Polymer Bulletin 32, 281–287 (1994)

Polymer Bulletin

Synthesis and bromination of di-, tri- and tetra-methyl substituted poly(aryl ether ether ketone)s

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ABSTRACT: The title polymers have been prepared by nucleophilic substitution of 2,3-dimethyl- and trimethylhydroquinone, and 3,3'-dimethyl- and 3,3',5,5'-tetramethylbiphenol with difluorobenzophenone. These polymers have been brominated to various degrees of substitution. The dimethyl PEEK can only be monobrominated; trimethyl PEEK yields mono- and dibromomethyl functional groups in the ratio 2:1. These results can be explained by steric hindrance to dibromination of the vicinal methyl groups. Dimethyl- and tetramethylbiphenyl PEEK can be dibrominated completely.

INTRODUCTION

Poly(aryl ether ether ketone)s have reached commercialization as high performance polymers with an interesting combination of desirable properties. For certain applications modified polymers containing particular functional groups are required.[1] However, the nucleophilic substitution reaction used to prepare the polymers limits the use of functionalized monomers.[2,3] Furthermore, because poly(ether ether ketone)s are insoluble in common organic solvents it is difficult to functionalize preformed polymers. In previous work, therefore, we have chosen to functionalize methyl substituted poly(ether ether ketone), MePEEK. The methyl group is a latent functional group. Bromomethyl- and dibromomethyl poly(ether ether ketone) intermediates have been prepared.[4,5] The bromomethyl intermediate affords hydroxymethyl substituted PEEK, acetic acid PEEK and quaternary ammonium derivatives. The dibromomethyl intermediate affords aldehyde and carboxylic acid derivatives of PEEK.

It has been observed, however, that there are limits to the degree of bromination that can be achieved. Complete dibromination of MePEEK is possible,[5] but monobromination is limited to about 50% of the methyl groups. Higher degrees of substitution lead to a mixture of mono- and dibromo- substitution.[4] In order to overcome this limitation we have studied poly(aryl ether ether ketone)s with multiple methyl groups in the ether-aryl-ether segment of the polymer backbone.

In this paper we describe the synthesis of di- and trimethyl PEEK and of di- and tetramethylbiphenyl PEEK. The product distribution of bromination reactions is also discussed.

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*Co-op student 1993

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EXPERIMENTAL PART

Monomers were purchased from Aldrich. Difluorobenzophenone was recrystallized from ether, m.p. 110.6°C. 2,3-dimethylhydroquinone was recrystallized from toluene-isopropanol (5:2), m.p.: 228.6°C. Trimethylhydroquinone was recrystallized from toluene-ethanol (7:2), m.p.: 177.5°C. 3,3'-dimethylbiphenol was prepared from *o*-tolidine dihydrochloride using a modified version of the method of Kern *et al.* [6]. It was recrystallized from acidic water (H_3PO_4) and methanol (10:1) and then from toluene, m.p.: 162.3-165.6°C. 3,3',5,5'-Tetramethylbiphenol was obtained from Mitsubishi Chemical Co. It was recrystallized from acetone-toluene (1:2), m.p. 232°C. Solvents were dried over CaH_2 and distilled. N-methyl-pyrrolidinone (NMP) was dried over CaH_2 and distilled from P_2O_5. Polymerizations were carried out as described previously [7-9]. Attention was paid not to have more than 5% excess K_2CO_3 to avoid very fast polymerization and depolymerization reactions.[9] Fractionations were performed in $CHCl_3$ with slow addition of methanol. The initial polymer concentration was 0.6% (w/v) or less. Fractions were redissolved in $CHCl_3$, filtered, precipitated in methanol and dried under vacuum at 60°C. ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ solutions with a Bruker AM-400 spectrometer. Size exclusion chromatograms were obtained with a Waters system with two microstyragel columns (10^4 and 10^5 Å) in THF at 35°C. The flow rate was 1 ml/min. A sensitive UV detector at 290 nm allows for the injection of very small samples (0.02 mg). Glass transitions were determined with a Du Pont 1090 DSC at 10°C/min heating rate. The first run was rejected in order to normalize the thermal history of the samples. Brominations were carried out on 1 or 2 gr. fractions as described previously.[4,5]

RESULTS AND DISCUSSION

MePEEK was previously described in the literature.[10] We observed that the nucleophilic substitution reaction used in the preparation of poly(aryl ether ether ketone)s are accelerated by the methyl substituents on the hydroquinone monomer. In general, high molecular weight polymers are obtained at low temperature (160-170°C) in short times. At the same time, the methyl substituted polymer shows a propensity to form a high molecular weight fraction.[9] A typical evolution of the polymerization, as monitored by SEC, is shown in Figure 1.

