Functionalization of Poly(aryl ether ether ketone) (PEEK): Synthesis and Properties of Aldehyde and Carboxylic Acid Substituted PEEK†

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ABSTRACT: Dibromomethyl substituted poly(aryl ether ether ketone) (PEEK) has been prepared from methylpoly(aryl ether ether ketone) by bromination with bromine. Hydrolysis of dibromomethyl-PEEK in aqueous NMP affords the aldehyde substituted PEEK. Oxidation of aldehyde PEEK with sodium chlorite gives the carboxylated PEEK. The carboxylic acid group is converted to the methyl ester. The structure of these polymers is characterized by IR, ^{1}H NMR, ^{13}C NMR, and size-exclusion chromatography. The glass transition temperatures and thermal stabilities have been determined by differential scanning calorimetry and thermogravimetry.

Introduction

Poly(aryl ether ketone) type polymers are high-performance engineering thermoplastics due to their crystallinity, reasonably high T_g, high T_m, and chemical stability. Among these polymers, poly(aryl ether ether ketone) (PEEK) is the most widely used material. For many applications, polymers with different structures and properties are desired. A variety of structurally modified PEEK type polymers has been reported.[1–4] Introducing different pendent groups into the polymer main chain has also been effected; pendent groups include sulfonic acid,[5,6] sulfonamide,[7,8] aminoaniline,[9] methyl, phenyl, and *tert*-butyl.[4,10–12]

We are interested in preparing high-performance polymers with functional groups on the polymer chain for specialty applications such as membrane materials. Due to the insolubility of PEEK polymer in common organic solvents, ordinary organic functionalization reactions such as chloromethylation cannot be used with PEEK. In a separate paper[13] we reported that, via the bromomethyl substituted PEEK prepared by bromination of methyl-PEEK, a variety of functional group substituted PEEK polymers can be prepared. In this paper, we report the synthesis of dibromomethyl substituted PEEK. Aldehyde and carboxylic acid substituted PEEK polymers are easily prepared via this dibromomethyl-PEEK intermediate.

Results and Discussion

Generally, there are two methods to functionalized polymers.[14] One is to use a functionalized monomer in the synthesis of the polymer. The other is to chemically modify the preformed polymer. PEEK type polymers are usually prepared under vigorous nucleophilic substitution conditions. It is difficult to avoid interference of the condensation reaction with the functional group on the monomer. For example, we failed to prepare the carboxylate ester substituted PEEK from methylcarboxylated hydroquinone and difluorobenzophenone under standard conditions. It is assumed that the ester group is cleaved under the basic polymerization condition. The stoichiometry of the reaction is thereby upset. Furthermore, the electron-withdrawing carboxylic group deactivates the hydroquinone monomer. In the second approach, the functionalization of preformed polymer is limited to the sulfonation of PEEK.[5,6] Due to the insolubility of PEEK in ordinary organic solvents, other types of functionalization are difficult to perform. In order to introduce functional groups into PEEK, we have used a combination of both methods in sequence. First, methylhydroquinone is used as the latent functionalized monomer to give methyl-PEEK (MePEEK). This polymer is then further reacted to introduce a variety of functional groups. The preparation and reaction on bromomethyl-PEEK have been described elsewhere.[13] Here we describe the synthesis of dibromomethyl-PEEK and its further conversion to aldehyde and carboxylic acid substituted PEEK.

Synthesis and Characterization of Dibrominated MePEEK. The bromination of MePEEK and following reactions are shown in Scheme I. Bromine is used as the brominating reagent. It is observed that long-wavelength UV light radiation favors the formation of dibrominated methyl-PEEK.[13] The reaction is carried out at high temperature and with excess bromine. The reaction results obtained under different conditions are summarized in Table I. Polymer 2 is isolated as a white material which is soluble in a common organic solvent such as chloroform and THF; no gellike material is found. The size-exclusion chromatography (SEC) results are shown in Figure 1; it can be seen that polymer 2 has an almost identical trace to the original MePEEK polymer 1. The SEC analysis results are given in Table II. In order to investigate the effect of bromination on the molecular weight of the polymers, the intrinsic viscosities of the polymers are measured and the results are used to obtain the real molecular weight by the universal calibration method. The results are given in Table II. It was previously shown that the universal calibration principle is applicable to MePEEK.[15] The ratio of the peak molecular weights of polymers 2 and 1 corresponds to that expected for a dibrominated polymer (460/302 = 1.5). This result suggests that there are no detectable degradation and cross-link reactions during the bromination.

Polymer 1 can be quantitatively brominated to dibrominated methyl-PEEK (2), as evidenced by ^{1}H NMR and ^{13}C NMR spectra. The ^{1}H NMR spectrum of 2 and its assignment is shown in Figure 2. The peak at 7.70 ppm was assigned to the ortho proton next to the dibromomethyl group. For the monobromomethyl unit, the ortho proton appears at 7.22 ppm.[13] The absence of this 7.22 ppm signal

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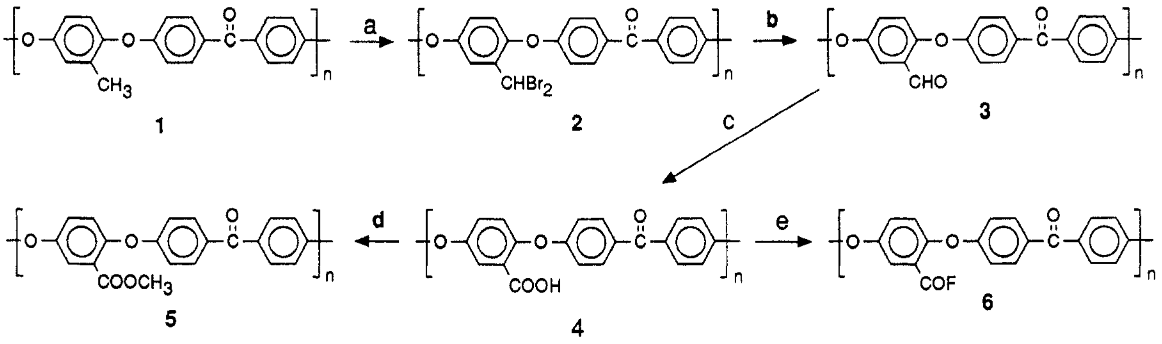
Scheme I



a. Br_2; b. H_2O; c. $NaClO_2$; d. $(CH_3)_3OBF_4$, $[(CH_3)_2CH]_2NC_2H_5$; e. SF_4

