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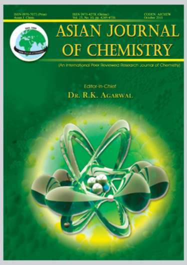

Synthesis and Characterization of Novel Fluorinated Polyurethane Elastomer Based on 1,4-*Bis*(4-amino-2-trifluoformethyloxyphenyl)benzene†

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A novel chain extender was synthesized containing fluorine element 1,4-*bis*(4-amino-2-trifluoromethyloxyphenyl)benzene (BAFB). Then BAFB was used to prepare a series of fluorine containing polyurethane elastomers (FPUEs) with different fluorine contents. The structures and properties of FPUEs were measured by fourier transform infrared spectroscopy, thermo-gravimetric analysis, microscale combustion colorimeter (MCC), water absorption test and contact angle measurement. The results show fluorine was incorporated into the polyurethane chains through the reaction between BAFB and prepolymers. Fluorine containing polyurethane elastomers show a better hydrophobic property, lower surface tension and better thermal stability due to the introduction of fluorine. The surface tension of FPUEs decreases from 29.8-20.8 mN/m with the F content increasing from 2.7-5.9 %. Furthermore, FPUEs also exhibit good flame resistance and the peak heat release rate (PHRR) of FPUE based on BAFB (466.2 W/g) is much lower than that of polyurethane elastomer without F element (537.2 W/g).

Key Words: Fluorine-containing diamine, Polyurethane, Surface tension, Heat resistance, Thermal stability, Flame resistance.

INTRODUCTION

Polyurethanes (PUs) are widely used because of their excellent mechanical properties such as abrasion resistance, toughness and tensile strength[1]. But their surface property, thermal stability and oxidative stability restrict their application. In order to overcome these problems, many researchers focus on synthesizing polyurethanes with special elements, such as fluorine element. The introduction of fluorine groups into the structure provides traditional polyurethanes with excellent mechanical properties, low surface force, high heat resistance and so on.

There are mainly three major methods of synthesizing fluorinated polyurethane by the introduction of fluorine containing soft segment, diisocyanates and chain extenders. Trombetta *et al.*[2] synthesized fluorinated polyurethane based on perfluoropolyether. Those FPUEs had quite low critical surface tension of wetting and high water and oil repellence. Takakura *et al.*[3] synthesized high performance antithrombus fluorine-containing polyurethane elastomers based on 2,2,3,3,4.4,5,5-octafluorohexamethylene diisocyanate. Wang[4] synthesized a series of FPUs using 2,2,3,3-tetrafluoro-1,4-butanediol as the chain extender and based on various soft segments. The result indicated that the crystallinity of hard segment domains declined with increasing soft segment length. At present, there have been few reports in the literature on synthesizing FPUEs by using short-chain fluorinated diamine. Furthermore, the flame retardant properties of the material has become more and more important, but the flame retardant properties of FPUEs have not been adequately investigated.

In this work, a fluorine containing diamine, 1,4-*bis*(4-amino-2-trifluoromethyloxy-phenyl)benzene (BAFB) was synthesized. Fluorinated polyurethane elastomers were prepared by using BAFB as chain extender. The structures and properties of FPUEs were studied by FTIR, TGA, microscale combustion colorimeter and contact angle measurement.

EXPERIMENTAL

2-Chlorobenzotrifluoride (99 % purity) was purchased from Huaian Yongchuang Chemical Co. Ltd. N,N-Dimethyl-

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formamide (DMF) (from Sinopharm Chemical Reagent Co. Ltd.) was purified by distillation under reduced pressure from calcium chloride. Hydrazine hydrate (80 % purity), $FeCl_3 \cdot 6H_2O$ (CR) (from Sinopharm Chemical Reagent Co. Ltd.), potassium carbonate (AR) and hydroquinone (AR) (from Guangdong Xilong Chemical Co. Ltd.) were used as received. Toluene diisocyanate (TDI) was purchased from Mitsui Chemicals. Polyoxypropylene glycol DDL (Mn = 1000, 2000, 3000) was obtained from Shandong Dexin Lianbang Chemical Co. Ltd. Poly(tetramethylene ether glycol) (PTMEG, Mn = 2000) was obtained from Zhejiang Dongyue Chemical Co. Ltd.

