Poly(ether imide)s having a pendant 3,5-bis(trifluoromethyl)phenyl group

Baijun Liu[1], Toshihiko Matsumoto[1], Shinji Ando[2]

[1] *Center for Nano Science and Technology, Tokyo Polytechnic University, Kanagawa 243-0297*
[2] *Dept. Organic and Polymeric Materials, Tokyo Institute of Technology, Meguro-ku, Tokyo 152-8552*
e-mail: matumoto@nano.t-kougei.ac.jp

Introduction

Aromatic polyimides are well known as a class of high performance polymers because of their outstanding properties. These materials are widely used in the aerospace and electronics industries. However, most polyimides are often insoluble and infusible in their fully imidized form. To improve the processability, numerous research efforts have been focused on synthesis of soluble and melt-processable polyimides, while maintaining their thermal stability and other excellent properties. The introduction of flexible linkages into the polymer chains is regarded as one of efficient approaches to increase their solubility and decrease their glass transition temperatures to a range, which facilitates their processing in melt.[1] The high thermal stability polymers with trifluoromethyl groups have received significant attention, due to their potential applications as microelectronic devices, optical wave-guide materials and gas-separation membranes.[2] The existence of cyano groups on the polymer chains may promote adhesion of the polymer to some substrates, transfer into other functional groups, and serve as a potential site for polymer crosslinking.[3]

In this study, a novel diamine, 1,4-bis[2'-cyano-3'(4"-aminobenzoxy)benzoxy]-2-[(3',5'-ditrifluoromethyl)benzyl]benzene (6FC-Diamine), containing flexible ether linkage, trifluoromethylated phenyl pendant groups, and cyano substituents, was synthesized and characterized. A series of aromatic polyimides derived from 6FC-Diamine were prepared for their potential applications as soluble high performance polymers.

Experimental

Monomer synthesis

Synthesis of 1,4-bis(2'-cyano-3'-fluorophenoxy)-2-[(3',5'-ditrifluoromethyl)phenyl]benzene (6FC-Trimer)

Into a 500ml three-necked flask equipped with a magnetic stirrer, a nitrogen inlet a dropping funnel, and a Dean-Stark trap with a condenser were placed 2,6-difluorobenzonitrile (41.7g, 0.30mol), anhydrous potassium carbonate (13.8g, 0.10mol), DMF (150ml), and toluene (70ml). The mixture was stirred and heated to reflux under a nitrogen atmosphere. A solution of 6F-PH (16.1g, 0.05mol) in DMF (80ml) was added dropwise into the mixture through the dropping funnel over 4 h. The reaction mixture was stirred for another 8h to ensure completion of the reaction. The mixture was concentrated to 100ml and poured into 1500ml of deionized water. The powder was washed with water and ethanol several times. The white powder was recrystallized from ethanol and sublimated.

Yield: 60%. m.p: 146 °C (DSC). IR (KBr): 2237 (-CN), 1245 (Ar-O-Ar), 1133 (-CF_3) cm^{-1}. ^1H NMR ($CDCl_3$, δ, ppm): 7.99 (s, 2H), 7.84 (s, 1H), 7.56-7.52(m, 1H), 7.44-7.39(m, 1H), 7.32 (s, 1H), 7.28-7.23 (m, 2H), 6.98(dd, J_1=8.5Hz, J_2=8.2Hz, 1H), 6.87(dd, J_1=8.2Hz, J_2=8.5Hz, 1H), 6.78 (d, J=8.5Hz, 1H), 6.54 (d, J=8.50 Hz, 1H).

Synthesis of 1,4-bis[2'-cyano-3'(4"-aminophenoxy)phenoxy]-2-[(3',5'-distrifluoromethyl)phenyl]benzene (6FC-Diamine)

6FC-Trimer (5.60g, 0.01mol), *p*-aminophenol(2.40g, 0.022mol), anhydrous K_2CO_3 (3.04g, 0.022mol), and NMP (35ml) were placed into a 100ml three-necked flask equipped with a magnetic stirrer, a nitrogen inlet and a Dean-Stark trap with a condenser under a nitrogen atmosphere. Toluene(65ml) was added through the Dean-Stark trap. The reaction mixture was allowed to reflux for 4h. The toluene was removed by the Dean-Stark trap. The mixture was stirred at 150°C for another 6 h. The resulting mixture was poured into 400ml of deionized water after cooling to room temperature. The precipitate was collected by filtration, washed thoroughly with water, and dried at 100°C in a vacuum oven. The product was crystallized from toluene to yield off-white crystals.

