



Study on Fluorine-Containing Polyurethane Elastomers Based on 2,2-Bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]hexafluoropropane†

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A series of fluorine-containing polyurethane elastomers (FPUEs) were synthesized from 2,2-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]hexafluoropropane (BAFPF₆P), which was made from 2-chlorobenzotrifluoride and 2,2-bis(4-hydroxyphenyl) hexafluoropropane and characterized by Fourier transform infrared spectroscopy, nuclear magnetic resonance, thermogravimetric analysis, microscale combustion calorimeter and contact angle measurement. The results show that the fluorine-containing polyurethane elastomers prepared from BAFPF₆P have good thermal stability and low surface tension. Furthermore, fluorine-containing polyurethane elastomers also exhibit good flame retardance and the peak heat release rate and total heat released of fluorine-containing polyurethane elastomer based on BAFPF₆P are much lower than those of polyurethane elastomer without the fluorine element.

Keywords: Fluorinated diamine, Fluorinated polyurethane elastomer, Surface properties, Flame retardancy.

INTRODUCTION

Polyurethane (PU) is widely applied in synthetic leathers, coatings, foams, adhesives, sealants, *etc.* due to its excellent properties. Fluorinated polyurethane (FPU) not only maintains the excellent properties of polyurethane but is also noted for some outstanding features such as low surface tension, low water absorption and good thermal stability; consequently, since the first patent about fluorinated polyurethane was published, it has attracted many scientists to do research in this area¹⁻⁴.

In this study, a series of fluorine-containing polyurethane elastomers (FPUEs) were synthesized from 2,2-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl] hexafluoropropane (BAFPF₆P) which was made from 2-chlorobenzotrifluoride and 2,2-bis(4-hydroxyphenyl)hexafluoropropane. The structure of BAFPF₆P was characterized by Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) and the surface tension, thermostability and flame retardancy of FPUEs were investigated.

EXPERIMENTAL

Synthesis of fluorinated polyurethane elastomers:

Polyester diol was heated to 110 °C, stirred and vacuumed for 2 h to remove trace water. When the temperature was reduced

to 70 °C, TDI was added and reacted for 2 h. The prepolymer was prepared. The synthesis route of BAFPF₆P is given in **Scheme-I**.

The molten chain extender (BAFPF₆P or MOCA) and prepolymer were fully mixed, then the mixture was casted on a Teflon plate at 70 °C for 2 h and 115 °C for another 2 h. Thus, the FPUEs were synthesized. Table-1 provides a description of the FPUEs and polyurethane elastomer.

Characterization: The contact angles of water and ethylene glycol on FPUE were measured with a JCZ 2000 contact angle goniometer at room temperature by the sessile drop method. The surface tension is calculated through the following equations:

$$\gamma_s = \gamma_s^d + \gamma_s^p$$
$$\cos \theta = \frac{2}{\gamma_L} [(\gamma_L^d \gamma_s^d)^{1/2} + (\gamma_L^p \gamma_s^p)^{1/2}] - 1$$

where γ_s is the elastomer surface tension, γ^d is the dispersion component, γ^p is the polar component, θ is the contact angle of polymer with liquid (water or ethylene glycol in this test), $\gamma_{H_2O}^d = 21.8 \times 10^{-3}$ N/m, $\gamma_{H_2O}^p = 51 \times 10^{-3}$ N/m, $\gamma_{EG}^d = 29.3 \times 10^{-3}$ N/m, $\gamma_{EG}^p = 19.0 \times 10^{-3}$ N/m.