Table I. NMR and Elemental Analysis Results of Polymer 2

		bromination level				elem anal.: found (calcd)		
sample	reaction condition	$-CBr_3$	$-CHBr_2$	$-CH_2Br$	$-CH_3$	% C	% H	% Br
2a	2.8 mol equiv of Br_2	0	0.51	0.48	0.01			
2b	3.5 mol equiv of Br_2, 0.5 h of UV after addition	0	0.88	0.12	0	53.79 (53.30)	2.89 (2.71)	33.75 (33.33)
2	4.0 mol equiv of Br_2, 1 h of UV after addition	0.03	0.97	0	0	53.59 (52.21)	2.47 (2.63)	34.33 (34.73)

Table II. SEC and Intrinsic Viscosity Results for Polymers 1–5

sample	V_e,[a] (mL)	$[\eta]$[b]	$M_w \times 10^{-4}$ [c]	$M_n \times 10^{-4}$ [c]	$M_p \times 10^{-4}$ [d]
1	40.02	0.63	7.73	3.76	3.17
2	39.73	0.53	8.99	4.19	4.74
3	41.03	0.47	5.39	2.0	2.44
4		0.78			
5	41.47	0.49	4.71	2.30	1.78

[a] In THF at 35 °C. [b] In NMP at 35 °C. [c] Apparent MW calculated based on polystyrene calibration. [d] Calculated by a universal calibration curve.[15]

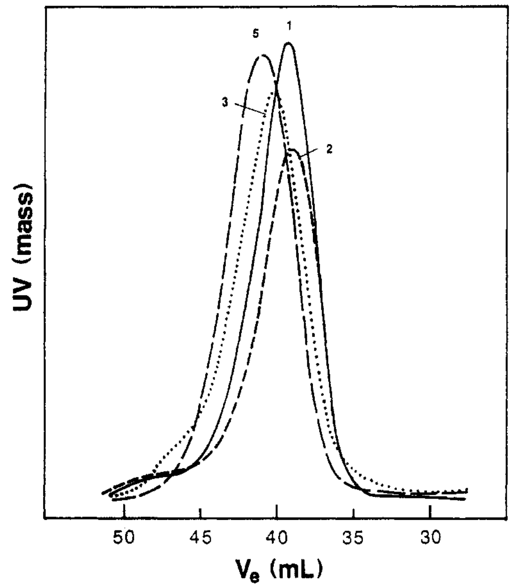


Figure 1. Size-exclusion chromatograms of 1–3 and 5.

indicates complete conversion to the dibromomethyl. There is also the possibility of a tribrominated methyl unit. The ortho proton on the tribromo unit could be shifted further downfield than the 7.70 ppm peak. A minor peak at 7.97 ppm can be observed, which is assigned to this ortho proton. Integration shows about 3% tribromination unit in polymer 2.

The ^{13}C NMR spectrum of 2 is shown in Figure 3. The assignment of this spectrum is completed based on the calculated values, and the results are listed in Table III. The C11 and C13 at 132–133 ppm split signals which are partly buried by other carbon signals in monobromomethyl-PEEK[13] can be seen clearly here. There is no obvious signal which can be assigned to the tribromomethyl carbon, due to its low level, in agreement with the ^1H NMR results. It is interesting to note that the ketone carbon peak at 193.9 ppm occurs as a triplet, in the intensity ratio 1:2:1. This can be attributed to the three possible dibromomethyl substitutions as depicted in Chart I. This split is not observed for methyl-PEEK or for monobromomethyl-PEEK.[13,15]

Polymer 2 is reasonably stable. After storage in the dark at room temperature for 2 months the SEC trace and following hydrolysis reaction results indicate that there is no detectable degradation.

Synthesis and Characterization of Aldehyde PEEK. There are several synthetic methods in general organic chemistry to convert the chloromethyl group to aldehyde. For reaction on polymers, DMSO has been used to oxidize the chloromethyl polystyrene to aldehyde polystyrene under basic conditions.[16] This method has also been used to convert chloromethyl polysulfone to aldehyde polysulfone, but the product was contaminated by other functional groups due to side reactions.[17] We have noticed that MePEEK polymer is not very stable when dissolved and heated under basic conditions.[13] Therefore, the DMSO method is not very suitable for converting bromomethyl-PEEK to aldehyde PEEK.

The hydrolysis of the dibromomethyl group produces dihydroxymethyl, which is converted to aldehyde on loss of H_2O. The conversion of dibromomethyl-PEEK to aldehyde PEEK (3) is carried out in an NMP solution containing 6% water (v/v) at 120 °C for 6 h. This system has been reported as a efficient method to hydrolyze alkyl halide.[18] There is no report using this system to hydrolyze the dihalomethyl group to aldehyde. However, the reaction conditions used here were adapted from a previous optimization of the methoxylation of monobromomethyl-PEEK.[13] A more dilute condition is needed to push the reaction to completion. SEC results and viscosity results shown in Table II indicate the molecular weight of 3 is slightly decreased from that of 2. It is likely that slight

