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Preparation and characterization of a polyphenylene ether and Nylon-6 block copolymer

Herbert S.-I. Chao and Thomas W. Hovatter

General Electric Corporation Research and Development Center, Schenectady, NY 12301, USA

Summary

A block copolymer of PPO® (1) and Nylon-6 was prepared through modification of the hydroxyl end group of the polyphenylene ether (PPE) with cyanuric chloride or 4,4'-difluorobenzophenone and subsequent anionic polymerization of ε-caprolactam using the modified PPE as the promoter. The pure copolymer was isolated by selective solvent extraction, using chloroform to remove PPE homopolymer and unreacted ε-caprolactam, and formic acid to remove Nylon-6 homopolymer. The copolymer has two melting points indicative of the Nylon and PPE segments. Its composition has been determined by carbon-13 NMR and elemental analysis.

Introduction

One way to improve the solvent resistance property of polyphenylene ether may be to disperse the resin in a crystalline polymer matrix such as Nylon-6 (poly-(ε-caprolactam)). Simultaneously, the relatively hydrophobic PPE resin can decrease the water absorption of Nylon-6 in the dispersion. However, physical blends of PPE and polyamides produce brittle materials which delaminate easily. A solution to the incompatability is to create a chemical linkage between the two polymers.(2) A copolymer may also serve as a compatibilizing agent for the homopolymers and blend properties may be tailored by controlling the copolymer content in the blend.

In this article, the preparation and analysis of a block copolymer of PPE and Nylon-6 is described.

Experimental

Commercially available compounds were used as received without further purification, unless noted. The PPO® was obtained from the General Electric Co., Selkirk, New York. The sodium hydride used was a 60% dispersion in mineral oil. The Nyrim® catalyst(3) was purchased from the Monsanto Chemical Company. The GC data was obtained with a Shimadzu GC-9A gas chromatograph using a Supelco 3% SE-30 (6' x 1/8") column or a Supelco SPB-1 (30 meter, 0.32mm I. D.) column with a Shimadzu C-R3A integrator. Fourier transform infrared spectra were obtained from a Nicolet 7199 spectrophotometer at one wavenumber resolution using CS_2 as the solvent for PPE resin. Melting points were obtained on a Thomas Hoover apparatus and are uncorrected. NMR spectra were obtained with a Varian XL-300 (^{1}H NMR, 300 MHz, ^{13}C NMR, 75 MHz) spectrometer and a Varian EM-390 (^{1}H NMR, 90 MHz) spectrometer relative to an internal tetramethylsilane standard. High resolution mass spectra were recorded on a VG ZAB2F spectrometer at a resolution of 10000 (10% valley).

A DSC thermogram of the copolymer was obtained using a DuPont 9900 with a 912 Dual Cell analyzer. A heating rate of 20 ^{o}C/min. was employed and the flow rate of nitrogen gas was 20 mL/min. TGA thermograms were obtained using a DuPont 9900 with a 951 Thermal Analyzer. The heating rate was 10 ^{o}C/min. and the nitrogen gas flow rate was 150 mL/min.

Promoter Efficiency Test

A standard test was carried out in a 25 mL Erlenmeyer flask in a nitrogen atmosphere. To 10.0 g (0.09 mol) of melted ε-caprolactam at 130 ^{o}C was charged 0.4 g (0.01 mol) of sodium hydride portionwise to generate sodium caprolactamide in ε-caprolactam. After hydrogen evolution ceased at 150 ^{o}C, the promoter (0.001 mol) was added all at once. The time span from promoter addition to polymer formation (based on viscosity buildup) was recorded, and was used to determine the efficiency of promoters. A promoter was considered a good candidate if the polymerization occurred within 60 seconds.

Synthesis of 2,4-dichloro-6-(2',4',6'-trimethyl)phenoxy-s-triazine (2).

In a three-necked round bottom flask were charged 20 mL of toluene and 0.80 g of NaH under N_2. To this suspension was slowly added a solution of 2.72 g (0.02 mol) of mesitol in 30 mL of toluene The mixture was heated to reflux to ensure the complete formation of sodium phenoxide and then cooled to -78 ^{o}C. The cyanuric chloride (1) was added as a solid, and the solution turned light orange. After stirring at -78 ^{o}C for another 15 minutes, the reaction mixture was gradually warmed to room temperature. The salt was removed by filtration, and the filtrate concentrated in vacuo to give 3.5 g of crude product. It was recrystallized from pet ether (b.p. 36-60 ^{o}C): m.p. 124-125 ^{o}C; ^{1}H NMR ($CDCl_3$) 2.1 (s,6H), 2.3(s,3H), 6.9 (s,2H); ^{13}C NMR($CDCl_3$) 16.10, 20.68, 128.93, 129.50, 136.20, 146.37, 170.62 and 173.09.