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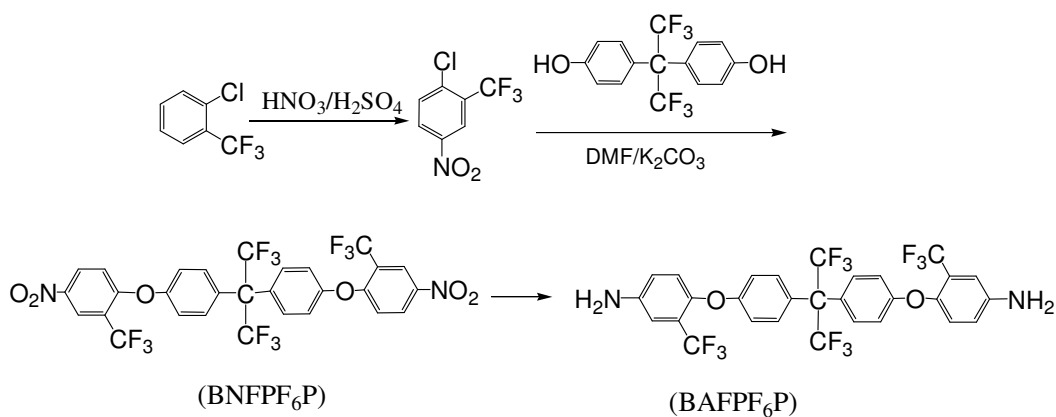
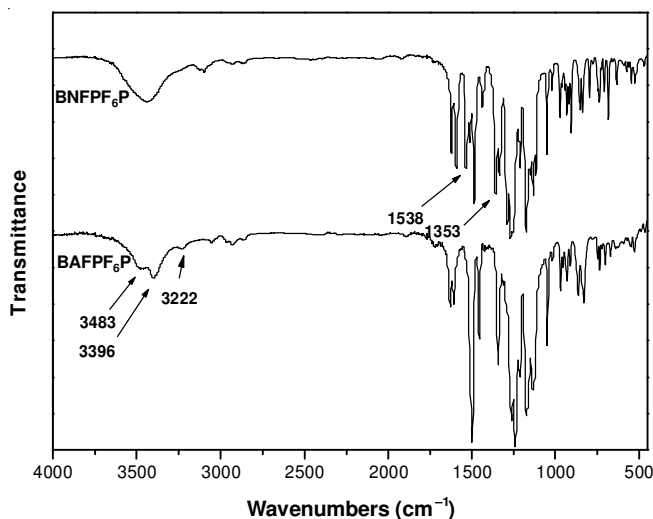
Scheme-I: Synthesis route of BAFPF₆P

TABLE-1 DESCRIPTION OF THE FPUES AND PUE				
Sample	Soft segment	R*	Chain extension coefficient*	Fluorine content wt. (%)
PUE	Polyester diol 1975	2.0	0.9	0
FPUE1	Polyester diol 1975	1.8	0.9	6.1
FPUE2	Polyester diol 1975	2.0	0.9	7.2
FPUE3	Polyester diol 1975	2.4	0.9	9.1

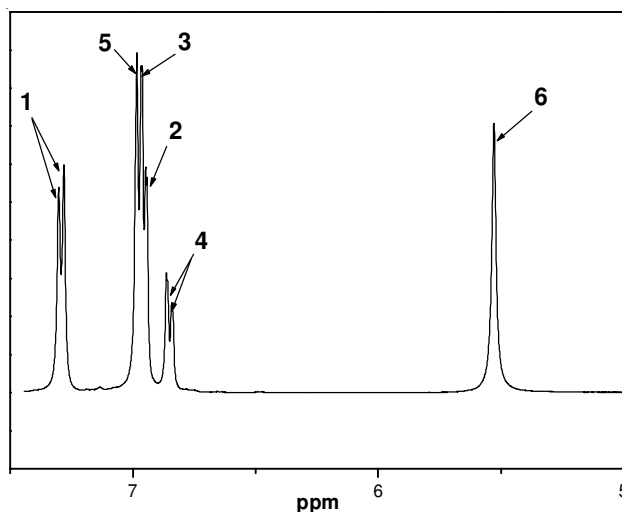
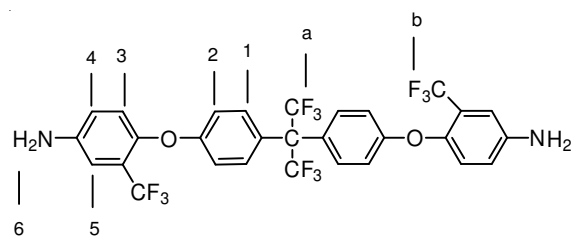
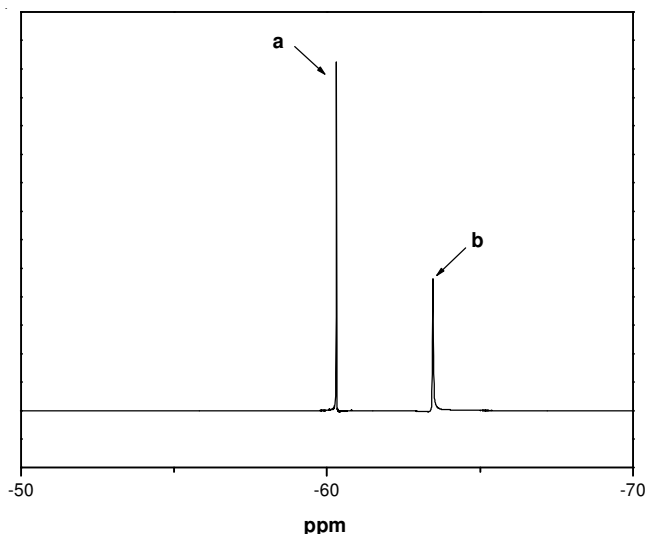
*R is the molar ratios of NCO of TDI and OH of soft segment. *Chain extension coefficient is the molar ratios of NH₂ of chain extender and NCO of prepolymer.