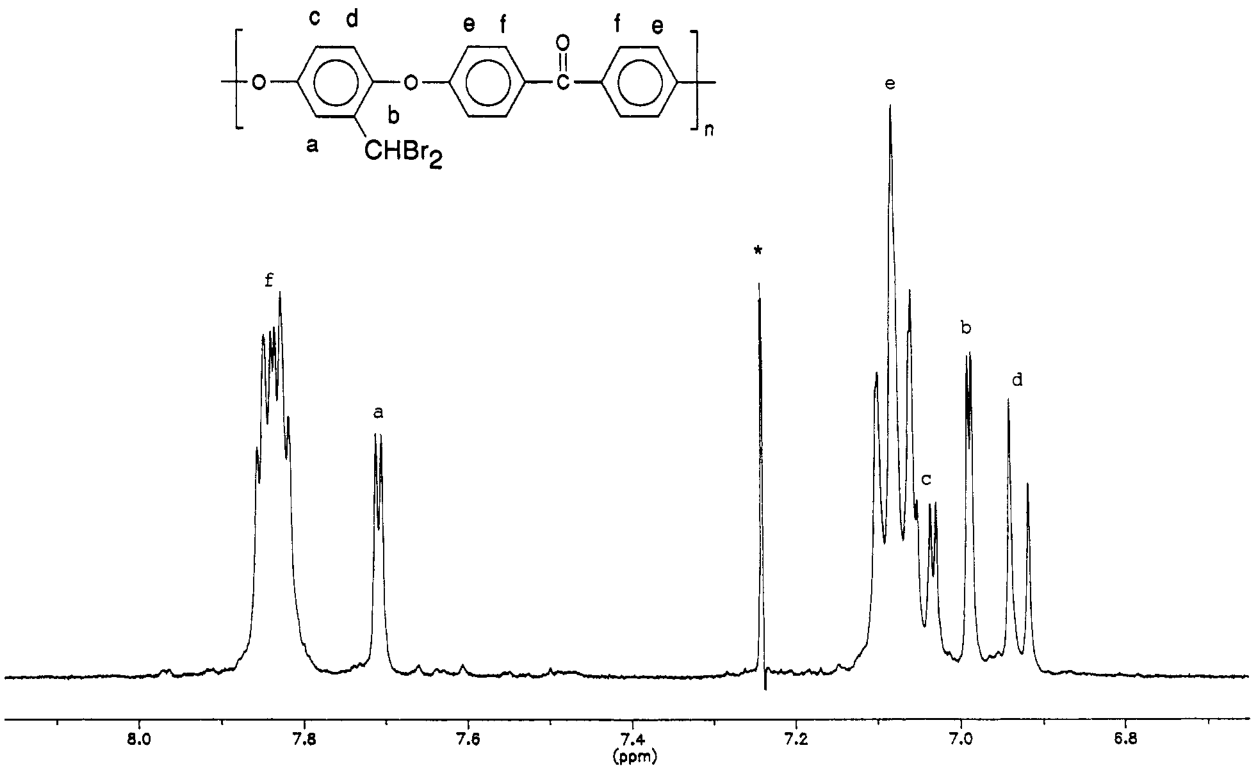


Figure 2. ^{1}H NMR spectrum of polymer **2** (*, solvent $CDCl_3$).

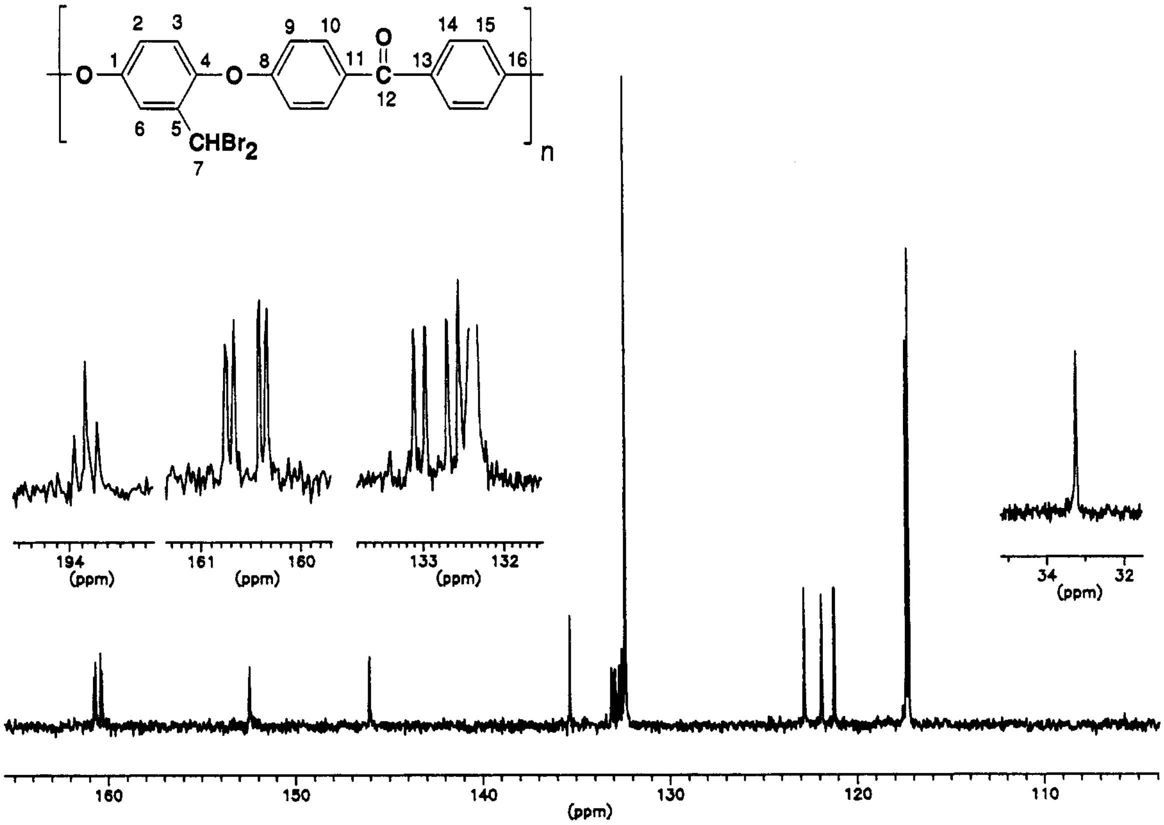


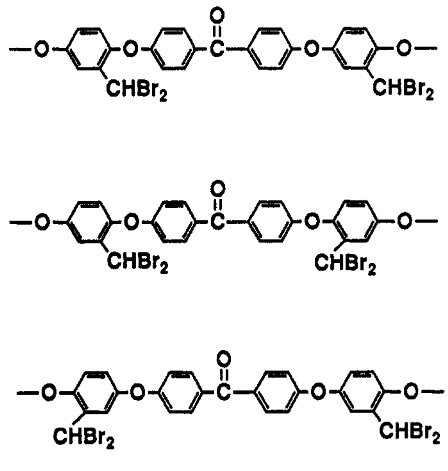
Figure 3. ^{13}C NMR spectrum of polymer **2** ($CDCl_3$ as solvent).

degradation occurs during the hydrolysis. Similar results are also observed for the methoxylation of monobromomethyl-PEEK. It has been concluded from the previous methoxylation study on a fractionated monobromomethyl-PEEK sample that the polymer chain undergoes a random rearrangement under the methoxylation reaction condition, together with a small molecular weight reduction in the presence of trace impurity.[13] It is assumed that a similar polymer chain rearrangement can occur under the hydrolysis condition of dibromomethyl-PEEK. We suspected that the degradation is due to some basic impurity in NMP at the initial stages of the reaction. As the reaction proceeds, released HBr neutralizes the base impurity and prevents further degradation. Therefore, several experiments were carried out with different amounts of HCl added at the beginning of the reaction. However, addition of HCl slows the reaction, and the molecular weight reduction is still observed. Thus, the possible basic impurity is not the reason of degradation. Polymer **3** can

