Soluble Polyimides from Unsymmetrical Diamine with Trifluoromethyl Pendent Group

Im Sik Chung and Sang Youl Kim*

Center for Advanced Functional Polymers, Department of Chemistry and School of Molecular Science (BK21), Korea Advanced Institute of Science and Technology, 373-1, Kusung-Dong, Yusung-Gu, Tae-jon 305-701, Korea

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Aromatic polyimides are well-known as highly heat-resistant materials and have been widely used in many applications such as electronics, coatings, composite materials, and membranes.1 Polyimides are often insoluble and infusible in their fully imidized form due to their rigid chain characteristics, leading to processing difficulties. Thus, polyimide processing is generally carried out with poly(amic acid) intermediate and then converted to polyimide via rigorous thermal treatment.2 However, this process has several inherent problems such as emission of volatile byproducts (e.g., H2O) and storage instability of poly(amic acid) intermediate.3

To overcome these problems, much research effort has been focused on synthesis of soluble and processable polyimides in fully imidized form without deterioration of their own excellent properties.4 Several approaches to soluble polyimides including introduction of flexible linkage5 or bulky substituents6 and use of noncoplanar7 or alicyclic8 monomers have been developed in the past decade. For example, the polyimides containing unsymmetrically structured aromatic ring with perfluoroalkoxy6a or phenyl6b-d groups showed enhanced solubility behavior. Most of the above approaches for soluble polyimides are aimed at reduction of several types of chain—chain interaction, such as chain packing (e.g., crystallinity) and charge transfer and electronic polarization interactions.2,9

In this communication, we describe our approach for soluble polyimide by introducing a trifluoromethyl group unsymmetrically into the polymer chains that may reduce interactions between polyimide chains.

4,4′-Diaminodiphenyl ether (4,4′-DDE) is widely used in synthesis of polyimides, but the polyimides synthesized from this diamine are insoluble or have poor solubility depending on dianhydride used. To increase solubility, we designed a new diamine monomer having the same structure with 4,4′-DDE except one trifluoromethyl group at the 2-position of the benzene ring. The new diamine monomer, 2-trifluoromethyl-4,4′-diaminodiphenyl ether (1), was prepared from 2-chloro-5-nitrobenzotrifluoride and 4-nitrophenol according to Scheme 1. 2-Chloro-5-nitrobenzotrifluoride was reacted with 4-nitrophenol in the presence of potassium carbonate to produce the dinitro compound, which was converted to the corresponding diamine monomer by reduction of the nitro groups.

First, new polyimides were prepared from 1 and commercially available aromatic dianhydrides, such as PMDA, BPDA, BTDA, and ODPA, via a one-pot synthetic method as shown in Scheme 2. The polymerization was carried out by reacting stoichiometric amounts of diamine monomer 1 with aromatic dianhydrides at a concentration of 12% solids in N-methylpyrrolidone (NMP). The ring-opening polyaddition at room temperature for 8 h yielded poly(amic acid) solutions. After dilution of the solution to 8–10%, subsequent cyclodehydration by heating at 190 °C for 12 h gave the fully imidized polyimides except that of PMDA. While the polyimide prepared from 1 and PMDA (2b) was precipitated during the imidization process presumably due to the rigid chain characteristics, the rest remained in solution after imidization. The degree of
imidization of the polyimides 2b determined with FTIR was 82%.\textsuperscript{10}

The polyimides were also prepared by a conventional thermal curing method to compare the differences by the imidization method. The poly(amic acid) solutions prepared as previously described were cast on a glass plate and then preheated in vacuo at 80 °C for 12 h to give the films of the poly(amic acids). Thermal conversion to polyimides was carried out at 300 °C under a flow of N\textsubscript{2}. The transparent, pale-yellowish, and finger-nail-creasable films were obtained in all cases. Poly(amic acid) 5a, which has relatively low inherent viscosity due to low reactivity of ODPA, gave a somewhat brittle film, but it became a flexible and tough film (5c) after fully imidized by thermal curing.

