Synthesis and Molecular Characterization of Narrow Molecular Weight Distribution Fractions of Methyl-Substituted Poly(aryl ether ether ketone)[†]

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ABSTRACT: Poly(aryl ether ether ketone) (PEEK) is a high-performance polymer. However, it is difficult to study the properties of PEEK because it has a high tendency to crystallize and is only soluble in strong acids at room temperature. Furthermore, the viscoelastic properties of the amorphous melt cannot be studied in the important $T_g < T < T_g + 175$ °C temperature range. Therefore, methyl-substituted poly(aryl ether ether ketone) (MePEEK) has been studied as a replacement for PEEK. The polymer has been fractionated and the fractions have been characterized by light scattering and intrinsic viscosity measurements in NMP and methanesulfonic acid. The results indicate that MePEEK is a freely rotating polymer with the characteristic ratio of $C_\infty = 2.44$. The molecular weight dependence of the glass transition temperature is established. The viscoelastic properties of the melts have been measured between 170 and 250 °C. The molecular weight between entanglements, $M_e = 1450$, has been calculated from the plateau modulus and is related to the molecular characteristics of the aryl–ether–ether–ketone chain.

Introduction

Poly(aryl ether ketone) type polymers are a class of high-performance engineering thermoplastics known for their chemical and thermal stability. Among these polymers, poly(aryl ether ether ketone) (PEEK) is the most widely used material. To obtain different properties and for different applications, structural changes have been introduced in the basic PEEK chain. Such structural changes have focused on the order and ratio of ether–ketone linkage,[1,2] on the ratio of meta and para phenyl substitution.[3] Groups with sp^3-hybridized atoms, such as $-CR_2-$ and $-SO_2-$, have also been introduced in the backbone.[4,5] Introduction of pendent groups onto the poly(aryl ether ether ketone) main chain is another structural change. Kricheldorf et al.[4] have synthesized a series of poly(ether ketone) type polymers with methyl or phenyl substituents by thermal condensation of silylated hydroquinones. Mohanty et al. have prepared PEEK with *tert*-butyl substituent groups.[6] This is an amorphous polymer that is very soluble in common organic solvents. Risse et al. have succeeded in removing the *tert*-butyl group by a reverse Friedel–Crafts reaction with trifluoromethanesulfonic acid as catalyst and solvent.[7] Bennett et al. have prepared low molecular weight amine-terminated methyl- and *tert*-butyl-substituted PEEKs and used them in epoxy/amine resins.[8] They have reported that the low molecular weight methyl-substituted PEEK is semicrystalline. Although a great number of structurally changed PEEK type polymers have been prepared, relative few molecular property studies have been conducted on these polymers.

Previously, we have studied the dilue solution properties[9] and melt crystallization kinetics[10,11] of narrow molecular weight distribution fractions of PEEK. However, due to the high tendency for crystallization of PEEK, the solution characterization is limited to highly protonating solvents such as methanesulfonic acid.[12] Furthermore, the high melting temperature of PEEK prevents a complete study of the viscoelastic properties of amorphous PEEK, and consequently only an indirect estimation could be made of the molecular weight between entanglements of PEEK, $M_e = 1300$ at 350 °C.[13] In this paper we report the synthesis and characterization of methyl-substituted PEEK (MePEEK). Introduction of one methyl group per repeat unit constitutes the smallest possible structural change and leaves the all-para aryl–ether–ether–ketone sequence unaltered. MePEEK has less tendency to crystallize than PEEK and has a lower melting point. This polymer has been fractionated, and the fractions have been characterized by light scattering and intrinsic viscosity measurements. The glass transition temperature (DSC) and viscoelastic properties of the amorphous melt are also described.

Experimental Section

Materials. Methyl hydroquinone (Aldrich) was recrystallized two times from a 5/1 (v/v) mixture of toluene and acetone (mp 130.3 °C). 4,4′-Difluorobenzophenone (Aldrich) was recrystallized from ether (mp 110.6 °C). K_2CO_3 was ground and dried at 100 °C for 2 days and cooled under vacuum. *N*-Methyl-2-pyrrolidinone (Aldrich; NMP) was dried overnight over CaH_2 and distilled under N_2 at reduced pressure over P_2O_5. Toluene was refluxed over CaH_2 and distilled. Methanesulfonic acid (99%; Aldrich; MSA) was distilled under N_2 at reduced pressure (bp <140 °C).

