

Synthesis and Characterization of Polyamides and Poly(amide-imide)s Based on Ether-Sulfone-Diamines

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Abstract: A series of polyamides and poly(amide-imide)s were prepared by the direct polycondensation of 4,4'-[sulfonylbis(1,4-phenyleneoxy)]dianiline or 4,4'-[sulfonylbis(2,6-dimethyl-1,4-phenyleneoxy)]dianiline with aromatic dicarboxylic acids and phthalimide unit-bearing dicarboxylic acids in a *N*-methyl-2-pyrrolidone (NMP) solution containing dissolved calcium chloride using triphenyl phosphite and pyridine as condensing agents. The inherent viscosities of the resulting polymers were above 0.45 dL/g and up to 1.70 dL/g. Except for the polyamides derived from terephthalic acid and 4,4'-biphenyldicarboxylic acid, all the other polyamides and all poly(amide-imide)s were readily soluble in polar organic solvents such as NMP, *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and *m*-cresol, and afforded transparent and tough films by solution-casting. Most of the polymers showed distinct glass transition on their differential scanning calorimetry (DSC) traces and their glass transition temperatures (T_g) stayed between 140–264 °C. The methyl-substituted polymers showed higher T_g s than the corresponding unsubstituted counterparts. The results of the thermogravimetry analysis (TGA) revealed that all the methyl-substituted polymers showed lower initial decomposition temperatures than the unsubstituted ones.

Keywords: Polyamides, Poly(amide-imide)s, Ether-sulfone-diamines, Methyl substituent, Solubility, T_g s.

Introduction

Aromatic polyamides (aramids) possess desirable characteristics such as high thermal stability and good mechanical properties [1,2]. Traditionally these materials have been infusible and only soluble in strongly acidic media; consequently potential applications have been limited. Therefore, several modifications of chemical structures have been used in order to lower the transition temperatures and to increase the solubility of aramids.

One approach to increase the solubility and processability of aramids is the introduction of kinked and flexible bridging units into the polymer chain so as to increase the overall chain flexibility [3-13]. However, the loss of thermal stability and significant decrease in mechanical properties on heating are almost always a consequence of the reduced

chain stiffness. The incorporation of sulfone groups into the macromolecular chain generally leads to an enhanced solubility, together with interesting properties such as increased T_g and higher thermo-oxidative stability. Hence, the goal of better solubility, together with higher retained thermal stability, could be achieved in preparing aramids containing both sulfone and flexible linkages like ether. Some aromatic polyamides bearing both aryl ether and sulfone links between amide groups have been reported in the literature [7-10]. Aramids of this general structure are of interest since they possess enhanced tractability and solubility characteristics, together with a moderately high T_g .

The presence of methyl substituents on a phenylene unit at *ortho* position to the ether linkage generally increases the T_g of the polymers, due to the increased barrier of the chain rotation [14,15].

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Very recently, we reported that methyl-substituted polyamides exhibited higher T_g s than the unsubstituted analogues [16,17]. Furthermore, the methyl-substituted aromatic poly(ether ketone)s were found to crosslink by radiation of ultraviolet light due to the presence of a sensitizing benzophenone structure [14,15]. In addition, some methyl-substituted polysulfones were found to exhibit more favorable gas separation properties as compared to their unsubstituted counterparts [18].