FTIR spectra of the poly(amic acids) show the absorption bands at 3400–2900 cm\textsuperscript{-1} corresponding to amide (–NH–) and acid (–OH) stretching, 1720 cm\textsuperscript{-1} corresponding to C=O stretching of carboxylic acid, 1660 cm\textsuperscript{-1} corresponding to C=O stretching of amide, and 1540 cm\textsuperscript{-1} corresponding to C–N stretching of amide. FTIR spectra of the polyimides show the absorption bands at 1780 (C=O asymmetric stretching), 1720 (C=O symmetric stretching), 1370 (C–N stretching), and 720 cm\textsuperscript{-1} (C=O bending) corresponding to the characteristic imide bands. FTIR spectra of the synthesized polyimides showed same patterns regardless of their imidization method. \textsuperscript{11}H NMR spectra of the poly(amic acids) showed the peak at 10.6 and 10.4 ppm corresponding to carboxylic acid (–COOH) protons. However, in the case of corresponding polyimides, \textsuperscript{11}H NMR spectra showed no amide and acid protons, indicating full imidization. Also, TGA and DSC measurements that did not show any transition corresponding to imidization imply that the polyimides prepared by using the solution imidization method were fully imidized in the case that precipitation did not occur during imidization.

The polyimides synthesized via the one-pot synthetic method (solution imidization method), 4b and 5b, are well dissolved in polar aprotic solvents and phenolic solvents at room temperature and form flexible and tough films by casting. Polyimide 3b is soluble in polar aprotic solvents only at elevated temperature, but gelation occurred below 120 °C even at low concentration (0.5 wt %), and 2b is not dissolved in any organic solvents though it is not fully imidized. The polyimides prepared by thermal curing have more poorer solubility in organic solvents than those prepared by the one-pot synthetic method. Polyimides 2c and 3c are not dissolved in any organic solvents, while 4c is only soluble in hot NMP and m-cresol. Polyimide 5c is soluble in polar aprotic solvents at elevated temperature.

Interestingly, the solubility of the polyimides prepared by the solution imidization method decreased and became comparable to that of the polyimides prepared by thermal imidization, when they are subjected to the thermal imidization condition of the corresponding poly(amic acids). One of the plausible explanations is that the thermal treatment may invoke a chain ordering of the polyimides that increases chain to chain interaction, but further studies are needed.

As mentioned above, polyimide synthesized from 1 and ODPA (5b) has the best solubility in organic solvents. To confirm the solubility enhancement effect of trifluoromethyl groups, the polymerization of 4,4'-DDE and ODPA was conducted by using the same method.\textsuperscript{11} But in this case, precipitation occurred during solution imidization in NMP at 190 °C, and the degree of imidization was 93%.\textsuperscript{10} This result clearly showed that introducing one trifluoromethyl group in the 4,4'-DDE structure significantly improved the solubility of the corresponding polyimides. The enhanced solubility is attributed not only to the bulkiness of the substituent but also to the unsymmetrical structure coming from the diaminemonomer.

Structural characterization of the synthesized polymers was also attempted with the X-ray method. The wide-angle X-ray diffraction patterns revealed that all of the polyimides were amorphous regardless of anhydride employed and imidization method.

Thermal properties of the polyimides were evaluated by TGA, DSC, and TMA. The thermal properties of the polyimides are summarized in Table 1. The 5% weight loss temperatures of the polyimides are in the range 539–582 °C in nitrogen and 530–548 °C in air. All of the polyimides showed high glass transition temperatures (T\textsubscript{g}’s) and low thermal expansion coefficient (CTE). The T\textsubscript{g}’s of these polymers are 346, 295, 268, and 246 °C for 2c, 3b, 4b, and 5b, respectively, and the CTE are 56.5, 47.5, 50.9, and 60.5 ppm/°C for 2c, 3c, 4c, and 5c, respectively. The difference of T\textsubscript{g} and CTE values was caused by the difference of chain rigidity due to different structure of the dianhydride employed, and their thermal properties are comparable to those of the polyimides synthesized from 4,4’-DDE.\textsuperscript{12}

In summary, a new series of soluble polyimides containing trifluoromethyl groups are prepared from 4,4’-DDE with trifluoromethyl group at the 2-position by using the one-pot synthetic method. The polyimides prepared by the solution imidization method were soluble in polar aprotic solvents except 2b while the polyimides synthesized by thermal imidization method had poor solubility or were insoluble. The polyimides have excellent thermal properties regardless of their imidization method, and their thermal properties are comparable to those of the polyimides without substituents. Further studies on the polyimides from unsymmetrical diamine monomers with various substituents are in progress.

