Synthesis and characterization of fluoropoly(amide–sulfonamide)s via polycondensation

Huan Chen, Hong Li, Supeng Pei, Xiaowen Wen, Yongming Zhang*

School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China

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ABSTRACT

Novel fluorine-containing polymers, fluoropoly(amide–sulfonamide)s were synthesized for the first time by polycondensation from β-hydroxytetrafluoroethanesulfonic acid sultone (TFE-sultone) and hexamethylenediamine. The chemical structures of the obtained F-PASAs were characterized by intrinsic viscosity measurements, GPC, FTIR, ^{1}H NMR, ^{19}F NMR and element analysis in detail. Thermal properties and optical property of F-PASAs were investigated by DSC, DMA, TGA and UV–vis spectra, respectively. The investigation indicated that these functional fluoropolymers in which there are both amide and sulfonamide linkages along the polymer main chains possessed distinctive structure as well as unique properties such as thermal properties, clean and high transparency and compatibility with nylons.

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1. Introduction

Polyamides have occupied a prominent position in the realm of polymers since their discovery by Carothers in 1934 [1,2]. Polyamides exhibit a relatively high modulus, toughness and strength, low creep and good temperature resistance that make them widely recognized and applied [3,4]. However, research in developing polyamides with new structures is relatively weak, in view of little variance in designing new monomers, especially in new diacid monomers. Meanwhile, an analogous kind of polymer named polysulfonamides is much less studied and applied since their synthesis by the interfacial polymerization of aliphatic diamines with disulfonyl chlorides [5,6]. Sulfonamides are known for their biological activity [7] and also are used as sorbents of metal ions, chelating agents [8] and in self-assembly [9]. A comparison of the chemical properties of amides and sulfonamides suggests that polysulfonamides would have some advantages as compared with polyamides [10,11]. For example, sulfonamides are much more resistant to hydrolysis than amides [12]. However, there are only a few examples of sulfonamide polymers dating from the early 1960s [13]. It is mainly due to the lack of disulfonyl monomers, the difficulty to preserve such active monomers and to maintain the polymerization by sulfonamidation. The attempt to combine amide group with sulfonamide group gives birth to poly(amide–sulfonamide)s. This leads to a new class of polymer that in certain aspects

could bridge the gap between polyamides and polysulfonamides. Chan and colleagues [14–17] have reported poly(amide–sulfonamide)s as asymmetric membranes. They incorporated a sulfonamide group into a diamine, then enabled this diamine containing a sulfonamide group to react with a diacid chloride by amidation to yield poly(amide–sulfonamide)s, which were found to be useful materials in separation processes.

Polycondensation is a fundamental way of polymerization, which is widely used to prepare many kinds of common polymers, such as polyamides, polyimides and polyesters. Intense research activity still continues in this area of polymer science with combination of different repeating units [18–21]. However, there are few random and alternating copolymers in which the two repeating units have different functional groups for the difficulty of simultaneously performing two different reactions, such as amidation simultaneously with sulfonamidation. In addition, although the introduction of fluorine element always brings about uniqueness of the materials [22–24], such as making these material useful in microelectronics industry for their thermal stability and chemical compatibility [25] and as photoresists for their high transparency [26], it is rather difficult to incorporate fluorine element into the polymer structure. To tackle the difficulty of developing new structure for polyamides and polysulfonamides, performing two different reactions in polymerization process, as well as introducing fluorine element into polymer structure, we specially synthesized and applied a cyclic fluorine-containing monomer named β-hydroxytetrafluoroethanesulfonic acid sultone (TFE-sultone), which can be catalyzed to isomerize into a bi-functional compound containing acyl fluoride and sulfonyl fluoride at each

* Corresponding author. Tel.: +86 021 34202613; fax: +86 021 54742567.
  E-mail addresses: ym_zhangsjtu@yahoo.com.cn, ymzhang@sjtu.edu.cn (Y. Zhang).

end. Therefore we successfully synthesized fluoropoly(amide–sulfonamide)s (F-PASAs) by the reaction of hexamethylenediamine with TFE-sultone, achieving amidation simultaneously with sulfonamidation. To our knowledge, F-PASAs which contain both amide and sulfonamide linkages, as well as carbon–fluorine bonds have not been reported before.

In the present paper, we reported the synthesis and characterization of these novel F-PASAs. The chemical characterization of F-PASAs-I (prepared by interfacial polycondensation) and F-PASAs-S (prepared by solution polycondensation) was performed by intrinsic viscosity measurements, GPC, FTIR, (^{1}H and ^{19}F) NMR and elemental analysis techniques, while the thermal properties were tentatively investigated by DSC, DMA and TGA analysis. UV–vis spectrum was applied to characterize the optical property of the film of F-PASAs-S.

2. Experimental

2.1. Materials

Tetrafluoroethylene (TFE), sulfur trioxide (SO_3) and 1,1,2-tri-chloro-1,2,2-trifluoroethane (CFC-113) were kindly received from Dongyue Polymer Company (China). TFE was of 99.99% purity and was used as-received. SO_3 was freshly distilled immediately prior to use. CFC-113 was distilled and then stored over 4A molecular sieves before use. Hexamethylenediamine, triethylamine, dimethyl sulphoxide (DMSO) and 1,4-benzenediamine were purchased from Sinopharm (China), and were distilled before use.

