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Hwa-Jin Jeong[a]; Ken Iwasaki[a]; Masa-Aki Kakimoto[a]; Yoshio Imai[a]
[a] Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Meguro-ku, Tokyo, Japan

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SYNTHESIS AND CHARACTERIZATION OF NOVEL AROMATIC POLYETHERS FROM TETRAPHENYLATED FIVE-MEMBERED HETEROCYCLE-CONTAINING DIOLS AND ACTIVATED AROMATIC DIHALIDES

HWA-JIN JEONG, KEN IWASAKI, MASA-AKI KAKIMOTO,
and YOSHIO IMAI*

Department of Organic and Polymeric Materials
Tokyo Institute of Technology
Meguro-ku, Tokyo 152, Japan

ABSTRACT

New aromatic polyethers having inherent viscosities of 0.23–0.73 dL/g were synthesized from combinations of three tetraphenylated five-membered heterocycle-containing diols, 2,5-bis(4-hydroxyphenyl)-3,4-diphenyl-furan, -pyrrole, and -thiophene, and three activated aromatic dihalides, 4,4′-difluorobenzophenone, bis(4-hydroxy-phenyl) sulfone, and 2,6-difluorobenzonitrile, by aromatic nucleophilic substitution polycondensation. These aromatic polyethers, which have an amorphous nature, were soluble in a wide range of organic solvents. They had glass transition temperatures in the 182 to 250°C range with no weight loss below 400°C in either air or nitrogen atmospheres.

INTRODUCTION

Aromatic polyethers such as poly(ether ketone)s and poly(ether sulfone)s are an important class of high performance thermoplastic materials because of their attractive combination of physical and mechanical properties for use in a variety of industrial fields [1, 2]. Aromatic polyethers containing various heterocyclic units have also attracted considerable interest for potential electronics and aerospace applications in these years. The synthetic approach has involved the polycondensation of heterocycle-containing aromatic difluoro compounds with various bisphenols, where the heterocyclic ring activates the fluorine atom sufficiently to permit aromatic nucleophilic substitution by a bisphenolate, accordingly leading to the formation of a high molecular weight polymer. Heterocycles that have been incorporated into the backbone of aromatic polyethers by using this approach include oxadiazole [3–5], pyridazine [3], triazole [6], benzoxazole [7], benzothiazole [8], quinoxaline [9–11], isoquinoline [12], and phthalazine [13].

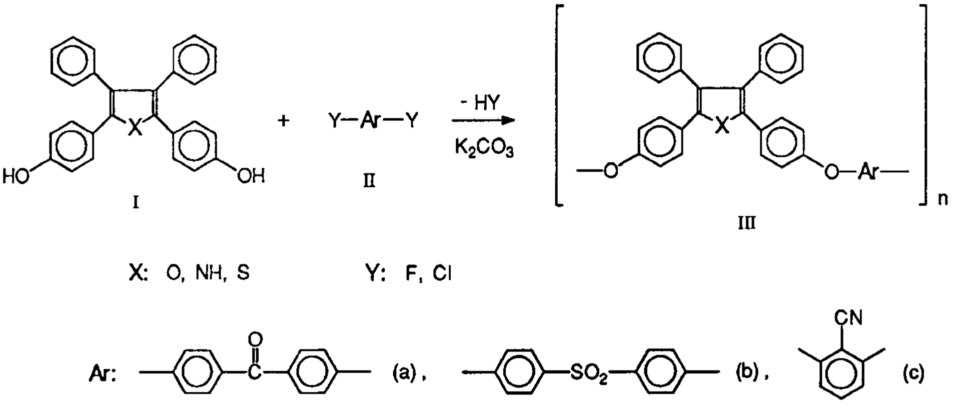
Alternatively, bisphenols containing preformed heterocyclic linkages such as imidazole [14], oxadiazole [15], quinoxaline [16], benzoxazole [17], and benzimidazole [18] have been synthesized and then subjected to polycondensation with various activated aromatic dihalides, producing high molecular weight aromatic polyethers. Both of these polycondensations were generally carried out by using potassium carbonate in polar aprotic solvents at elevated temperatures under nitrogen.