Fractionations were designed to yield two or three large fractions and to remove the low molecular weight (cyclic) material. Values of M_w/M_n are about 2-3. A summary of the fractions retained is given in Table I. The molecular weights are polystyrene equivalent peak maxima values. The true molecular weights are estimated to be about half of that value.[9]

All the polymers have resonances at 2.10-2.30 ppm from TMS in their ^1H NMR spectra due to the methyl protons. In the aromatic region, the protons ortho to ether linkages are observed at 6.6-7.0 ppm and the protons ortho to ketone are at 7.6-7.9 ppm. In the biphenyl PEEK samples the protons ortho to the phenyl-phenyl linkage are at 7.4-7.5 ppm.[11] Examples of ^1H NMR spectra are shown in Figure 2a.

The assignment of the ^{13}C NMR chemical shifts are given in Tables II. The spectrum of DMPEEK is particularly simple. Due to the symmetry in the repeat unit it consists of only 9 peaks. In MePEEK [9] and TMPEEK all carbons have different resonances. The splitting of the quaternary carbon observed in MePEEK.[9] (positions 1, 4, 6) is not seen

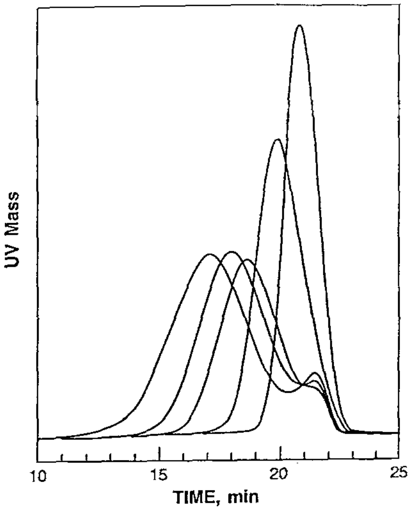


Figure 1
Evolution of molecular weight in the synthesis of dimethyl PEEK as monitored by SEChromatography.

Table I Fractions of methyl substituted PEEK

		$M_w \times 10^{-3}$[*]	Tg °C
DMPEEK	XA	130	177.6
	XB	66	176.5
TMPEEK	XA9	310	219.8
	XB9	139	218.1
	XC9	64	218.2
	XA16	193	218.7
	XB16	71	217.6
DMBPPEEK	XA	45	181.0
	XB	25	176.6
TMBPPEEK		58	266.5

* Polystyrene equivalent peak maxima values.

in TMPEEK. It is worth noting that TMPEEK has three different resonances for the three methyl groups. TMBPPEEK has also a highly symmetric repeat unit and 10 distinct carbon resonances. The ^{13}C NMR of DMBPPEEK has 12 resonances.

Brominations were performed as described previously.[4,5] The level of bromination was controlled by the stoichiometric ratio of bromine to methyl groups in the polymer. When the dibromomethyl group is the desired product, the reaction is performed under ultraviolet irradiation. The results of the bromination experiments are summarized in Table IV. The ratio of CH_2Br over CH_3 groups in the polymer can be determined from the intensities of the ^{1}H NMR resonances at 4.70 and 2.3 ppm respectively. See Fig. 2b. In MePEEK, the ^{1}H NMR resonance of the $CHBr_2$ group is found under the aromatic

