

## Synthesis and characterization of 1,3,4-oxadiazole-containing polyethers from 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole and various aromatic diols

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### SUMMARY:

Six 1,3,4-oxadiazole-containing polyethers with reduced viscosities of 0.65–1.17 dL · g<sup>-1</sup> were synthesized by high-temperature solution polycondensation of an activated difluoride, 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole, with aromatic diols possessing a variety of ring structures. The expected chemical structures were confirmed by IR and <sup>1</sup>H NMR spectroscopy and elemental analysis. Of all the polymers, two polyethers were highly crystalline and soluble only in limited solvents such as *o*-chlorophenol and conc. sulfuric acid. The other polyethers were amorphous and dissolved readily in a variety of organic media including polar aprotic solvents, phenols and chlorinated hydrocarbons. Colorless to slightly yellow-colored, transparent and tough films could be cast from the *N*-methyl-2-pyrrolidone or *o*-chlorophenol solutions. The mechanical properties were excellent and their tensile strength, elongation at break and tensile moduli were in the ranges of 53–80 MPa, 4–12% and 1.3–2.0 GPa, respectively. The amorphous polyethers had high glass transition temperatures of 195–259 °C. All the polyethers were highly thermally and thermooxidatively stable and exhibited no weight loss up to 400 °C, with 10% weight loss being recorded at 464–514 °C in air.

### Introduction

Aromatic polyethers are characterized as high-performance plastic materials with a favorable balance of physical, chemical and mechanical properties. A wide variety of aromatic polyethers have so far been synthesized, and the relationship between their primary structures and polymer properties has been studied extensively.

The method most frequently utilized for the preparation of aromatic polyethers is aromatic nucleophilic substitution polymerization, in which aromatic dihalides activated by strongly electron-accepting groups, most commonly a carbonyl or sulfone group, e.g., 4,4'-difluorobenzophenone and bis(4-chlorophenyl) sulfone, are used as partners of bisphenols. Dihalides containing heterocyclic nuclei, such as benzoxazole<sup>1,2)</sup> and phenylquinoxaline<sup>3)</sup>, are also used as activated monomers in this type of reaction. In these halides, the heterocycles not only serve as activating groups but also stabilize the negative charge of a Meisenheimer complex formed through the polymer-forming nucleophilic substitution reaction and, thereby, greatly promote polyetherification. Moreover, the resulting heterocycle-containing polyethers also have some of the favorable properties of heterocyclic polymers such as extremely high glass transition temperature (*T<sub>g</sub>*) and thermal stability, in addition to the inherent favorable properties of aromatic polyethers.

In the preceding paper<sup>4)</sup>, we reported that a series of high-molecular-weight polyethers containing 1,3,4-thiadiazole rings could be synthesized quite readily by fluorine displacement polymerization of a novel fluoride, 2,5-bis(4-fluorophenyl)-1,3,4-thiadiazole, with various aromatic diols under relatively mild conditions, i.e., 150–160°C. This implies that the activating group, 1,3,4-thiadiazole, effectively activates aromatic nucleophilic substitution. The 1,3,4-thiadiazole-containing polyethers obtained had high  $T_g$ 's of 204–299°C, and also showed good solubility in various organic media such as polar aprotic solvents, phenols and chlorinated hydrocarbons.

This article reports the synthesis and characterization of a series of 1,3,4-oxadiazole-containing polyethers **3a–3f** from activated difluoride, 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole (**1**), containing 1,3,4-oxadiazole, the oxygen analog of 1,3,4-thiadiazole, as an activating group and six kinds of aromatic diols **2a–2f** having a variety of ring structures. Several polyethers containing 1,3,4-oxadiazole nuclei have already been synthesized and characterized<sup>5,6)</sup>. However, no detailed properties, except thermal ones, of these polymers were disclosed.

