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Highly Fluorinated Polymers

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Unclas

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1.0 Introduction

Current work sponsored by the grant at Southwest Texas State University has shown progress in the following areas:

A.) Fluorinated poly(ether-ketone)s containing phosphorus;

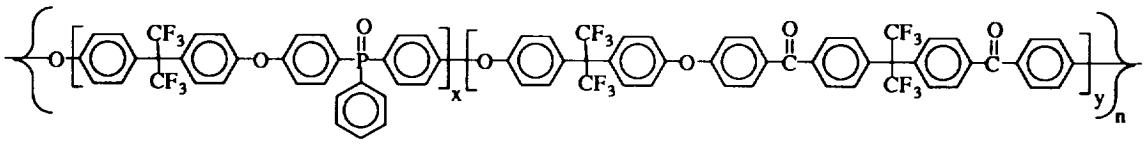
B.) Polyacrylates containing highly polar fluorinated pendant groups;

C.) Polyalkylene-and arylene- difluoroterephthalates

Each area is separately discussed in some detail below.

2.0 Fluorinated Poly(ether-ketone)s Containing Phosphorus

New phosphorus-containing fluorinated poly(ether-ketone)s (P-PEKs) of the composition shown below have been prepared and are currently undergoing characterization. The new polymers are easily soluble in $CHCl_3$,



(x=1, y=3), η_{inh} = 0.78dL/g, 52% Yield

(x=2, y=2), η_{inh} = 0.92dL/g, 71% Yield

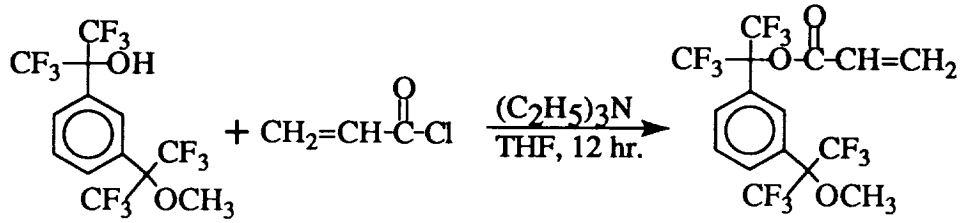
(x=3, y=1), η_{inh} = 0.85dL/g, 61% Yield

CH_3COCH_3, DMAC and THF and readily form tough, flexible films. The generic formula for the repeat unit shown is not meant to imply anything but the stoichiometric ratios of the monomers taken (i.e. the distribution of the phosphorus-containing repeat unit is random). Samples of these new P-PEKs have been submitted to NASA - Langley Research Center for further evaluation of their potential as coatings to be used in low earth orbit.

3.0 Polyacrylates Containing Highly Polar Fluorinated Pendant Groups

3.1 Polyacrylates Derived from 3-(Hexafluoro-2-methoxy-2-propyl)-1-(hexafluoro-2-hydroxy-2-propyl)benzene (1)

Compound **1** is prepared from commercially available 1,3-bis(hexafluoro-2-hydroxy-2-propyl)benzene by reaction with one equivalent of dimethyl sulfate under basic conditions. It is then converted to the acrylate monomer **2** as



1 **2** (1)

shown in eq 1. Polymerization of **2** has been affected both in bulk (12 hr. at 80°, 1:250AIBN) and in solution (36 hr. at 55°, l0 hr. at 90°, toluene, 1:50 AIBN). The results shown in Table I were obtained for both the homopolymer of **2** and its copolymers with methylacrylate (MA) and methylmethacrylate (MMA) in toluene solution.

Table I

Polyacrylates From Monomer **2**

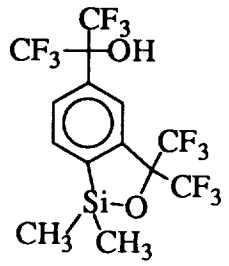
Monomer 2 (mol%)	**MA (mol %)**	**MMA (mol %)**	**η_{inh} (dL/g)**
25	75		0.41
50	50		0.36
75	25		0.31
50		50	0.38

Samples of these new polymers, along with analogous polymers derived from the methacrylate derivative of **1** will be submitted to NASA - Langley Research

Center for thermal analysis (TGA and DSC) in the near future. The polyacrylates prepared in this series are white solids which form clear melts and clear, but brittle films.

3.2 Silicon-Containing Polyacrylates

The reproducible synthesis of compound **3** and its conversion to monomer **4** has finally been accomplished. Earlier attempts to prepare **4** resulted in a



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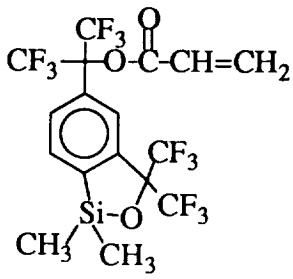

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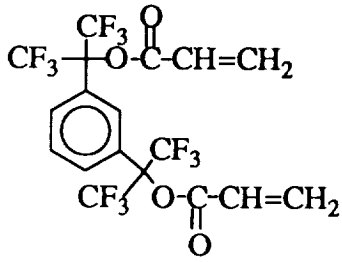

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product contaminated with low concentrations of **5** which, of course, causes crosslinked, insoluble polymers to be obtained. We can now reproducibly prepare pure **4** and report at this time that we have obtained both its homopolymer and 50:50 copolymer with methyl acrylate. Both polymers are soluble in common organic solvents and form brittle films (η_{inh} = 0.20 – 0.23 dL/g). Work in progress is directed toward increasing the molecular weight of these new materials.

4.0 Polyalkylene– and Arylene–difluoroterephthalates

As we have noted in earlier reports, we are completing work on the preparation of a series of polyesters derived from 2,5-difluoroterephthalic acid. We have chosen to study primarily those polymers for which data are available for the non-fluorinated terephthalates. Several samples of the new

difluororerephthalates have been submitted to NASA - Langley Research Center to obtain crystallinity measurements. We hope, eventually, to address the question of the effect of replacing the 2– and 5– hydrogens in terephthalic acid with fluorine. We are particularly interested in changes in T_g, T_m and percent crystallinity in the new polymers.