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PREPARATION AND CHARACTERIZATION OF NITRATED POLY(ARYL ETHER KETONE)

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ABSTRACT

The controlled nitration of poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) (PEEK) is reported. Polymers with five different levels of nitration were prepared. IR spectroscopic studies and elemental analyses were performed to determine the substitution pattern; thermal analyses determined the dependence of the glass transition temperature measured by DSC, and the degradation behavior on the level of nitration was measured by TGA, combined with other analyses. All nitration products were amorphous, with T_g going up and thermal stability going down with increasing nitration. Room temperature solubility in 14 solvent, with a range of solubility parameter values, has been evaluated and reported for the nitrated PEEKs.

INTRODUCTION

Poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) (PEEK) is a semicrystalline thermoplastic produced from hydroquinone and 4,4′-difluorobenzophenone. With a melting point (T_m) of ~335°C and a glass transition temperature (T_g) of 149°C, PEEK possesses excellent thermal stability, electrical properties, and chemical and flame resistance. However, there is a sharp drop in modulus and an increased tendency to creep above the T_g [1]. Several researchers have studied the properties of postpolymerization-modified PEEKs, either to take advantage of or to improve certain properties for specific applications.

Marvel and coworkers studied modifications of various poly(aryl ether ketones) by sulfonation with chlorosulfonic acid or sulfur trioxide/triethyl phosphate, with subsequent conversion to various sulfonamides [2–4]; they reported sizable increases in T_g (with the increases approximately proportional to the degree of substitution), significant decreases in thermal stability, and a decrease in molecular weight (as determined by solution viscosity). Karasz, MacKnight, and coworkers studied sulfonated PEEKs in both the polysulfonic acid and neutralized salt forms [5–8]; they reported that sulfonation in sulfuric acid was essentially free of degradation, provided the acid concentration was $<100\%$, and that the polymer was completely amorphous, except at very low sulfonation levels. For the free acid polymer, T_g increased monotonically with the degree of sulfonation; the neutralized salts (sodium and zinc) possessed even higher T_gs than the free acid polymer with the same sulfonation level. The thermal stability of the sulfonic acid polymer was found to be significantly less than that of the original PEEK; stabilities of the neutralized polymers were intermediate to the free acid and unmodified polymers. Strong evidence for crosslinking by sulfone formation was found when 100% sulfuric acid was used [6].

Several improvements of PEEK properties by crosslinking have been reported. Electron-beam-induced crosslinking of PEEK leads to slight increases in both T_g and shear modulus above T_g, as well as some chain scission [9]. Crosslinking by the inclusion of elemental sulfur (up to 2%) resulted in an increase in T_g of about 20°C, as well as a 50% increase in modulus at 200°C; chain scission was also observed [10, 11]. Use of an aromatic diamine for crosslinking by imine formation at the polymer carbonyl resulted in increases in T_g, dynamic storage modulus, and thermal stability over PEEK [12].

This paper describes the preparation and characterization of nitrated PEEK (NPEEK). This polymer possesses properties significantly different from PEEK and has potential uses as an intermediate for the inclusion of functional groups (such as amines) which could be used for crosslinking or other chemistry.

EXPERIMENTAL

Materials

PEEK powder was supplied by ICI, Wilton, England, with reported M_n and M_w values of 14,100 and 38,600, respectively. Methanesulfonic acid (MSA) (99%, Aldrich), nitric acid (assay 69.0–71.0%, Fisher), and all solvents (reagent grade or better) were used as received. Twice-distilled water was used for precipitation and washing.