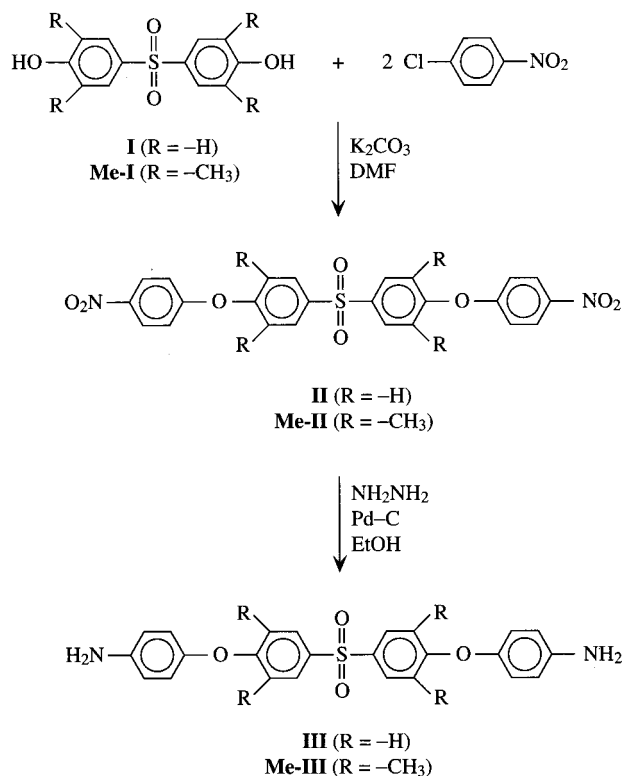
The present article deals with the preparation and basic characterization of new polyamides having ether and sulfone in the main chain, together with methyl substituents on the aromatic units. This combination was considered potentially attractive because the polymers were expected to exhibit a favorable balance of properties. For comparison, related polyamides without methyl substitution were also prepared and characterized. The synthesis and characterization of novel poly(amide-imide)s containing both ether and sulfone groups are also described.

Experimental

1. Materials

Following a well-developed method [19], ether-sulfone-diamine monomers, 4,4'-[sulfonylbis(1,4-phenyleneoxy)]dianiline (**III**) (mp. 188–189 °C) and 4,4'-[sulfonylbis(2,6-dimethyl-1,4-phenyleneoxy)]dianiline (**Me-III**) (mp. 186–188 °C), were prepared by aromatic nucleophilic chloro-displacement of *p*-chloronitrobenzene with 4,4'-sulfonyldiphenol (**I**) and 4,4'-sulfonylbis(2,6-dimethylphenol) (**Me-I**) in the presence of potassium carbonate, followed by palladium-catalyzed hydrazine reduction of the intermediate dinitro compounds, bis[4-(4-nitrophenoxy)phenyl] sulfone (**II**) and bis[3,5-dimethyl-4-(4-nitrophenoxy)phenyl] sulfone (**Me-II**). The synthetic route is outlined in Scheme 1, and details of the synthesis and characterization data of diamines **III** and **Me-III** have been described in the preceding paper [17].

All aromatic dicarboxylic acids were of high purity when received from manufacturers and were used without any further purification. They included terephthalic acid (**IV_a**) (from Wako), isophthalic acid (**IV_b**) (from Wako), 5-*tert*-butylisophthalic acid (**IV_c**) (from Aldrich), 4,4'-biphenyldicarboxylic acid (**IV_d**) (from Tokyo Chemical Industry Co.; TCI), 4,4'-oxydibenzoic acid (**IV_e**) (from TCI), 4,4'-(perfluoro-isopropylidene)dibenzoic acid (**IV_f**) (from Chriskev), 4,4'-sulfonyldibenzoic acid (**IV_g**) (from New Japan Chemical Co.), and 2,6-naphthalenedicarboxylic acid (**IV_h**) (from TCI). As de-



