

Polyetherketones, Polyacrylates and Supercritical CO₂ – Recent Results from SWT's Polymer Research Group

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1.0 Polyetherketones – PEK's

Aromatic polyetherketones, PEK's, because of their thermo-oxidative stability, high strength and resistance to harsh environments, can be used for advanced applications in the electronics and aerospace industries. Much current work on PEK's is directed toward the synthesis of more easily produced materials, which retain the excellent thermal stability of commercial materials.

1.1 Fluorine-containing PEK's

It has been found that certain backbone structures such as hexafluoroisopropylidene, HFIP, greatly improve the solubility of PEK's without reducing their stability¹. Recently we have determined that the HFIP group can be replaced by other functional groups to give PEK's which retain both good solubility and thermo-oxidative stability.

The effect of replacing the HFIP group in 12F-PEK, [Fig. 1: X = Y = >C(CF₃)₂] in the

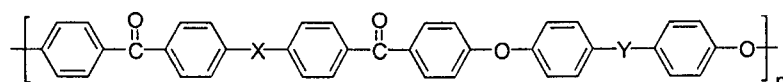


Fig 1: General PEK Formula

PEK structure and on the thermo-oxidative stability of the group used in the replacement. For example, changing X (Fig. 1) to >C(CH₃)₂ has very little effect on the TGA determined 10% weight loss temperature in either air or nitrogen (Table 1).

Table 1: Properties of Polyetherketones

X	Y	η_{inh}^a d/Lg	$T_g^{\circ C^b}$	TGA ^{°C} ^c		% Char Yield @800C
				Air	Nitrogen	
>C(CF ₃) ₂	>C(CF ₃) ₂	0.71	180	537	552	55
>C(CH ₃) ₂	>C(CF ₃) ₂	0.89	174	553	550	55
>C(CF ₃) ₂	>C(CH ₃) ₂	1.09	172	485	542	53
>C(CH ₃) ₂	>C(CH ₃) ₂	0.73	169	485	536	35

^a: measured in chloroform; ^b: measured at 10°C/min; ^c: measured at 20°C/min. 10% weight loss
 However, when the change is made in the Y position (Fig.1), the 10% weight loss temperature (TGA) in air drops by 50 to 70°C (Table 1)².

1.2. Silicon and Phosphorus-containing PEK's

In order to explore further the effect of substitutions in the X position of PEK's (Fig. 1), a dimethylsilyl analogue was prepared (Fig. 2).

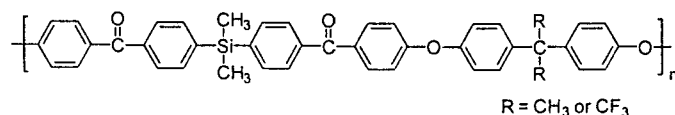


Fig. 2: Dimethylsilyl-substituted PEK's

In addition, the phosphorus-containing analogues were also prepared (Fig. 3). These film-forming, soluble phosphorus-containing polymers all show good thermal stability in both air (513-545°C) and nitrogen (528-549°C) according to TGA results. Char yields at 700°C ranged from 38-58% and Tg's 195-207°C.

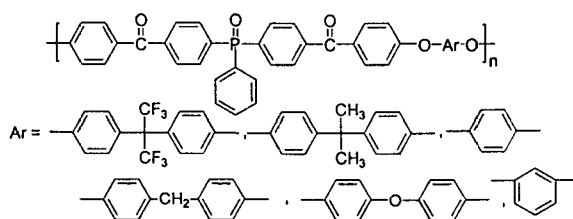


Fig. 3: Phosphorus-containing PEK's

The direct analogues to 12F-PEK in which the $>\text{Si}(\text{CH}_3)_2$ or $>\text{P}(\text{O})\text{C}_6\text{H}_5$ groups are substituted into the X position (Fig. 1) of the PEK structure are compared (Table 2).

Interestingly, the phosphorus-containing analogues show excellent thermal stability in air for $\text{Y}=>\text{C}(\text{CF}_3)_2$ or $>\text{C}(\text{CH}_3)_2$. However, the char yield is significantly less when $\text{Y}=>\text{C}(\text{CH}_3)_2$.

Table 2: Properties of PEK's

X	Y	$\eta_{\text{inh}}^{\text{a}}$ d/Lg	T_g^{c} °C ^b	TGA°C ^c 10%wt. loss		% Char Yield @800C
				Air	Nitrogen	
$>\text{C}(\text{CF}_3)_2$	$>\text{C}(\text{CF}_3)_2$	0.71	180	537	552	55
$>\text{C}(\text{CH}_3)_2$		0.89	174	553	550	55
$>\text{Si}(\text{CH}_3)_2$		0.29	154	482	513	52
$>\text{P}(\text{O})\text{C}_6\text{H}_5$		0.80	207	538	533	58 ^d
$>\text{C}(\text{CF}_3)_2$	$>\text{C}(\text{CH}_3)_2$	1.09	172	485	542	53
$>\text{C}(\text{CH}_3)_2$		0.73	169	485	536	55
$>\text{Si}(\text{CH}_3)_2$		0.15	115	510	527	47
$>\text{P}(\text{O})\text{C}_6\text{H}_5$		0.76	195	528	528	38 ^d

^a: measured in CHCl_3 ; ^b: measured at 10°C/min; ^c: measured at 20°C/min.; ^d: 700°C

The silicon results which show the $\text{Y}=>\text{C}(\text{CH}_3)_2$ analogue to have a higher 10% weight loss temperature by TGA in air than the $>\text{C}(\text{CF}_3)_2$ analogue suggest cleavage at silicon which might be initiated by HF released as polymer decomposes.