Equipment and Methods. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker AM-400 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1500 Fourier transform spectrometer. Size-exclusion chromatography (SEC) was performed on a Waters SEC system with differential refractometer and variable-wavelength UV/vis spectrometer detector accessories. The five microstyragel columns have nominal pore sizes of 500, 10^3, 10^4, 10^5, and 10^6 Å. The carrier solvents were THF at 1 mL/min at 35 °C or NMP at 1 mL/min at 52 °C. The elution volume was calibrated with narrow molecular weight distribution polystyrene standards. Light scattering was performed on a Brookhaven laser light scattering system in the static (Zimm) mode with 633-nm He-Ne laser light. Refractive index increments were measured with a Brice Phoenix differential refractometer. The Rayleigh ratio of toluene is taken as 14×10^{-6} cm^{-1}. All measurements were performed at 35 °C. Sample cells (o.d. = 15 mm) were made from flat-bottom NMR tubes and stoppered with ground glass caps. Samples were made in purified NMP and filtered through 0.2-μm Teflon filters. Intrinsic viscosities of the polymer solutions were determined with a semimicrodilution Ubbelohde viscometer. The solvent was NMP, and the solvent flow time was of the order of 220 s at 35 °C. In the case

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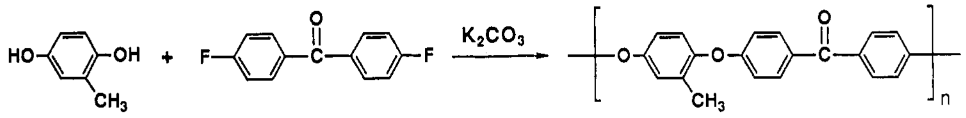
[†] Issued as NRC 35752.

Scheme I



of MSA, a single dilution was performed in the viscometer, and the solvent flow time was of the order of 210 s at 30 °C. Differential scanning calorimetry (DSC) measurements were made on a Dupont 1090 thermal analysis instrument. Polymer samples (4–5 mg) in aluminum pans were first heated to 260 °C at 10 °C/min and then quenched in liquid nitrogen to remove any possible crystallinity. The samples were then rescanned at 10 °C/min. The middle of the heat capacity change was used to determine T_g. Viscoelastic properties were measured with a Rheometrics mechanical spectrometer (605 M) in the oscillatory mode. One-inch diameter clear disks were prepared under reduced pressure at 180–190 °C. Samples were loaded at about 250 °C to erase all original crystallinity or structure. Master curves of the loss (G'') and storage (G') moduli against frequency were obtained by frequency–temperature superposition.

Synthesis of Methyl Poly(ether ether ketone) (MePEEK). A procedure developed by McGrath et al.[14] was followed. Methyl hydroquinone (12.414 g, 0.1 mol), 4,4′-difluorobenzophenone (21.82 g, 0.1 mol), K_2CO_3 (14.512 g, 0.105 mol), 175 mL of NMP, and 85 mL of toluene were charged into a four-necked 500-mL flask equipped with N_2 inlet, mechanical stirrer, thermometer, and Dean–Stark trap. The mixture was heated in a silicone oil bath. The temperature was raised to 143 °C in 0.5 h, when the toluene azetrope began to reflux, and then to 175 °C over a 2.5-h period to remove all water. The polymerization was continued for another 4–5 h while the temperature was slowly raised to 187 °C. The reaction mixture was cooled to room temperature, diluted with 400 mL of THF, and filtered to remove inorganic salts. Ten milliliters of acetic acid was added to the filtrate, and the polymer was precipitated in methanol. The white polymer was washed two times with boiling methanol and dried in a vacuum oven at 70 °C for 2 days: yield 95%; IR (film) 1654, 1599, 1487, 1416, 1381, 1307, 1276, 1227, 1190, 1161, 928 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.19 (s, 3H), 6.92–7.06 (m, 7H), 7.77–7.82 (m, 4H).

The molecular weight of low molecular weight polymer was controlled by replacing a calculated amount of 4,4′-difluorobenzophenone by 4-fluorobenzophenone.