Synthesis of 2-chloro-4,6-bis(2',4',6'-trimethylphenoxy)-s-triazine (3).

This compound was made in H_2O-acetone by following a literature procedure.(4) A preparative method in a non-aqueous solution was also developed. The reaction process was similar to the preparation of 6 except the molar ratio of 1 to mesitol became 1 to 2 respectively, and the reaction was conducted at room temperature for one hour. The recrystallized material (pet ether 60-110 ^{o}C) had a melting point of 198 ^{o}C (lit(4) 198-200^{o}C). ^{1}H NMR ($CDCl_3$) 2.1 (s,12H), 2.3 (s,6H), 6.9 (s,4H);

^{13}C NMR ($CDCl_3$) 16.04, 20.60, 129.04, 129.19, 135.61, 146.55, 172.05 and 173.83.

Synthesis of cyanuric chloride-modified PPE resin 4.

In 800 g of toluene was dissolved 200 g of PPE resin to form a 20% polymer solution. To this solution, 1 g of NaH was added portionwise. After all the H_2 evolution ceased (ca. 45 min), cyanuric chloride (4.61 g, 0.025 mol) was added as a solid. The reaction temperature was maintained at 75 °C overnight under nitrogen and then diluted with 1000 g of toluene to form a 10% polymer solution. The end-modified PPE resin was precipitated and washed with acetonitrile. The resulting modified polymer was dried in a vacuum oven at 100 °C overnight. The material had a nitrogen content of 0.47% (cf. nitrogen content in the unmodified resin is 0.13%).

Anionic Polymerization of ε-caprolactam promoted by 4.

To a dry 300 mL, three-necked flask fitted with a stirrer, a nitrogen inlet and a condenser were added 20 g of 4 and 70 g of ε-caprolactam. The suspension was heated to 180 °C for three hours to form a homogeneous solution. In a separate, dry 50 mL flask fitted with a magnetic stirrer and a N_2 inlet were placed 10 g of ε-caprolactam. To this flask at 130 °C was added 1.0 g of NaH. The catalyst solution was transferred to the PPE-caprolactam solution, and the oil bath temperature was maintained at 180 °C. In 30 seconds, the reaction became too thick to stir. It was then cooled and from the isolated material, 25-30% copolymer was recovered as determined by selective solvent extraction (vide infra). The elemental analysis of the isolated copolymer was 67.4% of carbon, 8.2% of hydrogen and 7.7% of nitrogen. After a straightforward calculation, the composition of the copolymer was found to be 66% nylon and 34% PPE resin by weight. DSC of the copolymer showed two distinct melting points at 220 °C (Nylon 6) and 267 °C (PPE).

Control experiment - Anionic polymerization of ε-caprolactam by phthalic anhydride.

The same experiment was conducted as above except unmodified PPE resin was used with 0.50 g (3.3 mmol) of phthalic anhydride as the promoter. The resulting material, as expected, contained only 1-2% PPE-Nylon 6 copolymer after selective solvent extraction.

General procedure for the determination of copolymer content.

The crude product was ground in a two speed Retsch grinder to a fine powder. It was extracted overnight in a Soxhlet apparatus with $CHCl_3$ to remove unreacted ε-caprolactam and homopolymer PPE resin. The residue in the thimble, after drying, was stirred overnight in formic acid to dissolve homopolymer Nylon 6. The PPE-Nylon 6 copolymer was recovered after filtration through a sintered glass funnel.

^{13}C NMR method of determining the composition of PPE-Nylon 6 copolymer.

A highly polar solvent combination, i.e., 1,1,2,2-tetrachloroethane/2,2,2-trichloroethanol (1:1 by volume) was used to dissolve the copolymer for NMR measurement. The sample was usually run overnight with the addition of small amount of chromium acetylacetonate as a relaxation agent. ^{13}C NMR assignment: (Nylon 6 portion) 25.20, 26.18, 28.68, 36.28, 39.48, and 174.72; (PPE portion) 16.77, 114.35, 132.41, 145.09, and 154.34. The ratio of Nylon 6 to PPE was determined by using the two peaks, 36.28 ppm and 145.09 ppm, to represent Nylon 6 and PPE, respectively. It should also be noted that the solvent had difficulty in dissolving copolymers having a very high Nylon 6 content.

Synthesis of 5.

