

# Syntheses and Properties of Related Polyoxadiazoles and Polytriazoles

E. R. HENSEMA,\* M. E. R. SENA,<sup>2</sup> M. H. V. MULDER,<sup>1†</sup> and C. A. SMOLDERS<sup>1</sup>

<sup>1</sup>University of Twente, Department of Chemical Technology, P.O. Box 217, 7500 AE Enschede, The Netherlands

<sup>2</sup>Instituto de Macromoléculas, Universidade do Rio de Janeiro/UFRJ, Ilha do Funao, Centro de Tecnologia, CEP 21945, Rio de Janeiro, Brasil

## SYNOPSIS

New aromatic poly-1,2,4-triazoles and poly-1,3,4-oxadiazoles are studied as thermally stable membrane materials. Various groups were introduced onto the pendant phenyl groups of poly-1,2,4-triazoles. Glass transition temperature, degradation temperature, and cold crystallization behavior were studied as a function of these groups. Cold crystallization appeared to be highly sensitive to macromolecular regularity. The solubility of poly-1,3,4-oxadiazoles was highly improved upon incorporation of 5-*t*-butylisophthalic, 1,1,3-trimethyl-3-phenylindane, 4,4'-(2,2'-diphenyl)hexafluoro propane, and diphenyl ether groups into the polymeric main chain, whereas the high glass transition temperatures and degradation temperatures typical for aromatic poly-1,3,4-oxadiazoles were maintained. © 1994 John Wiley & Sons, Inc.

**Keywords:** poly-1,3,4-oxadiazoles • polyhydrazide • poly-1,2,4-triazoles • cold crystallization

## INTRODUCTION

Aromatic poly-1,2,4-triazoles and poly-1,3,4-oxadiazoles are studied as new thermally stable membrane materials for gas separation applications, especially poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazole], which is known for its excellent gas separation properties.<sup>1</sup> The use of these polymers as membrane materials is hampered due to their poor solubility, which limits the number of possibilities of fabricating membranes with a desired morphology, like asymmetric structures. For example, poly(*p*-, *m*-phenylene)-1,3,4-oxadiazole is soluble only in concentrated sulphuric acid, which is a very difficult solvent to handle in practice.

In this article we wish to report the syntheses and physical properties of poly-1,3,4-oxadiazoles and poly-1,2,4-triazoles where various functional groups are incorporated *into* and *onto* the polymer backbone with the aim of increasing their solubility while

maintaining their thermal stability. The relationship between the gas separation properties and these molecular structures was also studied and is reported elsewhere.<sup>2</sup>

The solubility of polymers is often increased when flexible bonds, large pendant groups, or polar substituents are incorporated in the polymer backbone. The introduction of large pendant bulky groups along the polymer backbone results in a less ordered polymer matrix increasing the solubility characteristics. This is nicely illustrated by the fact that poly(*p*-, *m*-phenylene)-1,3,4-oxadiazoles are soluble only in concentrated sulphuric acid while poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazoles], having an extra pendant phenyl group, are also soluble in *m*-cresol and formic acid.

Solubility is also highly increased if, instead of aromatic groups, aliphatic groups are incorporated into the polymer backbone, but a significant reduction in thermal stability is also observed. Incorporation of aliphatic groups for that reason was avoided. (Nonetheless, cyclohexane was incorporated as a comparison to the aromatic poly(*p*-, *m*-phenylene-1,3,4-oxadiazoles.)

A number of authors have reported poly(1,3,4-oxadiazoles) with increased solubility characteris-

\* Present address: CIBA-GEIGY AG, Central Research Laboratories, CH-4002 Basel, Switzerland.

† To whom correspondence should be addressed.

tics. Iwakura has, for example, reported poly-1,3,4-oxadiazoles where the phenylene ring has been replaced by a pyridine ring. These polymers are soluble in formic acid, DMF and DMSO. However, these polymers were not synthesized and studied here, since low inherent viscosities were reported.<sup>3</sup>

Russian workers have developed so called "Cardo" poly-1,3,4-oxadiazoles containing a bulky phthalide group. Poly-1,3,4-oxadiazoles containing this group have been studied extensively and the preparation of porous membranes of poly-1,3,4-oxadiazoles containing this group has been patented.<sup>4</sup>

The functional groups that were incorporated into poly-1,3,4-oxadiazoles and poly-1,2,4-triazoles in this study, together with their syntheses, are represented in Figure 1.

A number of reaction routes are known for the preparation of these polymers.<sup>5</sup> Poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazoles] with alternating *para*- and *meta*-phenylene groups were prepared by means of a reaction of aniline and aniline derivatives