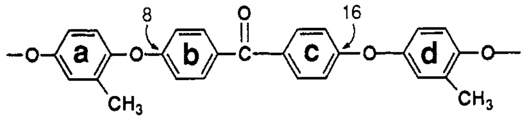
Fractionation of MePEEK. MePEEK was fractionally precipitated from a 0.4% solution in chloroform by the addition of methanol and varying the temperature between 39 and 35 °C. The low molecular weight polymer sample is first dissolved in hot NMP and then diluted with chloroform. Some low molecular weight fractions precipitate out as white solid powders. The fractionation was monitored with SEC. The fractions were diluted or redissolved in chloroform and precipitated in methanol. The precipitate was washed with methanol and dried in vacuo at 60 °C.

Results and Discussion

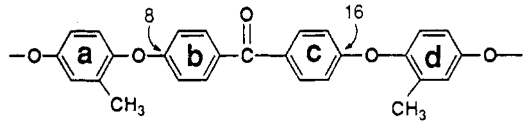
The synthesis of methyl poly(ether ether ketone) is given in Scheme I. The progress of polymerization was monitored by SEC. In the literature, normally 1.3–3 mol equiv of K_2CO_3 base is used in similar reactions.[6–8] In early experiments, 1.6 mol equiv of K_2CO_3 base was used. The polymerization is very fast under this condition. In the time required to remove H_2O, the SEC trace indicated that a very high molecular weight polymer had been achieved. However, on continued heating the molecular weight drops quickly and significantly. It was assumed that the large excess of base causes depolymerization. Since the rates of polymerization and depolymerization are very fast under this reaction condition, it was difficult to terminate the reaction at the optimum time. In order to control the polymerization process, a slower reaction rate is preferred. A small excess of K_2CO_3, 1.05 mol equiv, was used subsequently. The reaction rate is slower under this condition, and after complete removal of H_2O 4–5-h heating is required in order to obtain a high molecular weight polymer.

Bulky substituents, such as *tert*-butyl or phenyl, have been introduced into the hydroquinone unit of the PEEK polymer to increase its solubility.[6,7] The smaller methyl group increases the solubility of PEEK in NMP sufficiently and permits the synthesis of high molecular weight MePEEK at relative low temperatures. MePEEK is soluble in chloroform and dichloromethane at room temperature and is soluble in 1,2-dichlorobenzene at elevated temperatures. MePEEK is soluble in NMP upon heating to 70 °C and can be diluted with THF for SEC experiments in THF.

The IR spectrum of MePEEK is essentially identical with that of the pure PEEK spectrum. A weak band at 1381 cm^{-1} absent in PEEK is assigned to the methyl group symmetric deformation. Although this polymer has been prepared previously,[4,8] no NMR spectral data have been reported. The ^{1}H-NMR spectrum shows a single peak at 2.19 ppm, which is assigned to methyl protons. In the aromatic region, signals representing four protons at 7.8 ppm are assigned to the protons next to the carbonyl, while other signals at 6.9–7.1 ppm are for the rest of the protons. The aromatic region of the ^{13}C-NMR spectrum of MePEEK is shown in Figure 1. The assignment of the spectrum is listed in Table I. The calculated chemical shift values for these carbons are also listed.[15] Several interesting features can be seen from Figure 1. First, from the intensity of these signals, it is very easy to distinguish the tertiary carbons and quaternary carbons as well as the signals which belong to two overlapping carbons. This assignment has been proved by a DEPT[16] experiment. Second, due to the random distribution of methyl groups in the ortho or meta position of the hydroquinone unit, carbons 8 and 16, and 11 and 13, all experience a different chemical environment, which causes the small split for these carbons. For example, in structures A and B, the methyl position on the "a" ring distinguishes carbon 8 from carbon 16. Furthermore, the different positions of the methyl on the "d" ring split the signal of carbon 8. The signal of carbon 11 is buried under the strong signal from carbon 14 at 132.2 ppm. Third, there is no split observed for carbons 1 and 4. It is concluded that the isomeric methyl substitution causes splitting of the quaternary carbons whenever the distance is 3 or less phenyl rings. Similar splitting effects have also been observed in the ^{13}C-NMR spectrum of sulfonated PEEK.[17]



