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New spirodilactam polymers

Hui Zhou [a], Emilio Bucio [c], Sreenu R. Venumbaka [a,*], John W. Fitch [a], Patrick Cassidy [b]

[a] *Institute for Environmental and Industrial Science, Texas State University-San Marcos, CEN 340, 601 University dr., San Marcos, TX 78666, United States*
[b] *Department of Chemistry and Biochemistry, Texas State University-San Marcos, San Marcos, TX 78666, United States*
[c] *Instituto de Ciencias Nucleares, UNAM, México D.F. 04510, Mexico*

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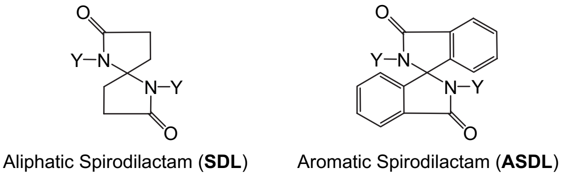
Abstract

New polyether and poly(ether ketone)s containing the rigid 1,6-diazaspiro[4.4]nonane-2,7-dione (spirodilactam) core in the backbone are described. The polymers are soluble in common solvents from which clear, colorless films are readily cast. Excellent thermo-oxidative stability is shown by all of the systems studied with TGA stabilities up to 595 °C or 598 °C in air and argon respectively. Dielectric constants ranged from 2.53 to 3.00 and water absorption results were nil to 3.6%.

Keywords: Spirodilactam; Thermo-oxidative stability; Polyetherketones

1. Introduction

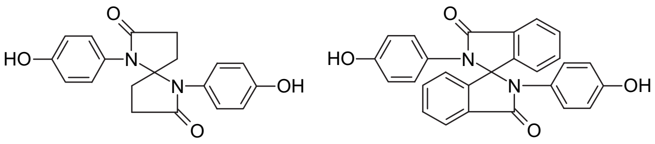
A new class of monomers containing the rigid 1,6-diazaspiro[4.4]nonane-2,7-dione (spirodilactam) core structure has recently been described [1]. Polymers containing this spirodilactam structure in the backbone generally have good thermal stability with relatively high glass-transition temperatures as well. Both aliphatic and aromatic spirodilactam moieties are known (Fig. 1), and the substituent Y groups shown in the figure can be varied widely to give a large number of classes of spirodilactam-derived monomers.



Aliphatic Spirodilactam (**SDL**) Aromatic Spirodilactam (**ASDL**)

Fig. 1. Spirodilactam structures. Y: functional aromatic or aliphatic group (*e.g.* hydroxyaryl, carboxyaryl, alkenyl, alkynyl, *etc*.).

The preparation and partial characterization of the **SDL** and **ASDL** monomers and polymers were described by P.C. Wang of Shell Oil in a series of 49 US patents dating from 1989 to 1992 [2]. Two phenolic spirodilactam-derived monomers [2d,2h,3–6], **1** and **2**, are particularly interesting because they are precursors to a variety of useful classes of polymers (*e.g.* polyarylates, polycarbonates, polysulfones, polyethers, polyetherketones, *etc*.).



1
SDL-diphenol

2
ASDL-diphenol

For example, **1** reacts with 4,4′-difluorobenzophenone to give a soluble thermoplastic polyetherketone with a glass-transition temperature of 232 °C [2g] or with 2,6-dichlorobenzonitrile to give a polyether with $T_g = 267$ °C and possessing good tensile properties [2e]. These results suggest that polyethers and polyetherketones derived from **1** or **2** should have excellent properties suitable for high-performance applications.

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* Corresponding author. Tel.: +1 512 245 2672; fax: +1 512 245 1892.
E-mail address: reddy@txstate.edu (S.R. Venumbaka).

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At this time we wish to report the syntheses and characterization of these new polymers, some of which exhibit extraordinary thermo-oxidative stability as indicated by TGA.

2. Experimental

2.1. Materials

N,*N*-Dimethylacetamide (DMAc), toluene, anhydrous potassium carbonate, 4,4′-difluorobenzophenone, and decafluorobiphenyl were obtained from Aldrich Chemical Company and used as received. Aromatic and aliphatic spirodilactam-derived diphenols were obtained from Shell Chemical Company, and used as received. 2,2-Bis[4-(4-fluorobenzoyl)phenyl]hexafluoropropane (6FBFP) was synthesized in our laboratory [7]. Synthesis of 1,3-bis(1,1,1,3,3,3-hexafluoro-2-pentafluorophenylmethoxy-2-propyl)benzene was as described earlier [8].

2.2. Characterization

^{1}H NMR spectra were obtained on a 400 MHz Varian Fourier Transform NMR Spectrometer. FTIR spectra were obtained on the Perkin–Elmer Spectrum One FTIR spectrometer. TGA data were obtained using a TA Instruments, Inc. TGA Q50. Differential scanning calorimetry was obtained from a TA Instruments, Inc. DSC2920 Modulated DSC. Molecular weights of polymers were determined by Waters Millennium 32 GPC System using a series of Waters Styragel columns with polystyrene standards. The mobile phase is chloroform at a flow rate of 1.0 mL/min. Dielectric constants (determined at 8–12 GHz and reported at 10 GHz) were determined by the NASA Langley Research Center on stacked films of several mils each. The water absorption of the polymers was studied by drying a thin film to constant weight and placing these samples (1 cm^2) in deionized water for 48 h after which they were wiped dry, air dried and weighed. The experiment was repeated three times and the average results are reported.