2.2. Methods

2.2.1. Monomer synthesis
The method of preparing TFE-sultone has been developed and discussed in Refs. [27,28]. The reaction must be carried out very carefully because of the latent explosiveness of mixtures of TFE and SO_3 [29]. A typical procedure is as follows. Under ambient temperature, freshly distilled liquid SO_3 (240 g, 3.0 mol) was charged into a dry autoclave of 1 L volume. The autoclave was then evacuated to remove most of the air present at low temperature. TFE of 99.99% purity was then carefully added through a valve in about 2 h. The total addition of TFE is 300 g. The temperature of the reaction mixture was strictly kept at 20–30 °C. After the addition, the mixture was kept stirring for another 2 h. TFE-sultone (bp 42 °C) was collected through distillation. However, as TFE-sultone is easily isomerized into fluorosulfonyldifluoroacetyl fluoride, the collected product became a mixture of TFE-sultone and fluorosulfonyldifluoroacetyl fluoride (bp 30 °C), which was used as diacid monomer. The total gain in weight is 491 g (yield: 90.9%). ^{19}F NMR (400 MHz, CDCl$_3$, ppm) (see SI1, Supporting information): 7.03(t, 2F), −2.89(t, 2F); 11.76(q, 2F), −117.88(t, 1F), −135.96(t, 1F). FTIR (liquid film, cm^{-1}): 1776 (C=O), 1445 and 1235 (O=S=O), 1150 and 633 (CF$_2$).

2.2.2. Polymer synthesis
The F-PASAs were successfully synthesized by interfacial polycondensation and solution polycondensation according to Scheme 1, respectively. Bulk polycondensation was also carried out, but yield no polymer products. Aromatic fluoropoly(amide–sulfonamide)s (A-F-PASAs) were tentatively synthesized through solution polycondensation by using 1,4-benzenediamine as diamine monomer.

A typical polymerization procedure for the synthesis of F-PASAs by interfacial polycondensation is as follows. Hexamethylenediamine (0.58 g, 5 mmol) and a variable amount of triethylamine (5–10 mmol) were dissolved in 25 ml distilled water.

The mixed solution was designated as solution A. Separately, the prepared monomer (0.90 g, 5 mmol) was dissolved into CFC-113 (25 ml) at 5.0 °C, and this solution was called solution B. Solution B was then introduced dropwise into solution A with intense stirring. After addition, the mixed solution was kept stirring for another 8 h. During this period, triethylamine was added to maintain 7 of pH. A flow of N$_2$ was introduced to further remove produced hydrogen fluoride (HF). The resulting products were introduced into a separating funnel, washed three times with excess ethanol and distilled water to remove impurities, and dried in vacuum at 50 °C.

A typical polymerization procedure for the synthesis of F-PASAs by solution polycondensation is as follows. Hexamethylenediamine (0.58 g, 5 mmol) and a variable amount of triethylamine (5–10 mmol) were dissolved in 25 ml DMSO. The prepared monomer (0.90 g, 5 mmol) was charged into this solution with intense stirring. After addition, the mixed solution was kept stirring for another 8 h at 20.0 °C. During this period, triethylamine was added to remove produced HF. A flow of N$_2$ was introduced to further remove produced HF. The reaction mixture was precipitated into methanol, and the products were filtered, washed and dried in vacuum at 50 °C. The typical procedure to yield aromatic fluoropoly(amide–sulfonamide)s (A-F-PASAs) is the same as this solution polycondensation method except using 1,4-benzenediamine as diamine monomer.

A typical trial to yield products by bulk polymerization is as follows. Hexamethylenediamine (0.58 g, 5 mmol), a variable amount of triethylamine (5–10 mmol) and the prepared monomer (0.90 g, 5 mmol) was charged into a 100 ml round-bottom flask equipped with a stirrer at 5.0 °C. The reaction was kept by stirring for 8 h, and maintained under a flow of N$_2$. The yellow sticky products were collected, washed and dried in vacuum at 50 °C.

2.2.3. Film preparation
The film of F-PASAs-S was prepared by casting the solution of F-PASAs-S in DMSO at concentration of 20 wt% onto clean quartz glass slide. The blend of F-PASAs-S and polydodecamide (PA-12) was prepared by solution mixing the F-PASAs-S and PA-12 (25 wt% of F-PASAs-S) in m-cresol at 60 °C and then casting onto glass slide.