A



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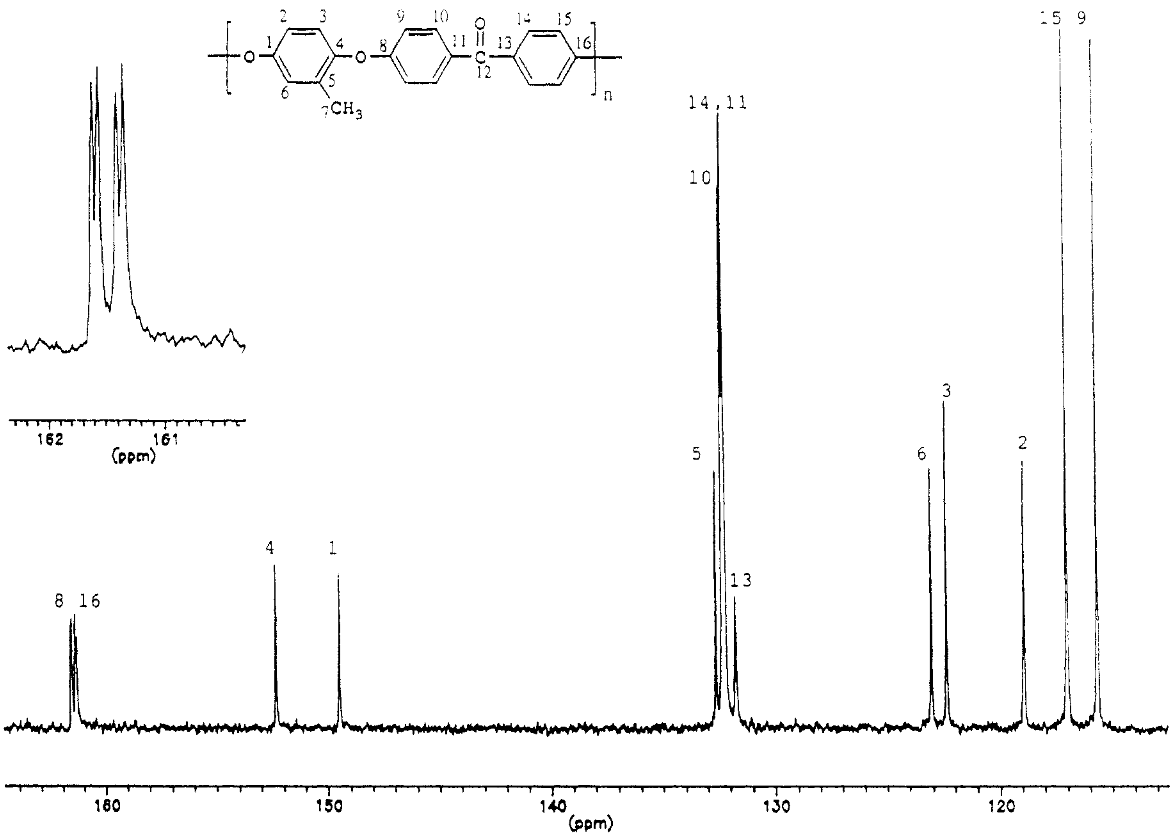

Figure 1. ^{13}C-NMR spectrum of MePEEK.

Table I. Assignment of ^{13}C-NMR Signals of MePEEK

carbon	(calcd)[15]	(MePEEK)
1	152.3	149.48
2	116.2	118.93
3	119.3	122.35
4	152.9	152.33
5	128.6	132.63
6	119.9	123.03
7		16.31
8	161.8	161.59
		161.52
9	119.2	115.65
10	129.0	132.34
11	132.5	132.24[a]
12		194.15
13	132.5	131.77
		131.70
14	129.0	132.24
15	119.2	117.00
16	161.8	161.38
		161.31

[a] Split is obscured by overlap with signal of C14.

Table II. Molecular Characteristics of MePEEK Fractions

sample	d*n*/d*c*,[a] mL/g	M_w[b]	$A_2 \times 10^3$,[b] mL·mol/g^2	V_e[c]	M_w/M_n[d]
FW58B3	0.188	123 600	1.27	7.33	1.33
FW58B4		85 500	1.43	7.53	1.18
FW58B5		58 800	1.22	7.75	1.19
FW58B6	0.185	33 800	1.48	8.00	1.19
FW59B2	0.185	23 800	1.61	8.21	1.27
FW59B3		13 550	1.81	8.53	1.20
FW59B4		8 020	2.01	8.89	1.18
FW59B5		4 950	2.16	9.16	1.11
FW59B6	0.180	3 450	2.34	9.49	1.12

[a] In NMP at 35 °C with λ = 633 nm. [b] In NMP at 35 °C. [c] In NMP at 52 °C. [d] Corrected for zone spreading. See text.