Synthesis of 1,4-*bis*(4-amino-2-trifluoromethyloxyphenyl)benzene (BAFB): 2-Chlorobenzotrifluoride (80 mL) and concentrated sulfuric acid (60 mL) were introduced into a three-neck round bottom 500 mL glass flask equipped with a thermometer and a mechanical stirrer. The mixture of concentrated sulfuric acid (90 mL) and concentrated nitric acid (90 mL) were added continuously to the flask at a constant rate over a period of 0.5 h. Then the mixture was maintained at 45 ºC for 4 h. The mixture was poured into an excess amount of ice-water after the reaction ended. The formed precipitate was collected and washed with water to neutral. The crude product was purified by vacuum distillation to acquire 2-chloro-5-nitro-trifluoromethylbenzene (CNFB) with a yield of 91.3 %.

2-Chloro-5-nitro-trifluoromethylbenzene (CNFB) (136.5 g) dissolved in DMF (200 mL), potassium carbonate (45.5 g) and hydroquinone (70.0 g) were introduced into a glass flask equipped with a thermometer and a mechanical stirrer. The mixture was stirred and kept at 130 ºC for 24 h. Then the reactants was cooled and filtered to extract precipitate. The solvent (DMF) was removed by vacuum distillation to get the crude product. The crude product was recrystallized with 2-methoxyethanol to produce light yellow crystals and dried by vacuum to obtain 1,4-*bis*(4-nitro-2-trifluoformethyloxyphenyl)-benzene (BNFB) (69.4 % yield).

1,4-*Bis*(4-nitro-2-trifluoformethyloxyphenyl)benzene (BNFB) (140.2 g) dissolved in 2-methoxyethanol (270 mL), activated carbon (10 g) and $FeCl_3 \cdot 6H_2O$ (1.3 g) were added to a four-neck, round-bottom 500 mL glass flask equipped with a thermometer, a reflux condenser and a mechanical stirrer. The mixture was first heated slowly to 110 ºC. Then the hydrazine hydrate (40 mL) was added continuously to the flask at a constant rate over a period of 2 h. The reaction mixture was stirred for 10 h with micro-reflux. After cooling to room temperature, the mixture was filtered and the filtrate was poured into 600 mL HCl (20 %), then ammonium hydroxide solution (20 %) was added to adjust the pH to 11-12 for the precipitate. The precipitate was filtered and recrystallized with ethanol. A brown crystalline solid (BAFB) was collected by filtration and dried under reduced pressure (yield: 89.4 %). **Scheme-I** shows the route of synthesizing BAFB.

Synthesis of fluorine containing polyurethane elastomers (FPUEs): Poly(tetramethylene ether glycol) (PTMEG) or polyoxypropylene glycol (DDL) was heated to 110-120 ºC, stirred and vacuumed for 2 h to remove trace water. Thereafter, vacuuming was stopped and nitrogen gas charged into the reactor. When the temperature was reduced to 70 ºC, toluene diisocyanate (TDI) was added and reacted for 2 h. Then, the prepolymer removed bubbles by vacuum.

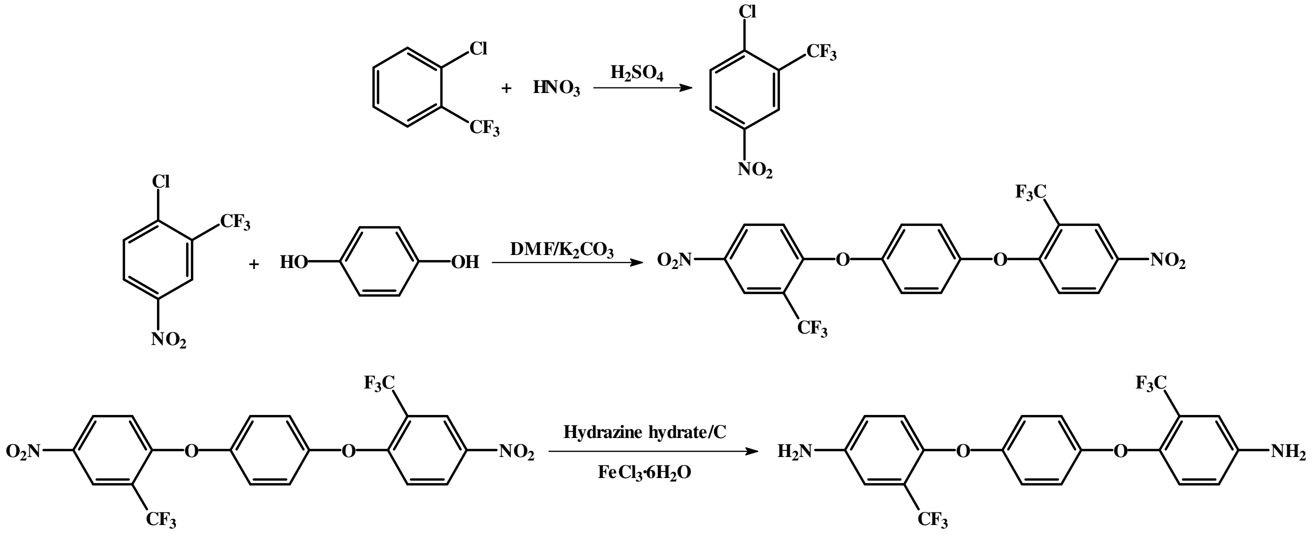
The chain extender and prepolymer were mixed and stirred fully. Then the mixture was casted on a teflon plate at 70 ºC for 6 h and put in an oven at 115 ºC for 2 h. Finally, the FPUEs were synthesized. Table-1 shows the description of FPUEs and polyurethane.