Yield: 45%. Mp: 245 °C (DSC). Anal. Calcd. for $C_{40}H_{24}F_6N_4O_4$ (738.63 g/mol): C, 65.04%; H, 3.28%, N, 7.59%. Found: C, 65.10%; H, 3.40% N, 7.60%. IR (KBr): 3471 and 3374 ($-NH_2$), 2233 (-CN), 1245 (Ar-O-Ar), 1130 ($-CF_3$) cm^{-1}. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.03(s, 2H), 7.85(s, 1H), 7.32-7.16(m, 5H), 6.93(d, J=8.5Hz, 2H,), 6.87(d, J=8.55Hz, 2H), 6.71(d, J=8.5Hz, 2H), 6.69(d, J=8.8Hz, 1H,), 6.54(d, J=8.2Hz, 1H), 6.48(d, J=8.5Hz, 1H), 6.38(d, J=8.8Hz, 1H), 6.33(d, J=8.2Hz, 1H), 3.70(s, 4H, $-NH_2$).

Polymer procedures

As a typical procedure for the preparation of polyimides, the synthesis of 6FC-6FDA is given as follows: 6FC-Diamine (0.7386g, 1mmol), and NMP (4ml) were placed into a 30ml three-necked flask equipped with a magnetic stirrer and a nitrogen inlet under a nitrogen atmosphere. After the diamine was entirely dissolved, 6FDA (0.4440g, 1mmol) was added to the solution. The mixture was stirred at room temperature for 24 h to yield poly(amic acid) solution. The solutions were cast on a glass plate, and then heated under vacuum by the following procedure: 80 °C/3h, 110 °C/0.5h, 150 °C/0.5h, 180 °C/0.5h, 210 °C/0.5h, 240 °C/0.5h, and 270 °C/0.5h. After curing, the polyimide film was removed by immersing the glass plate in boiling water. All of the other polyimides were synthesized by a similar procedure.

6FC-6FDA. IR (film): 2232 (-CN), 1783, 1729(C=O), 1374(C-N-C), 1243 (Ar-O-Ar), 1139 ($-CF_3$) cm^{-1}. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.21(s, 2H, H-6, H-4), 8.14 (s, 1H, H-5), 8.10 (d, J=7.8Hz, 1H, H-13), 7.90(s, 1H, H-1), 7.66-7.62(m, 5H, H-12, H-14, H-8), 7.58-7.50(m, 7H, H-10, H-3, H-10', H-8', H-2), 7.38 (d, J=9.0Hz, 2H, H-11), 7.25 (d, J=8.8Hz, 2H, H-11'), 6.89(d, J=8.5Hz, 1H, H-7), 6.82(d, J=8.3Hz, 1H, H-9), 6.72(d, J=8.3Hz, 1H, H-7'), 6.68(d, J=8.3Hz, 1H, H-9').

Results and Discussion

Monomer synthesis

The diamine monomer, 6FC-Diamine was synthesized *via* two-step aromatic nucleophilic substitution reactions. The first step is a substitution reaction of (3,5-difluoromethyl)phenylhydroquinone with a large excessive 2,6-difluorobenzonitrile in the presence of K_2CO_3, to yield the bisfluoro-compound (6FC-Trimer). In a similar way, 6FC-Diamine was prepared by the substitution reaction of 6FC-trimer and *p*-aminophenol. The structures of 6FC-Trimer and 6FC-Diamine were confirmed IR and ^{1}H NMR spectroscopy. In the IR spectra, 6F-Trimer shows the characteristic absorption bands at 2237 cm^{-1} due to stretching of cyano groups, at 1245 cm^{-1} due to aryl ether linkages, and at 1133 cm^{-1} corresponding to trifluoromethyl groups. Compared with 6FC-Trimer, the FTIR of 6FC-Diamine exhibits the characteristic absorption bands of amino groups at 3471 and 3374 cm^{-1}. The signal at 3.70 ppm in the ^{1}H NMR is peculiar to the amino group.

Preparation of Polymers

Polyimides were prepared according to a typical two-step polymerization method. The structures of poly(ether imide)s and their abbreviations are illustrated in **Fig.1.** The transparent, flexible and good-quality films were obtained in all cases. The resulting polyimides had inherent viscosities of 0.41-0.64 dL/g. The structures of polyimides were characterized by FTIR and ^{1}H NMR spectra. The FTIR spectra of polyimides exhibited the characteristic imide absorptions at 1777-1783(ν_{as} $_{C=O}$), 1719-1730($\nu_{s\,C=O}$), and 1374-1375(ν $_{C\text{-}N\text{-}C}$) cm^{-1}. The ^{1}H NMR spectra of the polyimides are agreed with their respective structures.

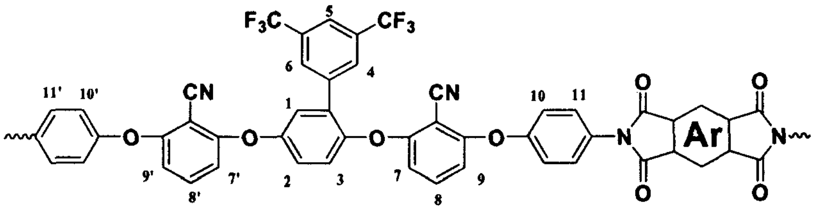

Fig.1. The structures of poly(ether imide)s and their abbreviations.