Nitration

Polymers with five different degrees of nitration were prepared; the degree of nitration of the polymer was controlled by varying the quantity of nitric acid introduced. Samples of PEEK powder were dissolved in MSA (c = 50.0 mg/mL) and stirred at room temperature until completely dissolved (~24 hours); the solutions were deep red and transparent. Separately, a certain volume of nitric acid and an equal volume of MSA were mixed and allowed to equilibrate for 15 minutes. Ratios of the volume of nitric acid (in mL) to amount of PEEK (in g) were (1) 0.10, (2) 0.20, (3) 0.25, (4) 0.50, and (5) 0.75. The acid mixtures were added dropwise to the respective polymer solutions with continuous stirring to ensure homogeneity. Upon addition of the nitric acid, the colors of the solutions gradually changed from red to brown. Precipitation was observed for reactions (4) and (5) (highest nitric acid/PEEK ratios). In (4), a small amount of yellow precipitate evolved over time, and the solution became cloudy; in (5), a larger amount of yellow precipitate appeared within 5 minutes of addition of the nitric acid, and the entire solution became opaque. No precipitation was observed in the other three polymer solutions (lowest HNO_3/PEEK ratios). Stirring was continued for 30 minutes, all at ambient temperature and pressure, after the addition of the nitric acid.

Complete polymer precipitation was achieved by dropwise addition of each solution to water (water:acid volume ratio >5:1), with the mixtures chilled to ensure complete precipitation. Each polymer was collected by filtration, washed with a 50:50 (v/v) mixture of water and methanol to remove acid, shredded in a blender (as needed), and washed thrice more with the water/methanol mixture. The nitrated polymers (NPEEKs) were dried under vacuum at 100°C for 24 hours, then stored in a vacuum desiccator over calcium sulfate until used.

Characterization Methods

Elemental analyses of the modified PEEKs were performed by the University of Massachusetts Microanalysis Laboratory; carbon, hydrogen, and nitrogen analyses were conducted using a Control Equipment Corp. Elemental Analyzer, utilizing a modified Pregl-Dumas (combustion) technique. As a proper reference, the analysis of the parent PEEK showed no nitrogen present.

The infrared (IR) spectra were obtained using an IBM IR/32 FT-IR instrument with continuous dry nitrogen purge before (~30 minutes) and during scanning. The spectra were taken at room temperature in the range of 4000–40 cm^{-1} with 2 cm^{-1} resolution, and were signal averaged from at least 200 scans. All samples were prepared by casting from dimethyl acetamide onto KBr pellets; the polymer solutions were heated as necessary to achieve complete solubility for casting.

The T_g and melting behavior of samples were determined by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-4. Calibrations for temperature and heat flow were made prior to sample analysis using indium, tin, and zinc samples. Samples (4–12 mg) were heated under nitrogen at a standard scanning rate of 20°C/min up to 400°C for virgin PEEK, 300°C for the nitrated PEEKs, and 250°C for the reduced NPEEKs. All samples were scanned twice to allow for the removal of residual water, with results determined from the second heating scan.

Thermogravimetric analyses (TGA) were carried out using a Perkin-Elmer TGS-2 with a heating rate of 20°C/min in the 50–850°C range. Sample sizes were 5–10 mg; a helium atmosphere was used for all samples. Study of the mechanism of degradation was made using an NPEEK sample with the highest degree of nitration. A partially degraded sample was prepared by using the TGS-2 (heating rate: 20°C/min) in the 50–450°C range; the composition of the resulting material was determined by elemental analysis.

Polymer solubilities were determined for 14 common solvents at a concentration of 1% (w/v) at room temperature. Solvents studied were (in order of increasing Hildebrand solubility parameter): toluene, chloroform, chlorobenzene, acetone, nitrobenzene, *m*-cresol, pyridine, dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), dimethylformamide (DMF), benzyl alcohol, formic acid, methanol, and water.

Solution viscosity measurements were made using an Ubbelohde viscometer in a constant temperature bath (26.00 ± 0.25°C). For each pure solvent and polymer concentration, 4-7 measurements were made, with averaged values used in calculations. Intrinsic viscosities were calculated by taking the limit of the inherent viscosities as the polymer concentration was extrapolated to zero; four polymer concentrations were studied: 0.150, 0.200, 0.250, and 0.300 dL/g.

RESULTS AND DISCUSSION

The nitrated PEEKs were recovered as pale pink-orange powders, the polymer color changing systematically (from pink to orange) with increasing HNO_3/PEEK ratio. The degrees of nitration (X_{NO_2}), defined as the average number of nitro groups per polymer repeat unit, were calculated from the nitrogen/carbon ratios of the products; the results are listed in Table 1.