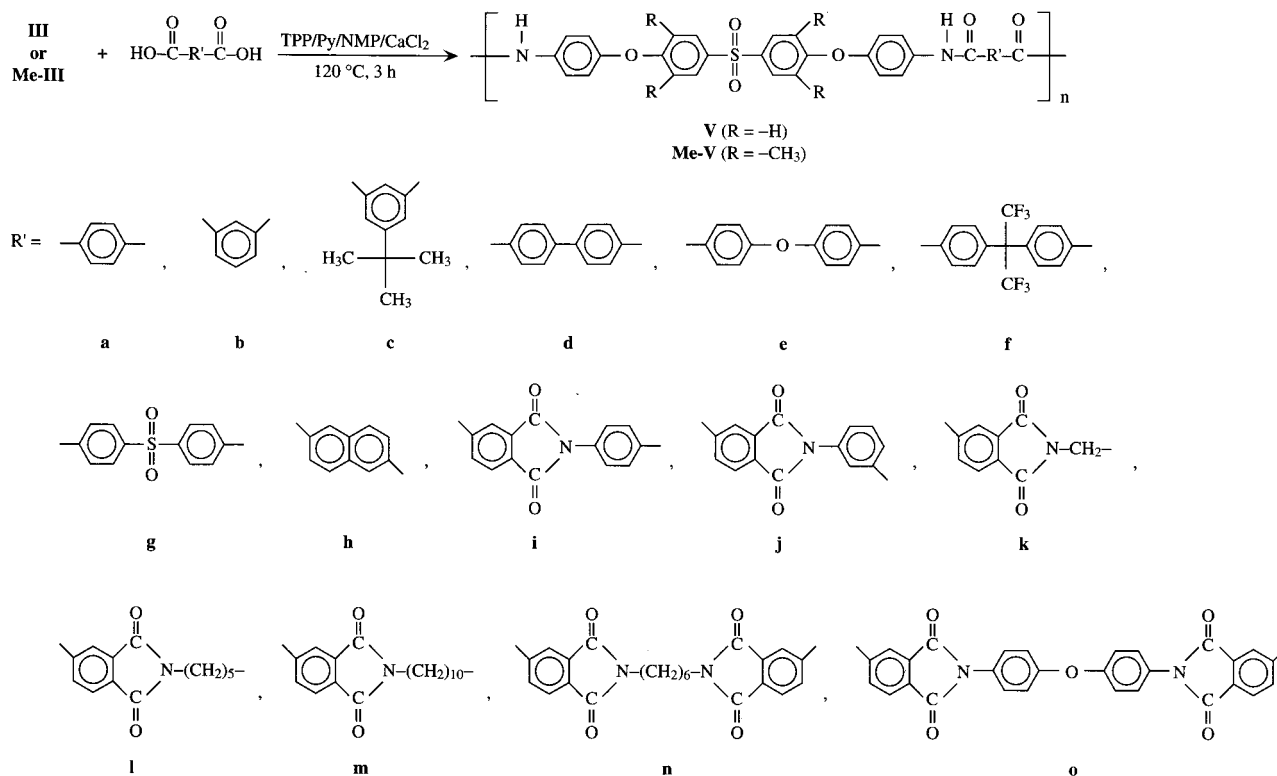
Scheme 1

scribed previously [20,21], imide-dicarboxylic acids **IV_i** (mp. 372 °C), **IV_j** (mp. 402 °C), **IV_k** (mp. 268 °C), **IV_l** (mp. 204 °C), and **IV_m** (mp. 162 °C) were synthesized by condensation of trimellitic anhydride with *p*- and *m*-aminobenzoic acids, glycine, 6-aminocaproic acid, and 11-aminoundecanoic acid, respectively. Bis(trimelli-timide)s **IV_n** (mp. 306 °C) and **IV_o** (mp. 378 °C) were prepared from the condensation of trimellitic anhydride with 1,6-hexamethylenediamine and 4,4'-oxydianiline, respectively, in a molar ratio 1 : 2, according to the method described previously [22].

N-Methyl-2-pyrrolidone (NMP) and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Triphenyl phosphite (TPP) was purified by distillation under reduced pressure. Calcium chloride was dried under a vacuum at 180 °C for 10 hr.

2. Typical polymerization procedure

A mixture of 1.25 mmol of a diacid or an imide-diacid, 1.25 mmol of a diamine, 0.4 g of calcium chloride, 0.9 mL (2.5 mmol) of triphenyl phosphite, 1.0 mL of pyridine, and 2.5 mL of NMP was heated with stirring at 120 °C for 3 hr. The viscosity of the solution drastically increased during the reaction. The obtained polymer solution was slowly



Scheme 2

poured into 400 mL of stirred methanol, producing a fiber-like stringy precipitate which was washed thoroughly with methanol and hot water, collected by filtration and dried. Yields were usually quantitative.