2.3. Measurements

Fourier transform infrared (FTIR) spectroscopy measurements of F-PASAs were performed on a Perkin Elmer Paragon 1000 FTIR spectrometer with 4 cm^{-1} resolution. FTIR spectroscopy measurements of monomers were recorded on a Bruker Tensor 27 FTIR spectrometer equipped with ATR accessory. The (^{1}H and ^{19}F) NMR spectra were collected on a Varian-Inova Mercury-Plus 400 instrument, using TMS as inner reference or trifluoroacetic acid as external reference. Gel permeation chromatography (GPC) measurements were conducted on a Perkin Elmer Series 200 instrument equipped with a Waters ultrasryra gel column and a differential refractometer detector. Dimethyl formamide (DMF) was used as the eluent at a flow rate of 1.0 ml/min. The intrinsic viscosity was determined in DMSO at a concentration of 0.5 g/dL in an Ubbelohde viscometer thermostated at 25.0 °C. Quantitative elemental analysis (element C, N, S) was performed on an Elementar Vario EL III element analyzer. F elemental analysis was performed by oxygen flask combustion method. DSC measurements were run on a Perkin Elmer Pyris 1 system with a heating rate of 10 °C/min under N$_2$ atmosphere. DMA measurements were carried out on a Perkin Elmer DMA 7e in a tensile mode using rectangular sample $(10 \times 5.0 \times 1.0 \pm 0.02 \text{ mm}^3)$ at a constant frequency of 1 Hz and heating rate of 3 °C/min. The range of temperature was 5–140 °C. TGA measurements were performed on
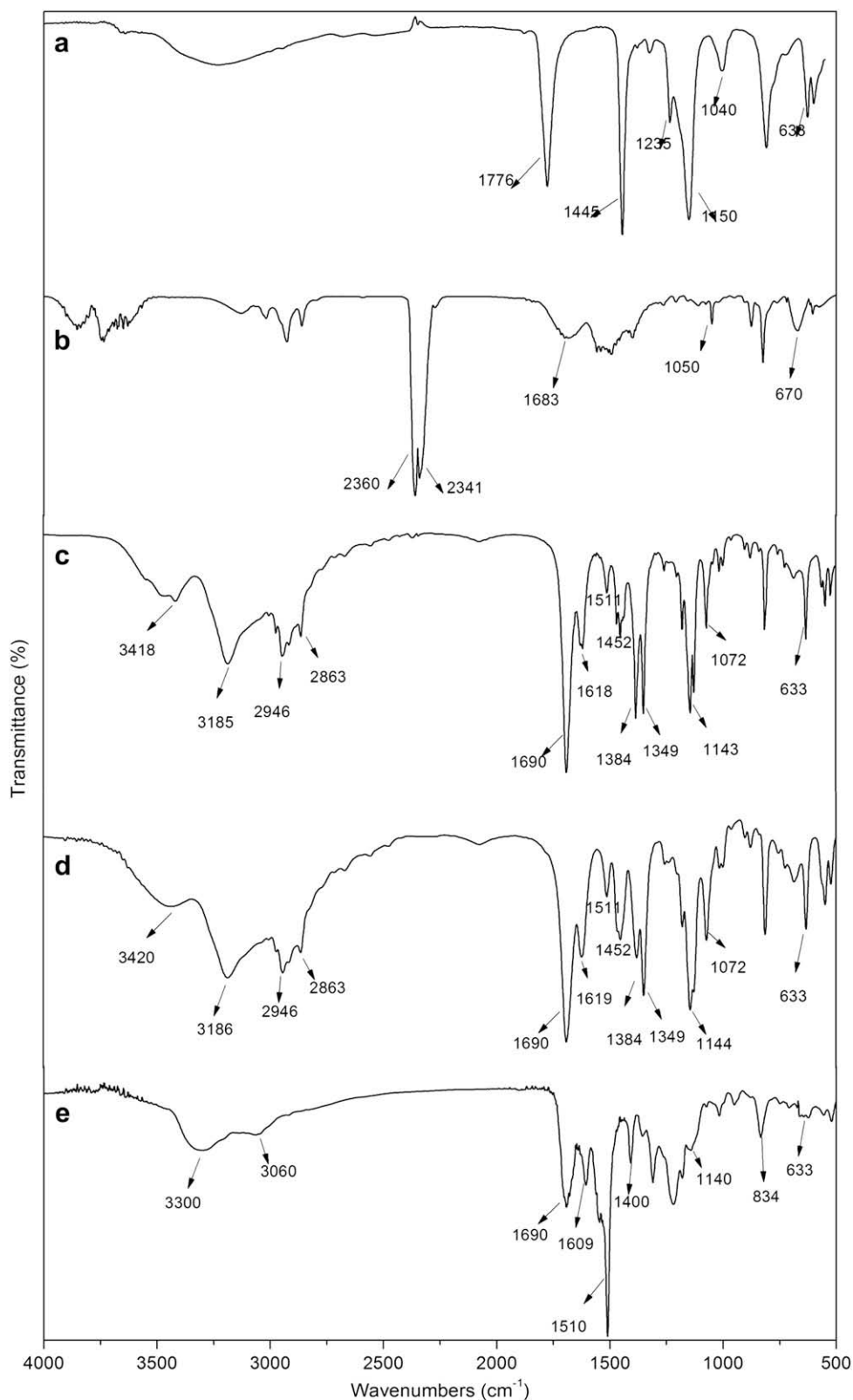
Scheme 1. Synthesis of fluoropoly(amide–sulfonamide)s.

a Perkin Elmer TGA 7 at a heating rate of 20 °C/min under N_2 flow. UV–vis spectra of films were recorded on a Purkinje General TU-1901 spectrophotometer. The solubility was evaluated by charging approximately 5 mg polymer into 2 ml solvents respectively under stirring overnight at ambient temperature.

3. Results and discussion

3.1. Polymer synthesis

Firstly, we have performed bulk polymerization of the prepared monomer with hexamethylenediamine and only yellow sticky products were collected. The FTIR spectrum of the yellow sticky products showed the characteristic bands of $>$C=N- group at 2341 cm^{-1}, 2360 cm^{-1} (stretch of NH$^+$) and 1683 cm^{-1} (stretch of C=N) [30] shown in Fig. 1(b). Gibbs and coworker [31] found that α-sulfamylperfluoroheptanamidine was obtained in good yield when anhydrous ammonia reacted with perfluoro-1-heptene sultone. And the conversion of imino group to amide group which was achieved by treatment with aqueous acid made α-sulfamylperfluoroheptanamidine convert to α-sulfamylperfluoroheptanamide which contains both amide and sulfonamide group. According to their proposed mechanism, the yield of yellow sticky products is understandable because no aqueous present in bulk polymerization. In addition, the failure to yield polymer through bulk polymerization might due to partly high concentration of reactants and primary products which impede the propagation to yield polymer chain.

Therefore, aqueous hexamethylenediamine solution was employed in the interfacial polycondensation. Meanwhile as the solubility of TFE-sultone in CFC-113 [32] is relatively high, we have made CFC-113 as the solvent of organic phase. Expectedly, F-PASAs were successfully prepared by interfacial polycondensation, but F-PASAs-I were oligomers according to their molecular weight. The stoichiometric balance and the purity of the two monomers are the two crucial factors affecting the molecular weight of the products formed by polycondensation. Therefore, the molar ratio of hexamethylenediamine and prepared monomer was kept at 1:1 under the same concentration on the basis of careful distillation of hexamethylenediamine and solvent before use. As the sulfonyl

fluoride group is less reactive towards nucleophilic attack as compared to the acyl fluoride group [31], the reaction time was extended to over 8 h.

