Polymer Bulletin 61, 569–580 (2008)
DOI 10.1007/s00289-008-0984-9

Polymer Bulletin

Synthesis and characterization of novel fluorinated azopolyamides

Qingming Zhu[a], Lijie Dong[a,b], Yongsheng Niu[a], Chuanxi Xiong[a,b] (✉), Yun Liu[a], Jingtao Liu[a], Liping Liu[a], Benqin Shu[a]

[a] School of Materials Science and Engineering, Wuhan University of Technology,
Wuhan 430070, P. R. China
[b] State Key Laboratory of Advanced Technology for Materials Synthesis and Processing,
Wuhan University of Technology, Wuhan 430070, P. R. China
E-mail: polymerlab@whut.edu.cn; Fax: +86-27-87652879

Received: 19 June 2008 / Revised version: 7 August 2008 / Accepted: 11 August 2008

Summary

Novel soluble fluorinated azopolyamides **4a-d** were synthesized by reacting 2-trifluoromethyl-4,4'-diaminodiphenyl ether **2** with various azodibenzoyl chlorides **3a-d** using the low temperature solution polycondensation technique. The fluorinated diamine **2** was prepared through the nucleophilic substitution reaction of 4-nitrophenol and 2-chloro-5-nitrobenzotrifluoride via catalytic reduction catalytic reduction with hydrazine and Pd/C. All of the fluorinated azopolyamides exhibited excellent solubility at room temperature in strong polar solvents such as *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and *N*-methyl-pyrrolidinone (NMP). Inherent viscosities of the azopolyamides were found to range from 0.85 to 1.35 dl/g, and those azopolyamides could be cast into flexible and tough films from DMAc solutions. The azopolyamides showed that the glass transition temperatures (T_g) were between 231 and 259ºC, and the char yields of all the azopolyamides except for **4d** at 800ºC in nitrogen atmosphere were above 47%. Furthermore, all the azopolyamides exhibited thermal and photochromic properties.

Keywords

Fluorinated azopolyamides; High solubility; Thermal properties; Photochromic behavior

Introduction

Wholly aromatic polyamides (aramids) have already been noted for their high thermal stability, chemical resistance and outstanding mechanical properties[1-3]. However, they are usually difficult to process due to their high softening or melting temperatures and insolubility in common organic solvents, caused by stiffness of the backbone and strong hydrogen bonding[4,5]. Therefore, many approaches to improve the solubility of aromatic polyamides including incorporation of flexible linkages[6-8] or molecular asymmetry[9-12] or pendant groups[13,14] and addition of non-coplanar conformation[15-17] have been investigated.

Recently, polyamides derived from ether-bridged diamines with trifluoromethyl (CF_3) groups have attracted considerable attention[18,19]. Incorporation of the bulky fluorine groups would increase the free volume of the polymers, so improving some properties such as solubility, gas permeability, optical transparency, and flame resistance. Moreover, it also decreases the dielectric constants, water absorption, and refractive indices because of the small dipole and the low electronic polarizability of the C-F bond[20-22]. On the other hand, the aromatic azo linkages in the main chain of these polyamides have a special effect on their photochromic properties. Some of the interest in this kind of polymers is due to their possible use as high grade pigments of good fastness to light and as materials which exhibit photochromic and photocontractile behavior.

As part of an effort to gain the high performance polymers for advanced micro-electronics applications such as photoswitching, optical storage and other electrooptic devices[23,24], novel soluble fluorinated azopolyamides **4a-d** derived from 2-trifluoromethyl-4,4'-diaminodiphenyl ether **2** with various azodibenzoyl chlorides **3a-d** were synthesized by the low temperature solution polycondensation technique. The solubility, thermal properties, and optical properties of the resultant polymers were investigated.