Table III. Assignment of ^{13}C NMR Signals of Polymers 2, 3, and 5

	2 (–CHBr$_2$)		3 (–CHO)		5 (–COOCH$_3$)	
carbon no.	calcd	obsd	calcd	obsd	calcd	obsd
1	152.7	146.05	153.5	152.66	152.3	150.64
2	119.0	121.95	125.3	127.52	123.7	125.34
3	119.7	122.86	120.5	118.75	119.3	122.89
4	152.4	152.48	153.5	154.32	153.5	152.37
5	128.5	135.36	128.3	128.86	121.4	125.37
6	119.4	121.26	120.5	122.26	120.5	124.40
7		33.22	192.0	187.90	166.8	164.65
8	161.8	160.78	161.8	160.83	161.8	161.90
		160.70		160.71		161.76
9	119.2	117.28	119.2	117.54	119.2	116.16
10	129.0	132.39	129.0	132.49	129.0	132.36
11	132.5	133.12	132.5	133.26	132.5	132.97
		132.99		133.09		132.78
12		193.97		193.92		194.00
		193.88		193.80		
		193.79		193.68		
13	132.5	132.71	132.5	132.92	132.5	132.11
		132.57		132.76		131.93
14	129.0	132.39	129.0	132.41	129.0	132.30
15	119.2	117.40	119.2	117.63	119.2	117.47
16	161.8	160.44	161.8	160.58	161.8	160.67
		160.36		160.48		160.53
–OCH$_3$						52.44

Chart I



be fully dissolved in chloroform to form a clear solution, and no gellike material is observed.

The IR spectrum of 3 is shown in Figure 4, in which a strong and sharp band at 1693 cm^{-1} is consistent with the aldehyde carbonyl stretch band. A combination band at 2859 and 2754 cm^{-1} is observed which is typical for aldehyde and is due to the Fermi resonance.[19]

The ^{1}H NMR spectrum of polymer 3 is shown in Figure 5 which is consistent with the proposed structure. The peak at 10.34 ppm is assigned to the aldehyde proton. The peak at 7.62 ppm is assigned to the "a" proton, and the peak at 7.35 ppm is assigned to the "c" proton which is shifted to lower field by the para-aldehyde group. The conversion of the dibromomethyl group to the aldehyde group is completed under the reaction condition used as evidenced by ^{1}H NMR. The tribromomethyl group should be transformed into the carboxylic acid group. Due to its low level, no signal could be observed for the carboxyl unit. Elemental analysis results show that no bromine remains in the polymer. The ^{13}C NMR spectrum of polymer 3 is shown in Figure 6. The assignment of the spectrum is listed in Table III. Similar to polymer 2, the ketone carbon peak is also a triplet.

Synthesis and Characterization of Carboxylated PEEK. The synthesis of carboxylated PEEK polymer has been attempted previously[13] by oxidation of the monobromomethyl-PEEK with the quaternary ammonium salt of permanganate. Due to the insolubility of the resulting polymer in a proper solvent, the product was poorly characterized and only the IR spectrum indicated the incorporation of the carboxylate group. When the oxidation is carried out starting from methyl ether substituted PEEK to carboxylic ester PEEK, a severe molecular weight drop is observed. This suggests that the polymer in solution is not stable toward a strong oxidizing reagent such as permanganate.

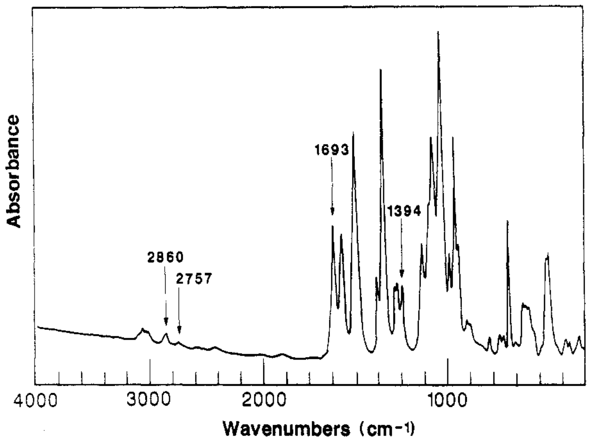


Figure 4. IR spectrum of polymer 3.

Generally, aldehydes are easily oxidized to carboxylic acids, and there are many methods for this transformation in organic chemistry.[20] In the case of PEEK, the crucial question is the proper choice of solvent and reaction conditions. Several of the oxidation reactions require expensive reagents, and some are carried out in basic conditions. Sodium chlorite is chosen as the oxidant because of the mild condition needed for this reaction.[21,22] A modified procedure has been developed using aqueous NMP as the solvent and DMSO as the scavenger for NaOCl and ClO$_2$ which are the byproducts of the reaction. Monosodium phosphate is used as the buffer to keep the reaction medium neutral. The reaction progress has been monitored by IR spectra. The conversion of aldehyde to carboxylic acid is indicated by the carbonyl band shift from 1693 to 1730 cm^{-1}. The IR spectrum of 4, shown in Figure 7, also shows another broad band from 2500 to 3300 cm^{-1} which is assigned to the hydrogen-bonded –OH stretch. Polymer 4 is slightly yellow and soluble in THF. An attempt to obtain a SEC trace of 4 was unsuccessful, due to the absorption of the carboxylate polymer onto the Styragel column. The intrinsic viscosity of 4 in NMP is higher than that of the other polymers. This may be due to association or to a polyelectrolyte effect.

In order to facilitate the characterization of polymer 4, its ester derivative is desired. A chlorosilane-promoted esterification with trimethylchlorosilane and methanol in THF[23] to esterify 4 is unsuccessful. The methyl ester is prepared with trimethyloxonium tetrafluoroborate and *N*,*N*-diisopropylethylamine.[24] The isolated polymer 5 is soluble in chloroform, dichloromethane, and THF. The IR spectrum of 5, shown in Figure 8, shows a carbonyl stretch band at 1735 cm^{-1}. There is no –OH band indicating that the esterification is completed. The ^{1}H NMR spectrum of 5 is shown in Figure 9. The singlet at 3.75 ppm is assigned to the methyl ester proton. The singlet at 7.67 ppm is assigned to the "a" proton. The two doublets at 7.28 and 7.15 ppm were assigned to the "c" and "d" protons, respectively; they are both shifted to lower field by the carboxyl ester substitution. The integration of the spectrum is consistent with the peak assignment.