Temperature had a great influence on the interfacial polymerization. It is believed that the low temperature might suppress some side reactions normally induced by the initial heat released by the exothermic polymerization. However, the lowest temperature possible for the polymerization was restricted by the freezing point of the solvents (i.e. 0 °C for water, −35 °C for CFC-113). Similarly, the highest temperature for the polymerization was restricted by the boiling point of monomers (i.e. 30 °C for fluorosulfonyldifluoroacetyl fluoride) and the hydrolysis of the monomers. The effect of temperature on the molecular weight of F-PASAs is presented in Table 1. The reaction at temperature higher than 10 °C was found to be unsuccessful and no polymers, or even oligomers were obtained. This may be due to much greater tendency of the hydrolysis of the bi-functional monomers compared to reaction with diamine over 10 °C. Good results were achieved for the reaction at the range of 0 °C and 10 °C. This range was just the optimal temperature range for the rearrangement of TFE-sultone to fluorosulfonyldifluoroacetyl fluoride [27]. At higher temperature in this range, more F-PASAs-I would dissolve in water phase, which permitted relatively a little higher molecular weight.

Solution polycondensation was also performed to yield F-PASAs-S. As shown in Table 1, the lower temperature was beneficial for the polymerization by suppressing some side reactions, while the lowest temperature was restricted by the freezing point of DMSO (18.5 °C). Therefore, the reaction at 20 °C gained F-PASAs-S with higher intrinsic viscosity compared to that at higher temperature. Moreover, the intrinsic viscosities of F-PASAs-S were much higher than those of F-PASAs-I. F-PASAs-S became insoluble in common solvent such as DMF, THF and water, which precludes the conventional measurement of GPC to directly get molecular weight. Therefore, molecular weights of F-PASAs-S were calculated on the basis of the relationship of log M_n and log [η] of F-PASAs-I. A-F-PASAs was also prepared by solution polycondensation under typical condition using 1,4-benzenediamine as diamine monomer, and its molecular weight is listed in Table 1.

Also, pH and acid acceptor had a great influence on both interfacial and solution polycondensation. As for interfacial

Fig. 1. FTIR spectra of prepared monomer (a), product prepared by bulk polymerization (b), F-PASAs-I (c), F-PASAs-S (d) and A-F-PASAs (e).

polycondensation, at the beginning of the reaction, the pH was relatively high due to the presence of hexamethylenediamine in the aqueous phase. Then as the reaction continued, diamine was consumed, leading to a decrease of pH, which was also favored by

the release of HF produced during the polycondensation and transferred to the aqueous phase via the assistance of water or hexamethylenediamine [33]. HF can be neutralized in the aqueous phase by an inorganic or organic base. However, our attempt to use

Table 1
Synthesis of F-PASAs via interfacial and solution polycondensation.

Polymer	Run[a]	Temperature (°C)	M_n (g/mol)	$[\eta]$ (dL/g)[c]	M_w/M_n[b]
F-PASAs-I	1	0.0	0.16×10^4 [b]	0.09	1.11
	2	3.0	0.23×10^4 [b]	0.11	1.08
	3	5.0	0.28×10^4 [b]	0.14	1.06
	4	8.0	0.28×10^4 [b]	0.14	1.06
	5	10.0	0.30×10^4 [b]	0.15	1.04
	6	Higher than 10.0	–[d]	–[d]	–[d]
F-PASAs-S	1	20.0	1.51×10^4 [e]	0.60	–[e]
	2	23.0	1.49×10^4 [e]	0.58	–[e]
	3	25.0	1.43×10^4 [e]	0.57	–[e]
A-F-PASAs	1	20.0	0.60×10^4 [b]	–	1.27

[a] Polymerization time, 8 h; the molar ratio of TFE-sultone and hexamethylene-diamine/1,4-benzenediamine, 1:1.

[b] Measured by GPC using DMF as eluent under 25.0 °C.

[c] Intrinsic viscosity was determined at 25.0 °C in DMSO by the single point method.

[d] No polymer products were collected.

[e] The polymer was insoluble in DMF or THF; the M_n was calculated on the basis of the relationship of log M_n and log $[\eta]$ of F-PASAs-I (see SI2, Supporting information).

NaOH and Na_2CO_3 as acid acceptor turned out to be unsuccessful as only carboxylates or sulfonates were collected and characterized by strong infrared absorption at 1661 cm^{-1}, 1398 cm^{-1}, 1238 cm^{-1} and 1033 cm^{-1}. This was consistent with the fact that strong acceptors may cause a decrease of both yield and molecular weight of the products [10]. Therefore, triethylamine was chosen as acid acceptor for both interfacial and solution polycondensation. In addition, triethylamine catalyzed the rearrangement of TFE-sultone to fluo-rosulfonyldifluoroacetyl fluoride as illustrated in Scheme 1. It was also found that adding triethylamine step by step during the process was better than adding all triethylamine into the system at the very beginning for one time. The necessary amount of tri-ethylamine for catalyzing isomerization of TFE-sultone was very small, and the high concentration of the triethylamine might promote the hydrolysis of the sulfonyl fluoride group and the acetyl fluoride group.

