A High-Performance Electrostatic Stabilizer for Poly(ether ether ketone) Particles

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Aqueous dispersion prepregging offers a relatively new alternative for processing graphite fiber reinforced, polymer matrix composites. This method, however, requires the matrix resin to be in the form of small particles in a stable aqueous suspension. This paper describes the development of a high-performance suspension stabilizer, poly(pyridine ether-*co*-ether ether ketimine). Acid hydrolysis of poly(pyridine ether-*co*-ether ether ketimine) to poly(pyridine ether-*co*-ether ether ketone) also results in protonation of the pyridine moiety. Therefore, the polymer can function as an electrostatic stabilizer. This general process can be used to form self–stabilizing particles of the pyridine-containing copolymer or for developing stable aqueous suspensions of preformed poly(ether ether ketone) (PEEK) particles.

1. Introduction

Aqueous dispersion prepregging is a relatively new method for applying high performance polymers to graphite fiber tow, which could potentially circumvent many of the environmental and processing problems prominent in melt and solution prepregging. The method, however, requires the matrix resin to be in the form of small particles dispersed in a stable aqueous suspension.[1–5] This paper focuses on the development of a high-performance stabilizer which can be used for suspending poly(ether ether ketone) (PEEK) particles in water (forming stable colloids), thereby facilitating the development of processes for aqueous dispersion prepregging.

Homopolymerization of 4,4′-difluoro-*N*-benzohydroxylideneaniline and hydroquinone, as well as the copolymerization of these monomers with 4,4′-difluorobenzophenone has been established.[6–8] The hydrolysis of these soluble materials to the semicrystalline, insoluble poly(arylene ether), PEEK, in the form of submicron size particles has also previously been reported.[9] Suspensions of these particles in water were demonstrated, but the suspending agents used were poly(amic acid)s at basic pHs, and these materials are not chemically stable under such conditions.[4,9] Because of the elevated use temperatures in the targeted applications of the final composites prepared from these resins, thermo-oxidative stability of all components involved is also a desirable property.

The new stabilizer is a copolymer formed from 4,4′-difluoro-*N*-benzohydroxylideneaniline, 2,6-dichloropyridine and hydroquinone formed according to the scheme outlined in Figure 1. This copolymer forms self-stabilizing particles upon hydrolysis (Figure 2). Alternatively, it can be adsorbed onto PEEK particles from 1-methyl-2-pyrrolidinone (NMP) and subsequently acid hydrolyzed to a poly(pyridine ether-*co*-ether ether ketone) copolymer where the pyridine units have been protonated. In this latter process, the copolymer containing the protonated pyridine units forms an electrostatic stabilizer on the surface of the PEEK particles. It is also believed that pyridine units might exhibit specific interactions with the carbon fiber and therefore provide a good interface between the matrix and the fiber.[10]

Nucleophilic aromatic substitution reaction conditions for incorporating pyridine units into the polyarylene ether ketimine backbone structure, using 2,6-dichloropyridine as the comonomer, have been established. Conversion of the ketimine to the ketone with concurrent pyridine protonation produce a material which functions as a high performance stabilizer for PEEK in water. Dynamic thermal gravimetric analyses of these stabilizers, in air, indicate that significant weight loss does not occur until well above 500 °C. This suggests that these materials may be stable to consolidation temperatures of high-performance polymer matrix composites.

2. Experimental Section

2.1. Materials. 4,4′-Difluorobenzophenone was kindly supplied by ICI Inc. and purified by recrystallization from ethanol. Aniline (Aldrich) was purified by vacuum distillation from calcium hydride. Toluene was purified by washing twice with sulfuric acid, followed by water, 5% sodium bicarbonate, and then water. This was first dried over calcium sulfate and then phosphorus pentoxide and distilled from sodium. The 1-methyl-2-pyrroli-

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[1] Davis, R. M.; Texier, A.; Yu, T. H.; Lyon, K.; Gungor, A.; McGrath, J. E.; and Riffle, J. S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33*, 416.

[2] Texier, A. Ph.D. Thesis, Department of Chemical Engineering, Virginia Polytechnic Institute and State University, 1991.

[3] Lyon, K. R.; McGrath, J. E.; Gungor, A.; Texier, A.; and Davis, R. M. *SAMPE Proc.* **1992**, 37.