In a three-necked 100 mL flask equipped with a condenser, a nitrogen inlet, and a stirring bar were charged 50 g of ε-caprolactam, and 1.36 g (0.01 mol) of mesitol. The flask was heated to 100 °C to melt the contents, and then 0.44 g (0.01 mol) of NaH was added. After H_2 evolution ceased, the mixture was heated to 150 °C and 2.18 g (0.01 mol) of 4,4'-difluorobenzophenone (6) was added. The reaction was continued for another hour at 150 °C before it was cooled to room temperature. The reaction mixture was then diluted with water and extracted with CCl_4. The organic layer was concentrated after drying ($MgSO_4$) to obtain crude 5 as a thick oil in 85 % yield. The purity of 5 was found to be higher than 90% through a capillary GC analysis. An analytically pure sample was obtained through a preparative GC collection. ^1H NMR ($CDCl_3$) 2.1 (s,6H), 2.3 (s,3H), 6.8-7.2 (m,6H), 7.7-7.9 (m,4H); FT-IR (neat): 2921, 1657, 1600, and 1238 cm^{-1}; HRMS calcd for $C_{22}H_{19}O_2F$ m/e 334.1370, found m/e 334.1370.

A one-step reaction for the modification of PPE resin with 4,4'-difluorobenzophenone in ε-caprolactam and the copolymer formation thereof.

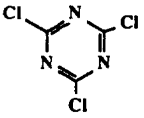
To a three-necked flask equipped with a mechanical stirrer, a condenser, and a nitrogen inlet were added 140 g of ε-caprolactam and 40 g of PPE resin. The temperature of the oil bath was raised to 180 °C to melt the contents and form a homogeneous solution. To the solution was added 0.12 g (0.003 mol) of NaH to generate sodium phenoxide. After 15 minutes of stirring, 0.58 g (0.003 mol) of 4,4'-difluorobenzophenone was added, and the capping reaction was conducted for 30 minutes. Finally, 0.92 g (0.023 mol) of NaH was added to finish the copolymer formation.

Results and Discussion

During the anionic polymerization of ε-caprolactam, the addition of a promoter such as an acyl chloride, anhydride, or isocyanate can significantly lower the reaction temperature from 250°C to about 130°C.(5) Since PPE resin and ε-caprolactam form a homogeneous solution at 120°C, a homopolymer blend was prepared by adding sodium hydride base and a promoter (e.g. phthalic anhydride) to the solution at 150°C. This method generated a physical blend of PPE and Nylon 6. The attachment of a promoter group to PPE resin end groups should effect the formation of a PPE-Nylon 6 block copolymer through anionic polymerization. Two compounds, cyanuric chloride and 4,4'-difluorobenzophenone were selected as the linking molecules for the copolymer. A phenyl ester-like linkage is expected to form as the phenolic end group of PPE reacts with cyanuric chloride, and it is known to be relatively labile to basic medium. On the other hand, an ether linkage will be produced as the PPE end group reacts with 4,4'-difluorobenzophenone, and it should be more stable in the anionic polymerization conditions.

Cyanuric chloride

Cyanuric chloride 1 and the model compounds 2 and 3 (prepared from 1 with mesitol to model the reaction with the PPE end group) were excellent promoters. Starting with 20% by weight cyanuric chloride-modified PPE resin 4 in ε-caprolactam, and 1% by weight NaH, the reaction product contained 25-30% by weight of PPE-Nylon copolymer after selective solvent extraction. When a control experiment was conducted with unmodified PPE resin and phthalic anhydride to promote the Nylon 6 formation, the final blend contained only 1-2% of copolymer.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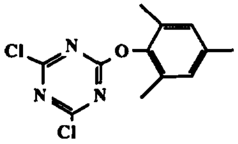
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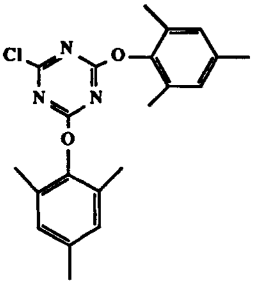
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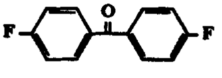
4,4'-Difluorobenzophenone

Both 6 and 7 were less efficient promoters in the standard promoter test. For 6, the viscosity build up required 4 minutes, and for 7, a higher temperature (170 $^{\circ}$C) was needed to initiate the reaction. When the Nyrim base was used instead of sodium hydride, 6 and 7 did not show any promoting ability even at 220°C.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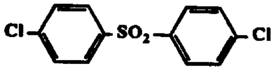
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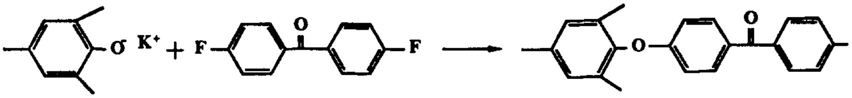
In toluene, the sodium salt of mesitol failed to displace the fluorine of 6 (eq. 1), even with the addition of tetrabutylammonium bromide as a phase transfer catalyst. However, 5 could be selectively generated in ε-caprolactam by addition of one equivalent of NaH to the mesitol solution. This reaction apparently occurred due to the large pK_a difference of phenol and ε-caprolactam. At 150 °C, the nucleophilic displacement went smoothly to generate 5 as the major component. Based on the model compound studies, commercial PPE resin (1) was dissolved in ε-caprolactam and then one molar equivalent, based on PPE end groups, of both sodium hydride and 6 were sequentially added. After 30 minutes, a large excess of sodium hydride was added to finish the ε-caprolactam polymerization. Through selective solvent extraction, 25% copolymer was isolated from the final crude material. This experiment demonstrates the feasibility of a one-step process for the preparation of PPE-Nylon 6 copolymer.