Room temperature solubilities of the five NPEEKs are given in Table 2. The parent PEEK is soluble only in strong acids (at room temperature) and in aprotic solvents (e.g., benzophenone, 1-chloronaphthalene, diphenyl sulfone) at elevated temperatures (>190°C); it is completely insoluble in seven solvents, resulting in partial or full solubility of the NPEEKs. Nitration sufficiently alters the chemical nature and chain regularity of PEEK to overcome its strong intercrystalline forces and the limited polarity, resulting in enhanced solubility.

From the solubility tests, a solubility parameter value for NPEEK in the range of 10.0-12.0 $(cal/cm^3)^{1/2}$ seems reasonable, with the specific value of the parameter increasing within this range with higher degrees of nitration. This compares to a calculated value of 10.5 $(cal/cm^3)^{1/2}$ for fully amorphous PEEK, determined by Small's method, and NPEEK values of ~10.6 ($X_{NO_2} = 0.42$) and 11.0 ($X_{NO_2} =$ 2.79) [13].

Evidence that a single solubility parameter cannot completely define NPEEK solubility was indicated by the behavior with three different solvents, all with a

TABLE 1. Nitrated PEEK: Synthesis Conditions and Characterization

Sample	mL HNO_3/g PEEK	X_{NO_2}
(1)	0.10	0.42
(2)	0.20	0.82
(3)	0.25	1.15
(4)	0.50	2.15
(5)	0.75	2.79

TABLE 2. Solubility of Nitrated PEEKs[a]

Test solvent	Solubility parameter	X_{NO_2} 0.42	0.82	1.15	2.15	2.79
Toluene	8.9	I	I	I	I	I
Chloroform	9.3	SW	PS	PS	I	I
Chlorobenzene	9.5	I	I	I	I	I
Acetone	9.9	I	I	I	I	I
Nitrobenzene	10.0	SW	PS	S	S	S
m-Cresol	10.2	SW	PS	S	PS	SW
Pyridine	10.7	I	SW	S	S	S
Dimethylacetamide	10.8	SW	PS	S	S	S
Dimethylsulfoxide	12.0	I	PS	S	S	S
Dimethylformamide	12.1	I	I	PS	S	S
Benzyl alcohol	12.1	I	I	I	I	I
Formic acid	12.1	I	I	I	I	I
Methanol	14.5	I	I	I	I	I
Water	23.4	I	I	I	I	I

[a] I = insoluble, SW = swollen, PS = partially soluble, S = soluble. Solvent solubility parameter in $(cal/cm^3)^{1/2}$.

solubility parameter of 12.1 (DMF, benzyl alcohol, and formic acid). Although all of the NPEEKs were completely insoluble in the latter two solvents, behavior in DMF changed from insoluble to partially soluble to soluble with increased nitration. Closer examination of NPEEK solubility reveals an important trend; with the exception of nitrobenzene, for which NPEEK solubility might be explained by the adage "like dissolves like," the solvents which swelled or dissolved the NPEEKs can all be classified as polar and nucleophilic. The interactions between the polymer and solvent, leading to the swelling and dissolution observed, can be explained as electronic interactions between nucleophilic and electrophilic (the nitrated phenylene rings of the polymer) moieties.

The change in the electronic nature of PEEK with increasing nitration is consistent with the precipitation observed during some of the nitration reactions. Dissolution of PEEK in MSA can be attributed to nearly complete protonation of the ketone moieties (electrophilic addition of H^+), with potential resonance stabilization from the adjacent phenylenes [14]. Nitration of a phenylene ring preempts the ability of that ring to stabilize the adjacent charge; with increasing nitration of a chain, the number of possible protonation sites is decreased until a threshold fraction of rings is nitrated. At that point, sufficient interactions between the polymer and the solvent to keep the chain in solution no longer exist, and precipitation begins. This explains why precipitation was not observed for three of the NPEEK syntheses (X_{NO_2} = 0.42, 0.82, 1.15), and why partial (X_{NO_2} = 2.15) and nearly complete (X_{NO_2} = 2.79) precipitation were observed at higher levels of nitration.