[4] Towell, T. W.; Hirt, D. E.; Johnston, N. J. *Int. SAMPE Tech. Conf.* **1990**, *22* (*Adv. Mater.*), 1156.

[5] Hirt, D. E.; Marchello, J. M.; Baucom, R. M. *Int. SAMPE Tech. Conf.* **1990**, *22*, (*Adv. Mater.*), 360.

[6] Mohanty, D. K.; Lowery, R. C.; Lyle, G. D.; McGrath, J. E. *Int. Sampe Conf.* **1987**, *32*, 408.

[7] Lyon, K. R.; Mohanty, D. K.; Lyle, G. D.; Glass, T.; Marand, H.; Prasad, A.; McGrath, J. E. *Int. SAMPE Conf.* **1990**, *36*, 417.

[8] Roovers, J.; Cooney, J. D.; Toporowski, P. M. *Macromolecules* **1990**, *23*, 1611.

[9] Brink, A. E.; Gutzeit, S.; Lin, T.; Marand, H.; Lyon, K.; Hua, T.; Davis, R.; Riffle, J. S. *Polymer* **1993**, *34*, 825.

[10] Nardin, M.; Asloun, E. M.; Schultz, J. *Surf. Interface Anal.* **1991**, *17*, 485.

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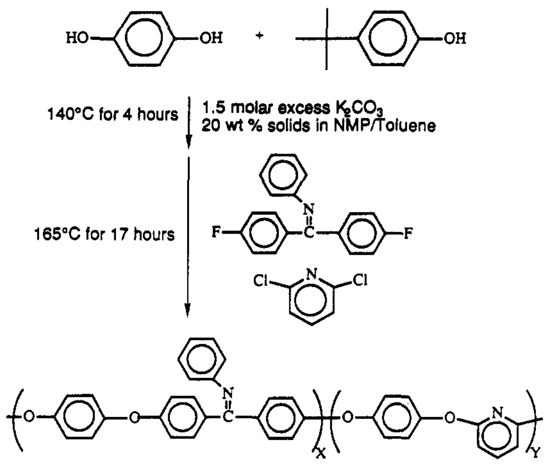

Figure 1. Synthesis of poly(pyridine ether-*co*-ether ether ketimine).

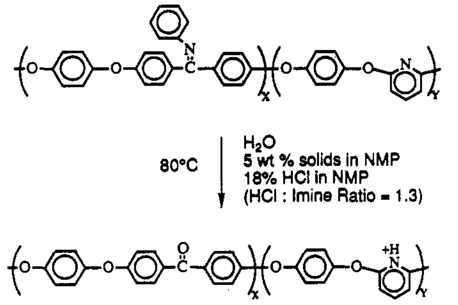

Figure 2. Acid hydrolysis of poly(pyridine ether-*co*-ether ether ketimine) copolymer to poly(pyridine ether-*co*-ether ether ketone) copolymer.

Table I. Monomer Melting Points

monomer	experiment (°C)[a]	literature (°C)	ref
dichloropyridine	87.6–88.4	87–88	17
ketimine	110.5–112.5	111–113	6
hydroquinone	174.8–177.3	174.4–176.6	17

[a] Determined at 1 °C/min.

dinone (NMP) was purchased from Aldrich and purified by vacuum distillation from phosphorus pentoxide. *N,N*-Dimethylacetamide (DMAC) purchased from Fisher, was purified by vacuum distillation from calcium hydride. Molecular sieves (4 Å) were purchased from Aldrich and regenerated by heating to 180 °C in vacuo. Potassium carbonate was dried under vacuum at 180 °C. Hydroquinone was purchased from Aldrich (99.9+% purity) and used as received. 2,6-Dichloropyridine (Aldrich) was recyrstallized from absolute ethanol. 4,4'-Difluoro-*N*-benzohydroxylideneaniline, the ketimine monomer, was synthesized and purified as previously reported.[9] The purity of the monomers was checked by measuring their melting points at a heating rate of 1 °C/min. These values, along with reported values are tabulated in Table I.