2.3. Polymerization

Polymerizations were conducted in a reactor fitted with a Dean–Stark water trap under argon atmosphere. In a typical reaction, the aromatic spirodilactam diphenol, **2**, (2.0000 g, 4.6035 mmol), anhydrous K_2CO_3 (1.2725 g, 9.2070 mmol), DMAc (20 mL) and toluene (10 mL) were allowed to react at reflux for 4 h. 2,2-Bis[4-(4-fluorobenzoyl)phenyl]hexafluoropropane (6FBFP) (2.5248 g, 4.6035 mmol) was then added; the reflux was continued for 0.5 h after which time the toluene was removed by distillation, and the polymerization was then completed at 165 °C for an additional 4 h. After cooling, the solution was added dropwise into water with vigorous stirring, and the precipitated polymer was collected by filtration. It was dried, dissolved in chloroform and reprecipitated into methanol. The polymer was dried under vacuum at room temperature overnight.

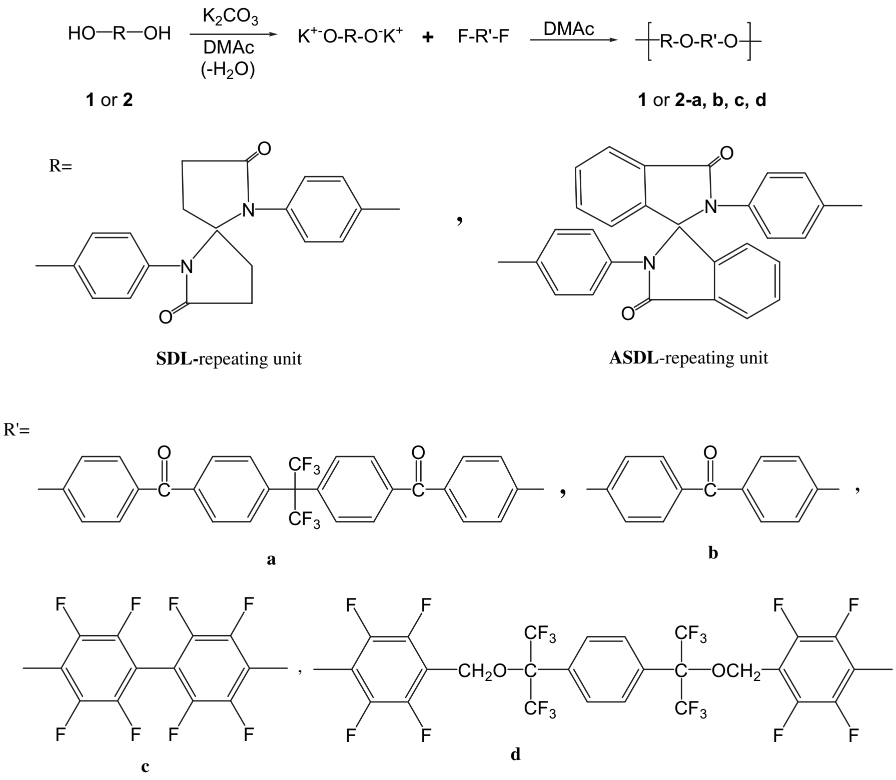
3. Results and discussion

Polymers derived from the diphenol monomers, **1** and **2**, were prepared according to the standard protocol of nucleophilic displacement of fluoride ion from an activated fluoromonomer by a preformed diphenoxide ion in DMAc (Scheme 1) [7]. Although the reactions occurred readily in reasonable yield, some care was required to prevent multiple substitution and resultant crosslinking with monomers **c** and **d**. The polymers were isolated as white fibrous materials by precipitation from chloroform into methanol. Selected results for the **SDL**-derived polymers are found in Table 1 while those for the **ASDL**-derived series are in Table 2. All of the polymers are soluble in many organic solvents and form clear and flexible films.

Diphenol **1**, derived from the aliphatic spirodilactam structure, exhibits somewhat greater reactivity than its aromatic analogue, **2**. Whereas **1** reacts with decafluorobiphenyl at 60 °C for 16 h to give **1c** ($M_w = 6.46 \times 10^4$); reaction at higher temperatures leads to gel formation. In contrast, the reaction of **2** with decafluorobiphenyl at 165 °C for 40 h yielded **2c** ($M_w = 6.56 \times 10^5$), a soluble film-forming material. Similarly, whereas **2** reacts with monomer **d** at 60 °C (24 h) to give soluble film-forming **2d**, it was necessary to prepare **1d** at room temperature to avoid gel formation. It is noted that the polydispersity for **2c** is 13.2, a very large number, which could imply some hyperbranching resulting from some multiple displacement of fluoride ion from decafluorobiphenyl. However, the ^{19}F NMR spectrum of **2c** clearly and simply shows 4,4′-disubstitution has been the dominant reaction occurring in the decafluorobiphenyl monomer. The spectrum gives a single peak in the aromatic fluorine region with very low intensity noise (<1%) in the vicinity. These very weak minor signals are interpreted as arising from additional fluorine displacement leading to a negligible amount branching.