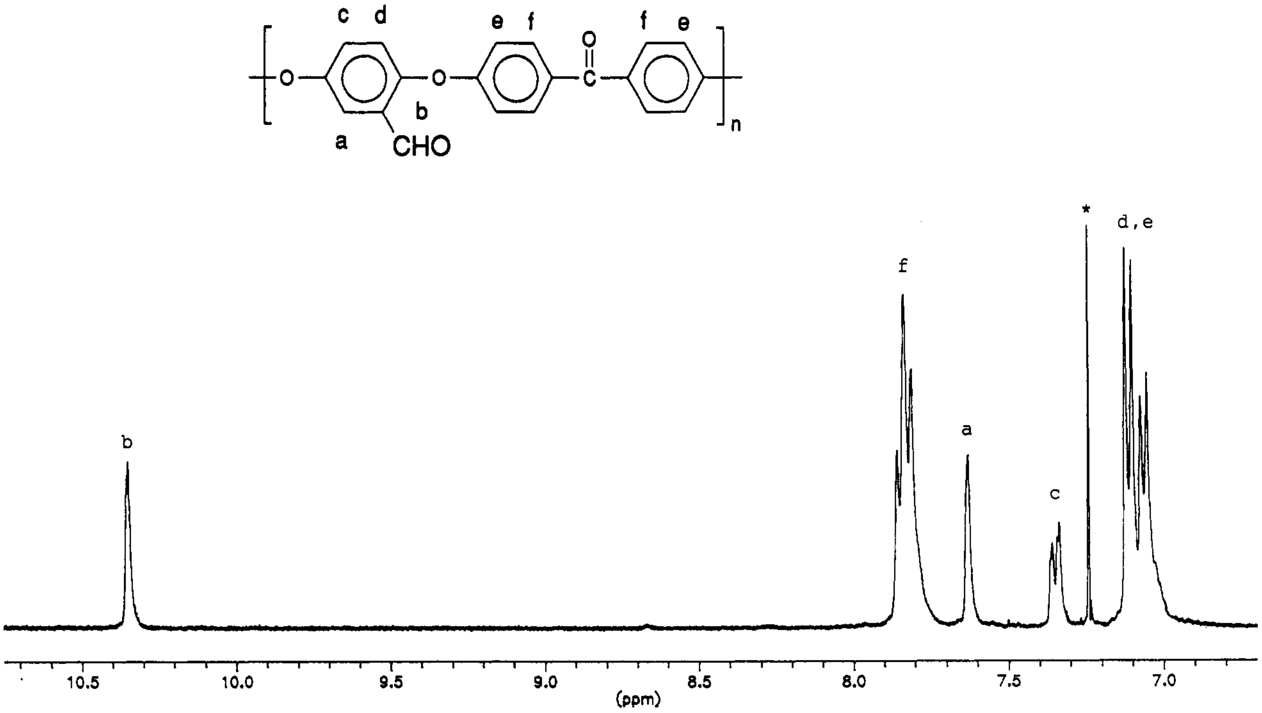


Figure 5. ^1H NMR spectrum of polymer **3** (*, solvent $CDCl_3$).

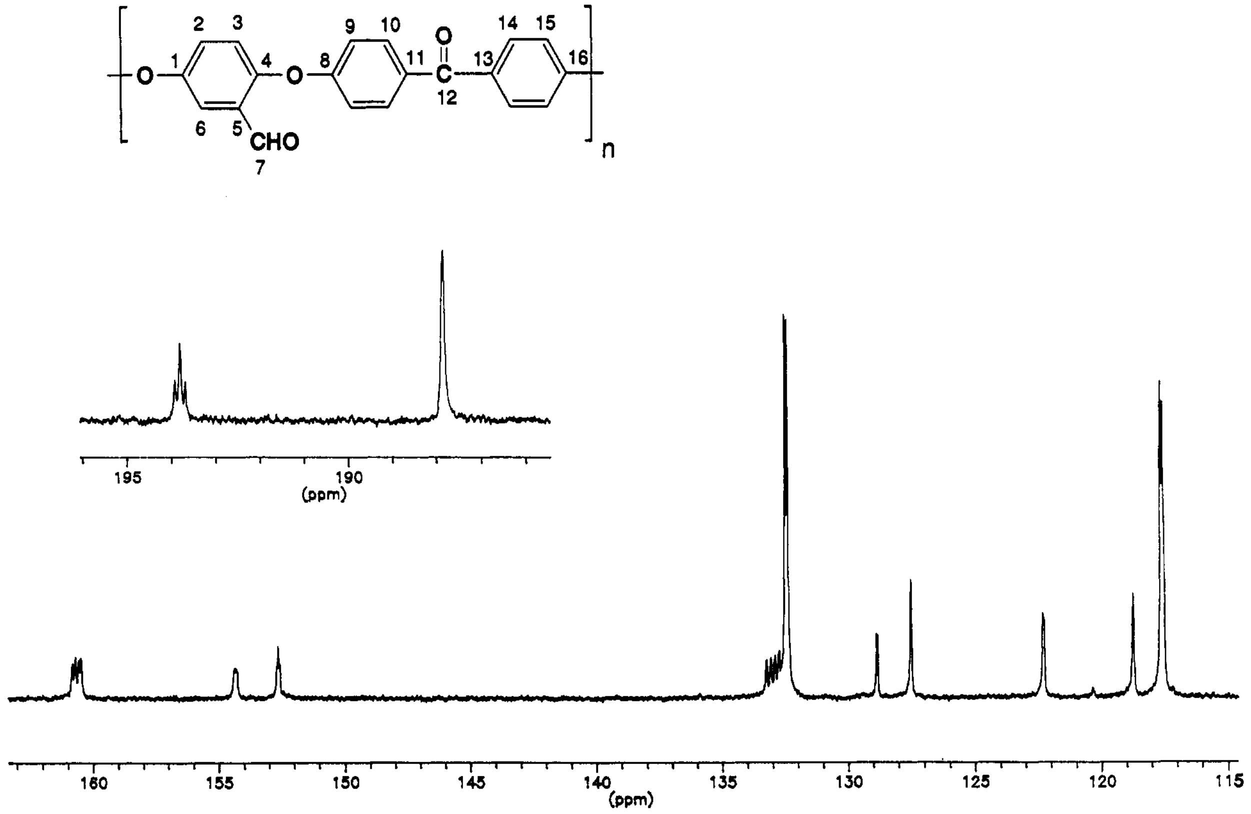


Figure 6. ^{13}C NMR spectrum of polymer **3** ($CDCl_3$ as solvent).

The ^{13}C NMR spectrum of **5** is shown in Figure 10. The assignments of the signals are listed in Table III. The signal at 164.67 ppm is assigned to the carboxylate carbon, and the signal at 52.47 ppm is assigned to the methyl ester carbon. The ketone carbon triplet, observed in **2** and **3**, is not observed here. The split of the carbon signals of C8, C11, C13, and C16 can be seen very clearly here and also in samples **2** and **3**. The SEC and viscosity result in Table II shows that there is a slight molecular weight reduction for polymer **5**, despite the mild oxidation step.