TABLE-1
THEORETICAL COMPOSITION OF POLYURETHANE

Sample	Soft segment	Molar ratio of TDI/soft segment (R)	Chain extension coefficient (δ)[a]	Fluorine content (%)
PUE	PTMEG-2000	2	0.9	0
FPUE1	PTMEG-2000	2	0.9	3.7
FPUE2	DDL-1000	2	0.9	5.9
FPUE3	DDL-2000	2	0.9	3.7
FPUE4	DDL-3000	2	0.9	2.7

[a] Chain extension coefficient is the molar ratios of NH_2 of chain extender and NCO of prepolymer; and all the chain extenders used here are BAFPP except for PUE of MOCA.

Characterization: The FTIR spectra of diamine were recorded by pressing potassium bromide troche and the FTIR



Scheme-I: Synthesis route of BAFB

spectra of elastomers were recorded by attenuated total reflection (ATR) using a MAGNA-IR 750 FTIR Spectrometer (Thermo Scientific, Waltham, MA, USA). The scanning range was between 4000 and 500 cm^{-1} at a resolution of 4 cm^{-1}. 32 scans were averaged for each sample.

A Bruker Avance AV 400 MHz spectrometer was used to obtain ^1H NMR spectrum for which DMSO-d_6 was used as solvents using tetramethylsilane and trichlorofluoromethant as internal standards, respectively.

Contact angles were measured with a JC2000D contact angle goniometer (Shanghai Zhongcheng Digital Technical Equipment Co. Ltd., Shanghai, China). The samples were flattened on the sample stage. Contact angles were measured on 1 pL of solution with H_2O and EG. Images were immediately caught.

Water absorption tests were according to ASTM D570. The water absorption was calculated according to the following formula:

$$\text{Water absorption} = \frac{(M_2 - M_1)}{M_1} \times 100\ \%$$

in which M_1 is the former weight and M_2 is the weight after immersion in water.

TGA was carried out using a NETZSCH STA 409PC/PC analyzer (Selb, Germany) from 30-700 ºC at a linear heating rate of 10 ºC/min under a nitrogen flow. The nitrogen flow was 25 mL/min. Samples were measured in a sealed alumina pan with a mass of about 10 mg.

The flammability property was characterized by a Govmark microscale combustion calorimeter (MCC-2, Farmingdale, NY, USA) based on the principle of oxygen consumption. The samples were heated with a linear heating rate of 1 ºC/s in a pyrolyzed furnace.

RESULTS AND DISCUSSION

Characterization of 1,4-*bis*(4-amino-2-trifluoromethyloxyphenyl)benzene (BAFB) and fluorine containing polyurethane elastomers (FPUEs): Fig. 1 shows the FTIR spectrum of BNFB. The nitro absorption peaks at 1530 and 1350 cm^{-1} are due to the asymmetric and symmetric stretching of $-NO_2$ group, respectively and these are not observed in BAFB. 1,4-*Bis*(4-amino-2-trifluoromethyloxyphenyl)benzene shows typical N-H stretching absorption peaks at 3453 and 3362 cm^{-1} and N-H bending absorption peaks at 1632 and 823 cm^{-1}. In addition, the C-F stretching vibration absorptions from $-CF_3$ are observed at 1160 and 1128 cm^{-1}. In fact, the C-F absorptions from $-CF_3$ become a wide absorption band as its multiple stretching vibration which is in agreement with the literature[5].