RESULTS AND DISCUSSION

Characterization of BAFPF₆P: The chemical structures of BNFPF₆P and BAFPF₆P were identified by FTIR (Fig. 1), ¹H NMR (Fig. 2) and ¹⁹F NMR (Fig. 3).

Fig. 1. FTIR spectra of BNFPF₆P and BAFPF₆P

The FTIR of BNFPF₆P in Fig. 1 shows that there are nitro absorption peaks at 1538 cm⁻¹ which is from -NO₂ asymmetric stretching and 1353 cm⁻¹ which is from symmetric stretching. But the two peaks disappear in the FTIR of BAFPF₆P, which shows that the reduction of -NO₂ has happened; In the meantime, the typical N-H stretching absorptions at 3483 and 3396 cm⁻¹, N-H bending absorption at 1634 cm⁻¹ are found in the FTIR of BAFPF₆P, which indicates the -NH₂ has arisen.

Fig. 2. ¹H NMR spectrum of BAFPF₆PFig. 3. ¹⁹F NMR spectrum of BAFPF₆P

All the above results indicate that BNFPF₆P completely converts into BAFPF₆P. The peaks at 1502 cm⁻¹ is a characteristic absorption peak of the benzene ring. The C-F multiple stretch bending absorptions from -CF₃ are observed between 1300 and 1100 cm⁻¹.

The ¹H and ¹⁹F NMR of BAFPF₆P are shown in Figs. 2 and 3, respectively. The structure of BAFPF₆P molecule is symmetrical and all the hydrogen can be divided into six types for different chemical environments. The ratio of the integral height of H₁:H₂:H₃:H₄:H₅:H₆ is 4:4:2:2:2:4, which is identical with the number of hydrogen atoms of BAFPF₆P. In Fig. 3, two peaks are found at -60.28 and -63.44 ppm, indicating that the fluorine atoms are in two different chemical environments. The ratio of the integral height Fa and Fb is equal to 1, which is in accordance with that of the designed product.

Thermal property of FPUEs: T₁₀, T₅₀ and T_{max} are the temperature of 10 %, 50 % and max weight loss of the sample, respectively. The T₁₀ and T₅₀ of FPUE2 are higher than those of polyurethane elastomer, meanwhile the char yield of FPUE2 (19.6 %) is higher than that of PUE (14.9 %). It can be concluded that FPUE2 has a better thermal stability than PUE (Table-2).