The transformation of the carboxylic acid group to carbonyl fluoride is a unique way to characterize the carboxylic acid functional group. In the IR spectrum, carbonyl fluoride has a sharp strong peak in the 1800-cm^{-1} area with no interference from other functional groups. The conversion of carboxyl-PEEK polymer **4** to the carbonyl fluoride substituted PEEK (**6**) is carried out with SF_4.[25] The IR spectrum of **6**, shown in Figure 11, shows a strong sharp peak at 1821 cm^{-1}. The original carbonyl band and the broad –OH stretch band have disappeared completely. This indicates that the carboxylic acid group on PEEK can be quantitatively transformed to the carbonyl fluoride.

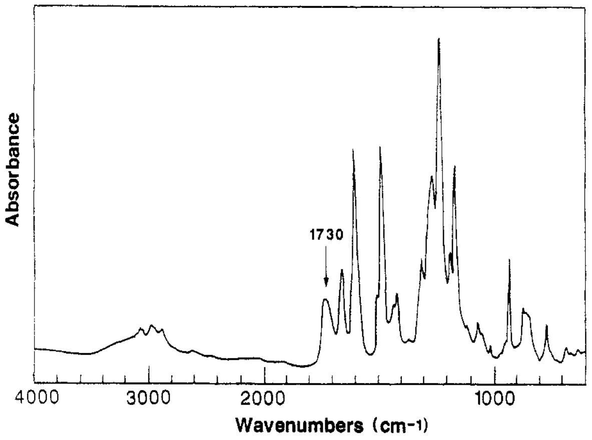


Figure 7. IR spectrum of polymer 4.

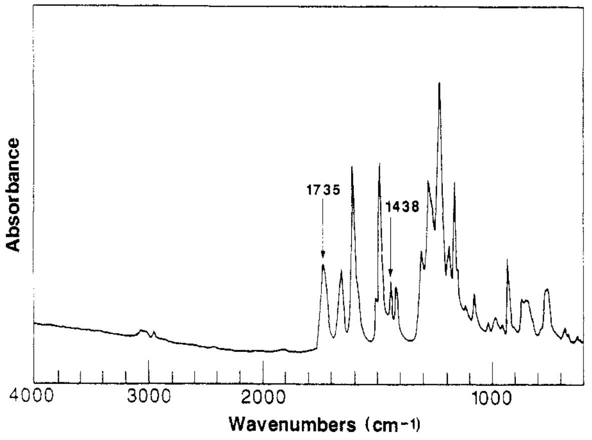


Figure 8. IR spectrum of polymer 5.

The one-pot reaction is also performed to convert polymer 2 directly to polymer 4 without isolating polymer 3. After the hydrolysis reaction is completed, sufficient monosodium phosphate is added to the reaction mixture to neutralize the released HBr. Then the sodium chlorite and DMSO are added to continue the oxidation reaction. The same carboxylated PEEK polymer is isolated from the one-pot reaction, and the yield is higher than that in the two-step procedure.

Thermogravimetric Analysis and Differential Scanning Calorimetry. Thermograms for polymers 1–5 are shown in Figure 12. The onset of decomposition temperatures is listed in Table IV. The dibromomethyl-PEEK (2) shows an initial mass loss at 250 °C of ca. 32%. This corresponds to the loss of bromine. The second thermal degradation occurs between 450 and 500 °C and extends to the polymer degradation. The aldehyde PEEK (3) shows a slight weight loss at 290 °C, that could be due to decomposition of the small amount of carboxyl group which is formed in the hydrolysis of the tribromomethyl group. The major weight loss occurs above 400 °C, indicating that the aldehyde PEEK is fairly thermally stable. The carboxylic acid substituted PEEK (4) is less stable, due to the loss of the carboxylate group. For the esterified polymer 5, a much improved thermal stability is observed. This polymer decomposed at a temperature above 400 °C, comparable to that of aldehyde PEEK.

A low carbon content is found in the elemental analysis of 4 (see the Experimental Section). The hydrophilic properties of the carboxylic acid group make it difficult to dry the polymer thoroughly. This effect can be seen in the TGA trace. The initial weight loss of 4 corresponds to the loss of water.

DSC is used to determine the glass transition temperature of these polymers. The results are listed in Table IV. The dibromomethyl-PEEK has a higher T_g than MePEEK. This effect can be explained by the increased bulkiness of the pendent group which would reduce cooperative mobility. The aldehyde PEEK has a higher T_g which could be attributed to the polar group interaction between polymer chains. This interchain interaction is largest in the case of carboxylic acid PEEK (4; T_g = 220 °C), where strong interchain hydrogen bonding is expected. T_g of the esterified polymer 5, where no hydrogen bonding remains, is 157 °C, which is comparable to that of polymers 1 and 2.

Conclusions

The new synthetic strategy has been developed to functionalize PEEK. The bromination of methyl-PEEK can lead to an intermediate dibromomethyl-PEEK which is useful for further functionalization. Aldehyde substituted PEEK can be obtained via hydrolysis of dibromomethyl-PEEK. Carboxylic acid substituted PEEK can be obtained by mild oxidation of aldehyde PEEK. The methyl ester of carboxylated PEEK is also prepared. These polymers have been characterized by IR and NMR spectra, SEC, and elemental analysis. The thermal properties of these polymers can be well explained by their chemical structures. Aldehyde and carboxyl functional group substituted PEEK may have potential applications in membranes.

Experimental Section

Materials and Methods. The preparation of MePEEK was reported elsewhere.[15] *N*-Methyl-2-pyrrolidinone (Aldrich; NMP) was dried overnight over CaH_2 and distilled under N_2 at reduced pressure over P_2O_5. All other organic solvents were purified according to standard procedure. Sodium chlorite was from Matheson. Trimethylchlorosilane was from Petrarch Systems. Trimethyloxonium tetrafluoroborate and *N,N*-diisopropylethylamine were from Aldrich. All these reagent were used as received. All reaction temperatures are the bath temperatures.

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1500 FTIR spectrometer from polymer sample films. Size-exclusion chromatography was performed on a Waters SEC system with differential refractometer and variable-wavelength UV/vis spectrometer detector accessories. Five Styragel columns with nominal pore sizes of 10^6, 10^5, 10^4, 10^3, and 500 Å were used. THF was the eluent at 1 mL/min at 35 °C. The SEC was calibrated with polystyrene standard samples, and the apparent molecular weights were calculated with the Waters Millennium 2010 software. Intrinsic viscosities of the polymer solutions were determined in a semi-micro dilution Ubbelohde viscometer. The solvent was NMP, and the solvent flow time was on the order of 220 s at 35 °C. DSC and TGA measurements were made under N_2 on a Du Pont 1090 thermal analysis instrument.