3.2. Polymer characterization

3.2.1. Fourier transform infrared (FTIR)

Fig. 1 presents the FTIR spectra of the prepared monomer (a), product of bulk polymerization (b), F-PASAs-I (c), F-PASAs-S (d) and A-F-PASAs (e). F-PASAs-I and F-PASAs-S showed similar infrared absorption spectrum. Compared with Fig. 1(a), in Fig. 1(c) and Fig. 1(d), it can be seen that acetyl fluoride band at 1776 cm^{-1} in Fig. 1(a) disappeared and a strong band at 1690 cm^{-1} (amide I) appeared, which is characteristic of C=O bands of amide groups in spectra of F-PASAs. This absence and appearance indicated that the interfacial polycondensation and solution polycondensation occurred. Other bands characteristic of amide I were also seen at 3418 cm^{-1} due to the N–H stretch. The F-PASAs were also charac-terized with the transmittance of mono-substituted amide linkages at 1511 cm^{-1} (amide II, C–N stretch) and frequency doubling band of amide II at 3185 cm^{-1}. Meanwhile the characteristic bands of sulfonamide linkage in F-PASAs can also be seen clearly. The char-acteristic bands of sulfonamide in F-PASAs were seen at 1349 cm^{-1} and 1384 cm^{-1} (split of asymmetrical stretch of –SO_2N–) and 1143 cm^{-1} (symmetrical stretch of –SO_2N–). For comparison, the asymmetrical and symmetrical stretch bands of –SO_2– in prepared monomer in Fig. 1(a) lied at 1445 cm^{-1} and 1235 cm^{-1}, respectively, the same as shown in Ref. [34]. In addition, the band at 1072 cm^{-1} associated with CF_2 functionality [35]. Lower wave number absorption band for CF_2 wag at 633 cm^{-1} was also observed indi-cating that linear groupings in the polymeric structure encounter weak hindrance to the molecular vibration modes [36,37]. The

bands at 2946 cm^{-1}, 2843 cm^{-1} and 1452 cm^{-1} were the charac-teristic bands of –$(CH_2)_6$– in hexamethylenediamine, which further confirmed that interfacial polycondensation and solution poly-condensation had occurred. Fig. 1(e) displays the FTIR spectrum of A-F-PASAs. The presence of amide group and sulfonamide group was verified by the absorption at 1690 cm^{-1} (amide I), 1510 cm^{-1} (amide II), 3300 cm^{-1} (N–H stretch), 1400 cm^{-1} and 1140 cm^{-1} (–SO_2N–), meanwhile the absorption at 3060 cm^{-1}, 1510 cm^{-1} and 834 cm^{-1} proved the presence of benzene ring.

The vibrational band at about 1618 cm^{-1} corresponded to –NH_2 vibrations, which indicated that the F-PASAs prepared probably be capped by unreacted hexamethylenediamine at both sides leaving –NH_2 at the terminals. Besides, the inexistence of bands near 1200 cm^{-1} and 1050 cm^{-1} excluded the possibility that the terminal groups are –SO_3H [38]. In addition, the absence of vibrational bands corresponding to –COOH groups can be observed, suggesting that the terminal groups of F-PASAs are amine groups [39].

3.2.2. Nuclear magnetic resonance (NMR)

The chemical structures of F-PASAs have been resolved by ^{1}H NMR and ^{19}F NMR. Fig. 2 presents the ^{1}H NMR spectrum of F-PASAs-I dissolved in D_2O. As shown in Fig. 2, five peaks (marked peaks a–e) due to the protons of the methylene from the hexa-methylenediamine units appeared in the intensity ratio of 2:1:1:1:1 at 1.26 ppm, 1.44 ppm, 1.53 ppm, 2.86 ppm and 3.11 ppm, respectively. Peaks a–c were found to be quintets, while peaks d and e were triplets. The triplets (peaks d and e) of methylene protons attached to sulfonamide group and amide group appeared at 2.86 ppm (t, 2H, –CH_2) and 3.11 ppm (t, 2H, –CH_2). The remaining aliphatic protons were in the range of 1.2–1.6 ppm. No signals of NH proton were observed (Fig. 2), which maybe result from the chemical shift of active hydrogen in the structure in D_2O. Therefore, the ^{1}H NMR spectrum of F-PASAs-I using DMSO-d_6 as solvent is provided in Fig. 3(a).

The peaks (still marked peaks a–e) in Fig. 3(a) due to the protons from the methylene protons from the hexamethylenediamine units were almost identical with the signals in Fig. 2, including their chemical shift, the pattern of the peak and the ratio of intensity. The protons attached to N appeared as broadened singlet (marked peak g) near 8 ppm. The small signal of singlet appeared near peak e at 2.98 ppm (marked peak f) was attributed to the active protons from the terminal group –NH_2. This was consistent with the inference about end group from the FTIR characterization. The F-PASAs-S were insoluble in water. So the ^{1}H NMR spectrum of F-PASAs-S using DMSO-d_6 as solvent is provided in Fig. 3(b).
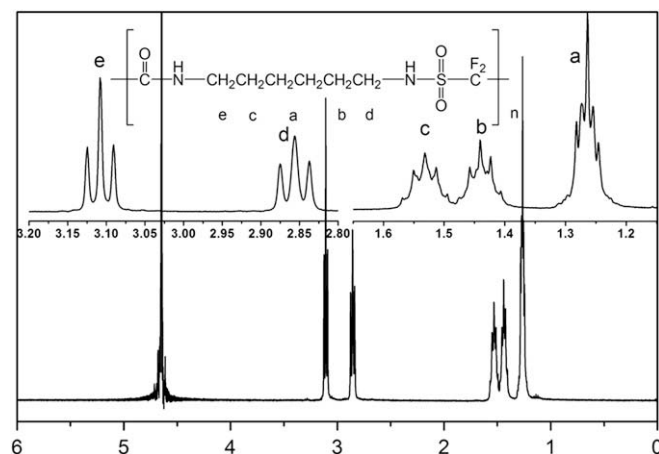