1.3 Aliphatic Pendant Groups

A series of PEK's was prepared in which the X-group (Fig. 1) is either HFIP, **6F** or $>C(CH_3)_2$, **6H**, and the Y groups contains either a $-C_{11}H_{23}$ or $-C_{17}H_{35}$ pendant function. The 10% weight loss values in air range from 464°C to 495°C and the value of T_g decreases as expected as the pendant function increases in length.

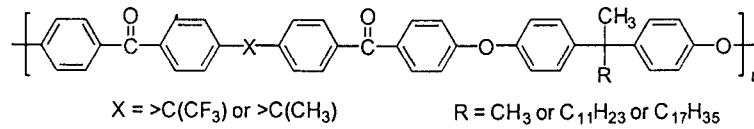


Fig. 4: Alkylated PEK's

1.4 Aryl-fluorine-containing PEK's

A novel series of fluorinated PEK's was prepared from pentafluorobenzoic acid as outlined in Scheme 3. These highly fluorinated polymers also show good thermal stability (499-599°C in N₂) and excellent char yields at 600°C (59-90%). The T_g 's ranged from 152 to 239°C.

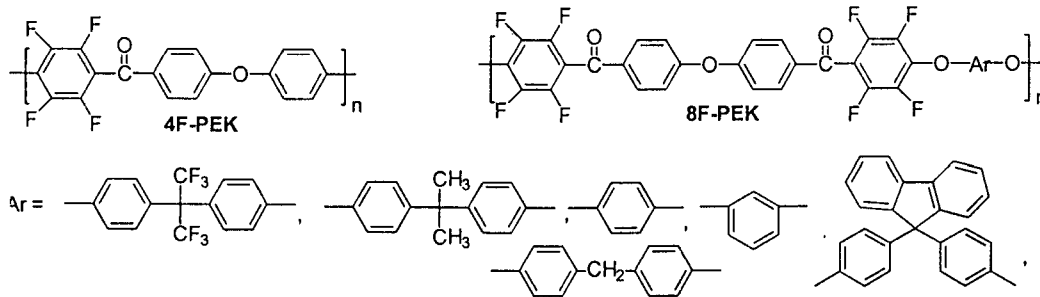


Fig. 5: PEK's Derived from Pentafluorobenzoic Acid

2.0 Polyacrylates

Recent work in our laboratories has been directed toward the preparation of fluorinated polyacrylates derived from hexafluoro-2-phenyl-2-propanol (HFAB)⁵⁻⁷. The HFAB-derived polyacrylates are generally water-clear, transparent, brittle, film-forming materials with TGA determined 10% weight loss temperatures ranging from 360 to 390°C. Typical results are exhibited by polymers derived from the unique silicon-containing monomer, **1** (Fig. 6).

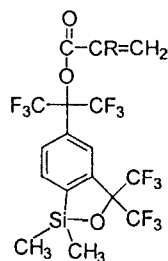


Fig. 6 Silicon-containing Acrylic Monomer (1)

Table 3 summarizes results for both the homopolymer of **1** and copolymer with methylacrylate.⁷ All polymerizations were conducted in bulk at 80-100°C using AIBN as initiator.

Table 3: Properties of New Silicon-containing Polymers

Mole % of 1	Mole % methyl acrylate	$[\eta]^a$ dL/g	TGA, N ₂ (10% wt. loss) ^o C	DSC, N ₂ T _g ^o C	Water Contact Angles ^b
100	—	0.20	386	67	106°
75	25	0.21	374	110	102°
65	35	0.25	371	78	99°
32	68	0.33	368	75	97°

a: measured at 25°C in THF at a concentration of 2.5 g/L. b: average of 10 measurements.

Water contact angles for these polymers suggest that the -CF₃ groups orient toward the surface in their films. Thermal stability decreases somewhat as methyl acrylate is added as a co-monomer, but remains acceptable even when **1** is present at only 30%. Molecular weights of the polymers as indicated by viscosity measurements are low for the homo polymer and increase with increasing methyl acrylate concentration. This behavior is characteristic of all HFAB-derived acrylates studied and likely occurs because of the steric crowding which arises from direct attachment of the HFAB moiety to the acrylate function.