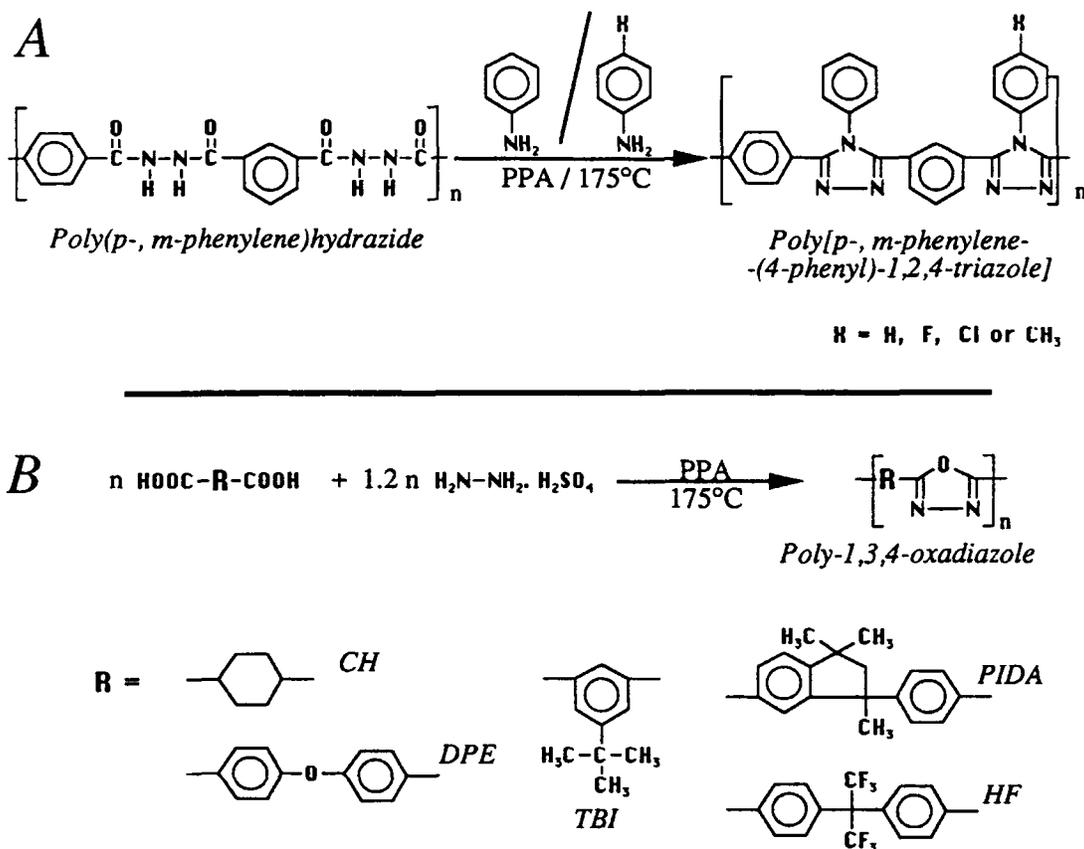
with poly(*p*-, *m*-phenylene)hydrazide in polyphosphoric acid [see Fig. 1 (A)]. Holsten and Lilyquist have studied this reaction extensively using polyhydrazide as a precursor polymer in combination with aniline.<sup>6</sup> Poly(*p*-, *m*-phenylene)hydrazide is prepared by means of a polycondensation reaction between terephthaloyl chloride and isophthaloyl dihydrazide.<sup>7</sup>

High molecular weight aromatic poly-1,3,4-oxadiazoles were prepared directly using various dicarboxylic acids and hydrazine sulphate as monomers [see Fig. 1 (B)]. This reaction route was originally reported by Iwakura et al.<sup>8</sup>

## EXPERIMENTAL

### Materials

A mixture of *cis*- and *trans*-1,4-cyclohexane dicarboxylic acid was purchased from Aldrich. The pure *cis*- (*c*-CH) and the *trans*-isomer (*t*-CH) were



**Figure 1.** (A) Preparation of aromatic poly[*p*-, *m*-phenylene(4-phenyl)-1,2,4-triazoles] out of a polyhydrazide in a reaction medium consisting of polyphosphoric acid and mixtures of aniline and *para*-substituted aniline derivatives. (B) Preparation of poly-1,3,4-oxadiazoles using dicarboxylic acids, R(COOH)<sub>2</sub>, and hydrazine sulphate as monomers.

obtained from this mixture by means of a treatment with chloroform.<sup>9</sup>

The dicarboxylic acids, 4,4'-diphenyl ether (DPE), 1,1,3-trimethyl-3-phenylindan-4',5-dicarboxylic acid (PIDA), and 5-*t*-butylisophthalic acid (TBI) are Amoco products and 4,4'-(2,2'-diphenyl)hexafluoropropane dicarboxylic acid (HF) was supplied by Hoechst. These dicarboxylic acids were used as received.

All other chemicals were supplied by Merck and were used as received, except NMP, which was distilled under reduced pressure over CaH<sub>2</sub>, lithium chloride, and dried in a vacuum oven at 150°C, and aniline, which was distilled under reduced pressure and its colorless distillate stored under nitrogen in a sealed flask in a refrigerator.

Isophthaloyl dihydrazide was prepared from isophthaloyl dimethyl ester and hydrated hydrazine.<sup>10</sup>

#### Poly(*p*-, *m*-phenylene)hydrazide Synthesis<sup>7,10</sup>

Isophthaloyl dihydrazide, 74.24 g (0.382 mol) and 16.21 g LiCl are dissolved in a 3-necked flask containing 600 mL of NMP at 60°C under dry nitrogen. After dissolution, the stirred solution is cooled to 0°C and 77.62 g (0.382 mol) of terephthaloyl chloride is added in four equal portions. Each following portion is added when the terephthaloyl chloride of the previous portion has completely dissolved. Total addition lasts approximately 2 h. The viscous solution is stirred overnight, and the polymer is precipitated and washed in hyperfiltrated water. After additional washing with ethanol, the polymer is dried in a vacuum oven at 150°C for at least 24 h.

Two batches of polyhydrazide were prepared having inherent viscosities of 0.86 and 0.82 dL/g, respectively (0.5 g polymer solution in 100 mL DMSO).

#### Poly-1,2,4-triazole Synthesis Using Polyhydrazide as a Precursor Polymer<sup>6</sup>

In a 3-necked flask, 310 g polyphosphoric acid (PPA) is heated to 150°C under nitrogen. Aniline, 76.65 g (0.823 mol), is added dropwise to the stirred solution, while maintaining the temperature at 150°C. After addition, the temperature is raised to 175°C, and 10 g poly(*p*-, *m*-phenylene)hydrazide is added. The reaction mixture is kept at this temperature for 140 h and poured into hyperfiltrated water and neutralized with sodium hydroxide under stirring. The product is washed in a 5% sodium hydroxide solution and washed twice in hyperfiltrated water. Subsequently, the product is extracted with

ethanol using a Soxhlet extractor after which it is dried in a vacuum oven at 150°C for 24 h. The product is dissolved in formic acid and insoluble parts are removed by means of filtration over a 5 μm filter. These solutions are directly used for poly-1,2,4-triazole film preparation, as will be discussed below.

The polymers were obtained in a good yield. Instead of aniline, also mixtures of aniline and aniline derivatives have been employed. In all cases, a ratio of 0.823 mol aniline and aniline derivative per 310 g PPA has been applied.