| Table 1. Physical Properties of the Synthesized Polyimides |
|--------------|--------------|------------|--------------|---------------|
| polyimides   | n_{in} (dL/g)| T_{g} (°C) | T\textsubscript{g} (°C) | CTE ppm/°C |
| PAA          | PI           | in N\textsubscript{2} | in air        |              |
| 2            | 0.43         | d          | 554          | 560          | 346         | 56.5       |
| 3            | 0.47         | e          | 582          | 561          | 295         | 47.5       |
| 4            | 0.45         | 0.61       | 539          | 530          | 268         | 50.9       |
| 5            | 0.27         | 0.63       | 653          | 548          | 246         | 60.5       |

\textsuperscript{1} Inherent viscosity, measured at a concentration of 0.5 g/dL in DMAc at 30 °C. PAA = poly(amic acid), PI = polyimide via one-pot synthesis. \textsuperscript{2} The 5% weight loss temperature. \textsuperscript{3} Measured by TGA at temperature range from 50 to 200 °C (thermal imidization). \textsuperscript{4} Insoluble. \textsuperscript{5} Gelation occurred below 120 °C. \textsuperscript{6} Measured by TMA (thermal imidization). \textsuperscript{7} Measured by DSC (solution imidization).

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sodium bicarbonate and brine repeatedly, and the chloroform solution was dried with anhydrous MgSO₄ and evaporated to obtain dinitro compound 2, which was recrystallized from methanol (19.4 g, 59.1 mmol, 90.6% yield); mp 70–72 °C. FTIR (KBr, cm⁻¹): 3086 (aromatic C–H); 1627, 1584, 1482 (aromatic C=C); 1521, 1347 (NO₂); 1248 (C–O–C); 1171–1113 (C–F). ¹H NMR (DMSO-d₆, 200 MHz, ppm): 8.60 (d, 1H, J = 2.63 Hz); 8.39 (dd, 1H, J = 9.08 Hz, J = 2.73 Hz); 7.12 (d, J = 9.02 Hz); 8.32, 8.28, 7.23, 7.19 (4H). ¹³C NMR (DMSO-d₆, 200 MHz, ppm): 159.56, 148.35 (q, J = 270.9 Hz), 145.44, 145.07, 124.60 (q, J = 270.9 Hz), 121.52, 120.77 (q, J = 29.7 Hz), 119.82, 119.22, 115.71, 111.62 (q, J = 5.03 Hz). HRMS (m/e): calcld for C₃₁H₁₅N₃F₃, 328.0370; found, 328.0302.

2-Trifluoromethyl-4,4′-diaminodiphenyl Ether (1). A mixture of the dinitro compound (15.0 g, 45.7 mmol), anhydrous SnC₂Cl (41.0 g, 216 mmol), and 250 mL of 95% ethanol was stirred until 200 mL of concentrated HCl was added slowly. After addition of HCl was over, the mixture was refluxed for 12 h. Excess ethanol was evaporated, and the remaining solution was poured into 400 mL of distilled water. The solution was basified with 10% NaOH solution, and the precipitate was filtered off, washed with hot water and cold methanol, and recrystallized from ethanol to give pale yellow product (10.3 g, 38.4 mmol, 84.0% yield). This yellow product (10.3 g, 38.4 mmol, 84.0% yield). This work was supported by Center for Advanced Functional Polymers (CAFPoly) at Korea Advanced Institute of Science and Technology (KAIST).

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References and Notes
at 1370 cm$^{-1}$ (imide C–N stretching) assuming 100% imidization of the polyimide obtained from conventional thermal imidization. The 1500 cm$^{-1}$ (aromatic C=C stretching) band was used as an internal reference to normalize the intensity of imide absorption band.

(11) The inherent viscosity of the poly(amic acid) is 0.48 dL/g in DMAc at 30 °C (0.5 g/dL). The precipitated polymer was not soluble in any organic solvents while PI4b was soluble in various organic solvents. The first scan of its DSC showed a maximum endothermic transition at 335 °C due to further imidization, but the second scan showed clearly a glass transition at 261 °C. The fully imidized form which has $T_g$ of 261 °C was also prepared by the thermal curing method, and it was not soluble in any organic solvents except in concentrated sulfuric acid.


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