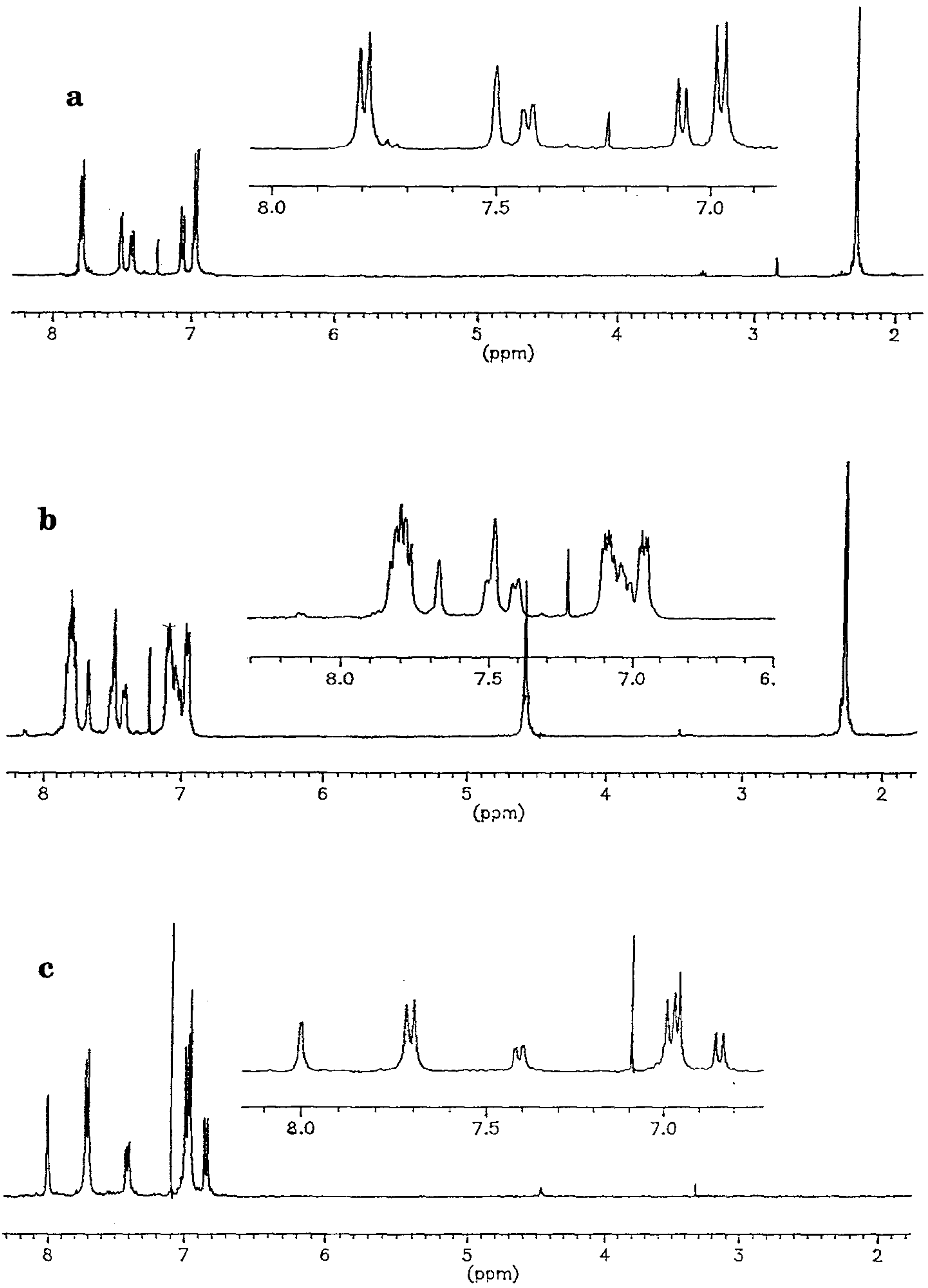
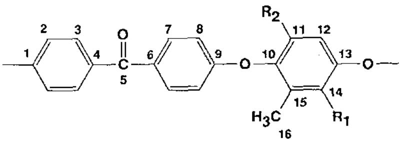
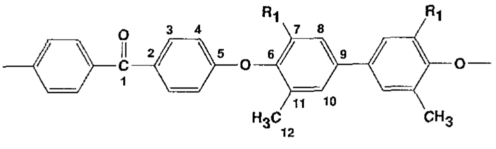


Figure 2 Example of ^{1}H NMR. Sample: dimethylbiphenyl PEEK.
a. homopolymer; b. partially brominated; c. fully dibrominated.

Table II Assignment of ^{13}C NMR Chemical Shifts (ppm from TMS)





#C	MePEEK [9]	DMPEEK	TMPEEK
	$R_1 = R_2 = H$	$R_1 = CH_3$ $R_2 = H$	$R_1 = CH_3$ $R_2 = CH_3$
1	161.38, 161.31	161.82	161.68
2	117.0	115.67	114.28
3	132.24	132.32	132.30
4	131.77, 131.70	131.75	128.61
5	194.15	194.17	194.17
6	132.24*	as C_4	129.87
7	132.34	as C_3	132.48
8	115.65	as C_2	115.67
9	161.59, 161.52	as C_1	161.25
10	152.33	149.87	149.93
11	122.35	119.59	131.99** 131.77** 131.46**
12	118.93	as C_{11}	121.01
13	149.48	as C_{10}	149.93
14	123.03	131.62	see C_{11}
15	132.63	as C_{14}	see C_{11}
16	16.31	12.91	12.67
R_1	-	as C_{16}	13.12
R_2	-	-	16.31

#C	DMBPPEEK	TMBPPEEK
	$R_1 = H$	$R_1 = CH_3$
1	194	194.25
2	131.90	132.46
3	132.32	131.44
4	115.99	114.31
5	161.56	161.15
6	152.63	150.05
7	121.13	131.47
8	125.88	127.78
9	137.40	137.86
10	(130.2)**	as C_8
11	(130.8)**	as C_7
12	16.29	16.29