## Experimental part

### Materials

Bisphenols such as 2,2-bis(4-hydroxyphenyl)propane (4,4'-isopropylidenediphenol) (**2a**), 2,2-bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane (4,4'-(1,1,1,3,3,3-hexafluoropropane-2,2-diyl)diphenol) (**2b**) (supplied by Central Glass Co., Ltd., Japan) and 3-(4-hydroxyphenyl)-1,1,3-trimethyl-5-indanol (**2c**) (provided by Mitsui Toatsu Chemical Industries, Ltd., Japan) were recrystallized from benzene. 9,9-Bis(4-hydroxyphenyl)-fluorene (4,4'-(9-fluorenylidene)diphenol) (**2d**), prepared according to the procedure of Morgan<sup>7)</sup> from 9-fluorenone and phenol, was purified by recrystallization from toluene; m.p. 223–224°C (ref.<sup>7)</sup> m.p. 224°C). Hydroquinone (**2e**) was recrystallized from acetone. 2,5-Bis(4-hydroxyphenyl)-1,3,4-oxadiazole (**2f**), synthesized according to the method of Iwakura et al.<sup>8)</sup> in four steps starting from *p*-hydroxybenzoic acid, was purified by recrystallization from methanol; m.p. 352–354°C (ref.<sup>8)</sup> m.p. 347°C).

Solvents such as *N,N*-dimethylacetamide (DMA) and tetrahydrothiophene 1,1-dioxide (TMS) were vacuum distilled under nitrogen. Diphenyl sulfone (DPS) was recrystallized from methanol. Toluene was distilled over sodium wire.

Potassium carbonate was dried at 200°C i. vac. just before use.

Other chemicals and solvents were used as received.

### Monomer synthesis

**2,5-Bis(4-fluorophenyl)-1,3,4-oxadiazole (1):** This compound was prepared according to the procedure of Popp<sup>9)</sup>. A mixture of 1,2-bis(4-fluorobenzoyl)hydrazine<sup>6)</sup>, synthesized from *p*-fluorobenzoyl chloride and hydrazine hydrate, (2.76 g; 0.01 mol) and polyphosphoric acid (80 g) was stirred at 100°C for 20 min and at 200°C for 1 h. The solution was then poured onto crushed ice to give a crystalline solid, which was filtered off, washed well with water and dried. Two recrystallizations from ethyl acetate afforded needle-like white small crystals. Yield: 2.04 g (79%); m.p. 202–204°C (ref.<sup>9)</sup> m.p. 202–203°C).

IR (KBr): 1420 cm<sup>-1</sup> (m; C=N).

$^1\text{H}$  NMR (dimethyl sulfoxide- $d_6$  (DMSO- $d_6$ )):  $\delta$  = 8,21 (dd;  $J$  = 14,4 Hz; aromatic ortho to oxadiazole) and 7,49 ppm (t;  $J$  = 17,8 Hz; aromatic meta to oxadiazole). Intensity ratio: 4:4.

### Polymerization

**Polyether 3a from 1 and 2a:** To a suspension of difluoride **1** (0,258 g; 1 mmol) and bisphenol **2a** (0,228 g; 1 mmol) in DMA (5 mL) and toluene (5 mL) was added powdered potassium carbonate (0,276 g; 2 mmol), and the mixture was agitated at 150 °C for 2 h under nitrogen to azeotrope off the water formed with toluene. The temperature was increased to 160 °C, and the mixture was allowed to react for 20 h. The resulting viscous solution was diluted with *N*-methyl-2-pyrrolidone (NMP) (10 mL), and then dropped into methanol (500 mL). The precipitated white fibrous polymer was collected, rinsed successively with hot water and hot methanol and vacuum dried. Yield: 0,442 g (99%). Reduced viscosity ( $\eta_{\text{red}}$ ) = 1,17 dL  $\cdot$  g $^{-1}$  (in NMP; conc.: 0,5 g  $\cdot$  dL $^{-1}$ ; at 30 °C).

IR (film): 1420 (m; C=N) and 1250 cm $^{-1}$  (vs; C—O—C).

$^1\text{H}$  NMR (CDCl $_3$ ):  $\delta$  = 8,06 (d;  $J$  = 8,4 Hz; aromatic ortho to oxadiazole), 7,28 (d;  $J$  = 8,1 Hz; aromatic meta to isopropylidene), 7,09 (d;  $J$  = 9,0 Hz; aromatic meta to oxadiazole), 6,99 (d;  $J$  = 8,6 Hz; aromatic ortho to isopropylidene) and 1,72 ppm (s; —CH $_3$ ). Intensity ratio: 4:4:4:4:6.