#### Poly-1,3,4-oxadiazole Synthesis<sup>8</sup>

In a 3-necked flask under a dry nitrogen flux, 0.05 mol dicarboxylic acid and 0.06 mol hydrazine sulphate are added to 155 g PPA. The mixture is homogenized under stirring and heated to the reaction temperature of 100–175°C and maintained at this temperature for 10–21 h. The reaction medium becomes very viscous with increasing reaction time. The polymer solution is precipitated in hyperfiltrated water and neutralized with sodium hydroxide. The product is repeatedly washed with hyperfiltrated water and dried in a vacuum oven at 60°C. The polymers were obtained in a quantitative yield.

#### Preparation of Homogeneous Films

##### Poly-1,2,4-triazoles

Homogeneous poly-1,2,4-triazole films are prepared from a 15 wt % polymer solution in formic acid. Inhomogeneities are removed from this solution by filtration over a 5 μm filter. The solution is cast on a glass plate using casting knives with slit heights of 0.3 and 0.5 mm, followed by evaporation of the solvent in a nitrogen atmosphere at room temperature. After evaporation, the glass plate is immersed into a water bath and the poly-1,2,4-triazole film is easily removed from the glass plate. Transparent films are obtained with thicknesses of 20–60 μm. The films are dried in a vacuum oven for at least 24 h at 150°C.

##### Poly-1,2,4-oxadiazoles

For PIDA-POD and HF-POD the same procedure was followed but in this case trifluoro acetic acid was used as a solvent. For CH-POD, DPE-POD, and TBI-POD, formic acid was used while for the 50/50 copolymer HF/DPE-POD, NMP was used as a solvent, which was evaporated at 150°C.

## Characterization

### Inherent Viscosity

The inherent viscosities are determined for 0.5 g polymer solutions in 100 mL solvent at 30°C. For the polyhydrazides, DMSO is used as a solvent, while, for the poly-1,2,4-triazoles and poly-1,3,4-oxadiazoles, formic acid was used. The inherent viscosities of PIDA-POD and HF-POD were determined in concentrated sulphuric acid, while, for the copolymer HF/DPE-POD, NMP was used as a solvent.

### Differential Scanning Calorimetry (DSC)

DSC measurements are performed on a Perkin-Elmer DSC-4 in combination with a System 4 Microprocessor Controller and a Thermal Analysis Data Station (TADS), model 3700. The polymer samples are placed in aluminium sample pans, and the temperature is increased with a heating rate of 20°C/min from 100°C to 400°C under a nitrogen purge gas stream. The sample is cooled with 320°C/min to 100°C and a second run is recorded from 100°C to 450°C again with a heating rate of 20°C/min, as glass transition temperature ( $T_g$ ), the midpoint of

the enthalpy change, is taken, which has been calculated by means of the TADS software.

### Thermogravimetical Analysis (TGA)

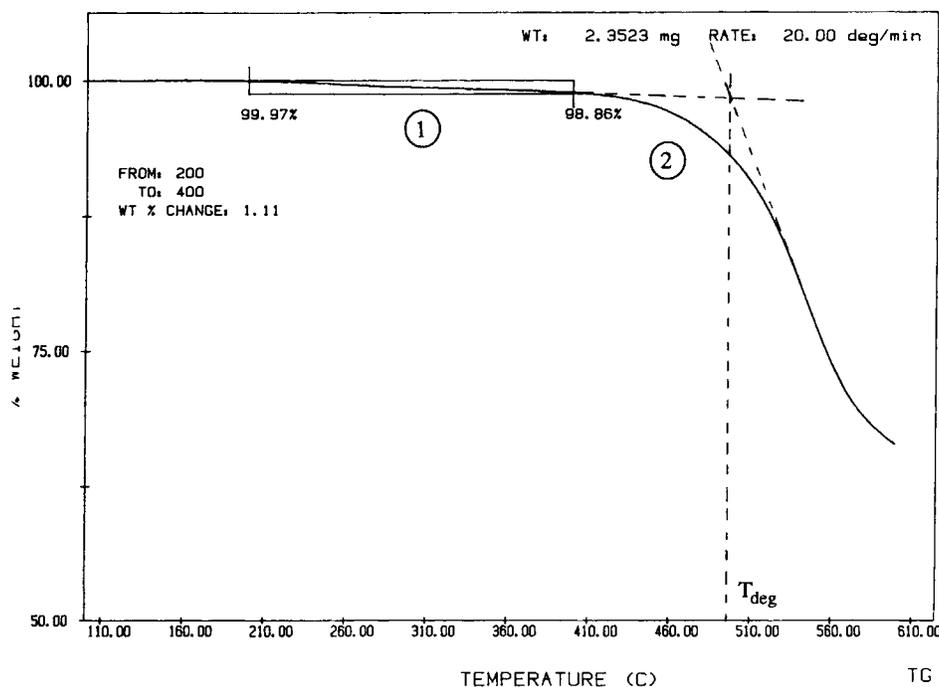
TGA experiments are carried out on a Perkin-Elmer TGS-2 in combination with a System 4 Microprocessor Controller and a Thermal Analysis Data Station (TADS), model 3700. Experiments are carried out under a nitrogen purge gas stream from 50 to 600°C. The temperature of the polymer samples is increased with a heating rate of 20°C/min and the weight loss has been monitored.

The degradation temperature ( $T_{deg}$ ), defined as the point of intersection of the tangents, in the thermogram was taken (see Fig. 2).

## RESULTS AND DISCUSSION

### Poly-1,2,4-triazoles via Polyhydrazides

The preparation of high molecular weight poly-1,2,4-triazoles using polyhydrazide as a precursor polymer was originally reported by Holsten and Lilyquist.<sup>6</sup> The reaction is carried out in PPA containing an



**Figure 2.** TGA thermogram of PT-p/m-25F recorded with a heating rate of 20°C/min from 100 to 600°C under nitrogen. Two phases of weight loss can be observed: (1) loss of water caused by the cyclodehydration of unclosed groups and (2) loss of volatiles caused by the degradation of the polymer. The degradation temperature ( $T_{deg}$ ) is defined as the intersection of the tangents.

excess of aniline. The ideal concentrations of the reactants were determined to be 10 g polyhydrazide and 0.823 mol aniline per 310 g PPA.