Experimental

Materials

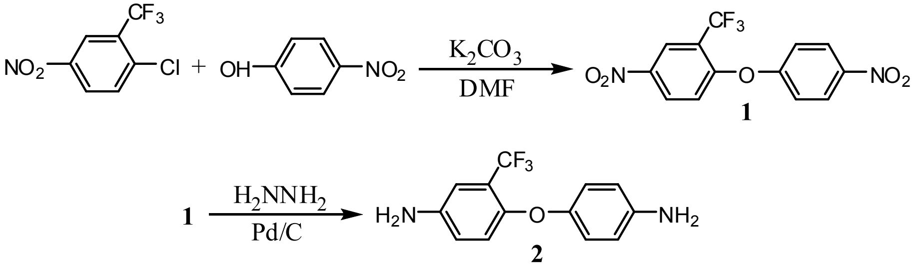
4-Nitrophenol (Sinopharm Chemical Reagent Co.) and 2-chloro-5-nitrobenzotrifluoride (Acros) were vacuum-distilled prior to use. Acids: 4-Nitrobenzoic acid (Sinopharm Chemical Reagent Co.), 3-nitrobenzoic acid (Sinopharm Chemical Reagent Co.), 2-chloro-4-nitrobenzoic acid (Alfa), and 3-methyl-4-nitrobenzoic acid (Jiangsu Shanda Chemical Co.) were used as received without further purifications. Anhydrous potassium carbonate (Shanghai Shiyi Chemical Reagent Co.), hydrazine monohydrate (Sinopharm Chemical Reagent Co.), dimethyl sulfoxide (DMSO; Shanghai Tingxin Chemical Plant), and 10% palladium on activated carbon were used as received. *N*,*N*-Dimethylacetamide (DMAc; Aldrich), *N*,*N*-dimethylformamide (DMF), and *N*-methyl-pyrrolidinone (NMP) were purified by distillation under reduced pressure over calcium hydride and stored over 4Å molecular sieves.

Instruments

Melting points were determined with a Kofler micro melting point apparatus and were uncorrected. Infrared (IR) spectra were recorded on a Perkin-Elmer 782 Fourier-Transform Infrared (FTIR) Spectrometer in KBr. ^1H NMR spectra were measured on a Bruker DPX-400 spectrometer with tetramethylsilane (TMS) as an internal standard. Elemental analyses were carried out on a Perkin-Elmer Model 2400 C,H,N analyzer. The inherent viscosities were determined at 0.5 g/dl concentration using an Ubbelohde viscometer at 30.0±0.1°C. Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer DSC7e in flowing nitrogen at a heating rate of 10°C/min. Differential scanning calorimetric (DSC) analyses were measured on a Perkin-Elmer DSC7e at a heating rate of 10ºC/min in flowing nitrogen (15 cm^3/min). Ultraviolet-Visible (UV-Vis) spectra were taken on a Shimadzu UV-2550 spectrometer in the region 200-600 nm with a Hand Ultraviolet Ray Examining Lamp (ZF-7) for UV irradiation (365 nm).

*Synthesis of 2-trifluoromethyl-4,4'-diaminodiphenyl ether (**2**)*

2-Trifluoromethyl-4,4'-diaminodiphenyl ether was synthesized according to a typical procedure, show in Scheme 1.



Scheme 1. Synthetic route of 2-trifluoromethyl-4,4'-diaminodiphenyl ether.

*2-Trifluoromethyl-4,4'-dinitrodiphenyl ether (**1**)*

A 300 mL three-necked flask was charged with 4-nitrophenol (13.91 g, 0.10 mol), 2-chloro-5-nitrobenzotrifluoride (22.56 g, 0.10 mol), potassium carbonate (13.82 g, 0.10 mol) and 100 mL of DMF. The solution was stirred at 120ºC for 12 h. This mixture was then poured into 440 mL of methanol/water (volume ratio 10/1) to give a solid, which was collected, washed thoroughly with methanol and hot water, and dried under vacuum at 60ºC. The solid was recrystallized from DMF/methanol to give fine, pale-cream crystals (26.89 g, 82% yield). Mp: 80-82ºC. FTIR (KBr): 1540, 1346 cm^{-1} (NO_2 stretch), 1290, 1246 cm^{-1} (C-O stretch), 1170, 1110 cm^{-1} (C-F stretch). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.59 ppm (1H, H_5), 8.54-8.57 ppm (1H, H_4), 8.35-8.38 ppm (2H, H_1), 7.44-7.60 ppm (3H, $H_{2,3}$). Anal. Calcd for $C_{13}H_7F_3N_2O_5$: C, 47.57%; H, 2.15%; N, 8.54%. Found: C, 47.59%; H, 1.98%; N, 8.72%.

*2-Trifluoromethyl-4,4'-diaminodiphenyl ether (**2**)*

The 2-trifluoromethyl-4,4'-dinitrodiphenyl ether (13.13 g, 0.04 mol) and 10% Pd/C catalyst (0.18 g) were dissolved in 100 mL of ethanol and hydrazine monohydrate was added into the reactor. The mixture was stirred at 70ºC for 4 h. The solution was filtered and the solvent was evaporated. The solid was purified by recrystallization from ethanol to give pale-cream crystals (9.12 g, 85% yield). Mp: 110-111ºC. FTIR (KBr): 3400, 3300, 3202 cm^{-1} (NH_2 stretch), 1264, 1229 cm^{-1} (C-O stretch), 1156, 1103 cm^{-1} (C-F stretch). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.86 ppm (1H, H_5), 6.73-6.76 ppm (1H, H_4), 6.64-6.68 ppm (3H, $H_{3,2}$), 6.52-6.54 ppm (2H, H_1), 5.26 ppm (2H, N-H_6), 4.92 ppm (2H, N-H_7). Anal. Calcd for $C_{13}H_{11}F_3N_2O$: C, 58.21%; H, 4.13%; N, 10.44%. Found: C, 58.30%; H, 3.86%; N, 10.66%.