(C $_{29}$ H $_{22}$ N $_2$ O $_3$ ) $_n$ (446,5) $_n$	Calc.	C 78,01	H 4,97	N 6,28
	Found	C 76,88	H 4,83	N 6,16

Other polyethers were also synthesized by analogous procedures.

### Polyether 3b from 1 and 2b:

IR (film): 1420 (m; C=N) and 1250 cm $^{-1}$  (vs; C—O—C).

$^1\text{H}$  NMR (CDCl $_3$ ):  $\delta$  = 8,13 (d;  $J$  = 8,8 Hz; aromatic ortho to oxadiazole), 7,44 (d;  $J$  = 8,6 Hz; aromatic ortho to perfluoroisopropylidene (perfluoropropane-2,2-diyl)), 7,18 (d;  $J$  = 9,7 Hz; aromatic meta to perfluoroisopropylidene) and 7,07 ppm (d;  $J$  = 9,2 Hz; aromatic meta to oxadiazole). Intensity ratio: 4:4:4:4.

(C $_{29}$ H $_{16}$ N $_2$ O $_3$ F $_6$ ) $_n$ (554,4) $_n$	Calc.	C 62,82	H 2,91	N 5,05
	Found	C 62,27	H 2,69	N 4,98

### Polyether 3c from 1 and 2c:

IR (film): 1420 (m; C=N) and 1240 cm $^{-1}$  (vs; C—O—C).

$^1\text{H}$  NMR (CDCl $_3$ ):  $\delta$  = 8,09 (d;  $J$  = 7,9 Hz; aromatic ortho to oxadiazole), 7,32–6,92 (m; phenylindane), 7,11 (d;  $J$  = 7,9 Hz; aromatic meta to oxadiazole), 2,42 (dd;  $J$  = 34,7 Hz; —CH $_2$ —), 1,75 (s; —CH $_3$ ), 1,44 (s; —CH $_3$ ) and 1,17 ppm (s; —CH $_3$ ). Intensity ratio: 4:7:4:2:3:3:3.

(C $_{32}$ H $_{26}$ N $_2$ O $_3$ ) $_n$ (486,5) $_n$	Calc.	C 78,99	H 5,39	N 5,76
	Found	C 78,07	H 5,08	N 5,53

### Polyether 3d from 1 and 2d:

IR (film): 1420 (m; C=N) and 1250 cm $^{-1}$  (vs; C—O—C).

$^1\text{H}$  NMR (CDCl $_3$ ):  $\delta$  = 8,03 (d;  $J$  = 8,4 Hz; aromatic ortho to oxadiazole), 7,75 – 6,88 (m; diphenylfluorene) and 7,24 ppm (d;  $J$  = 8,8 Hz; aromatic meta to oxadiazole). Intensity ratio: 4:16:4.

(C $_{39}$ H $_{24}$ N $_2$ O $_3$ ) $_n$ (568,6) $_n$	Calc.	C 82,38	H 4,25	N 4,93
	Found	C 80,79	H 3,88	N 4,82

*Polyether 3e from 1 and 2e:*IR (KBr): 1 420 (m; C=N) and 1 240 cm<sup>-1</sup> (vs; C—O—C).

(C <sub>20</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub> ) <sub>n</sub> (328,3) <sub>n</sub>	Calc.	C 73,16	H 3,68	N 8,53
	Found	C 72,21	H 3,42	N 8,35

*Polyether 3f from 1 and 2f:*IR (KBr): 1 420 (m; C=N) and 1 250 cm<sup>-1</sup> (vs; C—O—C).