2.2 Synthesis of Poly(pyridine ether-*co*-ether ether ketimine). The following is a procedure for the synthesis of a poly(pyridine ether-*co*-ether ether ketimine) via nucleophilic aromatic substitution in a polar aprotic solvent. The molecular weight is controlled to 20 000 g/mol by offsetting the stoichiometry according to the Carother's equation by adding the monofunctional endcapping agent *tert*-butylphenol. This example is for a copolymer containing 10 mol % 2,6-dichloropyridine and 90 mol % 4,4'-difluoro-*N*-benzohydroxylideneaniline (e.g., the ketimine monomer) for the activated dihalo monomers. Copolymers containing mole ratios of 2,6-dichloropyridine to ketimine of 20/80 and 30/70 were synthesized in a similar manner.

Hydroquinone (0.0628 mol, 6.9164 g), *tert*-butylphenol (0.0026 mol, 0.394 g) and potassium carbonate (0.0942 mol, 13.019 g) were dissolved in 50 mL of NMP in a four-neck 250-mL flask equipped with an overhead stirrer, Dean Stark trap, condenser, a nitrogen inlet, and a thermometer. Toluene (50 mL) was added as an azeotroping agent. The reaction mixture was heated to 140 °C for 3 h to dehydrate the system, and then to 165 °C. Once the reaction temperature equilibrated at 165 °C, 0.0574 mol (16.8413 g) of 4,4'-difluoro-*N*-benzohydroxylideneaniline and 0.0064 mol (0.9441 g) of 2,6-dichloropyridine were added with 70 mL of NMP. The reaction was allowed to stir for 17 h at 165 °C. The solution was then cooled to room temperature and diluted with 200 mL of tetrahydrofuran. The polymer was precipitated into methanol/water (80:20), Soxhlet extracted with methanol, and dried under vacuum.

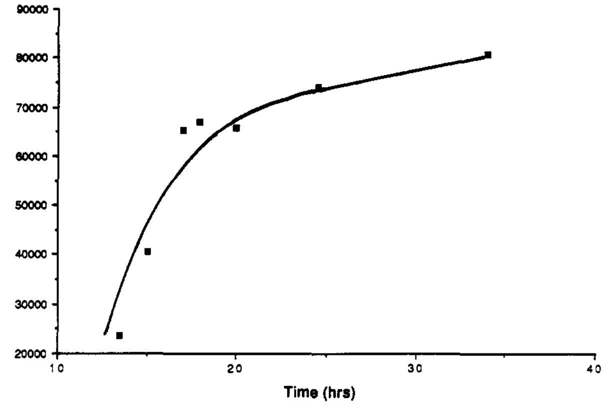

Figure 3. Dependence of weight average molecular weight on reaction time for the synthesis of poly(pyridine ether-*co*-ether ether ketimine) with 20% pyridine (determined by GPC with polystyrene standards).

2.3 Modified Synthesis of Poly(pyridine ether-*co*-ether ether ketimine). The following is the modified procedure for the synthesis of a poly(pyridine ether-*co*-ether ether ketimine) via nucleophilic aromatic substitution in a polar aprotic solvent. The molecular weight was uncontrolled, using a 1:1 stoichiometry. This example is for a copolymer containing 20 mol % 2,6-dichloropyridine and 80 mol % 4,4'-difluoro-*N*-benzohydroxylideneaniline (e.g., the ketimine monomer) for the activated dihalo monomers. Due to the anticipated long reaction time, DMAC was used instead of NMP to minimize the degredation of the solvent. Controlled molecular weight polymers (Dp = 66, and 40) of the same composition were made in a similar manner using *tert*-butylphenol as the endcapping agent.

Hydroquinone (0.0500 mol, 5.5056 g), 4,4'-difluoro-*N*-benzohydroxylideneaniline (0.0400 mol, 11.7326 g) and potassium carbonate (0.0750 mol, 10.3650 g) were dissolved in 90 mL of DMAC in a four-neck 250-mL flask equipped with an overhead stirrer, Dean Stark trap, condenser, a nitrogen inlet, and a thermometer. Toluene (50 mL) was added as an azeotroping agent. The reaction mixture was heated to 140 °C for 3 h to dehydrate the system and then to 160 °C. Once the reaction temperature equilibrated at 160 °C, 0.0100 mol (1.4799 g) of 2,6-dichloropyridine were added with 30 mL of DMAC. The reaction was allowed to stir for 35 h at 160 °C. Samples were taken as a function of time, cooled to room temperature and precipitated into methanol/water (80:20). Gel permeation chromatography analysis was preformed on each sample using polystyrene standards to approximate the molecular weight. This approximate molecular weight was plotted vs. reaction time (Figure 3).