Synthesis of azodibenzoyl chlorides

4,4'-Azodibenzoyl chloride (**3a**) was prepared as described earlier:[25] mp: 164-166ºC. Anal. Calcd for $C_{14}H_8Cl_2N_2O_2$: C, 54.72%; H, 2.62%; N, 9.12%. Found: C, 54.96%; H, 2.67%; N, 9.48%.

3,3'-Azodibenzoyl chloride (**3b**) was synthesized as previously reported:[25,26] mp: 101-102ºC. Anal. Calcd for $C_{14}H_8Cl_2N_2O_2$: C, 54.72%; H, 2.62%; N, 9.12%. Found: C, 55.09%; H, 2.69%; N, 9.54%.

3,3'-Dichloroazobenzene-4,4'-dicarboxyl chloride (**3c**) and *2,2'-dimethylazobenzene-4,4'-dicarboxyl chloride* (**3d**) were obtained according to our previous works[27].

Polymer synthesis

The polymers were prepared by a low temperature solution polycondensation reaction. The detailed procedure is as follows: 2-trifluoromethyl-4,4'-diaminodiphenyl ether (3.0 mmol) was dissolved in 15 mL *N,N*-dimethylacetamide (DMAc) containing LiCl (5%) in a 100 mL three-necked flask with stirring. After the mixture was completely dissolved, pyridine and azodibenzoyl chloride (3.2 mmol) were added. The solution was stirred for 2 h in a nitrogen atmosphere at -5-0ºC and then poured on to 500 mL of deionized water. The precipitated polymer was washed with water and acetone, collected by filtration and dried at 120ºC for 24 h under vacuum to leave a light yellow solid.

Results and Discussion

Synthesis of monomers

The diamine 2-trifluoromethyl-4,4'-diaminodiphenyl ether **2** was prepared from 2-chloro-5-nitrobenzotrifluoride and 4-nitrophenol due to a two-step synthetic route as shown in Scheme 1. In the first step, the 4-nitrophenolat anion, which was formed by reacting 4-nitrophenol with potassium carbonate, underwent nucleophilic chloro displacement reaction with 2-chloro-5-nitrobenzotrifluoride to yield the dinitro **1**, 2-trifluoromethyl-4,4'-dinitrodiphenyl ether. The diamine **2** was obtained in high yields by the catalystic reduction of the dinitro **1** with hydrazine hydrate and Pd/C catalyst in refluxing ethanol. The chemical structures of dinitro **1** and diamine **2** were confirmed by elemental analysis, FTIR, and ^{1}H NMR. The elemental analysis data of the dinitro and the diamine were found to correspond well with the calculated values for their structures. Fig 1 displays the FTIR spectra of the dinitro and the diamine. The nitro group of dinitro **1** gives two characteristic bands at 1540 and 1346 cm^{-1} (NO_2 asymmetric and symmetric stretching, respectively). The characteristic absorption of nitro group disappeared and the characteristic bands of amino group at 3400, 3300 and 3202 cm^{-1} (N-H stretching) appeared after reduction. The ^{1}H NMR spectra of the dinitro and the diamine are illustrated in Fig 2. The absorption signals of aromatic protons of dinitro **1** appeared in the range of 7.44-8.59 ppm, and those of diamine **2** shifted to high field between 6.52-6.86ppm caused by the electron-donating nature of the amino group.