3. Measurements

The infrared spectra were recorded on a Jasco FT/IR-7000 Fourier-transform infrared spectrometer. The inherent viscosities were measured at 0.5 g/dL concentration using a Cannon-Fenske viscometer at 30 °C in DMAc-5 wt% LiCl. The thermal transitions were investigated by a Sinku Riko DSC-7000 differential scanning calorimeter coupled to a Sinku Riko TA-7000 thermal analysis controller at a heating rate of 20 °C/min in flowing nitrogen. The glass transition temperatures (T_g) were read at the midpoint of the baseline shift and were taken from the second heating trace after rapid cooling from approximately 400 °C. Thermogravimetry analysis (TGA) data were obtained on a Rigaku Thermoflex TG 8110 coupled to a Rigaku TAS-100 thermal analysis station. Experiments were carried out on 9-11 mg samples heated in flowing nitrogen or air (50 cm³/min) at a scan rate of 20 °C/min. Wide-angle X-ray diffraction patterns were recorded on a Rigaku Geiger Flex D-Max IIIa X-ray diffractometer, using Ni-filtered Cu-K α radiation (1.5418 Å). The

scan rate was 2°/min over a 2 θ range of 5°-40°. An Instron universal tester model 1130 with a load cell of 5 kg was used to study the stress-strain behavior of the samples. A crosshead gauge length of 2 cm and an extension rate of 5 cm/min were used. Measurements were performed with film specimens (0.5 cm wide, 6 cm long, and about 0.1 mm thick) and an average of at least five individual determinations was used.

Results and Discussion

1. Polymer synthesis

Polyamides **V_{a-h}** and **Me-V_{a-h}** and poly(amide-imide)s **V_{i-o}** and **Me-V_{i-o}** were synthesized by the phosphorylation polyamidation of diamines **III** and **Me-III** with various aromatic dicarboxylic acids and imide-ring preformed dicarboxylic acids, as shown in Scheme 2. Table I summarizes the results of the polycondensation. All the polymerization reactions proceeded homogeneously in solution without precipitation. Polymers having inherent viscosities of 0.45-1.70 dL/g were obtained, indicative of moderate to high molecular weights. Except for the polyamides of terephthalic acid and 4,4'-biphenyldicarboxylic acid, all the polymers afforded good-quality, creasable films by solution-cast-

Table I. Inherent viscosities and film quality of polyamides and poly(amide-imide)s.

Polymer ^(a) code	$\eta_{inh}^{(b)}$ (dL/g)	Film ^(c) quality
V _a	0.96	brittle
V _b	0.78	flexible
V _c	0.45	flexible
V _d	1.09	brittle
V _e	0.84	flexible
V _f	0.64	flexible
V _g	0.74	flexible
V _h	1.14	flexible
V _i	0.77	flexible
V _j	0.67	flexible
V _k	0.58	flexible
V _l	0.99	flexible
V _m	0.80	flexible
V _n	0.84	flexible
V _o	0.82	flexible
Me-V _a	0.87	brittle
Me-V _b	0.59	flexible
Me-V _c	0.64	flexible
Me-V _d	1.06	brittle
Me-V _e	0.99	flexible
Me-V _f	0.78	flexible
Me-V _g	0.90	flexible
Me-V _h	1.70	flexible
Me-V _i	0.77	flexible
Me-V _j	0.73	flexible
Me-V _k	0.96	flexible
Me-V _l	0.82	flexible
Me-V _m	0.64	flexible
Me-V _n	0.88	flexible
Me-V _o	0.90	flexible

(a) Polymerization was carried out with 1.25 mmol of each diamine and diacid monomer, 2.5 mmol (about 0.9 mL) TPP, 1 mL pyridine, 0.3–0.5 g of CaCl₂, and 2–5 mL of NMP at 120 °C for 3 hr.

(b) Measured at a concentration of 0.5 g/dL in DMAc/5 wt% LiCl at 30 °C.

(c) Films were cast by slow evaporation of polymer solutions in DMAc.

ing.