We have incorporated aniline in combination with aniline derivatives and studied the effect on the physical properties of the polymers prepared. The effects on the gas separation properties of these poly-1,2,4-triazoles are reported elsewhere.<sup>2</sup>

Poly-1,2,4-triazoles were prepared from two batches of polyhydrazides having inherent viscosities of 0.86 and 0.82 dL/g.

### Elemental Analysis

Elemental analysis of C, H, and N were carried out. In Table I, the C/N and C/H ratio of the elemental analysis of the polyhydrazides and the poly-1,2,4-triazoles are given.

The experimental values found were somewhat lower than the theoretical ones. Nevertheless, the C/N and C/H ratios are close to their theoretical values indicating residual impurities, most likely to be polyphosphoric acid.<sup>13</sup> Polyhydrazide and poly-1,2,4-triazole are prepared reproducibly, as is indicated by the elemental analysis of PH-*p/m*-1, PH-*p/m*-2, PT-*p/m*-1, PT-*p/m*-2, and PT-*p/m*-3.

The chlorine contents of PT-*p/m*-25Cl and PT-*p/m*-50Cl were determined to be 4.52 and 8.21 wt %, respectively. This indicates that incorporation of chloro aniline is favored over aniline itself, since

incorporation based on stoichiometric concentrations in the reaction medium would have yielded theoretical chlorine values of 3.89 and 7.5 wt %, respectively.

Aniline or its derivatives forms a complex with PPA. This complex is in equilibrium with the free amines. Since only free amines can react with polyhydrazide, relatively more free chloro aniline must be available than can be accounted for on the basis of the ratio of aniline/chloro aniline present in the reaction medium. This means that equilibrium between complex and free amine has shifted in the direction of the latter one being chloro aniline. Similar incorporations are assumed to have taken place in the case of PT-*p/m*-75Cl, PT-*p/m*-25F, and PT-*p/m*-50F.

### Cyclodehydration

The results obtained with TGA and DSC techniques are given in Table II. In Figure 2, a TGA run of PT-*p/m*-25F is represented, and in Figure 3, two successive DSC curves of this poly-1,2,4-triazole are represented.

Unclosed 1,3,4-oxadiazole and 1,2,4-triazole groups can be present in the final product. During a TGA experiment a distinct weight loss is observed, phase 1 in Figure 2, attributable to the loss of water formed during the cyclodehydration of 1,3,4-oxadi-

**Table I.** Inherent Viscosities and Elemental Analyses of Polyhydrazides and Poly-1,2,4-triazoles

Polymer	Contents Aniline/ Aniline Derivative <sup>a</sup>	$\eta_{inh}^b$ (dL/g)	C/N <sup>c</sup> (Found)	C/N <sup>c</sup> (Theor.)	C/H <sup>c</sup> (Found)	C/H <sup>c</sup> (Theor.)
PH- <i>p/m</i> -1		0.82	3.50	3.43	15.66	15.89
PH- <i>p/m</i> -2		0.86	3.50	3.43	14.32	15.89
PT- <i>p/m</i> -1	100% aniline	0.85	4.05	4.00	17.99	18.53
PT- <i>p/m</i> -2	100% aniline	0.94	4.06	4.00	19.42	18.53
PT- <i>p/m</i> -3	100% aniline	1.01	4.13	4.00	19.57	18.53
PT- <i>p/m</i> -25Cl	25% <i>p</i> -Cl	0.94	4.07	4.00	17.09	19.07
PT- <i>p/m</i> -50Cl	50% <i>p</i> -Cl	0.80	4.08	4.00	16.97	19.64
PT- <i>p/m</i> -75Cl	75% <i>p</i> -Cl	0.80	4.08	4.00	20.70	20.24
PT- <i>p/m</i> -100Cl	100% <i>p</i> -Cl	0.78	4.16	4.00	21.62	20.84
PT- <i>p/m</i> -25F	25% <i>p</i> -F	0.99	4.07	4.00	19.27	19.08
PT- <i>p/m</i> -50F	50% <i>p</i> -F	1.10	4.05	4.00	19.11	19.65
PT- <i>p/m</i> -100F	100% <i>p</i> -F	0.95	4.07	4.00	19.95	20.85
PT- <i>p/m-p</i> -Me	100% <i>p</i> -Me	1.12	4.36	4.28	17.08	16.26
PT- <i>p/m-o</i> -Me	100% <i>o</i> -Me	0.98	4.21	4.29	17.44	16.26

<sup>a</sup> Proportions aniline/aniline derivative added to the reaction medium, for example PT-*p/m*-75Cl means that a mixture consisting of 25% aniline and 75% *p*-chloro aniline is applied, *p*-F stands for *p*-fluoro aniline, *p*-Me is *p*-toluidine, and *o*-Me is *o*-toluidine.

<sup>b</sup> Inherent viscosities were determined from polymer solutions (0.5 g/dL) at 30°C. DMSO was used as solvent in the case of polyhydrazide and formic acid in the case of the poly-1,2,4-triazoles.

<sup>c</sup> Determined using elemental analysis (wt %/wt %).