The infrared spectra for a sequence of four nitrated PEEKs are shown in Fig. 1. Nitration would be expected to significantly alter the absorption pattern of PEEK [15] with the rise of $-NO_2$ (asymmetric and symmetric) and C—N stretching bands, changes in the aromatic C—H out-of-plane bending patterns (due to new aromatic substitution), and splitting of the ketone and ether bands. *Several* of these changes were clearly observed and definitely assigned; other lesser changes were also observed, but unambiguous assignments could not be made due to overlapping of vibrational modes.

A clear difference between the spectra of the substituted and unsubstituted PEEKs was the emergence of IR peaks at 1535 and 1349 cm^{-1} for all the nitrated polymers; these absorptions were assigned to the asymmetric and symmetric $-NO_2$ stretches, respectively [16, 17]. The intensities of these peaks varied proportionally with the degree of nitration relative to the intensity of an absorption from a moiety in the backbone (e.g., the carbonyl stretching band at 1665 cm^{-1}). Similar bands

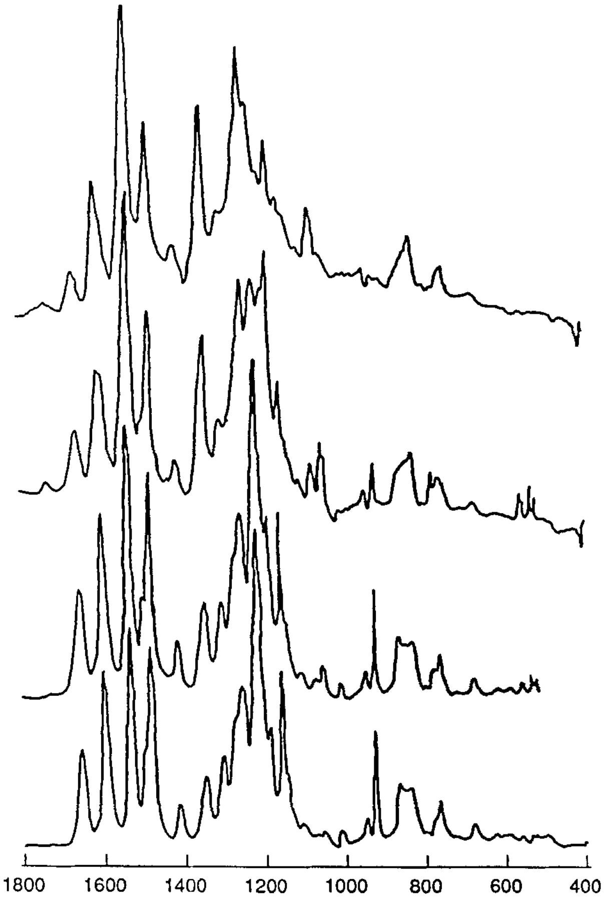

FIG. 1. Fourier-transform infrared spectrum of nitrated PEEKs, X_{NO_2} = 0.82, 1.15, 2.15, and 2.79 (bottom to top, in cm^{-1}).

are found in other nitrated aromatics, such as nitrobenzene (1527 and 1348 cm^{-1}); frequency shifts for the NPEEKs compared to other nitrated species resulted from the presence of additional substituents (ether and carbonyl linkages) found in these polymers.

The C—N stretching absorption appeared at approximately 835 cm^{-1}; this band was difficult to discern here due to overlapping absorptions of the aromatic C—H out-of-plane bending modes. Typical absorptions of this mode for two adjacent hydrogens (1,4-disubstitution) are in the 800-850 cm^{-1} range (848 cm^{-1} in the parent PEEK spectrum [15]) and at slightly higher frequencies for an isolated hydrogen (1,2,4-trisubstitution). As the positions and intensities of these latter bands are highly sensitive to the electronegativity of the substituents [16], the exact frequencies for these modes could not be discerned.