2.4. Hydrolysis of Poly(pyridine ether-*co*-ether ether ketimine). The following is a procedure for the conversion of the imine functionality to the ketone via acid hydrolysis. These conditions were previously optimized in terms of providing the smallest particle size, and for achieving quantitative hydrolysis to the ketone.[9] The acid hydrolysis conditions are such that the pyridine moiety in the backbone is also protonated during this procedure.

The purified, dried poly(pyridine ether-*co*-ether ether ketimin) (2 g) was dissolved in 38 mL of vacuum distilled NMP. Water (1.6 mL) was added to the solution and the mixture was equilibrated in an oil bath at 80 °C. Once this solution was homogeneous, 3 mL of an HCl/NMP solution (6 mL of 12.1 N

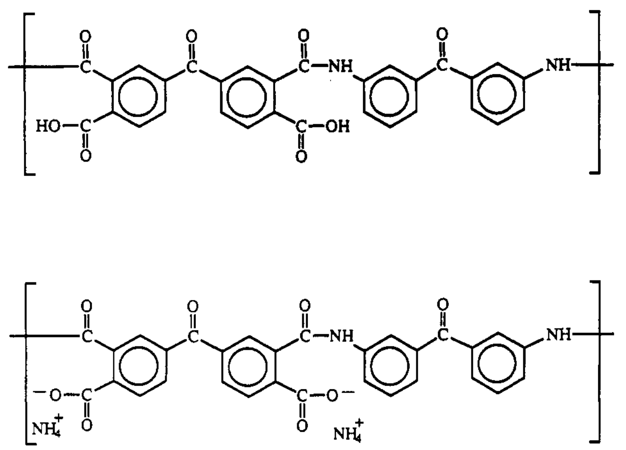

Figure 4. LaRC TPI poly(amic acid) and the ammonium salt.[4]

aqueous HCl in 24 mL of NMP) were syringed into the polymer solution while stirring continuously. The polymer typically precipitated immediately. The precipitate was then filtered and washed with water to remove both the solvent and acid. The washed "particles" were then suspended in water either without a stabilizer or using an aqueous solution of LaRC TPI polyamic acid and ammonium hydroxide (800 mL of water, 26.5 g of polyamic acid, and 7.2 mL of ammonium hydroxide) as a stabilizer[4] (Figure 4). Once the particles were suspended, they were sonicated for 3 min at 75 W to break up any aggregates. The particle size was then measured by a centrifugal particle size analyzer as described in the characterization section below.

2.5. Stabilization of PEEK Particles by Poly(pyridine ether-*co*-ether ether ketimine). PEEK particles formed from the previously reported procedure[9] were suspended in NMP with 10 wt % (compared to PEEK) of the poly(pyridine ether-*co*-ether ether ketimine) copolymer. The copolymer used contained a pyridine to ketimine ratio of 30/70. This suspension was stirred overnight, sonicated for 1 min at 75 W and then hydrolyzed as discussed previously. Following hydrolysis, the suspension was precipitated in water, washed exhaustively with deionized water, and collected as a paste. The particles were then measured by the particular size analyzer as described below.

2.6. Characterization. Thermal analysis was performed on a Perkin-Elmer Series 7 thermal analyzer. Thermal gravimetric analysis was obtained in air with a heating rate of 10 °C/min unless otherwise indicated. Differential scanning calorimitry was preformed in a nitrogen atmosphere also at a heating rate of 10 °C/min. Gel permeation chromatography was preformed on a Waters 150-C ALC/GPC chromatograph equipped with a refractive index detector and a Viscotek Model 100 differential viscometer, unless otherwise indicated. The mobile phase was NMP with a flow rate of 1 mL/min at 60 °C. The columns were Permagel with pore sizes of 500, 10^3, 10^4, and 10^5 Å. The injection volume was 200 μL with a sample concentration of 3 mg/mL. Nuclear magnetic resonance studies were preformed on a Varian Unity NMR spectrometer operating at 400 MHz. Particle size was measured by a centrifugal particle size analyzer (Model SA-CP3) by Shimadzu. This instrument measures the turbidity of the sedimenting suspension and utilizes Stokes law to correlate the sedimentation rate to particle size. The solvent density and viscosity as well as the density of the particle are required.[11] The solvent used was water (ρ = 0.998 g/mL, η = 0.938 cP). The density of the particle was approximatd by that of bulk poly(ether ether ketone) (1.3 g/mL).