**Table II.** Film Appearance and Thermal Properties of the Poly-1,2,4-triazoles<sup>a</sup>

Polytriazole	Film Appearance	$T_g^b$		$T_{cc}^c$ (°C)	$T_m^d$ (°C)	$T_{deg}$ (°C)	$\Delta w$ (200–400°C) (wt %)
		1 <sup>st</sup> Run (°C)	2 <sup>nd</sup> Run (°C)				
PT- <i>p/m</i> -1	Light yellow	264	- <sup>e</sup>	319	425	527	2.07
PT- <i>p/m</i> -2	Light yellow	267	282	324	427	524	1.65
PT- <i>p/m</i> -3	Light yellow	261	- <sup>e</sup>	315	425	521	1.82
PT- <i>p/m</i> -25Cl	Yellow	271	288	- <sup>e</sup>	- <sup>e</sup>	504	1.52
PT- <i>p/m</i> -50Cl	Deep yellow	269	276	- <sup>e</sup>	- <sup>e</sup>	489	2.30
PT- <i>p/m</i> -75Cl	Blue	271	278	- <sup>e</sup>	- <sup>e</sup>	484	1.45
PT- <i>p/m</i> -100Cl	Deep blue	274	279	373	423	486	1.77
PT- <i>p/m</i> -25F	Light yellow	257	266	344	407	507	1.11
PT- <i>p/m</i> -50F	Light yellow	269	273	- <sup>e</sup>	- <sup>e</sup>	479	1.13
PT- <i>p/m</i> -100F	Light yellow	276	283	- <sup>e</sup>	409	453	1.10
PT- <i>p/m-p</i> -Me	Light yellow	257	254	- <sup>e</sup>	- <sup>e</sup>	506	1.78
PT- <i>p/m-o</i> -Me	Light yellow	268	272	- <sup>e</sup>	- <sup>e</sup>	493	2.88

<sup>a</sup> DSC curves were recorded twice using the same sample. The first run from 100 to 400°C and the second run from 100 to 450°C. In all cases a heating rate of 20°C/min was used. After the first run the sample was cooled down with 320°C/min.

<sup>b</sup> All films were transparent except PT-*p/m*-100F, which was opaque.

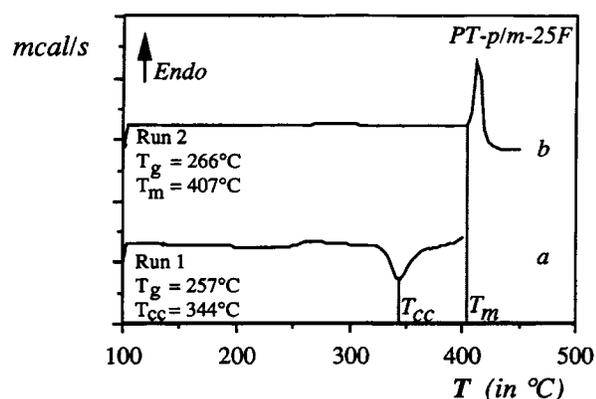
<sup>c</sup> The peak temperature of cold crystallization is given.

<sup>d</sup> The onset of the melting peak is given.

<sup>e</sup> No  $T_g$ , cold crystallization, or melting peak detectable using DSC techniques.

azole and 1,2,4-triazole groups. The reaction scheme of this ring closure is represented in Figure 4.

Weight loss occurring between 200°C and 400°C has been attributed to the ring closure reaction. In all cases, weight losses due to ring closure reactions are observed (see Table II), indicating that the reaction between aniline, aniline derivatives, and polyhydrazide at 175°C does not result in a fully converted product. Performing the reaction at higher

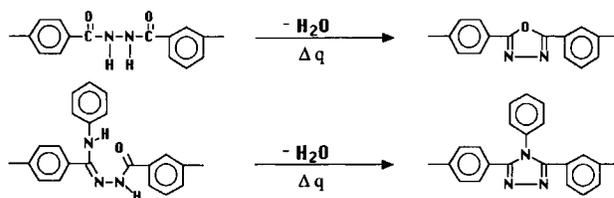


**Figure 3.** Two successive DSC curves of PT-*p/m*-25F recorded with 20°C/min under nitrogen. After the first run from 100 to 400°C (a) the sample is cooled with 320°C/min and the second run from 100 to 450°C is recorded (b).  $T_{cc}$  is the peak temperature of cold crystallization and  $T_m$  is the on-set temperature of melting.

temperatures results, however, in products with lower inherent viscosities.<sup>6</sup> In a thermogram of a fully converted poly-1,2,4-triazole this weight loss is, of course, absent. PT-*p/m-o*-Me shows the highest weight loss. In this case, the reaction between *o*-toluidine and polyhydrazide is most probably sterically hindered. Unclosed groups are also detectable by IR-spectrometry, since a carbonyl stretching absorption peak is observed in the IR-spectra at 1650  $\text{cm}^{-1}$ .

Unclosed rings are possible weak spots for thermal or chemical degradation. A heat treatment will force unclosed rings into their more thermally stable and chemically resistant closed ring forms.

Phase 2 in Figure 2 represents the loss of volatiles caused by the ultimate degradation of the polymer. Incorporation of aniline derivatives yields polymers with a slightly decreased thermal stability as compared to unmodified poly[*p*-, *m*-phenylene-(4-



**Figure 4.** Cyclodehydration of unclosed 1,3,4-oxadiazole and 1,2,4-triazole groups.

phenyl)-1,2,4-triazoles] (see Table II). From all polymers, except from PT-*p/m-o*-Me and PT-*p/m*-100F, flexible films were obtained by solvent casting techniques and these were investigated for their gas separation properties.<sup>2</sup> These films were also used for DSC experiments.

Each sample was subjected to two subsequent DSC heating runs, the first from 100 to 400°C after which the sample was cooled down within 320°C/min, followed by a second heating run from 100 to 450°C (see Fig. 3). In both experiments, a heating rate of 20°C/min was applied. The glass transition temperatures recorded during both runs are given in Table II.

The glass transition temperature is raised with the incorporation of fluoro and chloro aniline, obviously due to increased polar interactions. Incorporation of *o*-toluidine results in a decreased glass transition temperature compared to the unmodified poly-1,2,4-triazoles, PT-*p/m*-1, PT-*p/m*-2, and PT-*p/m*-3. Differences in glass transition temperatures are, however, small.

Except for PT-*p/m-p*-Me, the glass transition temperature of the second run is higher than the glass transition temperature of the "as-cast" film. This rise in glass transition temperature is obviously due to quenching effects during cooling,<sup>11</sup> and due to cyclodehydration of unclosed groups during the first DSC experiment in which a more flexible structure is converted into a rigid one. The effect of both quenching and ring closure on the glass transition temperature is nicely shown by the following experiment where a sample of PT-*p/m*-50Cl is subjected to a number of successive DSC heating runs, (see Table III). PT-*p/m*-50Cl was chosen for this experiment, since it has a relatively large number of unclosed rings, as indicated by its weight loss during the TGA experiments.