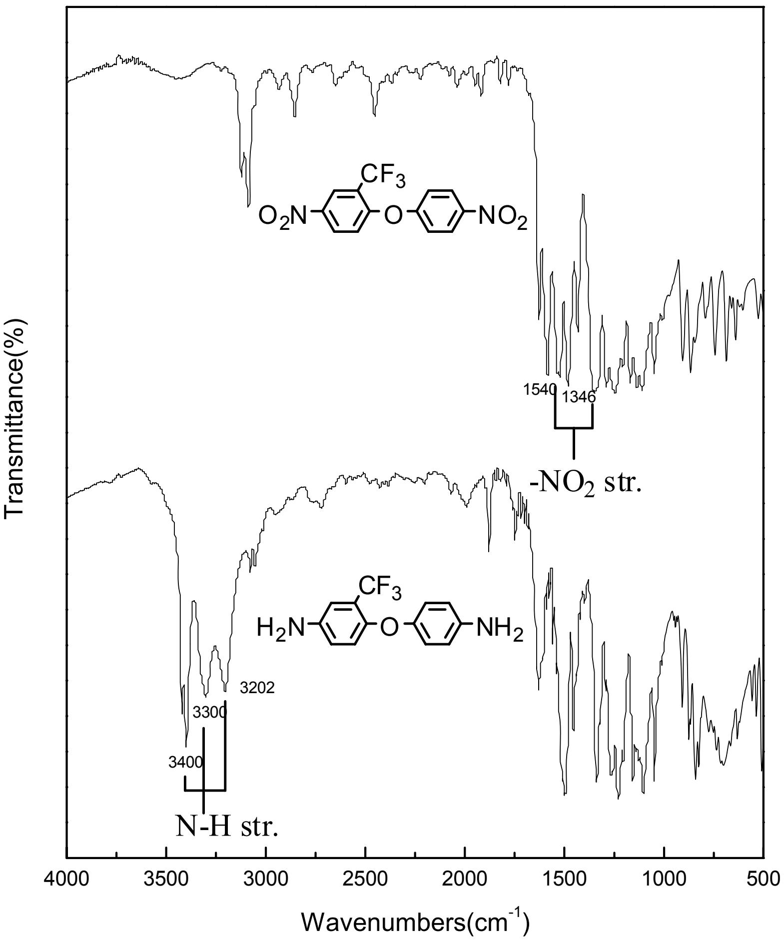


Fig 1. FTIR spectra of dinitro **1** and diamine **2**.

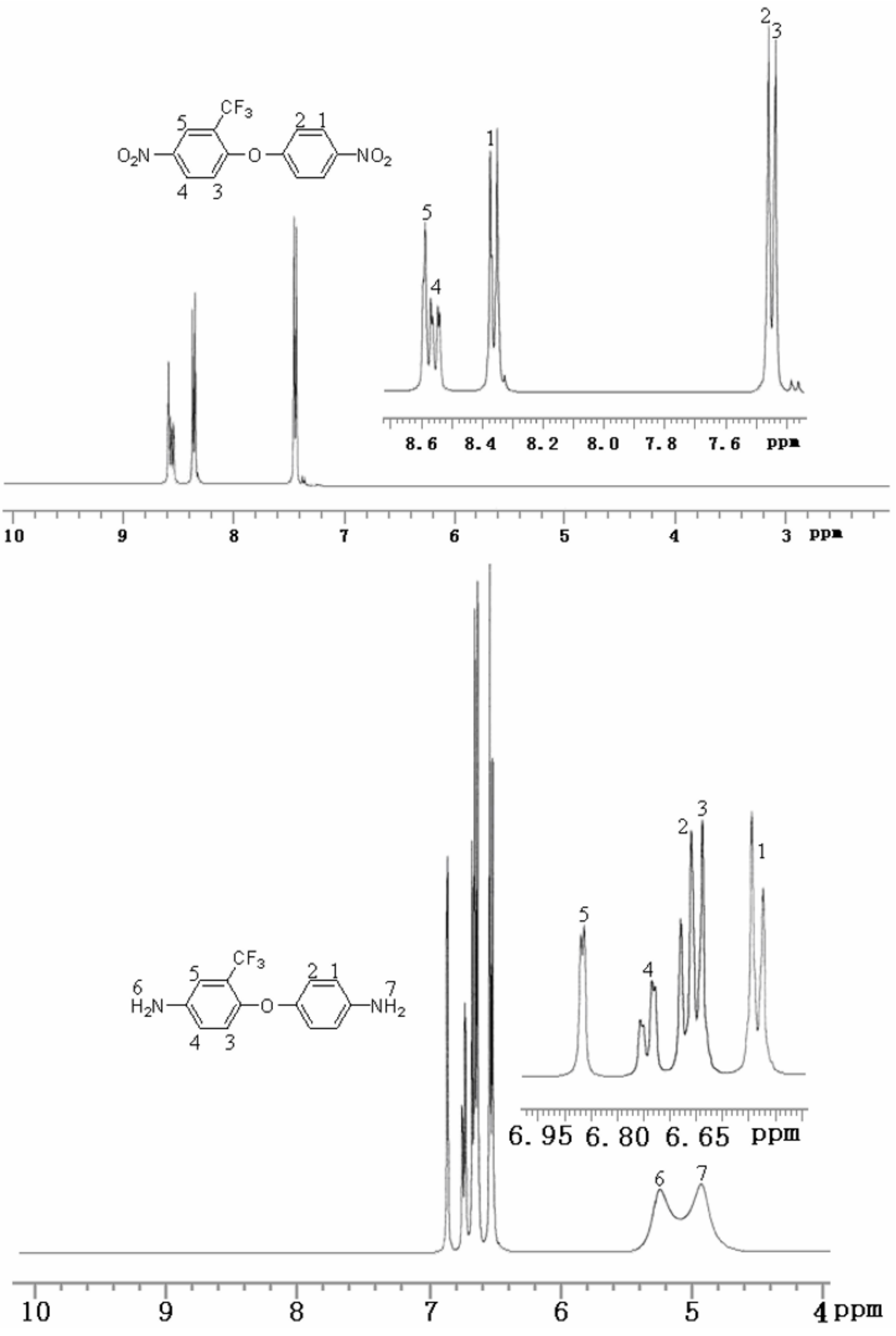
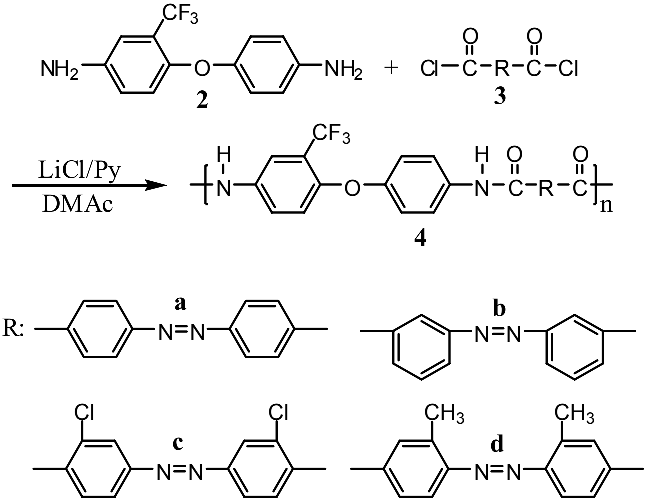