Sample	T ₁₀ (°C)	T ₅₀ (°C)	T _{max1} (°C)	T _{max2} (°C)	Char yield (%)
PUE	329	429.2	308.4	439.7	14.9
FPUE1	350.6	431.6	307.4	438.4	17.3
FPUE2	349	430.2	303	433	19.6
FPUE3	333.4	430.2	298.6	433	21.2

Flame retardant property of FPUEs: The THR and PHRR of FPUE2 are 15 KJ/g and 179.5 W/g, respectively. They are both lower than those of PUE which are 17.1 KJ/g and 275.6 W/g. FPUE2 and PUE have the same soft segment, R and Chain extension coefficient, with the only difference in the types of chain extender. It means that FPUE2 based on BAFPF₆P shows better flame retardation than PUE based on MOCA; in other words, the introduction of fluorinated chain extender improves the flame retardation.

From FPUE1 to FPUE3, the THR and PHRR decrease from 15.3 KJ/g and 244.4 W/g to 11 KJ/g and 119.1 W/g, respectively. The main reason for this is that, from FPUE1 to FPUE3, they all contain the same soft segment and chain extender, but the R increases from 1.8-2.4, so the increase in the fluorinated chain extender content gradually results in an increase in flame retardation (Fig. 4).

Surface property of FPUEs: The contact angle of PUE with water and ethylene glycol are 66.2 and 51.1° and the surface tension is 35.77 mN/m, while the surface tension of FPUE1, FPUE2 and FPUE3 is obviously lower. The surface tension of FPUE3 is just 18.18 mN/m, almost reduced 50 % compared with PUE. It shows that the introduction of fluorine to the polyurethane elastomer reduces the surface tension. The main reasons for this is that the CF₃ bears relatively low surface energy, so it is easy to migrate to and enrich on the surface, which results in the higher concentration of CF₃ groups on the surface than in bulk and then the FPUEs show excellent low surface energy (Table-3).

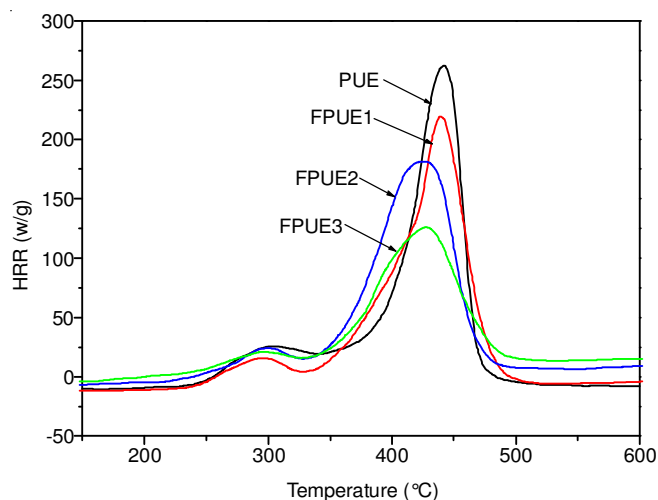


Fig. 4. MCC curves of FPUEs

Sample	Contact angle (°)		Surface tension ($\times 10^{-3}$ N/m)		
	Water	Ethylene glycol	γ^d	γ^p	γ
PUE	66.2	51.1	10.07	25.71	35.77
FPUE1	89.7	70	15.45	6.52	21.97
FPUE2	98.8	77	17.64	2.47	20.11
FPUE3	105.5	83.5	17.12	1.06	18.18

Conclusion

2,2-Bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]-hexafluoropropane (BAFPF₆P) was synthesized from 2-chlorobenzotrifluoride and 2,2-bis(4-hydroxyphenyl)hexafluoropropane and it was utilized as a chain extender to prepare a series of FPUEs. Through the FTIR and NMR analysis, the results demonstrate the structure of synthetic product is in accord with that of the expected design. The influence of fluorine on thermal stability, flammability and surface properties of the FPUE were investigated. The results show that the introduction of fluorinated chain extender can improve the surface properties efficiently. The surface tension of FPUE3 is almost reduced by 50 % compared with that of PUE. The results from TGA show that the introduction of fluorinated chain extender to the PUE improves the thermal stabilities; the THR and PHRR of FPUE2 are 15 KJ/g and 179.5 W/g, respectively, which indicates that the fluorinated chain extender incorporated contributes to improved flame-retardant properties. These properties should make these FPUEs attractive for practical applications.

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