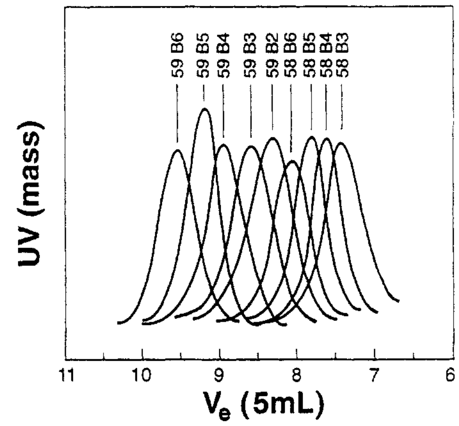

Figure 2. Size-exclusion chromatograms of MePEEK fractions in NMP.

Fractionation of high molecular weight whole polymer does not pose problems as the polymer can easily be dissolved in chloroform. However, low molecular weight whole polymer is first dissolved in a small amount of hot NMP and then diluted with chloroform. It has been observed that low molecular weight MePEEK tends to crystallize in contact with chloroform alone. Chlorinated hydrocarbons are known to promote the crystallization of PEEK.[18]

MePEEK samples are only partly soluble in THF, but it is possible to chromatograph MePEEK solutions in THF containing a trace of NMP when THF is the SEC eluent. The whole polymer and fractions were routinely characterized by SEC with THF as eluent. In order to exclude solubility problems, the fractions were also measured by SEC with NMP as eluent. There is a very good agreement between the THF and NMP SEC results. Figure 2 shows the profiles in NMP of the MePEEK fractions which have been used for further study. The SEC results obtained in NMP have been used to estimate the M_w/M_n ratios and are given in Table II. Narrow molecular weight distribution polystyrene standard samples have been used to calibrate the system. The apparent molecular weight

Table III. Dilute Solution Properties of MePEEK Fractions

sample	M_w	$[\eta]^a$	$k_H{}^a$	$[\eta]^b$
FW58B3	123 600	1.53	0.36	3.77
FW58B4	85 500	1.09_4	0.35	2.54
FW58B5	58 800	0.84_3	0.33	1.92
FW58B6	33 800	0.57_7	0.32	1.10
FW59B2	23 800	0.44_7	0.37	0.74
FW59B3	13 550	0.30_5	0.37	0.49
FW59B4	8 020	0.213_5	0.36	0.308
FW59B5	4 950	0.151	0.35	0.231
FW59B6	3 450	0.109_2	0.39	0.159

[a] In NMP at 35 °C (dL/g). [b] In MSA at 30 °C (dL/g).

distribution, M_w/M_n, for the polystyrene standard is between 1.05 and 1.07. Therefore, all the MePEEK M_w/M_n results have been reduced by 0.05 to account for zone spreading.

Initial light scattering measurements at 35 °C on FW59B2 dissolved in NMP by heating to 70 °C showed extremely high molecular weight. The strong increase of light scattered at low angles indicated that the solution contained a very small amount of large aggregates. These effects disappeared on heating the solution at 120 °C for 20 min, and normal, reproducible Zimm plots were obtained. Subsequently, all solutions were treated at 120 °C for 20 min before dilution and filtration. The weight-average molecular weight and the second virial coefficient for nine MePEEK fractions are given in Table II. From the angular dependence of light scattered the radius of gyration, $\langle R_G{}^2\rangle^{1/2}$, of FW58B3 is 19.6 nm. This value of $\langle R_G{}^2\rangle^{1/2}$, combined with values of M_w and A_2 for FW58B3, yields $\psi = A_2M_w{}^2/(4\pi^{3/2}N_A\langle R_G{}^2\rangle^{3/2}) = 0.19$. This value of ψ is typical for a linear polymer in a moderately good solvent.[19] Also the radius of gyration is 1.36 times larger than the hydrodynamic radius calculated by $R_v = (3[\eta]M/10\pi N_A)^{1/3}$, in good agreement with the theoretical value of Oono.[20] The mutual consistency of different dilute solution properties is gratifying. The molecular weight dependence of the second virial coefficient (Table II) is given by

$$A_2 = (1.23 \times 10^{-2})M_w{}^{-0.20}\ (\text{mL·mol/g}^2) \qquad (1)$$

The exponent is in agreement with the dependence expected for a random-coil polymer in a good solvent.