Additional absorption increased in intensity (relative to the 1665 cm^{-1} carbonyl peak) with increasing degree of nitration at 1081 cm^{-1} as assigned to the in-plane C—H bending for an isolated hydrogen (1,2,4-trisubstitution). This absorption was not identified in the spectra of sulfonated PEEK due to the presence of the symmetric $-SO_2-$ stretch at 1080 cm^{-1} [5]. Conversely, the absorptions at 1162 and 1145 cm^{-1} decreased in intensity with increasing levels of nitration and were assigned to the in-plant C—H bending for two adjacent hydrogens (1,4-disubstitution) [16].

Two spectral changes for absorptions associated with the ketone and ether moieties were observed. The peak at 1307 cm^{-1}, which has been described as a "motion of the carbonyl coupled with the rest of the molecule" [17], showed no measurable change from the *parent PEEK* for the spectra of the two lower degrees of nitration (X_{NO_2} = 0.82 and 1.15), but increased sharply in relative intensity for the two more highly nitrated polymers (X_{NO_2} = 2.15 and 2.79). Since no changes in the positions of either carbonyl band (1665 and 1307 cm^{-1}) were observed for any of the NPEEKs, the possibility of a side reaction of the ketone during nitration seems remote. There was no evidence of solution-soluble fragments. The observed intensity change is attributed to changes in that portion of the polymer involved in the coupled motion, i.e., the phenylene rings adjacent to the ketone. Since no significant difference in the peak intensity was observed for X_{NO_2} = 0.00 (parent), 0.82, and 1.15, but only for X_{NO_2} = 2.15 and 2.79 PEEKS, it is likely that no change in the oxy-1,4-phenylenecarbonyl rings occurs until further reaction, namely, nitration of these rings. Thus, it appears that, for a polymer repeat unit, the initial reaction occurs principally on the oxy-1,4-phenyleneoxy ring (i.e., the ring of highest electron density), with further reaction occurring on the two rings adjacent to the ketone (those of lower electron density).

Another difference observed in the NPEEK IR spectra was the change in the absorption observed in neat PEEK at 1227 cm^{-1}. This band initially broadened (X_{NO_2} = 0.83) and then split into two separate absorptions at 1211 and 1237 cm^{-1}. Although the exact identity of this band was uncertain, it may have resulted from a C—O ether vibration, a band known to be sensitive to ring substitution with electrophilic substituents [16].

All five nitrated PEEKs were determined to be completely amorphous and with T_gs of 156°C (X_{NO_2} = 0.42), 157°C (0.82), 154°C (1.15), 141°C (2.15), and 138°C (2.79), compared with a T_g of 149°C for the parent PEEK. The increase in T_g at lower nitration levels may result from a general hindering of rotation along the chain due to the presence of the moderately bulky nitro groups, similar to the increase observed with sulfonation [5]; unlike the $-SO_3H$ groups, however, the $-NO_2$ moieties are not thought to be involved in any polar/ionic interactions.

The decrease in T_g from a high of 157°C ($X_{NO_2} = 0.82$) to 138°C (2.79) suggests a decrease in average molecular weight caused by the chain-cleaving ipso nitration, which is known to occur commonly in aromatic nitrations [18-20]. In ipso substitution, a nitro group replaces an existing substituent on an aromatic ring; in the case of PEEK, this would be an ether or carbonyl, and would cleave the chain. In PEEK nitration, it would be expected to take place almost exclusively at the ipso carbon bonded to the carbonyl, as the resulting acylium ion would be a more stable leaving group than the aroxy cation produced by cleavage of the ether. Also, ipso substitution has been observed to take place readily at the carbonyl in the nitrations of substituted acetophenone and benzophenone [21], was not observed at the ether linkage in the nitrations of various diaryl ethers except with fuming nitric acid at elevated temperatures [22a, b, c], and was observed to take place exclusively at the aldehyde in asarylaldehyde rather than at any of the three methyl ether sites [23]. Solution viscosity measurements of the three most highly nitrated polymers in nitrobenzene (considered a noninteracting solvent) yielded intrinsic viscosities of 0.701, 0.250, and 0.133 dL/g for the $X_{NO_2} = 1.15$, 2.15, and 2.79 polymers, respectively, confirming the occurrence of ipso nitration and molecular weight reduction.