During the first run up to 300°C, a glass transition temperature of 268.5°C is measured. After cooling down with 320°C/min, the second run is recorded and the  $T_g$  has slightly increased, obviously due to

quenching of the sample during cooling. But further changes in runs 2, 3, and 4 are marginal. Due to the low end temperatures, no significant cyclodehydration reactions of the unclosed rings take place. Increasing the end temperature to 400°C results in a rise in  $T_g$ . During these runs the polymer undergoes cyclodehydration resulting in a more rigid polymer. This implies that the greater part of the ring closure reactions takes place when the polymer is in the rubbery phase. During runs 6 and 7 the polymer is likely to undergo also some degradation.

### Cold Crystallization

Cold crystallization is detected for a number of poly-1,2,4-triazoles during the first heating run of a DSC experiment. Cold crystallization of alternating poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazole] has extensively been studied by Gebben et al., who noticed that cold crystallization is observed only for poly-1,2,4-triazole films and not for the as-prepared reaction powder.<sup>12</sup> The process of cold crystallization also depends highly on the macromolecular structure of the polymers used. For example, cold crystallization is observed only for a poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazole] where *p*- and *m*-phenylene groups are present in an alternating fashion, and not if these groups are incorporated randomly.<sup>13</sup> A highly regular macromolecule is obviously a precondition for cold crystallization. A similar phenomenon is observed for the modified poly-1,2,4-triazoles as represented in Table II.

During the first DSC heating cycle, a number of poly-1,2,4-triazoles undergo cold crystallization in the rubbery phase. After heating to 300°C the polymer is quenched with 320°C/min to 100°C and subjected to a second heating cycle to 450°C. During cold crystallization the amorphous fraction in a polymer decreases, which results in a decreased heat capacity jump at the glass transition temperature. In the case of PT-*p/m*-1 and PT-*p/m*-2, this occurs to such an extent that the glass transition temper-

**Table III.** Influence of Subsequent Heating Runs on the Glass Transition Temperature of PT-*p/m*-50Cl

Heating Run	Limits	Glass Transition Temperature (°C)	Heating Run	Limits	Glass Transition Temperature (°C)
1	100–300	268.5	5	100–420	278.6
2	100–300	271.0	6	100–455	282.7
3	100–300	271.1	7	100–455	289.3
4	100–420	270.6			

ature is not detectable in the DSC curve of the second run. The crystalline fraction in poly-1,2,4-triazoles formed during cold crystallization melts in the second run as indicated by a clear melting peak [see Fig. 3 (B)]. The onset of this melting peak is given, since the peak temperature could not be indicated clearly in a number of cases due to simultaneously occurring degradation.

As said, the unmodified poly-1,2,4-triazoles undergo cold crystallization in the rubbery phase. Incorporation of *p*-chloro aniline in combination with aniline results in a less regular macromolecular structure and the possibility of undergoing cold crystallization vanishes. In the case of PT-*p*/m-100*p*-Cl the polymer becomes "regular" again and crystallization is observed. PT-*p*/m-25F undergoes cold crystallization indicating that incorporation of 25% *p*-fluoro aniline does not obviously result in a dramatic change in the macromolecular structure, due to the small amount and the relative small size of the fluorine atom. No cold crystallization is observed for PT-*p*/m-100F. Since the appearance of the "as-cast" polymer film is opaque, and since a melting peak is observed with an onset of 453°C, this polymer is believed to be already crystalline.

One also might expect cold crystallization for the regular PT-*p*/m-*p*-Me, but no cold crystallization or melting peak is observed in the DSC curve. The reason for this behavior is not understood.

### Other Pendant Groups

Since solubility is often enhanced when larger groups are incorporated onto the polymer backbone as pendant groups, we have investigated the possibility of incorporating biphenylic structures, like 1-naphthylamine, 4-phenoxy aniline, and 4-aminobenzotrifluoride, but in this case polymers with insufficient film-forming properties were obtained. During the reaction between amine and polyhydrazide, polymer degradation occurs due to the strong acidic environment of polyphosphoric acid. This degradation is kept to minimum if the reaction medium consists of 0.832 mol amine per 310 g PPA.<sup>6</sup> It, however, was not possible to dissolve these amounts of these high molecular weight amines in PPA. Another problem was the sublimation of these amines from the reaction mixture during the reaction, resulting in a further deviation from the ideal reaction conditions. Similar problems have been reported by Krongauz et al.,<sup>14</sup> who investigated the reaction between 1-naphthylamine and poly(*p*-phenylene-1,3,4-oxadiazole) also in PPA.

Incorporation of cyclohexylamine was also examined. During this reaction, only minor quantities of polyhydrazide are converted into the corresponding poly-1,2,4-triazole. In the case of a normal reaction behavior, the precursor dissolves completely in the course of the reaction and is converted into the corresponding poly-1,2,4-triazole. Due to the strong complex formation between polyphosphoric acid and cyclohexylamine,<sup>14</sup> the concentration of free amines is apparently too low to result in a successful reaction.

### Poly-1,3,4-oxadiazoles

Poly(*p*-, *m*-phenylene)-1,3,4-oxadiazoles are comparable with poly(*p*-phenylene) with respect to their thermal stability and chemical resistance, which is ascribed to the fact that the 1,3,4-oxadiazole ring is spectrally and electronically equivalent to the *p*-phenylene ring.<sup>15</sup> High thermal stability and chemical resistance is favored in most end-use applications. During processing, these characteristics can, however, be a major problem.