The intrinsic viscosities of the MePEEK fractions in NMP at 35 °C are given in Table III and plotted double logarithmically against the weight-average molecular weight in Figure 3. The Huggins constants are also listed in Table III. They range from 0.32 to 0.39. The Mark–Houwink–Sakurada relation is

$$[\eta] = (4.14 \times 10^{-4})M_w{}^{0.694} \qquad (2)$$

The intrinsic viscosities were also determined in MSA at 30 °C. The data are given in Table III and plotted in Figure 3. In MSA the Mark–Houwink–Sakurada relation is given by

$$[\eta] = (1.24 \times 10^{-4})M_w{}^{0.875} \qquad (3)$$

The data obtained with PEEK fractions[9] are also shown in Figure 3. One can see from Figure 3 that the intrinsic viscosity data of MePEEK and PEEK are in reasonable agreement.

The Stockmayer–Fixman method[21] has been used to estimate the unperturbed dimensions of MePEEK according to

$$[\eta]/M_w{}^{1/2} = K_\theta + 0.51\Phi_0 BM_w{}^{1/2} \qquad (4)$$

where K_θ is the Mark–Houwink–Sakurada constant for the θ condition. B is the parameter related to the polymer–solvent interaction. Φ_0 is the Flory constant relating the θ condition intrinsic viscosity of a polymer to its unperturbed end-to-end distance. Values of $[\eta]/M_w{}^{1/2}$ in NMP are plotted against $M_w{}^{1/2}$ as shown in Figure 4; $K_\theta = (1.64 \pm 0.1) \times 10^{-3}$ is obtained. A small correction for polydispersity is not justified in view of the uncertainty in K_θ. The unperturbed end-to-end distance per unit mass is obtained from

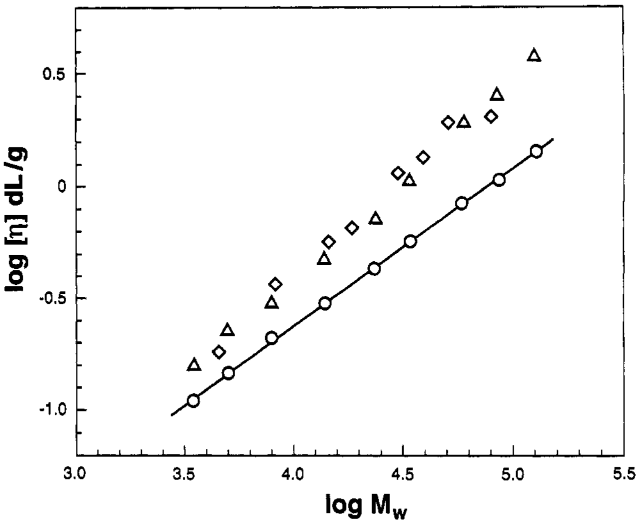

Figure 3. Double logarithmic plot of the intrinsic viscosity against molecular weight for MePEEK fractions: ○, MePEEK in NMP; △, MePEEK in MSA; ◇, PEEK in MSA.

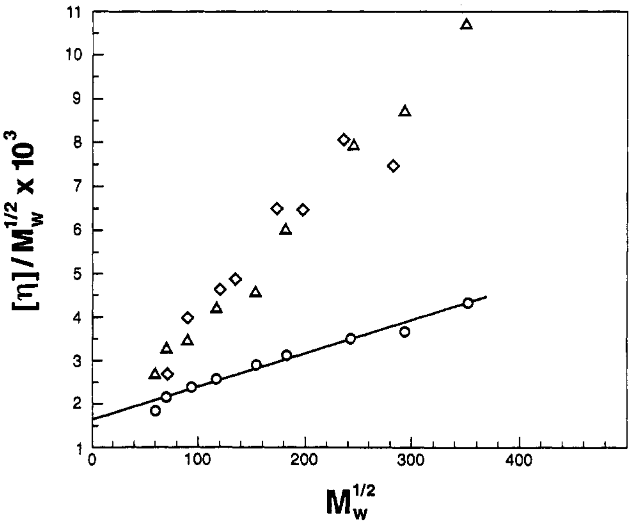

Figure 4. Stockmayer–Fixman plot for MePEEK fractions: ○, intrinsic viscosity in NMP; △, intrinsic viscosity in MSA; ◇, intrinsic viscosity of PEEK in MSA.