We have already reported the synthesis of a series of organic-soluble high temperature polymers such as aromatic polyamides [19–23], polyimides [24–27], and polyarylates [28–31] based on aromatic diamines and diols containing tetraphenylated five-membered heterocycles such as furan, pyrrole, and thiophene. In continuation to these studies, the present communication deals with the synthesis of novel aromatic polyethers derived from diol monomers bearing tetraphenylated five-membered heterocycles and activated aromatic dihalides as shown in Scheme 1.

EXPERIMENTAL

Materials

2,5-Bis(4-hydroxyphenyl)-3,4-diphenylfuran (**I-O**) [29], 2,5-bis(4-hydroxyphenyl)-3,4-diphenylpyrrole (**I-NH**) [30], and 2,5-bis(4-hydroxyphenyl)-3,4-diphenylthiophene (**I-S**) [31] were synthesized starting from 4-methoxydeoxybenzoin according to the procedures reported elsewhere. Compound **I-O**, mp 192–193°C (lit



SCHEME 1.

mp [29], 192–193°C); **I-NH**, mp 235–236°C (lit mp [30], 235–236°C); and **I-S**, mp 236–237°C (lit mp [31], 236–237°C).

4,4′-Difluorobenzophenone (**IIa-F**), 4,4′-dichlorobenzophenone (**IIa-Cl**), and bis(4-fluorophenyl) sulfone (**IIb-F**) were purified by recrystallization from ethanol, while bis(4-chlorophenyl) sulfone (**IIb-Cl**), 2,6-difluorobenzonitrile (**IIc-F**), and 2,6-dichlorobenzonitrile (**IIc-Cl**) were recrystallized from acetone. Solvents such as *N*-methyl-2-pyrrolidone (NMP) and toluene were purified by distillation over calcium hydride. Potassium carbonate was dried at 260°C for 18 hours under vacuum.

Polymerization

Three typical examples of the polymerizations are given below.

Polyether III-Oa from I-O and IIa-F

Into a 25-mL three-neck round-bottom flask fitted with a Dean–Stark trap, a condenser, a nitrogen inlet, and a thermometer were placed 1.618 g (4.0 mmol) heterocycle diol **I-O**, 0.873 g (4.0 mmol) aromatic difluoride **IIa-F**, 0.774 g (5.6 mmol) potassium carbonate, 8 mL NMP, and 4 mL toluene. The mixture was heated with stirring under nitrogen at 140–150°C for 3 hours and then at 180°C for 2 hours. During this period, the water formed was removed by azeotropic distillation with toluene. The reaction temperature was raised to 190–195°C and kept at that temperature for 2 hours. The resulting viscous reaction mixture was diluted with NMP and filtered to remove the potassium fluoride produced. The clear amber-colored solution was neutralized with a small amount of acetic acid and poured into 3 mL of a mixture of methanol and water (1:1 by volume). The precipitated polymer was collected by filtration and boiled in water for 1 hour. It was filtered and dried at 100°C for 10 hours under vacuum. The yield of the polymer was 2.07 g (89%). The inherent viscosity was 0.23 dL/g in NMP, measured at a concentration of 0.5 g/dL at 30°C. The infrared (IR) spectrum (KBr) exhibited an absorption band at 1675 cm^{-1} (C=O).

Analysis. Calculated for $(C_{41}H_{26}O_4)_n$: C, 84.52%; H, 4.50%. Found: C, 83.83%; H, 4.41%.

Polyether III-Na from I-NH and IIa-F

The polymerization was carried out with 1.614 g (4.0 mmol) heterocycle diol **I-NH**, 0.873 g (4.0 mmol) aromatic difluoride **IIa-F**, 0.774 g (5.6 mmol) potassium carbonate, 8 mL NMP, and 4 mL toluene under the same reaction conditions as above. The polymer weighed 2.14 g (92%) and had an inherent viscosity of 0.73 dL/g in NMP. The IR spectrum (KBr) showed an absorption band at 1680 cm^{-1} (C=O).

Analysis. Calculated for $(C_{41}H_{27}NO_3)_n$: C, 84.66%; H, 4.68%, N, 2.41%. Found: C, 83.55%; H, 4.52%, N, 2.67%.