In the ^1H NMR of BAFB (Fig. 2), the electron-donating effect of amino/ether groups and proton-donating effect of trifluoromethyl groups are demonstrated by the five groups of peaks: 6.83 ppm (H_b, 2H), 6.82 ppm (H_c, 2H), 6.85 ppm (H_a, 4H), 6.91 ppm (H_d, 2H), 5.42 ppm (H_e, 4H). The hydrogen peaks from H_b and H_c are in the upper-field as the shielding effect of the electron-donating effect of amino/ether groups and the hydrogen peaks from H_d are in the lower-field as the shielding effect of the proton-donating effect of trifluoromethyl groups. The hydrogen peaks from H_a between H_b and H_d indicate the multiple effect of ether groups and trifluoromethyl groups.

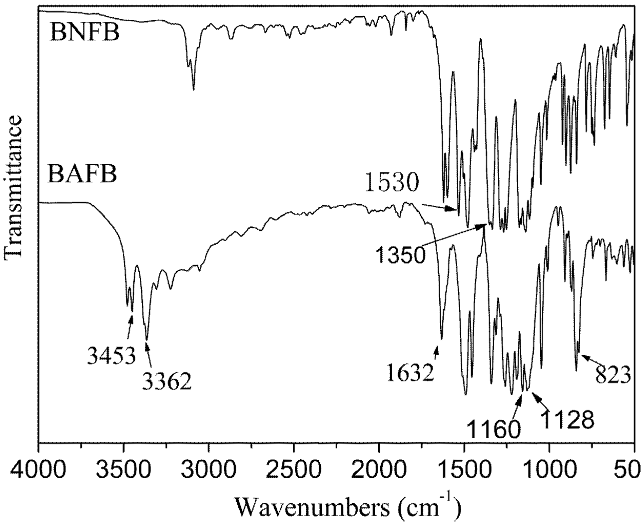


Fig. 1. FTIR spectra of of BNFB and BAFB

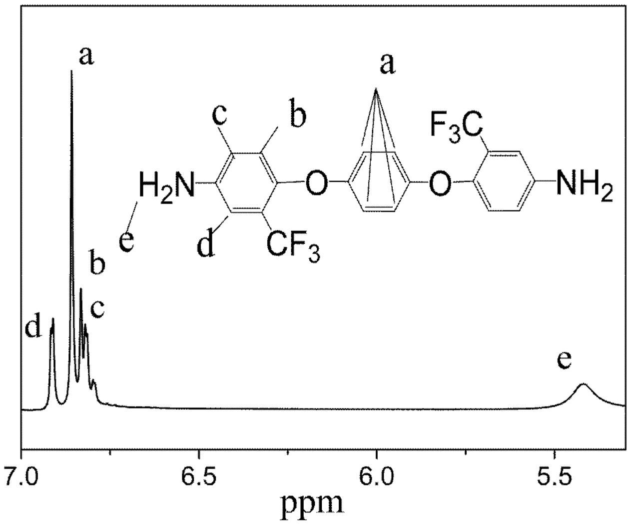


Fig. 2. ^1H NMR spectra of BAFB

The above analysis results are in good agreement with the chemical structure of BAFB.

Fluorinated polyurethane elastomers were characterized by FTIR. Urethane imino peaks at 3286 cm^{-1} (N-H, stretching), 1726 cm^{-1} (C=O, symmetric stretching) and 1110 cm^{-1} (C-O-C, stretching), suggest the formation of urethane group. Simultaneously, chain-extending reaction occurs which can be proved by the disappearance of the peak at 2270 cm^{-1} (-NCO, stretching). The peaks at 2971 and 2867 cm^{-1} are due to the stretching of CH_2 group. The C-F stretching vibration absorptions are not conspicuous as it may be overlapped[6] by the strong absorption of C-O-C around 1110 cm^{-1}.