$$\langle r^2\rangle_0/M = [K_\theta/\Phi_0]^{2/3} = 0.755\ \text{Å}^2 \qquad (5)$$

where the Flory constant $\Phi_0 = 2.5 \times 10^{21}$ for ordinary fractionated polymers, and the intrinsic viscosity is expressed in dL/g. The characteristic ratio for MePEEK can be obtained according to

$$C_\infty = \{\langle r^2\rangle_0/M\}(m_0/l_0{}^2) = 2.44 \qquad (6)$$

Because of the similar structure of MePEEK and PEEK, $l_0{}^2$, the mean-square main-chain bond length, has been calculated with the values quoted by Bishop.[12] $l_0{}^2 = (2a^2 + b^2)/3 = 31.18$ Å^2 ($a = 5.62$ Å is the bond length between ketone–ether and $b = 5.51$ Å is the bond length between ether–ether), and $m_0 = 302.3/3 = 100.8$. A value of 2.44 for C_∞ suggests that MePEEK is a freely rotating chain

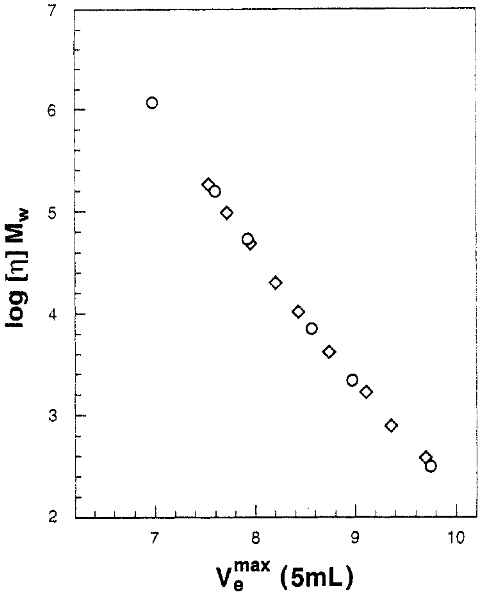

Figure 5. Universal calibration plot for SEC data obtained in NMP: ○, narrow MW distribution polystyrene standares; ◇, MePEEK fractions.

Table IV. Glass Transition Temperature of MePEEK Fractions

sample	M_w	M_n[a]	T_g, °C
FW58B3	123 600	92 900	153.5
FW58B4	85 500	72 450	153.0
FW58B5	58 800	49 400	152.4
FW58B6	33 800	28 400	151.1
FW59B2	23 800	18 700	146.2
FW59B3	13 550	11 300	144.0
FW59B4	8 020	6 800	138.6
FW59B5	4 950	4 450	132.2
FW59B6	3 450	3 100	123.5

[a] Based on M_w from light scattering and M_w/M_n from SEC.

with average ether and carbonyl bond angles of 115°. C_∞ = 2.44 is lower than the previous estimated of C_∞ = 3 of PEEK. This value of C_∞ was based on intrinsic viscosity measurements in MSA or mixed polar solvents.[9,12] As shown in Figures 3 and 4, the precision of the intrinsic visocities in these polar solvents makes accurate determination of K_θ difficult. Furthermore, the highly protonated state of PEEK-type polymers in these solvents may affect their conformation and invalidate the application of the Stockmayer–Fixman procedure. For the ketimine derivative of PEEK C_∞ = 3.0 has been obtained.[9] For the Radel-R polysulfone, which has a biphenyl unit along the chain and the sulfone group with bond angle of 104°, C_∞ = 1.96 has been obtained.[22] It should be noted that X-ray crystallographic data indicate that the bond angles in crystalline PEEK are 125–126°.[23-25]

The principle of universal calibration[26] is applicable to the SEC data obtained on MePEEK fractions in NMP at 52 °C. In Figure 5 the V_e^{max} of MePEEK fractions and polystyrene standards are plotted against log {[η]M_w}. Previously measured intrinsic viscosities of standard polystyrene in NMP have been used.[22]