Dibromomethyl-PEEK (2). MePEEK (10.0 g, 0.033 mol), 400 mL of 1,2-dichlorobenzene, and 50 mL of chlorobenzene were charged into a 1000-mL three-necked flask equipped with a N_2 inlet, addition funnel, and Dean–Stark trap. The mixture was heated in a silicone oil bath with stirring until all the polymer dissolved, and then the temperature was raised to 200 °C to distill off 50 mL of chlorobenzene to dry the reaction mixture. A long-wavelength UV lamp was used within 10 cm from the flask. While the temperature was kept at 170 °C, bromine (21.2 g, 0.132 mol, dried by shaking two times with concentrated H_2SO_4) was added dropwise during a 1-h period. When the addition was completed, the UV-illuminated reaction mixture was stirred at 170 °C for 1 h. The reaction mixture was cooled to room temperature and the polymer precipitated into 2 L of methanol. The polymer was redissolved in 350 mL of chloroform, filtered, and precipitated into 1.7 L of methanol. Polymer 2 was washed two times with boiling methanol and dried in a vacuum oven at 60 °C. Yield: 14.9 g (95%) of white polymer 2.

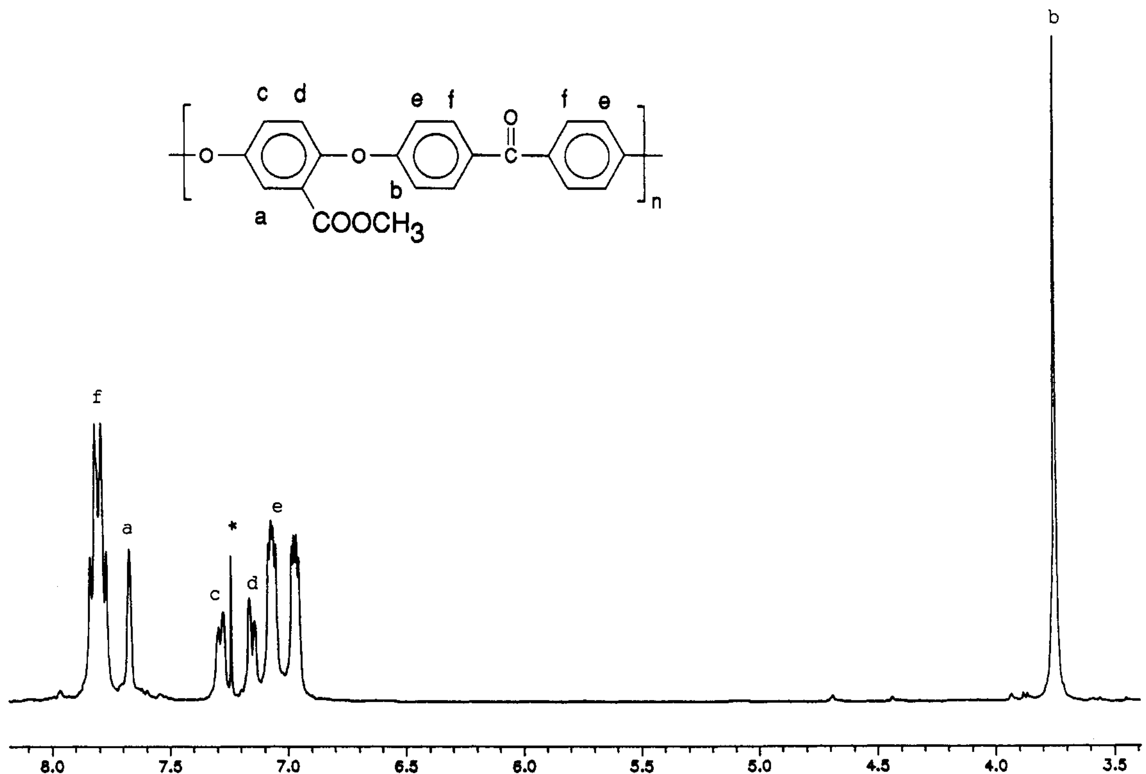


Figure 9. ^1H NMR spectrum of polymer **5** (*, solvent $CDCl_3$).

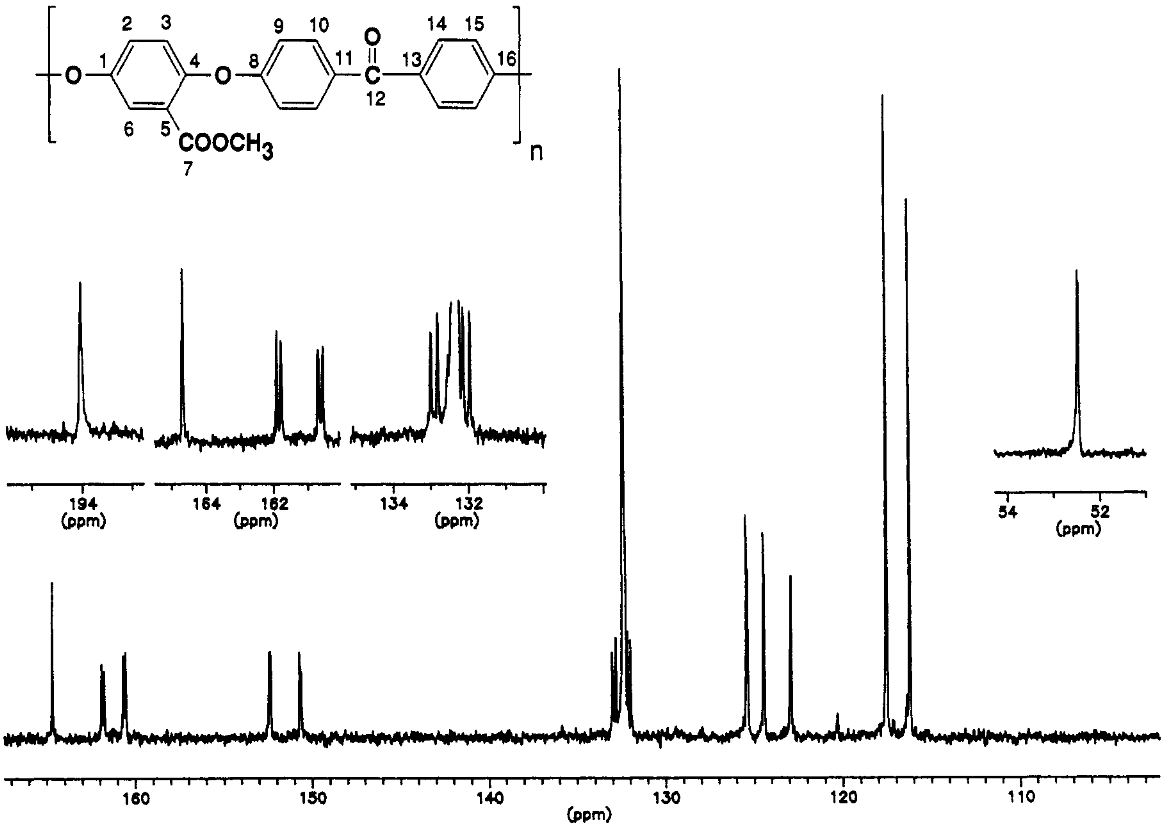


Figure 10. ^{13}C NMR spectrum of polymer **5** ($CDCl_3$ as solvent).