Table II. Characterization of Poly(pyridine ether-*co*-ether ether ketimine) Copolymers

mole % pyridine	$\langle M_n \rangle^a$	$\langle M_w \rangle^a$	T_g (°C)	5% wt loss (°C) (nitrogen)
10	7 100	14 300	143	522
20	11 200	22 700	144	509
30	11 100	22 300	135	488
20^b	34 900	65 700	154	502
20^c	19 500	38 800	146	
20^d	11 700	22 600		

[a] Obtained using GPC with universal calibration techniques.
[b] Extended reaction time (35 h), uncontrolled molecular weight.
[c] Extended reaction time (35 h), controlled to Dp = 66 (21 500 g/mol).
[d] Extended reaction time (35 h), controlled to Dp = 40 (13 000 g/mol).

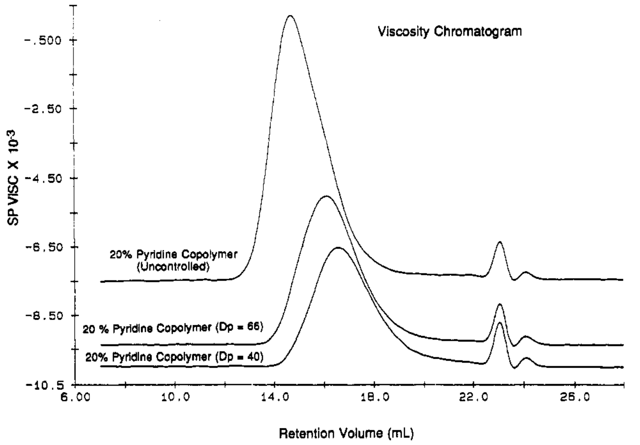

Figure 5. Gel permeation chromatography of poly(pyridine ether-*co*-ether ether ketimine) copolymers; Reaction time = 35 h. (a) Uncontrolled molecular weight. (b) Controlled molecular weight (Dp = 66). (c) Controlled molecular weight (Dp = 40): solvent = NMP, flow rate = 1 mL/min with universal calibration.

3. Results and Discussion

A series of poly(ether ether ketone)s with controlled, varied levels of 2,6-dichloropyridine incorporated as a comonomer have been synthesized in this work. Nucleophilic aromatic substitution polymerizations using dichloropyridine have been reported previously, but only low molecular weight materials were obtained.[12–14] We utilized gel permeation chromatography to evaluate the increase in molecular weight as a function of reaction time for reaction aliquots taken from a poly(ether ketone-*co*-ether pyridine) polymerization containing 20 mol % pyridine (Figure 3). This experiment indicated that, compared to many poly(arylene ether) polymerizations which react by nucleophilic aromatic substitution mechanisms, 2,6-dichloropyridine requires relatively long reaction times (≈35 h at 160 °C) for high, or controlled, molecular weights to be achieved. Table II outlines a comparison of targeted and experimental number average molecular weights for a series of pyridine containing polymers prepared using the 35-h reaction time vs 16 h. The empirical molecular weights shown in this table were calculated using a universal calibration method with a combination of concentration and viscosity GPC detectors. Controlled molecular weight (DP = 66 and 40) poly(pyridine ether-*co*-ether ether ketimine) copolymers with 20% pyridine were synthesized using the extended reaction time, and essentially the expected molecular weights were obtained (Table II and Figure 5).

Proton NMR chemical shifts for protons ortho to a pyridine nitrogen (δ 8.6 ppm) as compared to those ortho to the sulfone on diphenylsulfone (δ 7.95 ppm) suggest

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(11) Provder, T., Ed. *Particle Size Distribution: Assessment and Characterization*; ACS Symp. Series No. 332; American Chemical Society: Washington, DC, 1987.

(12) Kricheldorf, H. R.; Schwarz, G.; Erxleben, J. *Makromol. Chem.* **1988**, *189*, 2255.

(13) Kricheldorf, H. R.; Jahnke, P. *Polym. Bull.* **1991**, *27*, 135.