(C <sub>28</sub> H <sub>16</sub> N <sub>4</sub> O <sub>4</sub> ) <sub>n</sub> (472,4) <sub>n</sub>	Calc.	C 71,18	H 3,41	N 11,86
	Found	C 70,02	H 3,00	N 11,65

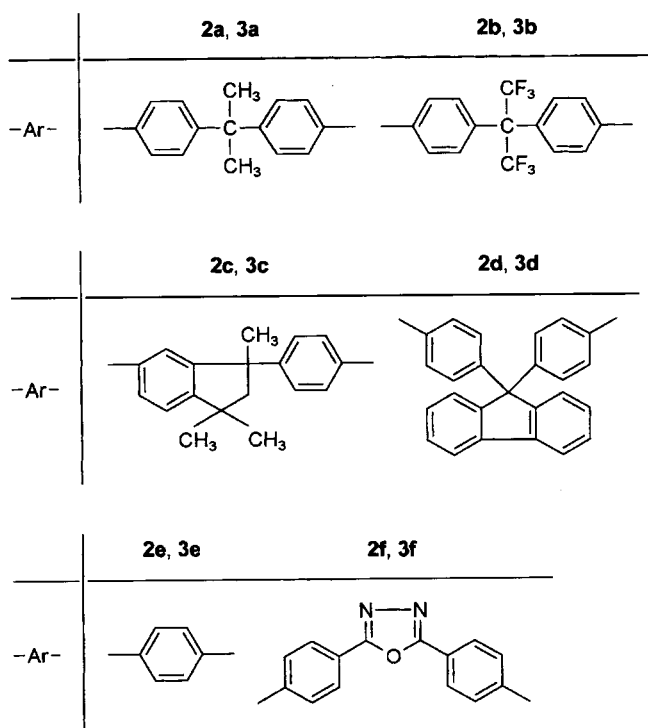
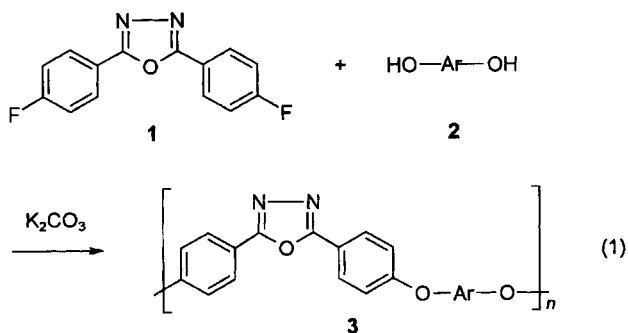
*Measurements*

IR spectra were recorded on a JASCO IR-810 spectrophotometer. <sup>1</sup>H NMR spectra were obtained on a JEOL JNM-FT 200 (for monomer **1**) or JEOL JNM-EX 90 FT-NMR spectrometer (for polymers **3**) at 200 or 90 MHz with tetramethylsilane as an internal standard. Elemental analysis was conducted with a Perkin-Elmer 240C elemental analyzer. Wide-angle X-ray diffraction diagrams were taken for powder specimens on a Rigaku Geigerflex Rad-γA X-ray diffractometer using Ni-filtered Cu-K<sub>α</sub> radiation (30 kV, 50 mA). Tensile properties were determined from stress-strain curves obtained with a Shimadzu Autograph S-100 at an elongation rate of 20% per min with film specimens (5 mm wide, 20 mm long, ca. 0.1 mm thick). Differential scanning calorimetry (DSC) and thermogravimetry (TG) were performed on powder specimens with a Perkin-Elmer DSC System 4 and a Seiko SSC 5200H Thermal Analysis System, respectively.

**Results and discussion***Polymer synthesis*

1,3,4-Oxadiazole-containing polyethers **3a–3f** were synthesized from 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole (**1**) with various aromatic diols **2a–2f** by high-temperature solution polycondensation in a polar solvent in the presence of anhydrous potassium carbonate, according to the conditions used for the preparation of 1,3,4-thiadiazole-containing polyethers<sup>4)</sup> from the same aromatic diols [Eq. (1)]. The reaction conditions and results are summarized in Tab. 1.

Under the same reaction conditions as for the corresponding 1,3,4-thiadiazole-containing polyethers<sup>4)</sup>, i.e., in DMA at 160 °C for 20 h for **2a–2d**, in TMS at 250 °C for 4 h for **2e** and in DPS at 250 °C for 4 h for **2f**, 1,3,4-oxadiazole-containing polyethers **3a–3f** were all successfully obtained in quantitative yields, and the reduced viscosities also reached to high values of over 0.6 dL · g<sup>-1</sup>, indicating that these polymers had high enough molecular weights. In these reactions, the polymerization variables, such as reaction temperature and time and monomer concentration, were not necessarily optimized. In the reactions with **2e** and **2f**, precipitation of polymers took place as the reaction progressed. Since DMA has a much lower boiling point than TMS and DPS, the molecular weights of the polymers **3e** and **3f** built-up in this medium were probably limited by the reaction temperature. Both the diols possess a highly conjugated aromatic or heterocyclic system in the molecules,



thereby presumably lowering the nucleophilicity of the hydroxyl groups, compared to the other four bisphenols.