Aldehyde PEEK (3). Polymer **2** (1.50 g, 3.15 mmol) was dissolved in 250 mL of NMP, and the solution was heated to 90 °C. A total of 16 mL of H_2O was added dropwise, and the reaction mixture was stirred at 120 °C for 6 h. The cooled solution was precipitated into a 500-mL mixture of isopropyl alcohol and hexane (1/1). The polymer was redissolved in 50 mL of chloroform, filtered, and precipitated into a 200-mL mixture of isopropyl alcohol and hexane. The polymer was washed two times with boiling methanol and dried in a vacuum oven at room temperature. A total of 0.92 g (92% yield) of white polymer **3** was obtained. Anal. Calcd for $C_{20}H_{12}O_4$: C, 75.94; H, 3.82. Found: C, 74.66; H, 3.56.

Carboxylic Acid PEEK (4). Polymer **3** (0.20 g, 0.63 mmol) was dissolved in 30 mL of NMP. A total of 10 mL of DMSO was added to the solution. Monosodium phosphate (0.10 g, 0.84 mmol) was dissolved in 0.5 mL of water and added dropwise to the solution. Sodium chlorite (0.22 g, 2.43 mmol) was dissolved in 1.5 mL of water and added dropwise to the solution. The reaction mixture was stirred at room temperature for 20 h. After acidification with HCl, the polymer was precipitated into

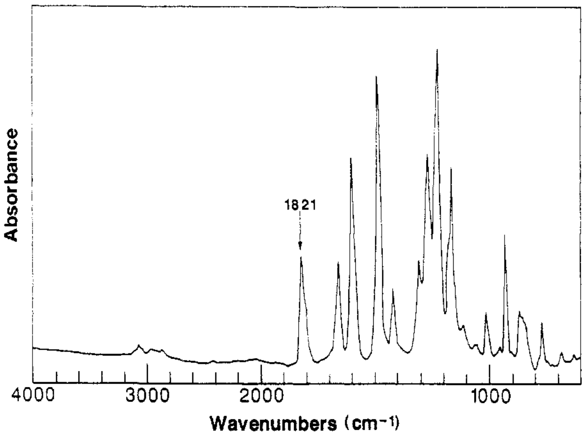


Figure 11. IR spectrum of polymer 6.

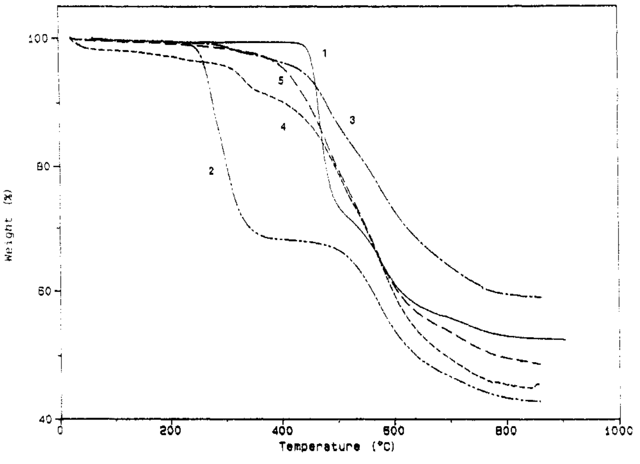


Figure 12. TGA thermograms of polymers 1–5.

Table IV. TGA and DSC Results for Polymers 1–5

sample	T_{de}, °C	T_g, °C	sample	T_{de}, °C	T_g, °C
1	451	150	4	312	210
2	255	169	5	413	157
3	445	175			

methanol. Polymer 4 was washed two times with boiling methanol and dried in a vacuum oven at 60 °C. 4 was obtained as a slightly yellow material. Yield: 0.17 g (81%). Anal. Calcd for $C_{20}H_{12}O_5$: C, 72.29; H, 3.64. Found: C, 69.60; H, 3.39.

One-Pot Reaction from 2 to 4. Polymer 2 (0.30 g, 0.63 mmol) was dissolved in 60 mL of NMP, and the solution was heated to 90 °C. A total of 4 mL of water was added dropwise, and the reaction mixture was stirred at 120 °C for 6 h. After the reaction mixture was cooled to room temperature, 10 mL of DMSO was added. Monosodium phosphate (0.20 g, 1.67 mmol) was dissolved in 0.3 mL of water and added to the reaction mixture. Sodium chlorite (0.22 g, 2.43 mmol) was dissolved in 0.7 mL of water and added dropwise to the reaction mixture, and then the reaction mixture was stirred for 20 h. The polymer was worked up as before. A total of 0.18 g (86% yield) of 4 was obtained.

Methyl Carboxylated PEEK (5). The reaction was carried out under nitrogen. Polymer 4 (0.20 g, 0.60 mmol) was suspended in 20 mL of dry dichloromethane. Trimethyloxonium tetrafluoroborate (0.12 g, 0.81 mmol) was added to the reaction mixture. *N*,*N*-Diisopropylethylamine (0.10 g, 0.78 mmol) was added via syringe. The reaction mixture was stirred at room temperature. After several hours the polymer and the tetrafluoroborate salt have dissolved. The stirring was continued for a total of 20 h. The mixture was precipitated into 100 mL of methanol. The polymer was washed one time with methanol, one time with water, and two times with boiling methanol and dried under vacuum at 60 °C. A total of 0.18 g (86% yield) of white polymer 5 was obtained. Anal. Calcd for $C_{21}H_{14}O_5$: C, 72.83; H, 4.07. Found: C, 73.34; H, 3.93.

Carbonyl Fluoride PEEK (6). Polymer 4 was dissolved in THF, and a film was cast from the solution. The film was dried under vacuum for 2 days. The film was charged into a polyethylene bottle, and the bottle was purged with nitrogen for 30 min and then purged with SF_4 for 5 min. The bottle was capped and left standing overnight. After the reaction was completed, the bottle was purged with nitrogen for 1 h and the film was dried under vacuum for 2 h. The film of polymer 6 was examined by IR spectroscopy.

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