Surface properties of fluorine containing polyurethane elastomers: Contact angle is a very important parameter as it can reflect the surface energy of materials directly. By measuring the contact angle, solid surface tension can be calculated by the following formula[7]:

$$(1+\cos\theta_{H_2O})\gamma_{H_2O} = \frac{4\gamma^{d}_{H_2O}\gamma^{d}}{\gamma^{d}_{H_2O}+\gamma^{d}} + \frac{4\gamma^{p}_{H_2O}\gamma^{p}}{\gamma^{p}_{H_2O}+\gamma^{p}} \qquad (1)$$

$$(1+\cos\theta_{EG})\gamma_{EG} = \frac{4\gamma_{EG}^{d}\gamma^{d}}{\gamma_{EG}^{d}+\gamma^{d}} + \frac{4\gamma_{EG}^{p}\gamma^{p}}{\gamma_{EG}^{p}+\gamma^{p}} \qquad (2)$$

in which $\gamma_{H_2O} = \gamma_{H_2O}^{d} + \gamma_{H_2O}^{p}$, $\gamma_{EG} = \gamma_{EG}^{d} + \gamma_{EG}^{p}$, $\gamma = \gamma^{d} + \gamma^{p}$, γ are the elastomer surface tension. γ^d is the dispersion component and γ^p is polar component. θ_{H_2O} and θ_{EG} are the contact angles of polymer with water and ethylene glyol, respectively. The numerical values used are $\gamma_{H_2O}^{d} = 21.8$ mN/m, $\gamma_{H_2O}^{p} = 51$ mN/m, $\gamma_{EG}^{d} = 29.3$ mN/m, $\gamma_{EG}^{p} = 19.0$ mN/m.

Table-2 shows the contact angle and surface tension results of PUE and FPUEs. It can be seen from Table-2 the contact angles of PUE with water and ethylene glycol are 67.3 and 52.7° and the surface tension is 38.7 mN/m. The surface tension of FPUE1 is only 24.5 mN/m, almost reduced by 40 % compared with that of PUE. It shows that the introduction of fluorine to the polyurethane elastomer reduces the surface tension. The surface tension of FPUE2, FPUE3 and FPUE4 increases gradually as the molecular weight of polyoxypropylene glycol increases (and the fluorine content decreases).

TABLE-2
CONTACT ANGLE AND SURFACE TENSION RESULTS OF PUE AND FPUES

Sample	Contact angle (°)		Surface tension (mN/m)		
	H_2O	EG	γ^d	γ^p	γ
PUE	67.3	52.7	11.4	27.3	38.7
FPUE1	89.8	78.4	6.4	18.1	24.5
FPUE2	97.8	79.1	10.1	10.7	20.8
FPUE3	88.2	78.7	5.6	19.9	25.5
FPUE4	80.1	69.6	7.4	22.4	29.8

Water absorption is an important parameter to characterize the hydrophobic properties of a material.

The water absorption of PUE1 is 4.9 % and that of FPUE1 is just 2.5 %, which decreases about half from the value of PUE. It can be concluded that the introduction of fluorine improves the hydrophobic properties effectively. The possible reason is that fluorocarbon groups migrate to and enrich on the outmost surface of FPUEs resulting in lower surface free energy of FPUEs[8], so the FPUEs show better hydrophobic properties.

Thermal property of fluorine containing polyurethane elastomers (FPUEs): The TGA representation temperature of PUE and FPUEs are shown in Table-3. T_{10}, T_{50} and T_{max} are the temperature with 10 %, 50 % and max mass loss of the sample. Comparing PUE with FPUE1, the initial decomposition temperature (T_{10}) of FPUE1 is 309 and 16 °C higher than that of PUE. The T_{50} and T_{max} of FPUE1 are 409 and 418 °C, also higher than those of PUE. It can be concluded that FPUE1 has a better thermal stability than PUE. The possible reason is that FPUE1 contains stronger polar -CF_3 group which increases hydrogen bonds between molecular chains and results in reinforcing the microphase separation, so more heat are needed to destroy the structure of FPUE. The initial decomposition temperature (T_{10}) of FPUE2 (290 °C) is much lower than that of FPUE4 (307 °C). With the hard segment content increasing, the initial thermal stability of polyurethane elastomer decreases. The reason for this is much more of biuret and urea-based carbamate were generated, which have poor thermal stability[9].

TABLE-3
TGA RESULTS OF PUE AND FPUES

Samples	v_T (°C/min)[a]	T_{10} (°C)	T_{50} (°C)	T_{max} (°C)
PUE	10.0	288	393	415
FPUE1	10.0	309	409	418
FPUE2	10.0	290	370	381
FPUE3	10.0	299	378	387
FPUE4	10.0	307	382	387

[a]v_T is the heating rate.