Poly(*p*-, *m*-phenylene)-1,3,4-oxadiazole can be obtained via a cyclodehydration reaction of the corresponding tractable polyhydrazide. However, solid state cyclodehydration of alternating poly(*p*-, *m*-phenylene hydrazide) yielded brittle membranes.<sup>13</sup>

Poly(*p*-, *m*-phenylene)-1,3,4-oxadiazoles prepared from isophthalic acid and terephthalic acid with hydrazine sulphate as monomers yielded polymers with higher inherent viscosities from which flexible membranes were prepared. Since this reaction gave poly-1,3,4-oxadiazoles with superior properties, it was also used to prepare poly-1,3,4-oxadiazoles with various other functional groups. The physical properties of these polymers were studied as a function of these functional groups. The poly-1,3,4-oxadiazoles were prepared from various dicarboxylic acids (see Fig. 1). These poly-1,3,4-oxadiazoles were, in turn, used as precursor polymers for the preparation of poly-1,2,4-triazole on which we hope to report in the future.

Fuming sulphuric acid is mostly favored over PPA as a reaction medium for the preparation of aromatic poly-1,3,4-oxadiazoles.<sup>16</sup> But in the case of 1,1,3-trimethyl-3-(*p*-carboxy-phenyl)-5-carboxyindan (PIDA), no polymer was obtained, possibly due to degradation of the monomer that contains aliphatic groups obviously susceptible to degradation in the strong acidic environment. Performing the reaction in PPA, a much milder dehydrating agent, resulted readily in a very viscous reaction medium and gave

**Table IV.** Elemental Analysis of Poly-1,3,4-oxadiazoles

Polymer	Dicarboxylic Acid	$\eta_{inh}^a$ (dL/g)	C/N (Found)	C/N (Theor.)	C/H (Found)	C/H (Theor.)
cCH-POD	c-CH	1.65	3.46	3.43	9.74	9.54
t-CH-POD	t-CH	2.81	3.61	3.43	8.94	9.54
c+t-POD	c+t-CH	1.56	3.42	3.43	8.72	9.54
PIDA-POD	PIDA	0.19 <sup>b</sup>	8.63	8.58	12.75	12.55
TBI-POD	TBI	0.38	5.64	5.15	11.65	11.92
HF-POD	HF	0.40 <sup>b</sup>	7.50	7.29	25.38	25.30
DPE-POD	DPE	0.37	6.05	6.00	15.38	20.87
HF/DPE-POD <sup>d</sup>	HF & DPE	2.44 <sup>c</sup>	6.26	6.64	16.88	23.08

<sup>a</sup> Inherent viscosity is determined in formic acid.

<sup>b</sup> Inherent viscosity is determined in concentrated sulphuric acid.

<sup>c</sup> Inherent viscosity is determined in NMP.

<sup>d</sup> Random copolymer of HF and DPE used in 40% and 60% molar amounts, theoretical values for the polymer elemental analysis were calculated assuming stoichiometric incorporation of both monomers.

a polymer with an inherent viscosity of 0.19 dL/g from which flexible films were prepared. To prevent monomer degradation, all syntheses represented in Figure 1 (B) were performed in PPA instead of fuming sulphuric acid.

Successful preparation of poly-1,3,4-oxadiazoles was confirmed by elemental analysis (see Table IV). Also in this case, the experimental C, N, and H values found were somewhat lower than the theoretical ones. Nevertheless, the C/N and C/H ratios are close to their theoretical values indicating residual impurities in the final product, most likely to be polyphosphoric acid.<sup>13</sup> Flexible films were obtained from all poly-1,3,4-oxadiazoles by solvent casting techniques.

In Table V, the glass transition temperatures and the degradation temperatures are given. Again samples are subjected to two successive heating runs, the first from 100 to 400°C, after which the sample is cooled down with 320°C/min to 100°C, followed by a second run with an end temperature of 450°C. Both scans were recorded with a heating rate of 20°C/min. These poly-1,3,4-oxadiazoles all have high glass transition temperatures. The first run yields the glass transition temperature of the as-prepared film. The glass transition temperature recorded during the second run is higher than the first. In this case, quenching effects and cyclodehydration of unclosed hydrazide groups into the more rigid 1,3,4-oxadiazole groups probably occur (see Fig. 4). In the second run, the glass transition temperature of a number of poly-1,3,4-oxadiazoles were not detectable with DSC techniques.

The thermal stability of these poly-1,3,4-oxadiazoles is slightly lower than those of the poly-1,2,4-

triazoles. Discriminating between weight loss due to cyclodehydration and degradation is in this case not possible to full satisfaction, since these two phases of weight loss shade off into one another.

### CH-POD

Preparation of alicyclic poly-1,3,4-oxadiazoles was originally reported by Iwakura et al.<sup>9</sup> Poly(1,4-cyclohexane)-1,3,4-oxadiazole was reported to be soluble in formic acid while good thermal stability was maintained. Incorporation of the flexible cyclohexane unit results in a decrease of the glass transition temperature compared to its aromatic counterpart, poly(*p*-phenylene)-1,3,4-oxadiazole. The degradation temperature is approximately 100°C lower than

**Table V.** Film Appearance and Thermal Properties of Poly-1,3,4-oxadiazoles

Polymer	Film Appearance	$T_g$		$T_{deg}$ (°C)
		1 <sup>st</sup> Run (°C)	2 <sup>nd</sup> Run (°C)	
c-CH-POD	Light yellow	179	- <sup>a</sup>	441
t-CH-POD	Colorless	179	- <sup>a</sup>	449
c+t-POD	Colorless	180	- <sup>a</sup>	449
PIDA-POD	Light yellow	300	330	488
TBI-POD	Colorless	315	- <sup>a</sup>	485
HF-POD	Colorless	287	295	479
DPE-POD	Colorless	333	361	496
HF/DPE-POD	Light yellow	339	- <sup>a</sup>	491

<sup>a</sup> No glass transition temperature detectable with DSC techniques.

found for poly(*p*-phenylene)-1,3,4-oxadiazole, being 542°C.<sup>13</sup> Our results on the thermal stability of CH-POD are in agreement with the observations of Iwakura et al.<sup>9</sup>

Cyclohexane-1,4-dicarboxylic acid was supplied as a mixture of *cis* and *trans* isomers. Both this mixture as well as the pure *cis*- and *trans*-isomers were used as monomers, resulting in three batches of poly(1,4-cyclohexane)-1,3,4-oxadiazole. Flexible films were obtained from all three polymers. No differences were detected between the three batches using elemental analysis, IR-spectroscopy, and DSC techniques.