Fig 2. ^{1}H NMR spectra of dinitro **1** and diamine **2**.

Polymer synthesis

Novel fluorinated azopolyamides **4a-d** were synthesized by a low temperature solution polycondensation reaction of diamine **2** with azodibenzoyl chlorides **3a-d** as displayed in Scheme 2. As shown in Table 1, the inherent viscosities of the azopolyamides were in the range of 0.85-1.35 dl/g. The molar masses were sufficiently high to form flexible and tough films from DMAc solutions. The viscosity decreased in the following order: **4c**, **4a**, **4d**, **4b**. The reason is the effect of the substituent on the electrophilicity of the carbonyl carbon, and the stronger the effect, the higher the viscosity. Compared with the polymer **4a**, the chlorine substituent of the polymer 4c is very electronegative, which can increase the electrophylic character of carbonyl carbon. On the contrary, the methyl groups of the polymer **4d** are electron-donors, which decrease the electrophylic character. The lowest viscosity for **4b** is due to the meta-oriented benzene ring in the polymer backbone, which reduced the rigidity



Scheme 2. Synthetic route of azopolyamides.

Table 1. Inherent viscosity and elemental analysis of azopolyamides

polymer	Inherent viscosity	Elemental analysis(%)				
	$\eta_{inh}{}^{a}$(dl/g)	Formula		C	H	N
4a	1.08	$(C_{27}H_{17}N_4O_3F_3)_n$	Calcd	64.54	3.39	11.16
		$(502.45)_n$	Found	64.68	3.12	10.96
4b	0.85	$(C_{27}H_{17}N_4O_3F_3)_n$	Calcd	64.54	3.39	11.16
		$(502.45)_n$	Found	64.72	3.08	11.02
4c	1.35	$(C_{27}H_{15}N_4O_3F_3Cl_2)_n$	Calcd	56.74	2.63	9.81
		$(571.34)_n$	Found	56.95	2.57	9.68
4d	1.06	$(C_{29}H_{21}N_4O_3F_3)_n$	Calcd	65.66	3.96	10.57
		$(530.51)_n$	Found	65.49	3.81	10.23

[a] Measured at a concentration of 0.5 g/dl in DMAc at 30°C

and the effective volume[28]. The results of elemental analyses of all the azopolyamides are also listed in Table 1. The elemental analysis values were in good agreement with the calculated values for the proposed structures.