(eq. 1)

5

The ^{13}C NMR spectrum of the isolated PPE-Nylon 6 copolymer (Fig. 1) shows 30% PPE and 70% Nylon 6 by weight. The thermogravimetric analysis of the copolymer (Fig. 2) showed that the material starts decomposing at 350 °C. DSC of the copolymer (Fig.3) showed a distinct melting point at 221 °C (Nylon 6) and a broad melting point between 250-260 °C (PPE).

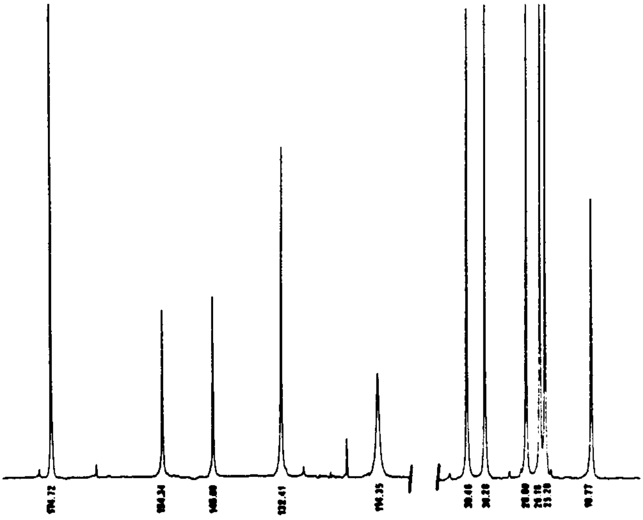


Figure 1. ^{13}C NMR spectrum of PPE-Nylon 6 block copolymer.

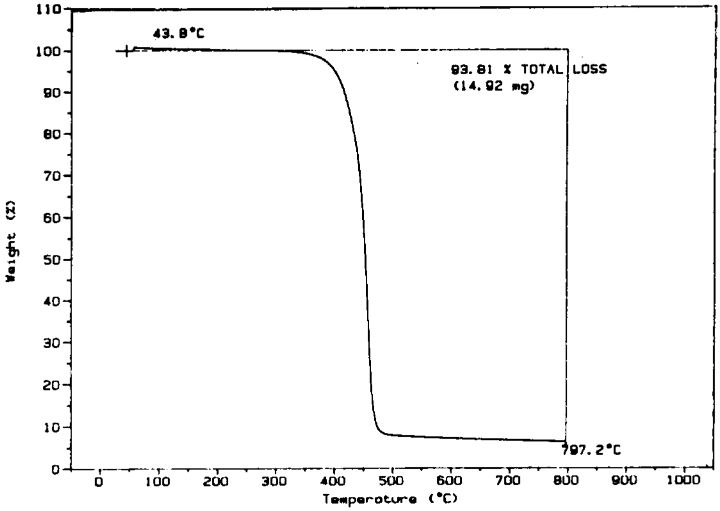


Figure 2. TGA thermogram of PPE-Nylon 6 block copolymer.

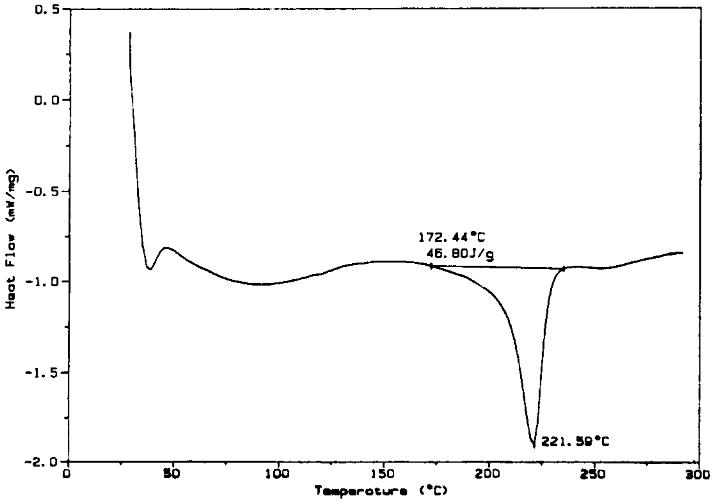


Figure 3. DSC thermogram of PPE-Nylon 6 block copolymer.

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References

1. PPO® is a registered trademark of the General Electric Company. It is a homopolymer of 2,6-xylenol, having a number averge molecular weight of 15,000-20,000.
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