC released a total heat of 125.2 mW, whereas the PC/FR-A system released 79.8 mW. It can be seen that the more stable was

Table 2. Results of Thermogravimetric Analysis and the LOI of Various PC Compositions

Samples	$T_{1\% \text{ mass loss}}$ (°C)	T_{max} (°C)	Peak rate (%/min)	Residues at 600 °C (%)	LOI (%)
PC	441.7	546.7	2.20	24.96	21.0
PC+0.05% FR-A	454.6	534.8	2.55	24.98	23.5
PC+0.1% FR-A	467.4	529.7	2.58	24.77	25.5
PC+0.1% PPFBS ^a	455.0	503.4	1.96	21.88	37.5
PC+0.1% KSS ^b	450.1	510.0	2.25	26.00	38.3

^aPPFBS (potassium perfluorobutane sulfonate), data taken from reference 15.

^bKSS (potassium diphenylsulfone sulfonate), data taken from reference 16.

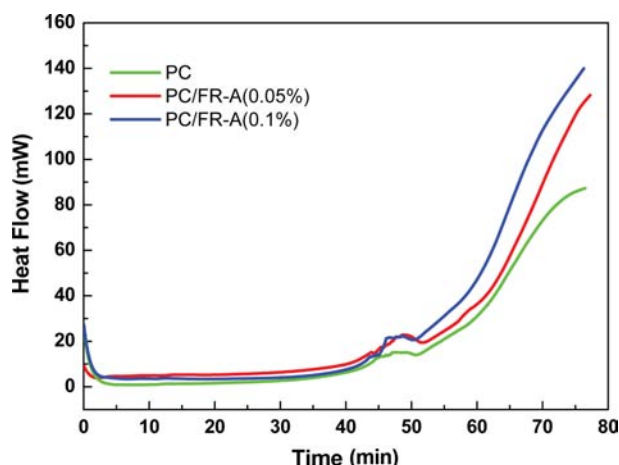


Figure 5. DSC curves of PC/FR-A (view of time).

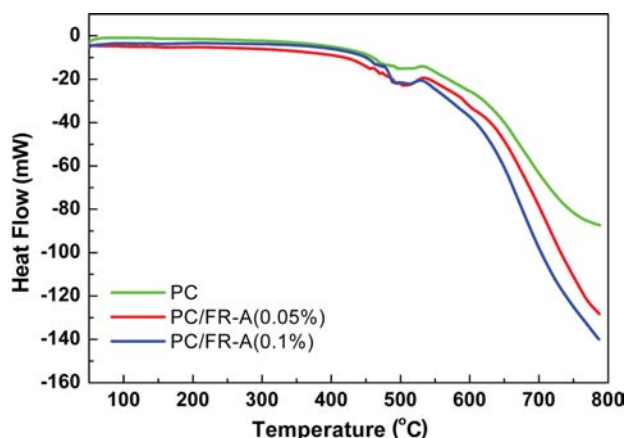


Figure 6. DSC curves of PC/FR-A (view of temperature).

the char generated in high temperature, the better flame retardancy was obtained. This indicated that a part of PC/FR-A had not completely combusted, possibly undergoing a char-forming process.

In PC/FR-A system, the retardant mechanism of PC/FR-A system was similar to KSS. This point was confirmed by the above TGA curves.¹⁷ It was supposed that the byproducts SO_2 and H_2O from the desulfonation of FR-A promote the PC degradation. The more amounts of sulfonate salts generated more SO_2 and H_2O to make PC degradation at lower temperature. Moreover, due to the increasing conjugation of the aromatic ring with $\text{C}=\text{O}$ and/or $\text{C}=\text{C}$ double bonds, the presence of a highly cross-linking aromatic ester and ether char inhibited the supply of flammable gas and heat transfer. It was known that the sulphonate flame retardant accelerates further carbonate-ether and Fries-type rearrangement of PC.¹⁸

Conclusions

A novel sulfonate flame retardant, 1,3,5,7-tetrakis(phenyl-4-sodium sulfonate) adamantane (FR-A), was successfully synthesized. The LOI measurements, TGA and DSC analysis showed that this novel sulfonate flame retardant had effective flame retardancy for PC. The flame retardancy of PC was improved obviously, and gave easily UL 94 V-0 rating with small amount of FR-A (0.08 wt%), have considerable increase in LOI by almost 5 units and confirmed the flame retardant.

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