Flame retardant properties of polyurethane elastomer (PUE) and fluorine containing polyurethane elastomers (FPUEs): Microscale combustion colorimeter (MCC) can be used to determine rapidly and efficiently the main combustion parameters of a variety of plastic, wood, textiles and so on. The peak of the heat release rate (PHRR) and total heat release (THR) have been found to be important parameters to evaluate fire safety[10]. Through Fig. 3 and Table-4, the PHRR and THR of PUE are 537.2 W/g and 23.0 KJ/g, but the values of FPUE1 which contain the same soft segment are 466.2 W/g and 22.9 KJ/g. The ignition temperature is corresponding to the temperature of maximum heat release rate. The ignition temperature of FPUE1 is higher than that of PUE. It means that the FPUE1 delayed the time to reach the maximum flammable gas release rate. The FPUE1 has better thermal stability which is also in good agreement with the TGA result. The THR of FPUE1 and PUE are almost the same, but the PHRR of FPUE-1 is much

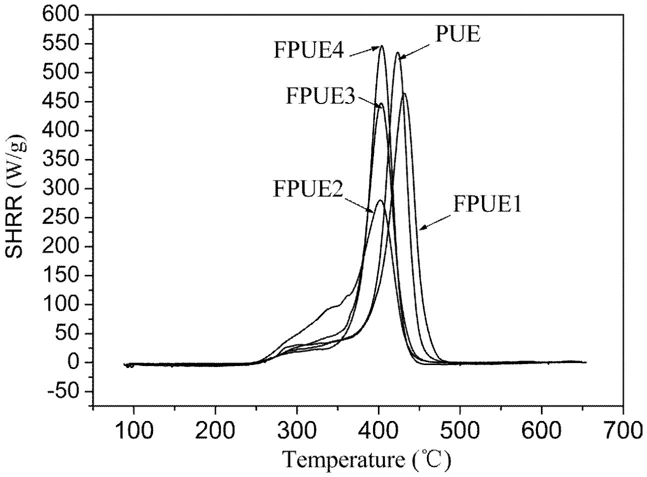


Fig. 3. SHRR curves of the PUE and FPUEs

TABLE-4
RESULTS OF MCC OF PUE AND FPUE

Samples	PHRR (W/g)	THR (KJ/g)	Ignition temperature (°C)
PUE	537.2	23.0	423.4
FPUE1	466.2	22.9	431.7
FPUE2	281.1	20.1	401.9
FPUE3	448.0	21.3	403.2
FPUE4	549.7	22.6	403.9

lower than that of PUE, FPUE1 shows better flame retardancy. The possible reason is that the degradation rate of FPUE1 decrease as its thermal stability increase, then the release rate of flammable gas decrease.

With the content of hard segment increasing the peak of the heat release rate (PHRR) and total heat release (THR) decrease from 549.7 W/g and 22.6 KJ/g to 281.1 W/g and 20.1 KJ/g (from FPUE4 to FPUE2), indicating that the flame retardant property of the FPUEs improves. The most likely reason is that the FPUEs based on BAFB first decomposed and formed a residue which prevent further decomposition of FPUEs. Increasing char formation can limit the production of combustible carbon-containing gases, decreases the THR on pyrolysis, as well as decreasing the PHRR. A higher char yield will enhance the flame retardancy[11]. The char yield of FPUE4 is 2.0 % and with the hard segment increase, the char yield of FPUE3 and FPUE2 reach 3.1 and 5.0 %, respectively. So FPUE2 show the best flame retardancy in the three FPUEs. It can be concluded that the flame retardation of FPUEs increases as the char yield increasing with the hard segments increasing.

Conclusion

1,4-*Bis*(4-amino-2-trifluoromethyloxyphenyl)benzene (BAFB) was synthesized from 2-chlorobenzotrifluoride and its structure was confirmed by FTIR, ^{1}H and ^{19}F NMR. The FPUEs prepared by using BAFB have a low surface tension, good hydrophobic property, high thermal stability and flame retardant properties. These FPUEs have low surface tension from 20.8-29.8 mN/m and low water absorption (FPUE1, 2.5 %). The initial degradation temperatures (T_{10}) of FPUEs in nitrogen from 298.5-311.6 ºC, all of them were much higher than that of PUE without F, which is due to the fact that the incorporation of stronger polar -CF_3 group increases hydrogen bonds between molecular chains. The initial thermal stability of polyurethane elastomer decreases with an increase in the hard segment content as much more poor stability biuret and urea-based carbamate are generated. The PHRR and THR of FPUE2 are 281.1 W/g and 20.1 KJ/g, exhibiting better flame retardancy than that of PUE. These properties should make these FPUEs attractive for practical applications.

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