The structure of the polymers was confirmed by means of IR and  $^1\text{H}$  NMR spectroscopy and elemental analysis. In the IR spectra, an intense absorption owing to aromatic ether groups at around  $1250\text{ cm}^{-1}$  appeared. The  $^1\text{H}$  NMR chart of polymer **3a** measured in  $\text{CDCl}_3$  is given in Fig. 1.

Four peaks are observed at  $\delta$  8,06, 7,28, 7,09 and 6,99 ppm, where the integration ratio is all unity. These peaks are all observed as doublets, and the coupling con-

Tab. 1. Reaction conditions and results of the synthesis of 1,3,4-oxadiazole-containing polyethers **3** by fluorine displacement polymerization of 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole (**1**) with aromatic diols **2**

Diol	Reaction conditions <sup>a)</sup>			Polymer <sup>b)</sup>	
	solvent	temperature in °C	time in h	No.	$\frac{\eta_{\text{red}}}{\text{dL} \cdot \text{g}^{-1}}$ <sup>c)</sup>
<b>2a</b>	DMA	160	20	<b>3a</b>	1,17
<b>2b</b>	DMA	160	20	<b>3b</b>	0,86
<b>2c</b>	DMA	160	20	<b>3c</b>	0,65
<b>2d</b>	DMA	160	20	<b>3d</b>	1,00
<b>2e</b>	DMA	160	20	<b>3e</b>	0,18 <sup>d)</sup>
<b>2e</b>	TMS	250	4	<b>3e</b>	0,86 <sup>d)</sup>
<b>2f</b>	DMA	160	20	<b>3f</b>	0,14 <sup>d)</sup>
<b>2f</b>	TMS	250	4	<b>3f</b>	0,61 <sup>d)</sup>
<b>2f</b>	DPS <sup>e)</sup>	250	4	<b>3f</b>	1,04 <sup>d)</sup>

a) The polymerization was carried out with **1** (1 mmol) and **2** (1 mmol) in the solvent (5 mL) in the presence of potassium carbonate (2 mmol) at 150 °C for 2 h and then at the designated temperature for the prescribed period under nitrogen.

b) All the polymers were obtained quantitatively.

c) Reduced viscosity was measured at a polymer concentration of 0,5 g · dL<sup>-1</sup> in NMP at 30 °C.

d) Measured in conc. sulfuric acid.

e) 5 g of DPS was used.

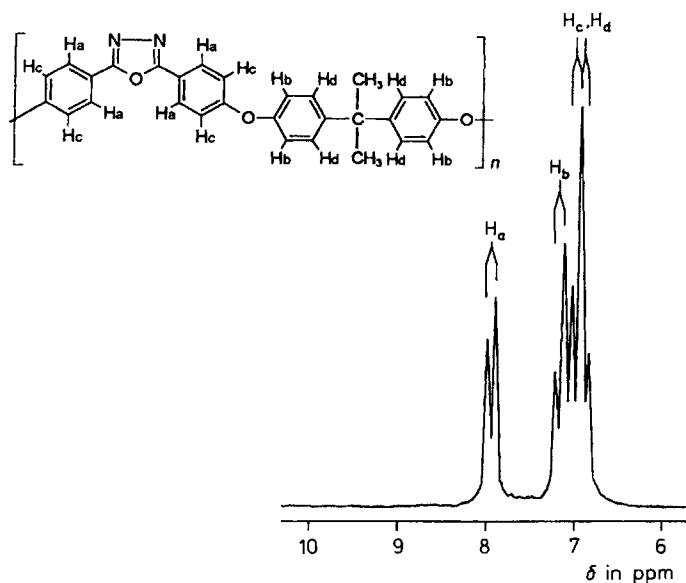


Fig. 1. 90 MHz <sup>1</sup>H NMR spectrum of 1,3,4-oxadiazole-containing polyether **3a** in CDCl<sub>3</sub> at room temperature (aromatic region only)