These polymers were characterized by IR spectroscopy. The IR spectra of all the polyamides showed characteristic amide absorptions around 3350 cm⁻¹ (N-H) and 1650 cm⁻¹ (C=O), and those of the poly(amide-imide)s showed additional characteristic imide ring absorptions near 1780 cm⁻¹ (asym. C=O stretching of imide ring), 1720 cm⁻¹ (sym. C=O stretching of imide ring), 1390 cm⁻¹ (C-N), and 720 cm⁻¹ (imide ring deformation). Other characteristic absorptions include aryl ether stretching near 1250 cm⁻¹ and S(=O)₂ stretching near 1300 and 1150 cm⁻¹.

2. Polymer characterization

Table II summarizes the solubility of the polyamides and poly(amide-imide)s. All the polymers

Table II. Solubility behavior of polyamides and poly(amide-imide)s.^(a)

Polymer	Solvent ^(b)					
	NMP	DMAc	DMF	DMSO	THF	<i>m</i> -cresol
V _a	+	+	-	-	-	+
V _b	+	+	+	+	-	+
V _c	+	+	+	+	-	+
V _d	+	+	-	-	-	+
V _e	+	+	+	+	-	+
V _f	+	+	+	+	+	+
V _g	+	+	+	+	-	+
V _h	+	+	+	+	-	+
V _i	+	+	+	+	-	+
V _j	+	+	+	+	-	+
V _k	+	+	+	+	-	+
V _l	+	+	+	+	+h	+
V _m	+	+	+	+	-	+h
V _n	+	+	+	+	-	+
V _o	+	+	+	+	-	+
Me-V _a	+	+h	-	-	-	-
Me-V _b	+	+	+	+	+h	+
Me-V _c	+	+	+	+	-	+
Me-V _d	+	+h	-	-	-	+
Me-V _e	+	+	+	+	-	+
Me-V _f	+	+	+	+	+	+
Me-V _g	+	+	+	+	-	+
Me-V _h	+	+	-	+	-	+
Me-V _i	+	+	+	+	-	+
Me-V _j	+	+	+	+	-	+
Me-V _k	+	+	+	+	-	+
Me-V _l	+	+	+	+	-	+
Me-V _m	+	+	+	+	+	+
Me-V _n	+	+	+	+	-	+
Me-V _o	+	+	+	+	-	+

(a) +: Soluble; +h: soluble on heating; -: insoluble even on heating.

(b) DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran; NMP: *N*-methyl-2-pyrrolidone.

were soluble in amide-type solvents such as NMP, DMAc, and most of them were soluble in DMF, DMSO, and *m*-cresol but were insoluble in THF. The lesser solubility of the polyamides derived from terephthalic acid and 4,4'-biphenyldicarboxylic acid is attributed to moderate crystallinity, as evidenced by the X-ray diffraction patterns [17]. Polyamides derived from 4,4'-perfluoroisopropylidenedibenzoic acid (IV_f) were soluble in THF, probably due to their nonplanar structures and low cohesive energies caused by the -CF₃ groups.

Most of the polyamides and all the poly(amide-imide)s exhibited amorphous X-ray diffraction patterns and could be solution-cast into transparent, flexible, and tough films. The tensile properties of these flexible films are given in Table III. The films had tensile strengths of 47–77 MPa, elongations at break of 6–46%, and initial moduli of 0.86–1.66 GPa.

Table III. Tensile properties of polyamide and poly(amide-imide) films.