The representative FT-IR spectrum of the azopolyamides is shown in Fig 3. The IR spectra of these azopolyamides exhibited characteristic absorption bands at around 1629 cm^{-1} (C=O stretching) and 3293 cm^{-1} (N-H stretching). Specific assignments of the -N=N- stretching was difficult because of the interference of the -C=C- stretching in aromatic rings[29-31]. All the azopolyamides also exhibited some strong absorption bands in the region of 1130-1330 cm^{-1} due to the C-O and C-F stretching. The disappearance of the characteristic frequencies of the primary amine group and the appearance of those for amide linkages confirms the formation of the azopolyamides. Fig 4 shows a typical ^{1}H NMR spectrum of azopolyamide **4a** in DMSO-d$_6$, where all the peaks have been assigned to the hydrogen atoms of the repeating unit.

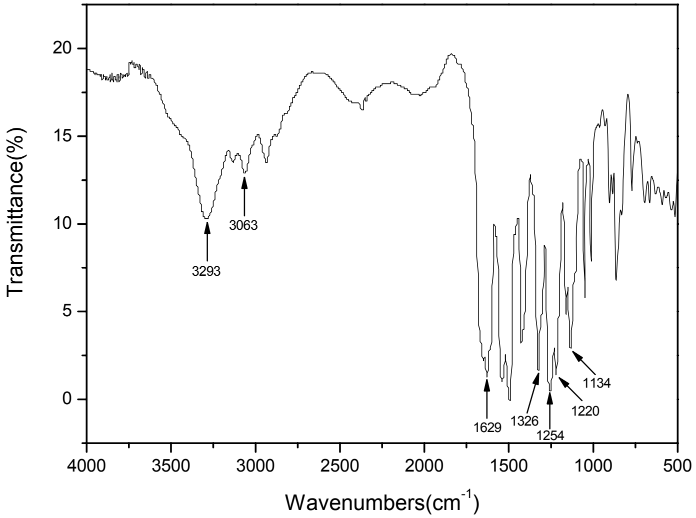


Fig 3. FTIR spectrum of azopolyamide **4a**.

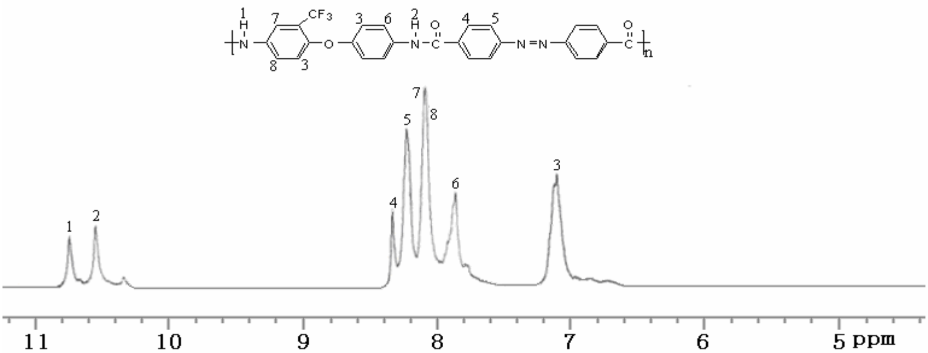


Fig 4. ^{1}H NMR spectrum of azopolyamide **4a** in DMSO-d$_6$.

Solubility properties

The solubility of the azopolyamides in various solvents is listed in Table 2. All the fluorinated azopolyamides **4a-d** showed an excellent solubility in aprotic polar solvents such as DMAc, DMF, NMP and DMSO and were completely insoluble in less aggressive polar solvents like acetone at room temperature. The good solubility of polymers could be apparently attributed to the molecular asymmetry and the presence of bulky CF_3 groups, which reduce the interchain interaction to enhance solubility. Because the bulky CF_3 groups appear to hinder the rotation of C-N amide bond and force the two phenyl rings into adopting a non-coplanar conformation[32].

Table 2. Solubility of azopolyamides[a]

Polymer	Solvents[b]						
	H_2SO_4	DMAc	DMF	NMP	DMSO	Acetone	Ethanol
4a	+++	+++	+++	+++	+++	-	-
4b	+++	+++	+++	+++	+++	-	-
4c	+++	+++	+++	+++	+++	-	-
4d	+++	+++	+++	+++	+++	-	-

[a] Qualitative solubility was determined with 10 mg of polymer in 1 ml of solvent at 25ºC. +++, very soluble; ++, soluble; +, slightly soluble; -, insoluble.

[b] DMAc, *N*,*N*-dimethylacetamide; DMF, *N*,*N*-dimethylformamide; NMP, *N*-methyl-pyrrolidinone; DMSO, dimethyl sulfoxide.