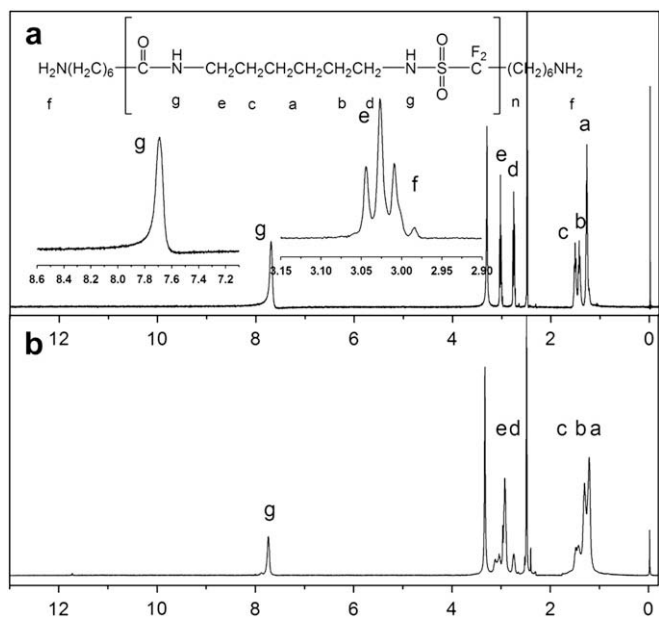**Fig. 2.** 400 MHz ^{1}H NMR spectrum of F-PASAs-I in D_2O.

Fig. 3. 400 MHz ^{1}H NMR spectra of F-PASAs-I in DMSO-d_6 (a) and F-PASAs-S in DMSO-d_6 (b).

The peaks showed similar chemical shift, but the pattern of peaks was not as clear as F-PASAs-I, which may result from the much higher molecular weight of F-PASAs-S.

The only signal showed in the ^{19}F NMR spectrum of F-PASAs-I using D_2O as a solvent (Fig. 4(a)) and F-PASAs-S using DMSO-d_6 as a solvent (Fig. 4(b)) revealed the only –CF$_2$– in the backbone derived from the TFE-sultone, which confirmed the existence of fluorine element and the occurrence of polycondensation.

3.2.3. Elemental analysis

Elemental analysis data of F-PASAs-I and F-PASA-S are listed in Table 2. As illustrated in Table 2, the found values were a little smaller than calculated ones, which may result from the moisture absorption of the polymer. In addition, the ratio of the found content between N and S ($10.37/11.81 = 0.878$ for F-PASAs-I; $10.38/$
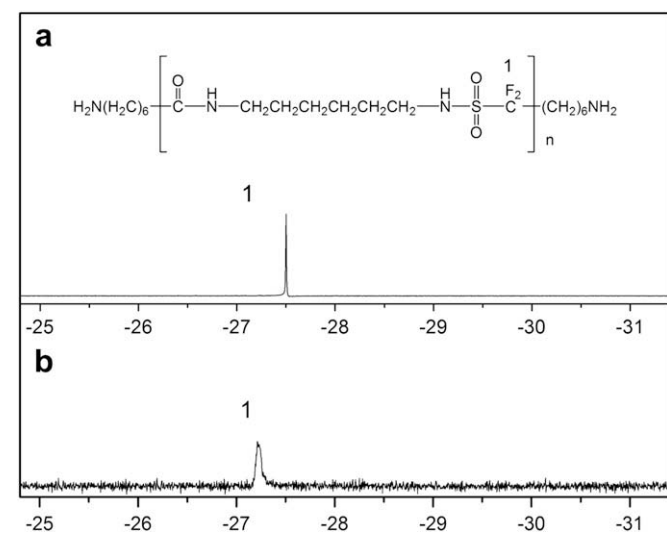
Fig. 4. 400 MHz ^{19}F NMR spectrum of F-PASAs-I in D_2O (a) and 400 MHz ^{19}F NMR spectrum of F-PASAs-S in DMSO-d_6 (b).

Table 2
Elemental analysis of F-PASAs-I and F-PASAs-S.

Polymer	Repeated unit		Elemental analysis (%)			
			C	N	S	F
	$C_8H_{14}O_3N_2SF_2$ (256.27)$_n$	Calc.	37.49	10.93	12.51	14.83
F-PASAs-I		Found	36.13	10.37	11.81	14.85
F-PASAs-S		Found	36.16	10.38	11.81	14.84

$11.81 = 0.879$ for F-PASAs-S) was a little larger than that of the relative atomic mass between N and S in repeated formula ($28.0134/32.065 = 0.874$). This originated from no consideration of end group when calculating repeated formula and indicated the existence of N in end group –NH$_2$ as inferred from the FTIR and NMR characterization. Meanwhile the ratio of the found content between C and N ($36.13/10.37 = 3.484$ for F-PASAs-I; $36.16/10.38 = 3.483$ for F-PASAs-S) was larger than that of the relative atomic mass between C and N ($8 \times 12.0107/(2 \times 14.0067) = 3.430$), which indicated that the end group –NH$_2$ was derived from the hexamethylenediamine units, showed as –(CH$_2$)$_6$NH$_2$. The chemical structures of the newly synthesized polymers were confirmed by the good agreement of the elemental analysis values with those of the calculated values.

3.2.4. Solubility

The solubility of F-PASAs-I and F-PASAs-S in various solvents was carefully evaluated and summarized in Table 3. For comparison, the solubility of PA-6.6 in various solvents was also summarized, part of the data was from Ref. [2]. It was found that like polyamides and polysulfonamides, the F-PASAs-I and F-PASAs-S are soluble in such powerful solvents as m-cresol, formic acid and sulfuric acid. As polysulfonamides are normally soluble in electron-donor solvents such as DMF and pyridine, polyamides dissolve readily in acidic solvents as just mentioned [5], it was expected that the F-PASAs would be soluble in both kinds of solvents, as F-PASAs contained both groups. F-PASAs-I which were oligomers found themselves soluble in both electron-donor solvents and acidic solvents, which was consistent with the fact that the F-PASAs-I contain both the sulfonamide group of acidic nature and the amide group in which the carbonyl parts have the predominant nucleophilic nature. However, F-PASAs-S were found to be insoluble in DMF and pyridine even at elevated temperature, which resulted from much higher molecular weight, as well as the relative weak acidity of sulfonamide group. Besides the chemical composition, molecular weight played an even greater role in

Table 3
Solubility of F-PASAs in various liquids. Key: (−) insoluble, (+) soluble.