* part of split obscured by C_3
** not assigned

protons ortho to ether. In extensively dibrominated samples it occurs as a doublet at 6.98 ppm.[5] Analysis of the extent of dibromination is best done on the isolated doublet of the proton ortho to the $CHBr_2$ group at 7.70 ppm.[4,5] For the cases at hand, well resolved resonances are observed for the $CHBr_2$ proton at 6.62 pm in TMPEEK and at 6.92 ppm for DMBPPEEK. See Fig. 2c. The proton ortho to the $CHBr_2$ group is shifted downfield to 7.62 ppm in TMPEEK and to 8.15 ppm for DMBPPEEK. See Fig. 2b and 2c. Both resonances can be used to determine the extent of dibromination. No dibromination is observed in DMPEEK. The levels of bromination were confirmed by elemental analysis, see Table III.

A few comments on the bromination results are in order. When only low levels of bromination are desired the product distribution is practically identical with that

Table III Bromination of Methyl Substituted PEEK

Substrate	Br_2/CH_3 eq.	CH_3	CH_2Br	$CHBr_2$	C/H/Br (%)	
					calc[d]	obs.[e]
MePEEK [4]	1.0	0.28	0.60	0.12		
DMPEEK	1.0	0.01	0.99	-	53.37/2.99/33.48	53.40/2.76/33.98
TMPEEK	0.2	0.77	0.23	trace	68.67/4.53/14.33	68.44/4.28/15.22
	1.0	0.23	0.71	0.06	50.16/2.97/37.77	50.48/2.92/37.46
DMBPPEEK	0.6	0.50	0.42	0.07	67.23/3.94/18.88	67.59/3.74/19.11
TMBPPEEK	1.0	0.26	0.60	0.14	49.89/2.96/40.28	50.04/2.86/40.76
MePEEK [5]	4.0	-	-	0.97[c]		
DMPEEK	4.0	trace	0.97	0.03	52.67/2.93/34.37	52.70/2.82/34.20
TMPEEK	4.0[a)]	trace	0.73	0.27		
	4.0[b)]	trace	0.74	0.26	42.04/2.28/48.05	42.07/2.07/48.11
DMBPPEEK	4.0	-	0.05	0.95	46.32/2.32/44.51	46.46/1.90/44.46

a) High polymer concentration causes polymer precipitation during bromination.
b) 1/2 polymer concentration. No phase separation during bromination.
c) Remainder is CBr_3[5].
d) Based on NMR analysis.
e) Elemental analysis.

obtained with MePEEK. However, DMPEEK can only be monobrominated. This is presumably due to the ortho substitution of the two methyl groups. Steric hindrance prohibits the formation of dibromomethyl group. This polymer can therefore be used to prepare the monobrominated intermediate with degrees of substitution between zero and two without interference of dibrominated product.

Extensive bromination of TMPEEK yield 73% monobromination and 27% dibromination. The latter is close to 1/3 and suggests that the methyl group alone is available for dibromination. This agrees with the results obtained with DMPEEK. DMBPPEEK can be fully dibrominated. This polymer is therefore a candidate if one desires a degree of substitution, DS, equal to 2.0 uncontaminated by the monobromoderivative. With TMBPPEEK a DS = 4.0 can presumably be obtained in a similar way. Fractional DS's of the dibromoderivative are however not possible without contamination by the bromomethylgroup.

The glass transitions of the high molecular weight fractions of the methyl substituted PEEK polymers are given in Table I. The Tg increases with methyl substitution from Tg = 152°C [12] for unsubstituted PEEK and 154.5°C for MePEEK.[9] The Tg of DMBPPEEK is remarkably low. The high Tg of these polymers is advantageous.

ACKNOWLEDGEMENT

We thank Mitsubishi Petrochemical Co., Ltd. for the 3,3',5,5'-tetramethylbiphenol sample, Mr. J. Bornais for NMR spectra, and Mrs. A. Webb for the elemental analysis.

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11. ^{1}H NMR ($CDCl_3$, 400 MHz); DMPEEK: δ 2.15 (s ,6H), 6.90 and 6.92 (d, 4H), 6.91 (s, 2H), 7.77 (d, 4H). TMPEEK: δ 2.07 (s, 3H), 2.09 (s, 3H), 2.11 (s, 3H), 6.80 (s, 1H), 6.83 (d, 2H), 6.91 (d, 2H), 7.78(m, 4H). DMBPPEEK: δ 2.27 (s, 6H), 6.97 (d, 4H), 7.07 (d, 2H), 7.42 (dd, 2H), 7.50 (s, 2H), 7.79 (d, 4H) TMBPEEK: δ 2.19 (s, 12H), 6.87 (d, 4H), 7.33 (s, 4H), 7.78 (d, 4H).
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Accepted January 20, 1994 K