stants ( $J$  values) are in the order 8,4, 8,1, 9,0 and 8,6 Hz. These values are reasonable ones for non-equivalent ortho-protons. From these observations, four peaks are assigned to the corresponding aromatic protons<sup>4,10</sup>, as shown in the Fig. 1. The  $^1\text{H}$  NMR spectral data of  $\text{CDCl}_3$ -soluble polymers **3a–3d** are presented in the Experimental part. The spectra of **3b–3d** also exhibited the general AA'BB' patterns of para-disubstituted benzene rings in addition to the proton signals from the respective bisphenol residues in the aromatic region. The elemental analysis values were in fairly good agreement with the calculated ones.

### Polymer characterization

The solubility behavior of the 1,3,4-oxadiazole-containing polyethers is tabulated in Tab. 2.

Tab. 2. Solubility of 1,3,4-oxadiazole-containing polyethers **3** in various solvents<sup>a)</sup>

Solvent <sup>b)</sup>	Polymer					
	<b>3a</b>	<b>3b</b>	<b>3c</b>	<b>3d</b>	<b>3e</b>	<b>3f</b>
DMA	+	++	++	++	–	–
DMF	–	+	+	+	–	–
DMSO	–	–	+	–	–	–
HMPA	+	++	++	++	–	–
NMP	++	++	++	++	–	–
Nitrobenzene	+	++	++	+	–	–
<i>m</i> -Cresol	++	++	++	++	–	–
<i>o</i> -Chlorophenol	++	++	++	++	++	++
Phenol/ <i>sym</i> -Tetrachloroethane (3/2, v/v)	++	++	++	++	++	++
Dichloromethane	–	++	++	–	–	–
Chloroform	++	++	++	++	–	–
Tetrachloromethane	–	+	+	–	–	–
<i>sym</i> -Tetrachloroethane	++	++	++	++	–	–
Tetrahydrofuran	–	++	+	++	–	–
Conc. sulfuric acid	++	–	++	++	++	++

<sup>a)</sup> ++: Soluble at room temperature; +: soluble on heating; +–: partially soluble and/or swelling; –: insoluble.

<sup>b)</sup> DMA = *N,N*-dimethylacetamide; DMF = *N,N*-dimethylformamide; DMSO = dimethyl sulfoxide; HMPA: hexamethylphosphoric triamide; NMP = *N*-methyl-2-pyrrolidone.

The data clearly indicate the influence of the aromatic diol components used on the solubility nature. Polyethers **3e** and **3f** containing highly rigid *p*-phenylene and diphenyloxadiazole units<sup>11–13</sup>, respectively, in the polymer backbone were highly crystalline judging from their X-ray diffraction diagrams (Fig. 2), and were soluble only in *o*-chlorophenol, a mixture of phenol and *sym*-tetrachloroethane (3/2, v/v) and conc. sulfuric acid. In contrast, polyethers **3a**, **3b**, **3c** and **3d**, which contain bulky and distorted and/or unsymmetrical diphenylisopropylidene, diphenylhexa-

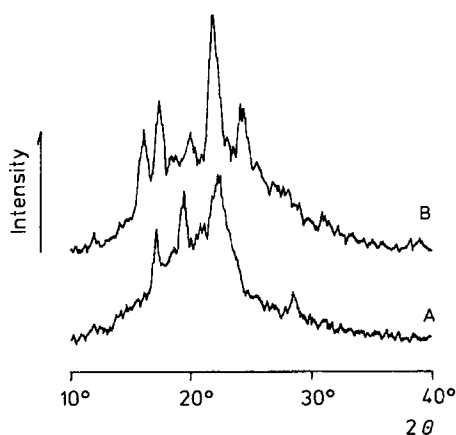


Fig. 2. The X-ray diffraction diagrams of 1,3,4-oxadiazole-containing polyethers. (A): **3e**; (B): **3f**

fluoroisopropylidene<sup>14-16</sup>), phenylindane<sup>14</sup>) and diphenylfluorene units<sup>14</sup>), respectively, were amorphous and also dissolved readily in a variety of organic solvents including NMP, *m*-cresol, chloroform and *sym*-tetrachloroethane at room temperature. Thus, the difference in the crystalline nature of these polyethers is well correlated to that of their solubility in organic media. The high-crystalline characteristics of **3e** and **3f** and their limited solubility behavior are apparently attributed to their stiff main-chain structures. The solubility behavior of these 1,3,4-oxadiazole-containing polyethers is quite similar to that of 1,3,4-thiadiazole-containing polyethers<sup>4</sup>).