Glass-transition temperatures do not depend on whether monomer **1** or **2** is used. This is not unexpected as both monomers possess very rigid structures. Co-monomer **d**, with a very flexible structure, yields polyethers with the lowest T_g values, 161 °C for **1d** and 167 °C for **2d**. T_g values for the other more rigid polymers range from 240 °C to 279 °C (Tables 1 and 2).

Thermo-oxidative stability as determined by TGA correlates well with structure. In general, polymers derived from the **ASDL**-diphenol, **2**, are more stable than those derived from the simple **SDL** monomer, **1**, as is expected from the aromatic version. Particular note is made of the outstanding stability of **2a** and **2b** which undergo their TGA determined 10% weight loss at about 600 °C in air (Table 2). Interestingly, the stabilities of **1a** and **1b** are higher in air than in argon and **2a** and **2b** are essentially the same within limits of experimental error. This can only be attributed to the fact that a more stable structure is created upon the oxidation of the ‘**a**’ and ‘**b**’ moieties, those with the aromatic ketones, where oxidative crosslinking may occur. The ‘**c**’ and ‘**d**’ units have only aromatic fluorine links and methylene



Scheme 1. Polymer synthesis.

groups, the former of which cannot crosslink with oxidative exposure and the latter of which undergoes oxidative chain cleavage.

Determinations of dielectric constants and water absorption were important for the possibility of use of these polymers for microelectronic technology, and the data correlate well with structure. In general, the **ASDL**-derived polymers exhibit lower water absorption than the simple **SDL** analogues. Neither polymer derived from the highly fluorinated monomer **d** showed any measurable water absorption. Polymers **1d** and **2d** also exhibit the lowest dielectric constants at 2.53 and 2.54 respectively. In general, the **SDL**- and **ASDL**-derived polymers exhibited very similar behavior for dielectric constant related to the structure variables.

Table 1
Selected results for spirodilactam (**SDL**)-derived polyethers and PEKs prepared from **1**

Result	Polymer			
	1a	**1b**	**1c**	**1d**
Reaction time (temp. °C)	4 h (165)	1.5 h (165)	16 h (165)	24 h (30)
Inherent viscosity (dL/g in $CHCl_3$)	1.03	0.71	0.40	0.28
$M_w \times 10^{-3}$ (polydispersity)[a]	613 (7.8)	116 (1.9)	64.6 (1.9)	43.1 (1.9)
T_g (°C)[b]	243	261 (232)[d]	276	161
TGA[c] (°C–10% wt. loss)				
Air	533	471	416	400
Argon	510	458	443	409
%CharYield (800 °C)				
Air	1	4	2	2
Argon	60	56	44	36
Dielectric constant (10 GHz)	2.74	2.93	2.67	2.53
%Water absorption	2.1	3.6	3.1	Nil

[a] Measured by GPC in THF.
[b] Measured by DSC (10 °C/min).
[c] Measured at 20 °C/min.
[d] Ref. [2g].

Table 2
Selected results for aromatic spirodilactam (**ASDL**)-derived polyethers and PEKs prepared from **2**

Result	Polymer			
	2a	**2b**	**2c**	**2d**
Reaction time (temp. °C)	4 h (165)	4 h (165)	40 h (165)	24 h (60)
Inherent viscosity (dL/g in $CHCl_3$)	0.43	0.20	0.23	0.29
$M_w \times 10^{-3}$ (polydispersity)[a]	59.8 (1.6)	35.5 (1.5)	656 (13.2)	139 (3.9)
T_g (°C)[b]	240	255	279	167
TGA[c] (°C–10% wt. loss)				
Air	595	618	499	409
Argon	598	613	501	474
%CharYield (800 °C)				
Air	17	40	1	36
Argon	66	67	51	38
Dielectric constant (10 GHz)	2.80	3.00	2.72	2.54
%Water absorption	1.2	1.9	1.2	Nil

[a] Measured by GPC in THF.
[b] Measured by DSC (10 °C/min).
[c] Measured at 20 °C/min.

4. Conclusions

The spirodilactam containing polyethers and poly(ether ketone)s studied are readily soluble in common organic solvents from which clear colorless films can be cast. TGA determined decomposition temperatures in air ranged from 533 °C to 400 °C in the **SDL** series (**1a–d**) and from 618 °C to 409 °C in the **ASDL** series (**2a–d**). Maximum thermo-oxidative stability is observed in the all aromatic series. Dielectric constants are all 3.0 or lower with **1d** and **2d** having the lowest at 2.5. Water absorption is lowest in polymers in the **ASDL** series and is nil in both of the polymers containing the highly fluorinated repeat unit **b** (Scheme 1).

Acknowledgements

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