(14) Kricheldorf, H. R.; Jahnke, P. *Makromol. Chem.* **1990**, *191*, 2027.

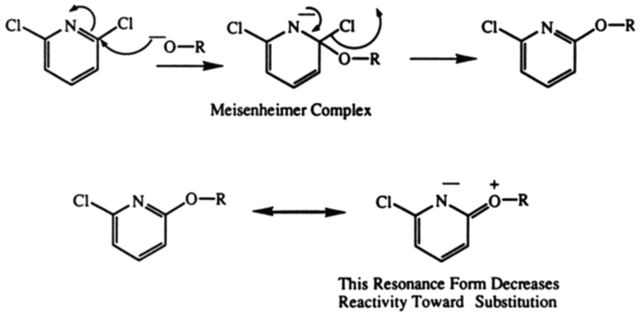

Figure 6. Substitution of 2,6-dichloropyridine.

Table III. Particle Size Analysis of Copolymers

mole % pyridine	median diameter with no stabilizer (μm)	median diameter with LaRC TPI PAA (μm)
0	flocculates	0.3
10	10.5	10.6
20	1.8	1.4
30	11.0	9.1

that the pyridine nitrogen should be more strongly activating toward nucleophilic aromatic substitution than a sulfone group.[15,16] This suggests that 2,6-dichloropyridine should undergo nucleophilic aromatic substitution under less stringent conditions that 4,4′-dichlorodiphenyl sulfone. However, after the first chloro group has been substituted with an ether on 2,6-dichloropyridine, a prominent resonance form exists that deactivates the pyridine ring from nucleophilic aromatic substitution of the second chlorine (Figure 6). Therefore, although substitution of the first chlorine on 2,6-dichloropyridine should be fast, substitution of the remaining chlorine may be correspondingly slow.

A series of copolymers were prepared using 4,4′-difluoro-(*N*-benzohydroxylideneaniline) (the ketimine), 2,6-dichloropyridine, and hydroquinone with systematically varied molar ratios of pyridine to ketimine (10/90, 20/80, and 30/70). All were shown to be amorphous by DSC (Table II) even though homopolymerization of 2,6-dichloropyridine and hydroquinone results in a semicrystalline polymer with T_g = 100 °C and T_m = 272 °C.[12] These amorphous materials are soluble in a variety of solvents including dipolar aprotic solvents (NMP, DMAc, DMSO), chloroform, and toluene.

Once the copolymers had been synthesized, they were hydrolyzed from the ketimine to the ketone form as previously reported.[9] Upon conversion to the ketone, the copolymers crystallized rapidly from the solution in the form of fine particles. This hydrolysis procedure also protonates the pyridine nitrogen in the backbone and provides electrostatic stabilization of the particles when dispersed in water (Table III and Figure 7). Interestingly, the smallest particles were derived from the polymer with the 20/80 pyridine to ketone ratio (the middle composition). It is hypothesized that this may be attributable to a combination of two opposing effects; increasing rates of crystallization with less pyridine units (note that 0% pyridine would be PEEK), but increased electrostatic stabilization with more pyridine. A detailed analysis of suspension stability as a function of chemical structure and charge will be the focus of considerable future work.