Problems with polymerization of bulky acrylate monomers are commonly observed^{8,9}. In order to address this problem a series of acrylate monomers containing a spacer-arm separating the bulky HFAB group from the acrylate function was prepared, characterized and polymerized (Fig. 7).

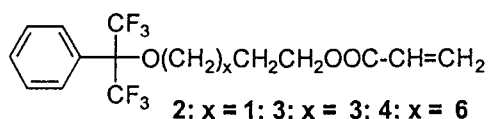


Fig. 7: Spacer-arm-containing acrylate monomers

The modified acrylates, **2**, **3**, and **4** all readily polymerize with the molecular weight increasing regularly with the value of x (Table 4). Interestingly, the thermal stability remains good in the series although the glass transitions are lowered dramatically.

Table 4: Spacer-arm-separated, HFAB-derived Polyacrylates

Monomer	η_{inh} (CHCl ₃) d/Lg	Mol. Wt. (x10 ⁵)	T _g ^o C ^a	TGA ^o C ^a (10% wt.loss)	Water Contact Angle
2	0.45	5.9	11	369	111
3	0.68	17.7	-2	368	108
4	0.71	19.3	-4	358	106

^a: measured at 20°C/min

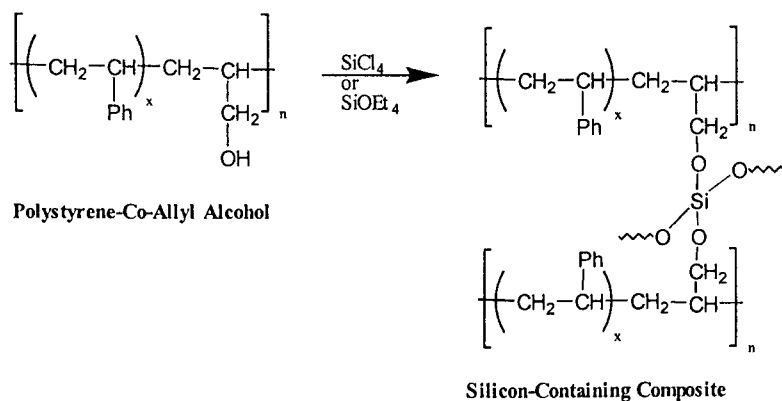
3.0 Syntheses in Supercritical Carbon Dioxide (SC-CO₂)

3.1 Polyacrylates

The solvent, SC-CO₂ has been investigated as a reaction medium for the polymerization of HFAB-derived acrylates using a peroxide initiator. Although the polymer obtained using this technique is very simply isolated by venting the CO₂, molecular weight remain low.

3.2 Silicon-Containing Networks (Blends by Infusion Polymerization)

A poly(styrene-co-allyl alcohol) (PSAA)/silica composite was obtained through a facile method involving infusion of silicon tetrachloride (SiCl₄) into a SC-CO₂-swollen PSAA matrix and subsequent hydrolysis and polycondensation of the silicon-containing penetrant (Scheme 1).



Scheme 1: Formation of the PSAA/SiO₂ Composite

Hydrolysis of the initially isolated material was effected by heating it with water (180°C) in a Parr bomb. The product obtained after the SC-CO₂-assisted infusion of the SiCl₄, but before hydrolysis in the digestion bomb was found to contain 15.75% silicon and 11.83% after hydrolysis. These results indicate that the infusion strategy was successful at impregnating the silicon-containing inorganic precursor into the organic PSAA matrix. Solubility studies also indicate formation of a crosslinked matrix structure. While the native PSAA copolymer readily dissolves in common solvents, formation of the organic/inorganic composite imparted solvent resistance to the hybrid material.

An examination of the thermal data (Table 5) reveals that infusion of the silicon tetrachloride with concomitant formation of the inorganic network results in a slight increase in thermal stability. But the char yield shows a significant increase. The higher thermal stability of the composite results from the crosslinked architecture and the formation of the thermally stable inorganic network.

The T_g of PSAA was observed at 64°C (Table 5), while the T_g was not distinguished in the DSC thermogram of the organic/inorganic composite. This observation is consistent with the dispersion of a silica network in PSAA at the molecular level¹⁴.

Table 5: Thermal Properties of PSAA and PSAA/SiO₂

Sample	T_g , °C	TGA, a °C		% Char yield at 600 °C,	
		air	nitrogen	air	nitrogen
PSAA	64	—	319	< 1	< 1
PSAA/SiO ₂	-	276	332	42	27

To investigate the dispersion quality of the silica network, the morphology of the PSAA/inorganic composites was studied by SEM showing an homogeneous dispersion of silica in the PSAA matrix. The micrographs reveal that the sizes of the silica particles are mostly in the range of 50-200 nm, indicating that the SC-CO₂-assisted infusion/hydrolysis strategy is a good method for preparing organic/inorganic composites. Examination by energy dispersive spectroscopy (EDS) of the central area of a cross section revealed that silicon could be detected throughout the bulk of the sample.

4.0 Acknowledgements

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