Thermal properties

The thermal properties of the azopolyamides **4a-d** were evaluated by means of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in a nitrogen atmosphere. The thermal behavior data of all the azopolyamides are summarized in Table 3. The fluorinated azopolyamides **4a-d** showed T_g values in the range of 231-259ºC. It can be seen that the T_g of the para-oriented azopolyamides was higher than that of the meta-oriented one **4b**, because the para-oriented azopolyamides are symmetric molecules but the meta-oriented azopolyamide is asymmetric molecule. The thermal stability of **4a-d** was examined by TGA measurements at a heating rate of 10ºC/min. All the azopolyamides exhibited excellent thermal stability with the

Table 3. Thermal properties of azopolyamides

Polymer	T_g[a](ºC)	T_5[b](ºC)	T_{10}[b](ºC)	Char yield[c](%)
4a	259	417	435	50
4b	231	396	411	47
4c	248	413	448	58
4d	250	392	447	4

[a] From DSC measurements conducted at a heating rate of 10ºC/min and a gas flow rate of 15 cm^3/min.

[b] Decomposition temperatures at which 5% weight loss (T_5) or 10% weight loss (T_{10}) were recorded via TGA at a heating rate of 10ºC/min.

[c] Residual weight percentage when the samples were heated to 800ºC in nitrogen.

decomposition temperatures at 5% weight loss (T_5) and 10% weight loss (T_{10}) between 392-417ºC and 411-448ºC in nitrogen atmosphere, respectively. Compared the char yields it was observed that the chlorine-substituted polymer **4c** was much more retardant than the methyl-substituted one **4d**, so all the azopolyamides except for **4d** had char yields above 47% at 800ºC in nitrogen. It implied that these azopolyamides with trifluoromethyl and non-coplanar groups in the polymer backbone showed high thermal stability.

Optical properties

The UV-Vis absorption spectra of azopolyamides **4a-d** in DMAc are shown in Fig 5. The absorptions were recorded at intervals of time until spectral variation was no longer evident. It was found that the shape of absorptions of the azopolyamides **4a**, **4b** and **4c** was almost the same. The intense absorption between 300 and 400 nm corresponding to the п→п* transition of *trans* form decreased while the weak absorption between 400 and 500 nm due to the n→п* electronic transition of the *cis* form increased with increasing irradiation times, which is a clear indication of the photoisomerisation of the azobenzene residues in the chain backbone. When kept in the dark at room temperature, the irradiated solutions returned completely to the *trans* conformation after 62-70 h. The two distinct isobestic points at 315 and 420 nm (**4a**), 302 and 406 nm (**4b**), 325 and 430 nm (**4c**) were observed. The presence of two isobestic points indicated that only photoisomerisation took place and no side

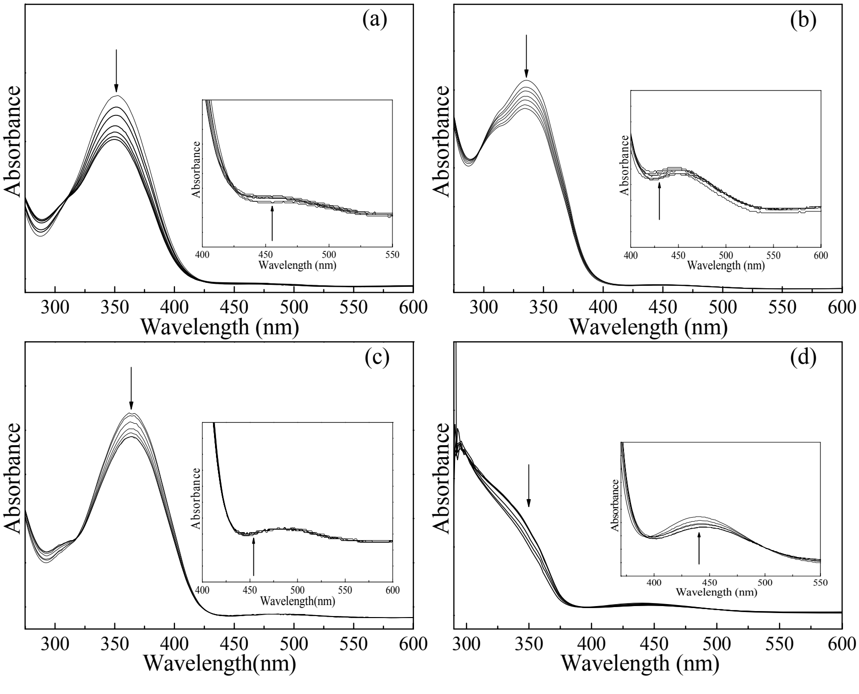


Fig 5. UV-Vis absorption spectral change of (a) **4a**, (b) **4b**, (c) **4c** and (d) **4d** in DMAc upon the UV light irradiation at 5, 10, 15, 20, 25, 30 min.

reactions such as photocrosslinking or photodegradation occurred. From Fig 5, it can easily be observed that the UV-Vis absorption spectrum of **4d** was different from that of **4a**, **4b** or **4c** just because the polymer **4d** was the lowest co-planar. In other words, it was due to the 2-position of methyl groups that affected the azo orbitals in the polymer backbone.