Thermal properties of polyimides

The thermal properties of polymers were evaluated by DSC and TGA (**Table 1**). The Tg's of polmers were in the range of 215-234 °C, and no melting enthoderms were observed in the DSC traces. These results could be explained by the presence of bulky pendant groups and flexible ether linkages, which inhibited the close packing of the molecular chains. All polymers possessed the lower Tg values because of the introduction of flexible linkages (added up to four or five ethers in every repeated unit). As expected, 6FC-PMDA with more rigid moieties had the highest Tg value, and 6FC-ODPA with more flexible linkages had the lowest Tg value. The curves of TGA showed that all the polymers had good thermal stability. The temperatures at 5% weight loss reached to 479-510 °C, and the temperatures of 10% weight loss were up to 507-536 °C in nitrogen. The good thermal stability is attributed the aromatic structure and strong C-F bonds.

Table 1 The inherent viscosity, thermal properties, and film quality of polyimides

polyimide	η_{inh}(dL/g) [a]	Tg(°C) [b]	TD_5(°C) [c]	TD_{10}(°C) [d]	Film quality
6FC-ODPA	0.44	215	479	507	clear, flexible
6FC-6FDA	0.51	232	510	536	clear, flexible
6FC-BTDA	0.41	217	490	524	clear, flexible
6FC-BPDA	0.59	228	495	527	clear, flexible
6FC-PMDA	0.64	234	480	515	clear, flexible

[a] polyimide, measured in DMAc, 0.5g/dL, 30°C [b] 20K/min in N_2
[c] 5%-weight loss and [d] 10%-weight loss temperatures, 10K/min in N_2

Solubility of polymers

The solubility of the polyimides obtained by thermal imidization method was investigated in various solvents. All of them could be soluble in polar aprotic solvents, such as NMP, DMAc, and DMF at room temperature, and soluble in DMSO on heating. Improved solubility was explained by the introduction of bulky pendant groups and flexible ether linkages. 6FC-6FDA, 6FC-ODPA and 6FC-BTDA could be dissolved in chloroform and THF at room temperature due to their more flexible backbones. Therefore, the transparent and flexible polyimide films could be obtained by the solution casting.

Optical properties and Dielectric constants of polymers

The UV-vis spectra showed that the cutoff wavelengths of polyimide films were from 315 to 373 nm. The cutoff wavelength of 6FC-6FDA is lower than that of other polyimides. The reason can be interpreted by the hexafluoroisopropyl moiety that can separate the chromaphoric groups and reduce electronic interaction. The dielectric constants of the polymer films were evaluated by the improved Maxwell equation (**Table 2**). The dielectric constants of polyimides were in the range of 2.69-2.84. The estimated values are lower than Kapton H ($\varepsilon \sim 3.5$ at 1 kHz), and Ultem ($\varepsilon \sim 3.15$ at 1 kHz). The low dielectric constants were attributed to the existence of trifluoromethyl groups. Highly fluorinated polymer, 6FC-6FDA had the lowest dielectric constant. They may be the promising processable high-temperature materials applied as microelectronic and optical devices.

Table 2 Optical properties and optically estimated dielectric constant

polyimide	n_{TE}	n_{TM}	n_{AV}	Δn	ε
6FC-ODPA	1.5980	1.5963	1.5974	0.0017	2.81
6FC-6FDA	1.5638	1.5625	1.5634	0.0013	2.69
6FC-BTDA	1.5994	1.5984	1.5991	0.0010	2.81
6FC-BPDA	1.6067	1.6055	1.6063	0.0012	2.84
6FC-PMDA	1.5935	1.5895	1.5922	0.0040	2.79

[a] in-plane, [b] out-of-plane refractive index. [c] averaged refractive index = $(2n_{TE}+n_{TM})/3$.
[d] birefringence = $(n_{TE}-n_{TM})$. [e] optically estimated dielectric constant = $1.1\,n_{AV}^{2}$.

Conclusions

A series of trifluoromethylated aromatic polyimides derived from a novel diamine were synthesized and characterized. The resulting polyimides had Tg's in the range of 215-234 °C. All the polymers had excellent thermal stability and good solubility. Good quality and flexible polyimide films could be produced by solution casting. The polymer films exhibited good optical transparency and low dielectric constants (2.69-2.84).

References

1. D.J. Liaw, B.Y. Liaw, *Macromol. Chem. Phys.*, **1998**,*199*,1473.
2. G. Maier, *Progress in Polymer Science*, **2001**; *26*: 3.
3. B.J. Liu, W. Hu, Z.H. Jiang, T. Matsumoto, *J. Photopolym. Sci. & Technol.*, **2003**, *16*, 261.