Polyether III-Sc from I-S and IIc-F

The polymerization was carried out with 1.682 g (4.0 mmol) heterocycle diol **I-S**, 0.556 g (4.0 mmol) aromatic difluoride **IIc-F**, 0.774 g (5.6 mmol) potassium carbonate, 8 mL NMP, and 4 mL toluene under the same reaction conditions as above. The yield of the polymer was 1.76 g (82%), and the inherent viscosity was 0.39 dL/g in NMP. The IR spectrum (KBr) exhibited an absorption band at 2238 cm^{-1} (C≡N).

Analysis. Calculated for $(C_{35}H_{21}NO_2S)_n$: C, 80.90%; H, 4.07%, N, 2.70%, S, 6.17%. Found: C, 79.37%; H, 4.01%, N, 3.50%, S, 5.80%.

Measurements

IR spectra were recorded on a Hitachi EP-G3 spectrophotometer. Differential scanning calorimetry (DSC) and thermogravimetry (TG) were performed with Shimadzu thermal analyzers DSC-41M and TGA-40M, respectively. The wide-angle x-ray diffraction patterns were recorded with a Rigakudenki XG x-ray diffraction apparatus using nickel-filtered CuK$_\alpha$ radiation (35 kV, 20 mA).

RESULTS AND DISCUSSION

Polymer Synthesis

A series of aromatic polyethers **III** were synthesized by the aromatic nucleophilic substitution polycondensation of the diol monomers containing tetraphenylated five-membered heterocycles; namely, furan, pyrrole, and thiophene (**I-O**, **I-NH**, and **I-S**) with activated aromatic dihalides (**IIa**, **IIb**, and **IIc**) in a mixed solvent system of NMP and toluene in the presence of potassium carbonate (Scheme 1). All the polymerizations proceeded in homogeneous solution. The results of the polymerizations are summarized in Table 1.

It is well known that the reactivity of the aromatic dihalides is dependent on both the activating group and the halide to be substituted. Although in the present case the activating groups (carbonyl, sulfone, and nitrile) had no marked effect on the viscosity values attained by the aromatic polyethers, a remarkable difference was observed in reactivity of the aromatic dihalides. The aromatic difluorides afforded aromatic polyethers with inherent viscosities of 0.23–0.73 dL/g, indicative of moderate to high molecular weights, and these viscosity values were much higher than those of 0.11–0.30 dL/g obtained for the polymers from the aromatic dichlorides. This is consistent with the fact that the fluoro group is more readily substituted than the chloro group under aromatic nucleophilic substitution conditions.

In addition, the tetraphenylpyrrole diol **I-NH** afforded the aromatic polyethers of **III-NH** series with the highest viscosity values of 0.37–0.73 dL/g, and the tetraphenylthiophene diol **I-S** and the tetraphenylfuran diol **I-O** produced polymers of the **III-S** and **III-O** series having the second highest (0.36–0.46 dL/g) and the lowest values (0.23–0.33 dL/g), respectively. The order of reactivity of these heterocycle diols with respect to the viscosity values attained by the aromatic polyethers is probably related to their basicity or nucleophilicity in polymer formation.

The formation of the aromatic polyethers was verified by means of IR spectroscopy and elemental analysis. The IR spectra exhibited a characteristic carbonyl absorption band at around 1675 cm^{-1} for the poly(ether ketone)s **III-Xa**, two sulfonyl bands at about 1320 and 1150 cm^{-1} for the poly(ether sulfone)s **III-Xb**, and a nitrile band at around 2240 cm^{-1} for the poly(ether nitrile)s **III-Xc**. The elemental

TABLE 1. Synthesis of Aromatic Polyethers[a]

Monomers		Polymer		
Diol	Dihalide	Code	Yield, %	η_{inh},[b] dL/g
I-O	**IIa-F**	**III-Oa**	89	0.23
I-O	**IIa-Cl**	**III-Oa**	82	0.11
I-O	**IIb-F**	**III-Ob**	88	0.33
I-O	**IIb-Cl**	**III-Ob**	83	0.13
I-O	**IIc-F**	**III-Oc**	92	0.25
I-O	**IIc-Cl**	**III-Oc**	90	0.18
I-NH	**IIa-F**	**III-NHa**	92	0.73
I-NH	**IIa-Cl**	**III-NHa**	85	0.13
I-NH	**IIb-F**	**III-NHb**	87	0.42
I-NH	**IIb-Cl**	**III-NHb**	86	0.30
I-NH	**IIc-F**	**III-NHc**	91	0.37
I-S	**IIa-F**	**III-Sa**	86	0.46
I-S	**IIa-Cl**	**III-Sa**	83	0.12
I-S	**IIb-F**	**III-Sb**	84	0.36
I-S	**IIb-Cl**	**III-Sb**	80	0.30
I-S	**IIc-F**	**III-Sc**	82	0.39

[a] Polymerization was carried out with 4.0 mmol of each monomer in 8 mL NMP and 4 mL toluene at 140°C for 3 hours and at 180°C for 2 hours under nitrogen.