Transparent, flexible and tough films with colorless to pale yellow color could be cast from the NMP solutions of amorphous polyethers **3a–3d**. Crystalline polyether **3f** also gave a clear film from *o*-chlorophenol solution. Tab. 3 lists the mechanical properties of the polyether films.

The films had tensile strength of 53–80 MPa, elongation at break of 4–12% and tensile moduli of 1.3–2.0 GPa. These tensile values are somewhat higher than those of 1,3,4-thiadiazole-containing polyether films<sup>4</sup>).

The thermal behavior data of the polyethers are also presented in Tab. 3. The  $T_g$ 's of amorphous polyethers **3a–3d** determined by DSC ranged from 195–259°C, depending markedly on the bisphenols used. The highest  $T_g$  of 259°C was observed for polyether **3d** containing highly bulky diphenylfluorene unit, followed by phenylindane-containing polyether **3c**, diphenylhexafluoroisopropylidene-containing polyether **3b** and diphenylisopropylidene-containing polyether **3a**. This decreasing order of  $T_g$  generally correlates with those of the bulkiness and rigidity of the aromatic units<sup>14</sup>). The  $T_g$  values of these polyethers are somewhat lower than those of the corresponding 1,3,4-thiadiazole-containing polyethers<sup>4</sup>) derived from the same bisphenols. The  $T_g$  of phenylindane-containing polyether **3c**, for instance, was 223°C, which is lower than that of the corresponding 1,3,4-thiadiazole-containing polyether<sup>4</sup>) by 17 K. No melting temperature was detectable for crystalline polyethers **3e** and **3f**. All the polyethers were stable up to 400°C in air, and the tempera-



Tab. 3. Mechanical and thermal properties of 1,3,4-oxadiazole-containing polyethers **3**

Polymer	Mechanical properties			Thermal properties		
	tensile strength in MPa	elongation at break in %	tensile modulus in GPa	$T_g^a)$ °C	$T_{10}^b)$ °C	RW <sup>c)</sup> in %
<b>3a</b>	74	5	1,6	195	479	85
<b>3b</b>	77	12	1,3	204	496	88
<b>3c</b>	53	5	1,3	223	474	75
<b>3d</b>	80	7	1,7	259	514	93
<b>3e</b>	— <sup>d)</sup>	—	—	— <sup>e)</sup>	464	63
<b>3f</b>	73	4	2,0	— <sup>e)</sup>	483	85

- a) Glass transition temperature was determined by DSC at a scan rate of 20 K · min<sup>-1</sup> under nitrogen.  
 b) Temperature at which 10% weight loss was recorded by TG in air at a heating rate of 10 K · min<sup>-1</sup>.  
 c) Residual weight at 500 °C.  
 d) No tough film was obtained.  
 e) No  $T_g$  was observed.

tures where 10% weight loss occurred were above 460 °C. The excellent thermal stability is almost comparable to that of 1,3,4-thiadiazole-containing polyethers<sup>4)</sup>.

## Conclusion

In this study, a series of 1,3,4-oxadiazole-containing polyethers was synthesized from 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole and aromatic diols having a variety of ring structures through fluorine displacement polymerization. In contrast to the usual poly(arylene ether) syntheses, the relatively lower reaction temperatures of 150–160 °C are sufficient to produce 1,3,4-oxadiazole-containing polyethers of high molecular weight. This implies that the electron-withdrawing group, 1,3,4-oxadiazole, effectively activates aromatic nucleophilic substitution. Most of the polyethers obtained are characterized by good solubility in organic solvents, excellent mechanical properties and high thermal stability, and, hence, considered to be one of the promising high-temperature film and plastic materials.

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