Solvent	PA-6.6 [2]	F-PASAs-I	F-PASAs-S
Chloroform	−	−	−
CFC-113	−	−	−
Ether	−	−	−
Ethanol	−	−	−
Acetone	−	−	−
THF	−	−	−
H$_2$O	−	+	−
DMF	−	+[a]	−
DMSO	−	+	+
Pyridine	−	+[a]	−
m-Cresol	+	+	+
Formic acid	+	+	+
Sulfuric acid	+	+	+
Hexafluoroisopropanol	+	+	+
Lubricant[b]	−	−	−

[a] Soluble at elevated temperature.
[b] Krytox (perfluoropolyether).

solubility of F-PASAs-S. In addition, although F-PASAs-I dissolved in electron-donor solvents, its solubility in electron-donor solvents was much less than in acidic solvents, which indicates the acidity of sulfonamide group is relatively weak. The more detailed knowledge of acidity of the acidic sulfonamide has been elucidated by Bell and Roblin [40].

Common organic solvents such as chloroform did not dissolve F-PASAs-S even at elevated temperatures as expected. Although DMSO did not dissolve PA-6.6, it dissolved both F-PASAs-I and F-PASAs-S greatly, mainly due to their similar counterpart –SO$_2$– according to the principle of "similarity and intermiscibility". While high fluorine content liquids such as perfluoropolyether lubricant and CFC-113 were not able to dissolve the F-PASAs, which might be ascribed to the low percents of the fluorine element in the polymer as shown from their structures and Table 2. The oligomer F-PASAs-I did dissolve into water. Consequently, we infer that the prepared F-PASAs-I are water-soluble due to the rather low molecular weight and the H-bond formed. The stability against acid–base hydrolyses and reactivity towards mercuric ions of sulfonamides [41] have made them as useful functional group for polymer sorbent [42], while sulfonamides are highly hydrophobic which is not desirable. The water-solubility of relative low molecular weight F-PASAs-I here may help to overcome this dilemma.

3.2.5. Thermal properties

The powders of F-PASAs-S were subjected to thermal analysis, and the DSC curve is shown in Fig. 5. It can be seen from Fig. 5 that F-PASAs-S did not show any crystallinity. This observation indicated that the crystallization of the F-PASAs become intensively difficult because of alternating array of amides group and sulfonamides group and the sequential isomers of polymer molecules. Unlike what Chan et al. have found [14], there was no an anonymous broad peak caused by the bound water which disturbed the determination of glass transition temperature, T_g of F-PASAs-S was clearly defined to be ca. 52.0 °C. The behavior of thermal transition was further confirmed by dynamic mechanic analysis (DMA). Shown in Fig. 6 is the dynamic mechanical spectrum of F-PASAs-S, which shows the storage modulus (E') and the loss factor (tan δ) as functions of temperature. F-PASAs-S exhibited a well-defined relaxation peak centered at ca. 50 °C, which is responsible for the glass-rubber transition. The alternating range of amides group and sulfonamides and the presence of regioisomers weakened the structure regularity and intermolecular H-bond to some extent. This was similar with what Groote and colleagues have found [43]. They found that
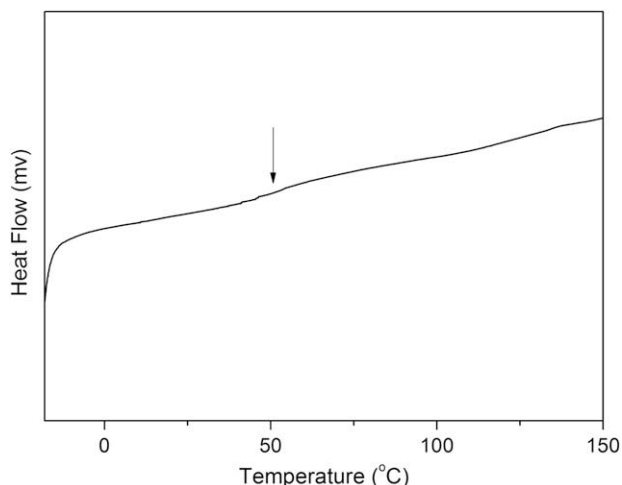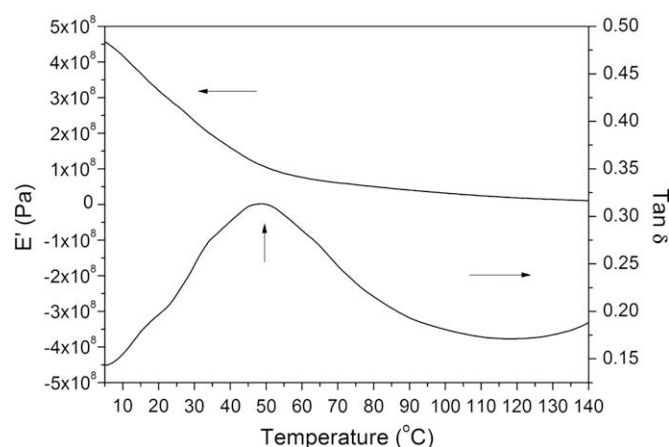

Fig. 6. DMA curve of F-PASAs-S.