The results of thermogravimetric analysis for PEEK (powder, as received) and two NPEEK samples are shown in Fig. 2. Comparisons of the NPEEKs with PEEK indicated that thermal stability decreased with increasing levels of nitration, and degradation of the NPEEKs, unlike PEEK, occurred with two weight loss

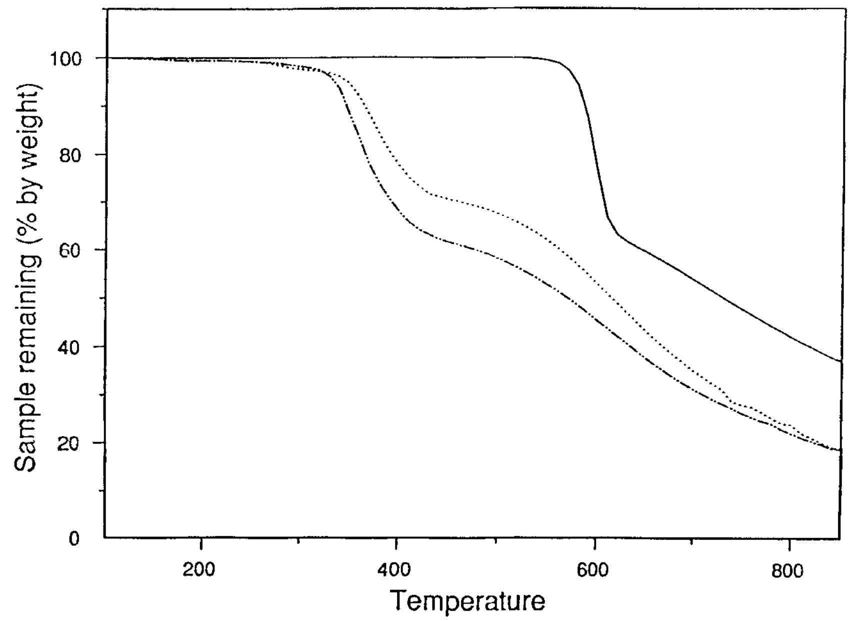

FIG. 2. Thermogravimetric analysis of PEEK (——), nitrated PEEK ($X_{NO_2} = 2.15$) (· · ·), and nitrated PEEK ($X_{NO_2} = 2.79$) (-·-·-).

TABLE 3. Thermogravimetry of PEEK and NPEEKs

X_{NO_2}	Nitro weight, %	Onset temperature, °C	"First step" weight loss, %
0.00	0.0	581	–
0.42	6.2	395	7.5
0.82	11.6	391	6.2
1.15	15.6	382	13.6
2.15	25.7	345	27.0
2.79	31.0	331	35.9

stages. The transition between these two stages occurred at about 420°C, independent of the degree of nitration. A summary of the polymer nitro group weight fractions, the degradation onset temperatures, and the "first stage" weight losses are listed in Table 3.

As the first stage might involve nitro group decomposition, an NPEEK sample (X_{NO_2} = 2.79) was partially degraded by stopping decomposition at 450°C. Elemental analysis of the recovered material revealed that only 45.5% (wt) of the nitrogen was lost in this decomposition stage, along with 21.0% (wt) of the carbon and just over 60% (wt) of the oxygen. Mass spectroscopy of low molecular weight models (such as substituted benzophenones, diphenyl ethers, and nitroaromatics) are all known to yield carbon monoxide upon decomposition, either by ring fragmentation or by elimination of the carbonyl (in the case of the benzophenones). This latter process is greatly enhanced by the presence of electron-withdrawing substituents such as nitro groups [24]. Calculations indicated that the NPEEK oxygen weight loss corresponded to losses through carbon monoxide (assuming all carbon was eliminated in this manner), nitric oxide, and nitrogen dioxide (both known to be eliminated from nitroaromatics, predominantly the latter). Thus, the "first stage" weight loss cannot solely be ascribed to nitro decomposition; its correlation with the level of nitration, however, may indicate the occurrence of a decomposition mode activated by nitro substituents, e.g., elimination of the carbonyl moiety as carbon dioxide.