Polymer	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)
V _b	59	13	0.86
V _c	61	9	1.11
V _e	57	35	1.26
V _f	52	13	1.32
V _g	54	12	1.19
V _h	69	46	1.22
V _i	56	22	1.49
V _j	77	8	1.66
V _k	55	11	1.16
V _l	59	19	1.25
V _m	47	14	0.97
V _n	53	20	1.35
V _o	60	24	1.06
Me-V _b	66	7	1.33
Me-V _c	89	8	1.44
Me-V _e	59	24	1.10
Me-V _f	59	15	1.05
Me-V _g	51	14	1.09
Me-V _h	73	13	1.50
Me-V _i	65	11	1.27
Me-V _j	61	10	1.17
Me-V _k	57	16	0.97
Me-V _l	66	7	1.17
Me-V _m	65	6	1.18
Me-V _n	62	9	1.00
Me-V _o	66	21	1.32

Thermal properties of all the polymers were evaluated by differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA). The T_g values of these polymers are summarized in Table IV. Polyamides and poly(amide-imide)s from diamine **Me-III** showed higher T_g s than those from **III** by 11~40 °C. This might be a consequence of higher restriction of mobility in the **Me-III** moiety which has four methyl groups hindering rotation at the ether sites. No discernible glass transitions were observed for the polyamides **V_a**, **V_c**, **Me-V_a**, **Me-V_c**, and **Me-V_h** by DSC. As expected, the introduction of an aliphatic segment decreased the T_g values, which were lowered with the increasing length of the methylene units.

From dynamic thermogravimetry, the temperatures at which 10% weight loss occurred in air or nitrogen and the char yield at 800 °C in nitrogen of all the polymers are summarized in Table IV. None of the polymers showed significant weight loss up to 400 °C in air or nitrogen. It is quite reasonable to conclude that the methyl-substituted polymers began to decompose at lower temperatures in comparison with the unsubstituted counterparts. The poly(amide-imide)s with polymethylene segments in the repeating unit such as **V_{l-n}** showed higher initial

Table IV. Thermal properties of polyamides and poly(amide-imide)s.

Polymer	$T_g^{(a)}$ (°C)	$T_d^{(b)}$ (°C)		Char yield ^(c) (%)
		in N ₂	in air	
V _a	— ^(d)	489	485	52.3
V _b	219	499	494	54.0
V _c	222	492	493	53.9
V _d	—	489	485	58.9
V _e	220	500	498	56.8
V _f	210	504	496	52.5
V _g	240	490	488	56.4
V _h	225	510	504	63.6
V _i	224	509	499	58.1
V _j	236	496	499	58.0
V _k	229	434	430	55.9
V _l	165	451	453	50.5
V _m	140	449	452	43.9
V _n	178	469	463	52.1
V _o	235	515	529	58.6
Me-V _a	—	419	423	51.3
Me-V _b	255	433	427	59.7
Me-V _c	252	441	435	54.0
Me-V _d	—	423	425	55.8
Me-V _e	235	427	430	57.1
Me-V _f	242	434	437	52.7
Me-V _g	251	434	427	62.5
Me-V _h	—	443	438	62.4
Me-V _i	264	436	432	59.2
Me-V _j	262	444	439	61.5
Me-V _k	255	409	414	50.0
Me-V _l	192	422	423	50.6
Me-V _m	162	418	422	37.4
Me-V _n	200	430	432	47.2
Me-V _o	256	445	446	61.3

(a) Baseline shift in the second heating DSC traces, with a heating rate of 20 °C/min.

(b) Decomposition temperatures at which 10% weight loss were recorded by TGA at a heating rate of 20 °C/min.

(c) Residual weight % when heated to 800 °C in nitrogen.

(d) Difficult to judge.

decomposition temperatures than those with only one methylene unit such as **V_k**. The result is similar to that found in the previous publication [21] and can be attributed to higher crystallinity.

Conclusions

A series of novel polyamides and poly(amide-imide)s bearing both ether and sulfone groups in the main chain were successfully synthesized by the direct polycondensation of 4,4'-[sulfonylbis(1,4-phenyleneoxy)]dianiline and 4,4'-[sulfonylbis(2,6-dimethyl-1,4-phenyleneoxy)]dianiline with several aromatic dicarboxylic acids and imide ring-preformed dicarboxylic acids, using triphenyl phosphite and pyridine as condensing agents. The polymers had inherent viscosities in the range of 0.45~1.70

dL/g. Most of them could be cast into flexible and tough films. The methyl-substituted polymers had higher T_g , but lower thermal stability than the corresponding unsubstituted polymers.

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