T_g of polydodecamide (PA-12) shifted from 50 °C to about 0 °C when adding benzenesulfonamides as plasticizers due to the less structure regularity and weaker intermolecular H-bond caused by adding of sulfonamides. This may lead to the potential application of F-PASAs acting as choice of blending candidates for common polyamides as many kinds of sulfonamides have already been industrial plasticizers for polyamides due to their good compatibility [44,45]. We found that the melting point of PA-12 was reduced by 15 °C when blending 25%(wt) (10 s-%, sulfonamide molar percentage) F-PASAs-S into PA-12 (see SI3, Supporting information), and Groote et al. found some benzenesulfonamides induced fall of 6 °C of melting point at 10 s-% [46].

Fig. 7 is the TGA curve of F-PASAs-S in N$_2$ atmosphere. Upon thermal decomposition in N$_2$ atmosphere with linear heating, F-PASAs-S showed three steps of weight loss, similar with that of nylon [47]. The first step which is evident on the derivative curve was attributed to the volatilization of residual moisture and low molecular weight oligomers. As summarized by Levchik et al. [48], the major decomposition of amide group in nylon lied in the range of 280–450 °C, the weight loss of F-PASAs-S started from ca. 300 °C and kept in this temperature range, which was the major decomposition step of F-PASAs-S because most material volatilized at this range of temperate. During the heating, probably a cross-linked structure was formed, and the rate of weight loss slowed down
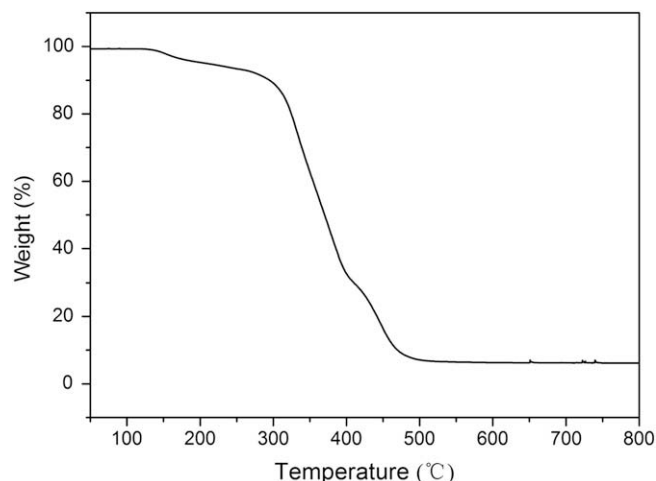

Fig. 5. DSC curve of F-PASAs-S.

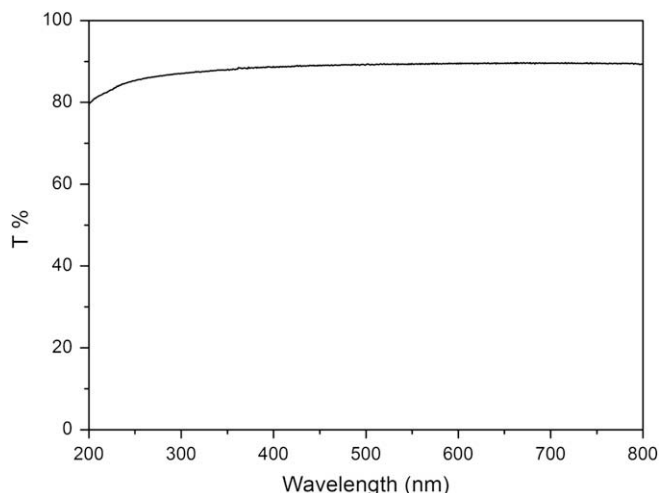**Fig. 7.** Thermal behavior of F-PASAs-S.

Fig. 8. UV–vis spectrum of F-PASAs-S casting film.

greatly at about 450 °C. On further heating, the cross-linked structure decomposed and yielded about 6.2% of thermally stable char.

3.2.6. Optical property

The optical property of the prepared F-PASAs-S was measured as film. Fig. 8 presents the UV–vis spectrum of the film casted from the solution of F-PASAs-S in DMSO. The film was colorless and transparent in the visible region and kept high transmittance even in the ultraviolet region. The film of F-PASAs-S showed good light transmittance of over 89% at wavelength higher than 450 nm, maintained near 85% at the range of 190–300 nm. High transparence of the F-PASAs film might mainly due to the amorphous morphology which is achieved by the presence of regioisomers of polymer molecules. High transparence might also due to the carbon–fluorine groups in backbones [26,49] and the relative big length of S–N bond and C–N bond in backbones [50]. In addition, the weak hindrance encountered by polymeric structure inferred from FTIR analysis contributed to the high transparency of F-PASAs. And You and colleagues recently found that sulfonyl group contained in the main chain of polyimides was responsible for their high transparence [51]. All these characteristics have made the F-PASAs possess outstanding transmittance comparable to that of siloxane resins [52] and inorganic glass [53].

4. Conclusions

Using polycondensation, novel fluoropoly(amide–sulfonamide)s were successfully obtained from the step copolymerization of hexamethylenediamine with β-hydroxytetrafluoroethanesulfonic acid sultone (TFE-sultone). The elemental analysis, FTIR, ^{1}H and ^{19}F NMR clearly demonstrated the structures of obtained F-PASAs as expected. The amide group, sulfonamide group and fluorine elements were identified to confirm the special structure of F-PASAs. The higher molecular weight F-PASAs-S possessed good thermal stability. F-PASAs can be used as functional blending component for common polyamides due to its low T_g, good compatibility and the incorporation of sulfonamide group. The high transparency of F-PASAs film demonstrated the function of carbon–fluorine group.

Acknowledgements

Appendix. Supplementary material

The supplementary material associated with this article can be found in the on-line version, at doi:10.1016/j.polymer.2009.07.008.

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