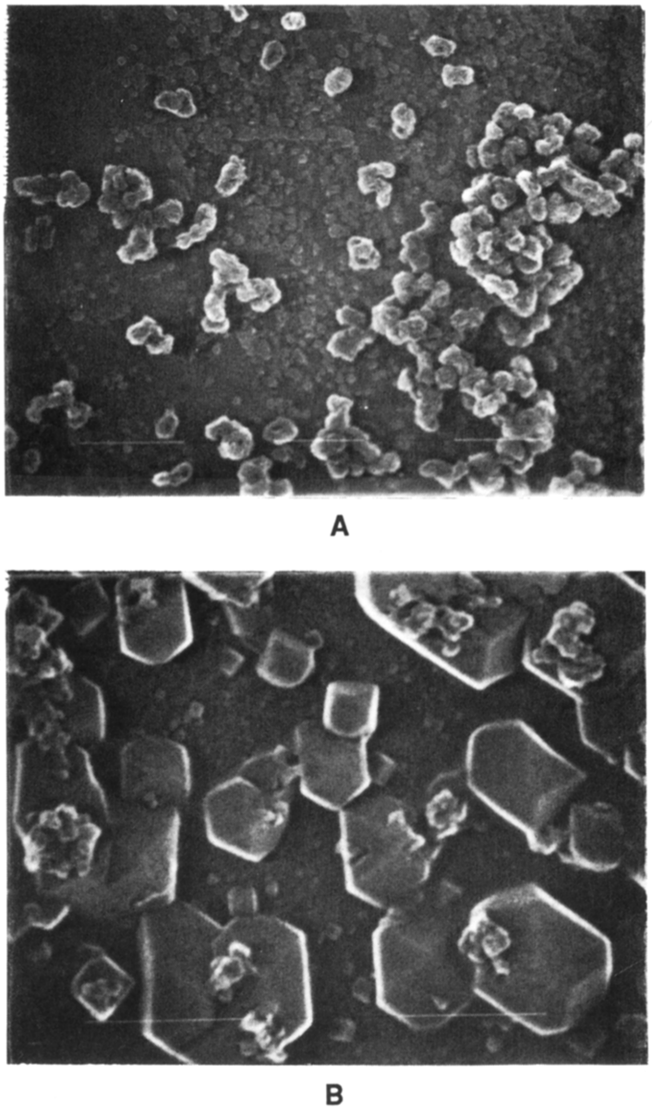

Figure 7. Scanning electron micrographs of 20% pyridine copolymer: (A) Magnification = 3 200 with 5-μm marker. (B) Magnification = 50 000 with a 0.5-μm marker.

Our major interests in these polymers were as suspension stabilizers for preformed PEEK particles. Aqueous suspensions were prepared using a range of PEEK particle sizes (0.3, 15, 100 μm). This was done by preparing a solution of the poly(pyridine ether-*co*-ether ether ketimine) polymer in NMP and adding the preformed PEEK particles. The ratio of stabilizer to PEEK particles was 10/90 by weight. These suspensions were stirred for 24 h to allow the stabilizer to adsorb onto the particle surfaces, then the copolymer stabilizer was acid hydrolyzed as done previously. When poured into water and sonicated, these particles formed a stable suspension. The larger PEEK particles (15 and 100 μm) settled out within a few hours, but upon agitation were easily resuspended. The smallest PEEK particles (0.3 μm) formed suspensions that were stable for 3–5 days but did eventually flocculate. For comparison, the same procedure was followed in the absence of the pyridine copolymer, and only flocculation occured (Table IV).

Thermal properties of the poly(pyridine ether-*co*-ether ether ketone) materials were probed using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) (Table V). Importantly, even with significant levels of pyridine incorporated into the polyarylene

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(15) Hedrick, J. L.; Labadie, J. W. *Macromolecules*, **1990**, *23*, 1561.
(16) Hedrick, J. L. *Polymer* **1992**, *33* (7), 1399.
(17) Perrin, D. D., Armarego, W. L. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: New York, 1988.

Table IV. Particle Size Data for PEEK Particles

particle size (μm)	stabilizer	median diameter (μm)[c]
0.3[a]	none	flocculates
0.3[a]	LaRC TPI PAA	0.3
0.3[a]	30% pyridine copolymer	1.1
15[b]	30% pyridine copolymer	14.8
100[b]	30% pyridine copolymer	100.5

[a] Previously determined (ref 9). [b] Received from ICI and sieved to this size. [c] Determined by particle size analyzer as described in the Experimental Section.

Table V. Characterization of Poly(pyridine-*co*-ether ether ketone) Copolymers

mole % pyridine	T_g (°C)	T_m (°C)	5% wt loss (°C)[a]
0	143	335	574
10	126	330	543
20	126	316	526
30	121	300	519

[a] Determined in air with a heating rate of 10 °C/min.

ether ketone backbone, the polymers readily crystallized, and melting points remained high. Additionally, significant weight loss was not apparent by dynamic TGA until temperatures in excess of 500 °C were reached.

4. Conclusions

A high-performance electrostatic stabilizer was developed by the incorporation of 2,6-dichloropyridine as a comonomer into poly(ether ether ketimine). This copolymer, upon hydrolysis, forms self-stabilizing particles. These copolymers can also be used as stabilizers for aqueous suspensions of preformed PEEK particles. There is ongoing work examing both the properties of suspensions using these materials, as well as the utility of these copolymers as binding agents in aqueous dispersion prepregging.

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