Conclusions

The fluorine-containing diamine, 2-trifluoromethyl-4,4'-diaminodiphenyl ether, was successfully synthesized from 4-nitrophenol with 2-chloro-5-nitrobenzotrifluoride. A series of novel soluble fluorinated azopolyamides were prepared from the diamine with various azodienzoyl chlorides by the low temperature solution polycondension technique. Because of the incorporation of CF_3 and aryl ether groups in the main chain, all the azopolyamides showed excellent solubility at room temperature. The data of TGA and DSC analyses revealed that these azopolyamides had good thermal stability. In addition, these polymers also exhibited photochromic behavior, due to the presence of the aromatic azo groups. These properties can make these polymers attractive for practical applications such as advanced microelectronic material.

Acknowledgements. This work was supported by the National Natural Science Foundation of China under No.50572081.

References

1. Dine-Hart RA, Moore BJC, Wright WW (1964) J Polym Sci Part B: Polym Lett 2:369
2. Frazer AH (1968) High-temperature Resistant Polymers, 1st edn. Wiley, New York
3. Preston J, Dobinson F (1964) J Polym Sci Part B: Polym Lett 2:1171
4. Yang HH (1989) Aromatic High-strength Fibers, 1st ed. Wiley, New York, p 33
5. Cassidy PE (1980) Thermally Stable Polymers, 1st ed. Marcel Dekker, New York, p 67
6. Bellomo MR, Pasquale GD, Rosa AL, Pollicino A, Siracusa G (1996) Polymer 37:2877
7. Johnson RA, Mathias LJ (1995) Macromolecules 28:79
8. Gaudiana RA, Minns RA, Rogers HG, Sinta R, Kalganarama P, McGrown C (1987) J Polym Sci Part A: Polym Chem 25:1249
9. In I, Kim SY (2006) Polymer 47:547
10. Serna F, García F, de la Peña JL, Calderón V, García JM (2007) J Polym Res 14:341
11. Turner SR, Perry RJ, Blevins RW (1992) Macromolecules 25:4819
12. Liou GS, Hsiao SH, Chen WC, Yen HJ (2006) Macromolecules 39:6036
13. Steuer M, Horth M, Ballauff M (1993) J Polym Sci Part A: Polym Chem 31:1609
14. Rogers HG, Gaudiana RA, Hollinsed WC, Kalyanaraman PS, Manello JS, McGowan C, Minns RA, Sahatjian R (1985) Macromelecules 18:1058
15. Liou GS, Fang YK, Yen HJ (2007) J Polym Res 14:147
16. Cimecioglu AL, Weiss RA (1992) J Polym Sci Part A: Polym Chem 30:1051
17. Imai Y, Maldar NN, Kakimoto M (1985) J Polym Sci Polym Chem Ed 23:1797
18. Liaw DJ, Huang CC, Chen WH (2006) Polymer 47:2337
19. Hsiao SH, Yang CP, Tsai CY, Liou GS (2004) Eur Polym J 40:1081
20. Matsuura T, Ando S, Sasaki S (1999) Synthesis and properties. In: Hougham G, Cassidy PE, Johns K, Davidson T (eds) Fluoropolymers. Kluwer Academic, New York, p 50
21. Yang CP, Chen RS, Chen KH, Chen YP (2002) J Chin Chem Soc 49:927
22. Yang CP, Su YY (2005) Eur Polym J 41:249
23. Hugel T, Holland NB, Cattani A, Moroder L, Seitz M, Gaub HE (2002) Science 296:1103
24. Ikeda T, Tsutsumi O (1995) Science 268:1873

25. Tomlinson ML (1964) J Chem Soc 756
26. Srinivasan M, Gopal J (1985) Chem Ind 339
27. Xiong CX, Niu YS, Zhou W, Dong LJ (2006) J Chem Res (S) 139
28. Balasubramanian M, Nanjan MJ, Santappa M (1982) J Appl Polym Sci 27:1423
29. Henniker JC (1967) Infra-red Spectrometry of Industrial Polymers, 1st ed. Academic Press, London, p 128
30. Bellamy LJ (1975) The Infra-red Spectra of Complex Molecules, 3rd ed. Chapman and Hall, London, p 369
31. Balasubramanian M, Nanjan MJ, Santappa M (1981) Makromol Chem 182:853
32. Qiu ZM, Wang JH, Zhang QY, Zhang SB, Ding MX, Gao LX (2006) Polymer 47:8444