[b] Measured at a concentration of 0.5 g/dL in NMP at 30°C.

TABLE 2. Solubility of Aromatic Polyethers[a]

	Polymer						
Solvent	**III-Oa** **III-Ob** **III-Oc**	**III-NHa**	**III-NHb**	**III-NHc**	**III-Sa**	**III-Sb**	**III-Sc**
N-Methyl-2-pyrrolidone	+ +	+ +	+ +	+ +	+ +	+ +	+ +
N,N-Dimethylacetamide	+ +	±	+ +	+ +	−	+ +	−
Pyridine	+ +	+ +	+ +	+ +	−	+ +	+ +
m-Cresol	+ +	+	+ +	±	+	+	−
sym-Tetrachloroethane	+ +	+ +	+ +	−	−	+ +	+ +
Dimethyl sulfoxide	+	+	+ +	+ +	−	+ +	−

[a] Solubility: + +, soluble at room temperature; +, soluble on heating; ±, partially soluble; and −, insoluble.

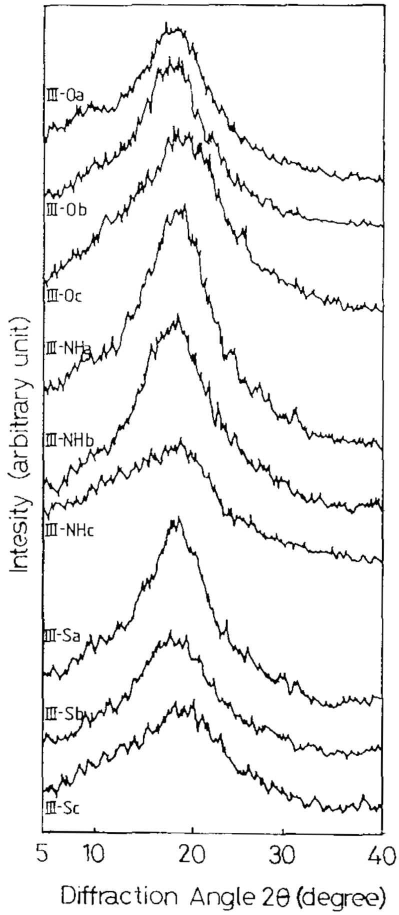


FIG. 1. X-ray diffraction diagrams of aromatic polyethers.

analysis values were in fairly good agreement with the calculated values for the polymers with the proposed structures.

Polymer Properties

The qualitative solubilities of the aromatic polyethers are shown in Table 2. It is evident that the solubility was dependent on the kinds of both heterocyclic ring systems and polar functional groups (activating groups for the aromatic dihalides) in the polymer structures. The tetraphenylfuran-based **III-O** series polyethers showed the highest solubility and were quite readily soluble at room temperature in a wide range of organic solvents such as NMP, *N*,*N*-dimethylacetamide, *m*-cresol, pyridine, and *sym*-tetrachloroethane. Of the other two aromatic polyethers, the tetraphenylpyrrole-containing **III-NH** series polymers were more soluble than the tetraphenylthiophene-bearing **III-S** series polymers. This high solubility behavior of the **III-O** series polyethers is presumably due partly to their lower viscosity values.

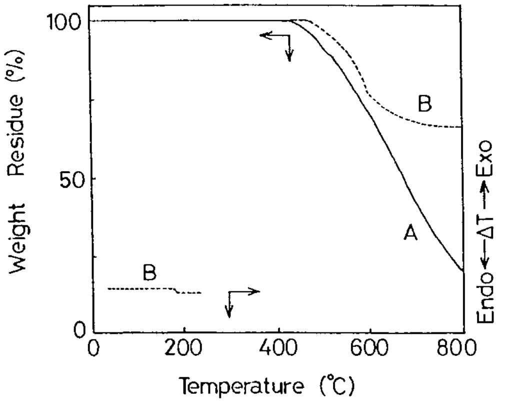


FIG. 2. DTA and TG curves for aromatic polyether **III-Oa** in air (A) and in nitrogen (B).