Iwakura synthesized two batches of poly(1,4-cyclohexane)-1,3,4-oxadiazole using the *cis*- and *trans*-isomers of 1,4-cyclohexane dicarboxylic acid and concluded that the two polymers had the same geometrical structure on the basis of their identical infrared spectrum, solubility, thermal stability, and crystallinity. He assumed that *cis*-1,4-cyclohexane was converted into the more stable *trans* isomer in the acidic environment of PPA.<sup>9</sup> The identical glass transition temperatures of our three batches of poly(1,4-cyclohexane)-1,3,4-oxadiazole endorses this assumption.

#### PIDA-POD

The 1,1,3-trimethyl-3-phenylindane unit is used as a solubility increasing unit for a number of polymers. For example, Ciba-Geigy's soluble polyimide "XU-218" also contains this bulky and asymmetrical moiety. We have investigated whether incorporation of this unit had the same effect on solubility behavior of the poly-1,3,4-oxadiazoles. Compared to the fully aromatic poly(*p*, *m*-phenylene)-1,3,4-oxadiazoles, the solubility is increased. PIDA-POD is, beside its solubility in concentrated sulphuric acid, also soluble in trifluoro acetic acid.

Using DSC techniques, a glass transition temperature of 330°C (second run, see Table V) was determined for PIDA-POD, which is comparable with the high  $T_g$  reported by Wilson<sup>17</sup> of 341°C (also second run) for a polyamide derived from 1,1,3-trimethyl-3-(*p*-aminophenyl)-5-indanamine and 1,1,3-trimethyl-3-phenylindan-4',5'-dicarboxylic acid.

#### TBI-POD

The preparation of TBI-POD using oleum as a reaction mixture has been reported in a patent by Stephens.<sup>18</sup> The preparation of flexible films from TBI-POD/*m*-cresol solutions is claimed in this patent.

We have initially performed this synthesis in PPA. After solvent casting from formic acid, a polymer with insufficient film-forming properties was obtained, possibly due to the low inherent viscosity. Using a mixture of sulphuric acid and chlorosulphonic acid as a reaction medium resulted in a polymer with a higher inherent viscosity, 0.7 dL/g. Flexible films were obtained from TBI-POD/*m*-cresol solutions after evaporation of the solvent.

#### HF-POD

Incorporation of the polar and bulky 4,4'-(2,2'-diphenyl) hexafluoropropane moiety into the polymer backbone of polyimides has shown to be an effective way of substantially increasing the solubility of these polymers.<sup>19</sup> The HF unit has also been incorporated into the polymer backbone of a poly-1,3,4-oxadiazole by Russian workers.<sup>20</sup> This poly-1,3,4-oxadiazole was prepared by cyclodehydration of a polyhydrazide. The polyhydrazide was, in turn, prepared by a low-temperature polycondensation of the dihydrazide and dichloride of 4,4'-(2,2'-diphenyl) hexafluoropropane dicarboxylic acid. We have prepared HF-POD directly by the less laborious one-step synthesis using 4,4'-(2,2'-diphenyl) hexafluoropropane dicarboxylic acid and hydrazine as monomers. Flexible films were cast from a HF-POD/trifluoro acetic acid solution.

The Russian workers reported a glass transition temperature of approximately 333°C with DTA for their poly-1,3,4-oxadiazole, which is somewhat higher than the value we have found using DSC (see Table IV). This may be due to the difference in preparation history of the polymer.

Solubility tests showed that HF-POD is soluble in THF, chloroform, NMP, *o*-dichloro benzene, and trifluoro acetic acid. The increased solubility of HF-POD compared to the other poly-1,3,4-oxadiazoles is believed to be a result of the more loosely packed polymer matrix, as was found by a Russian worker for trifluoromethyl containing polyamides<sup>20</sup> allowing enhanced solvent diffusion into the polymer matrix followed by its subsequent dissolution.

#### DPE-POD

Incorporation of the diphenyl ether unit results in a less rigid poly-1,3,4-oxadiazole as compared with the corresponding poly(*p*-phenylene)-1,3,4-oxadiazole. Elemental analysis indicates a surplus of hydrogen atoms. This deviation from the theoretical value may be due to a combination of the polymers hygroscopic nature and its relative small number of hydrogen atoms in comparison to carbon, resulting in a large relative error.

A glass transition temperature of 333°C was obtained for DPE-POD using DSC techniques; in the second run of the same sample a much broader glass transition area with a midpoint of approximately 361°C was found. These observations are in agreement with those of Korshak et al.<sup>21</sup> DPE-POD exhibits a good thermal stability as indicated by its high degradation temperature. During a TGA experiment, unclosed 1,3,4-oxadiazole groups undergo cyclodehydration.

Flexible films were cast from a polymer solution in formic acid. Beside its solubility in formic acid, DPE-POD is soluble in DMSO and NMP.

### HF/DPE-POD

Since DPE-POD and HF-POD are each other's extremes in permeability and selectivity,<sup>2</sup> the random copolymer HF/DPE-POD was also prepared using 40%/60% (mol/mol) mixture of both monomers in combination with hydrazine sulphate. Flexible films were cast from a polymer solution in NMP. The glass transition temperature and degradation temperature are in agreement with those of the homopolymers.

### CONCLUSIONS

The glass transition temperature, degradation temperature, and cold crystallization behavior of aromatic poly-1,2,4-triazoles have been studied, where various groups have been introduced onto the pendant phenyl group. Cold crystallization was observed only if macromolecular regularity was maintained to a large extent.

The solubility of poly-1,3,4-oxadiazoles was highly improved with the incorporation of 5-*t*-butylisophthalic, 1,1,3-trimethyl-3-phenylindane, 4,4'-(2,2'-diphenyl)hexafluoro propane, and diphenyl ether groups into the polymer main chain, whereas high glass transition temperatures and degradation temperatures typical for aromatic poly-1,3,4-oxadiazoles were maintained.

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