CONCLUSIONS

The first detailed study of NPEEK nitration has been performed; five degrees of polymer nitration were achieved. Infrared spectroscopy demonstrated that each of the three phenylene rings within the polymer repeat unit could be nitrated, according to stoichiometric reagent availability. A two-step nitration process is suggested, with initial substitution generally occurring on the oxy-1,4-phenyleneoxy ring and later reaction generally occurring on the phenylene rings adjacent to the carbonyl. Lower degrees of nitration resulted in increases in the T_g, while higher degrees of nitration ($X_{NO_2} > 1$) resulted in decreases in T_g. This was postulated to result from ipso substitution at the carbonyl, with resultant chain cleavage. Solution viscosity measurements confirmed the decreases in molecular weight at higher degrees of nitration. Nitrated PEEK was found to have a significantly lower thermal stability than PEEK, but was also significantly more soluble, primarily in polar, aprotic, electron-rich solvents.

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REFERENCES

[1] O. B. Searle and R. H. Pfeiffer, *Polym. Eng. Sci., 25*, 474 (1985).
[2] J. Lee and C. S. Marvel, *J. Polym. Sci., Polym. Chem. Ed., 22*, 295 (1984).
[3] T. Ogawa and C. S. Marvel, *Ibid., 23*, 1231 (1985).
[4] M. I. Litter and C. S. Marvel, *Ibid., 23*, 2205 (1985).
[5] X. Jin, M. T. Bishop, T. S. Ellis, and F. E. Karasz, *Br. Polym. J., 17*, 4 (1985).
[6] M. T. Bishop, F. E. Karasz, P. S. Russo, and K. H. Langley, *Macromolecules, 18*, 86 (1985).
[7] L. Leung, C. Bailly, J. F. O'Gara, D. J. Williams, F. E. Karasz, and W. J. MacKnight, *Polym. Commun., 28*, 20 (1987).
[8] C. Bailly, D. J. Williams, F. E. Karasz, and W. J. MacKnight, *Polymer, 28*, 1009 (1987).
[9] T. Sasuga and M. Hagiwara, *Ibid., 27*, 821 (1986).
[10] C.-M. Chan and S. Venkatraman, *J. Appl. Polym. Sci., 32*, 5933 (1986).
[11] C.-M. Chan and S. Venkatraman, *J. Polym. Sci., Polym. Phys. Ed., 25*, 1655 (1987).
[12] S. A. Thompson and R. J. Farris, *J. Appl. Polym. Sci., 36*, 1113 (1988).
[13] P. A. Small, *J. Appl. Chem., 3*, 71 (1953).
[14] M. Liler, *Reaction Mechanisms in Sulfuric Acid*, Academic Press, New York, 1971.
[15] H. X. Nguyen and H. Ishida, *Polymer, 24*, 1400 (1986).
[16] L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, Wiley, New York, 1954.
[17] K. Nakanishi and P. H. Solomon, *Infrared Absorption Spectroscopy*, 2nd ed., Holden-Day, San Francisco, 1977.
[18] D. V. Nightengale, *Chem. Rev., 40*, 117 (1947).
[19] R. B. Moodie and K. Schofield, *Acc. Chem. Res., 9*, 287 (1976).
[20] J. G. Traynham, *J. Chem. Educ., 60*, 937 (1983).
[21] L. Elion, *Rec. Trav. Chim. Pays-Bas, 43*, 867 (1924).
[22] (a) R. V. Henley and E. E. Turner, *J. Chem. Soc.*, p. 928 (1930). (b) D. L. Fox and E. E. Turner, *Ibid.*, p. 1115 (1930). (c) D. L. Fox and E. E. Turner, *Ibid.*, p. 1853 (1930).

[23] J. Van Alphen, *Rec. Trav. Chim. Pays-Bas, 46*, 195 (1927).
[24] H. Budzikiewicz, C. Djerassi, and D. H. Williams, *Mass Spectroscopy of Organic Compounds*, Holden-Day, San Francisco, 1967.

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