With respect to the polar functional groups, the solubility decreased in the following order: the poly(ether sulfone)s **III-Xb** > the poly(ether nitrile)s **III-Xc** > the poly(ether ketone)s **III-Xa**. This is consistent with the general observation that aromatic poly(ether sulfone)s are readily soluble while most aromatic poly(ether ketone)s are much less soluble in organic solvents. Transparent films could be cast from the *sym*-tetrachloroethane solutions of polymers **III-NHa** and **III-NHb** having inherent viscosities higher than 0.4 dL/g.

Figure 1 shows the wide-angle x-ray diffraction diagrams of the aromatic polyethers. All the polyethers had similar diffraction patterns with a broad peak at around 18° in 2θ, suggesting that they were essentially amorphous.

TABLE 3. Thermal Properties of Aromatic Polyethers

Polymer	T_g,[a] °C	T_{10},[b] °C In air	T_{10},[b] °C In nitrogen	Char yield,[c] %
III-Oa	182	515	550	66
III-Ob	196	490	525	57
III-Oc	217	525	540	69
III-NHa	243	535	605	77
III-NHb	244	475	540	65
III-NHc	250	455	565	76
III-Sa	213	590	590	65
III-Sb	235	570	570	54
III-Sc	238	560	580	76

[a] Determined by DSC at a heating rate of 20°C/min in nitrogen.

[b] Temperature at which 10% weight loss was recorded by TG at a heating rate of 10°C/min.

[c] Char yield at 800°C in nitrogen by TG.

The thermal behavior of these aromatic polyethers was evaluated by means of DSC and TG. Figure 2 shows typical DSC and TG curves of polyether **III-Oa**, and the glass transition temperatures (T_g) and 10% weight loss temperatures (T_{10}) of these polymers are summarized in Table 3. The present aromatic polyethers had T_gs in the 182–250°C range depending on the polymer structures. The T_gs of the structurally related polyethers decreased in the following order: the tetraphenylpyrrole-containing **III-NH** series polymers (243–250°C) > the tetraphenylthiophene-based **III-S** series polymers (213–238°C) > the tetraphenylfuran-bearing **III-O** series polymers (182–217°C). The low T_gs of the **III-O** series polyethers are probably attributed in part to their low molecular weights as evidenced by low viscosity values. In addition, the order of decreasing T_gs was observed to be the poly(ether nitrile)s **III-Xc** (217–250°C) > the poly(ether sulfone)s **III-Xb** (196–244°C) > the poly(ether ketone)s **III-Xa** (182–243°C). This is compatible with the general tendency for this type of polymer.

All the aromatic polyethers showed no weight loss below 400°C in air or nitrogen, and the T_{10} values in air and nitrogen were 455–590 and 525–605°C, respectively, indicating high thermal stability. In addition, the aromatic polyethers retained more than 54% in weight even at 800°C in nitrogen. The thermal stability with respect to T_{10} values and char yield at 800°C in nitrogen were in the following order: the tetraphenylthiophene-containing **III-S** series polymers > the tetraphenylpyrrole-based **III-NH** series polymers > the tetraphenylfuran-bearing **III-O** series polymers. This order of thermal stability was in good agreement with that for most of the aromatic polymers containing these heterocyclic units, which is due to the difference in inherent thermal stability among these five-membered heterocycles [22, 23].

CONCLUSIONS

New aromatic polyethers with inherent viscosities of 0.23–0.73 dL/g were prepared from three tetraphenylated five-membered heterocycle-containing diols and three activated aromatic dihalides by the aromatic nucleophilic substitution polycondensation in the NMP–toluene system in the presence of potassium carbonate at elevated temperatures. These aromatic polyethers were soluble in organic solvents and had both moderately high T_g values (182–250°C) and high thermal stability (no weight loss below 400°C). Therefore, they are organic-soluble high temperature plastic materials potentially useful in a variety of applications.

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