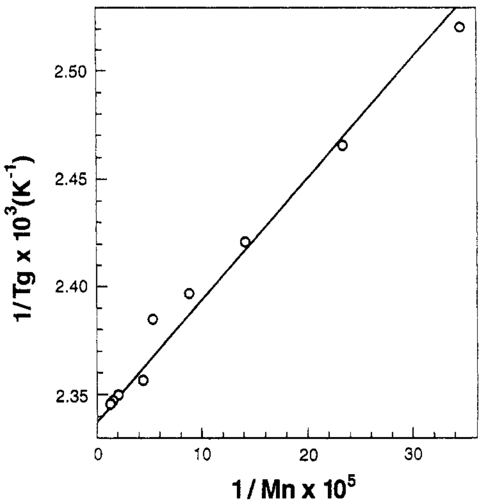

Figure 6. Ueberreiter–Kanig plot of glass transition temperature against molecular weight for MePEEK fractions.

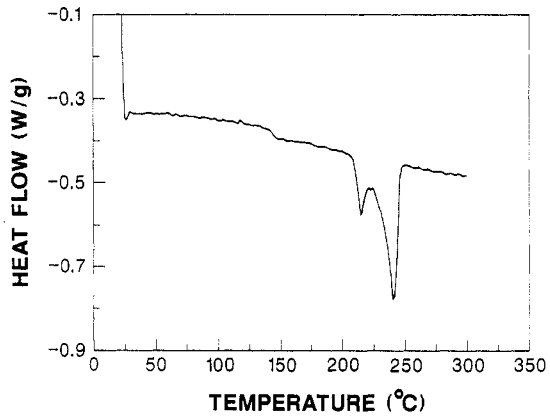

Figure 7. DSC trace of FW59B3.

The glass transition temperature of each fraction has been measured by DSC, and the results are listed in Table IV. The range of variation of T_g of MePEEK with different molecular weights is similar to that of PEEK.[10] The molecular weight dependence of T_g is shown in Figure 6 in the Ueberreiter–Kanig fashion as a plot of $1/T_g$ (K^{-1}) against $1/M_n$. M_n is calculated from the experimental values of M_w and M_w/M_n data in Table II obtained from SEC. The molecular weight dependence of T_g is given by

$$1/T_g = (2.338 \times 10^{-3}) + 0.625/M_n\ (\mathrm{K}^{-1}) \qquad (7)$$

Accordingly, T_g^∞ is 154.5 °C. T_g^∞ for PEEK is 152.2 °C,[10] and for *tert*-butyl PEEK T_g is 175 °C.[7]

The low molecular weight fractions of MePEEK have a tendency to crystallize during the heating process. Fraction FW59B3 was annealed at 200 °C for 60 min and was then scanned again. This DSC trace is shown in Figure 7. A double melting endotherm was observed between 200 and 250 °C with a maximum at 241 °C. The double melting process in PEEK is observed at much higher temperatures. It can be concluded that MePEEK can be crystallized under a narrow range of conditions. The crystallization window, i.e., the gap between T_g and T_m, is much smaller in MePEEK than in PEEK, and high molecular weight samples of MePEEK never combine the correct mobility and undercooling to crystallize to any extent. Some solvent treatments can broaden the crystallization window of MePEEK.[27]

The viscoelastic properties of MePEEK could be reproducibly measured on all fractions near 250 °C. Sample FW59B3 (M_w = 13 550) crystallized below 230 °C, but could be quenched at 172.7 °C in the rheometer. However, it cannot be ascertained that a small amount of crystallinity is not introduced during quenching. Sample FW59B2 (M_w = 23 800) was measured from 250 down to 161 °C, but measurements below 211 °C are affected by a very small amount of slow crystallization. Crystallization is first revealed by an increase of the low-frequency values of G'. No sign of crystallization has been observed during measurements on the other fractions.

Table V. Viscoelastic Properties of MePEEK at 250 °C

sample	M_w	η_0, P (250 °C)	T_g, °C	η_0, P (T_g + 90 °C)	$G_N^0 \times 10^{-7}$, dyn/cm²	log $\tau_{G''\max}$,[a] s	log $\tau_{G''=G'}$,[a] s
FW59B4	8 020	3.10×10^2 [b]	138.6	9.6×10^2			
FW59B3	13 550	2.2×10^3	144.0	5.9×10^3			-1.35_5
FW59B2	23 800	1.92×10^4	146.2	4.4×10^4		−1.10	−0.38
FW58B6	33 800	2.28×10^5	151.1	3.6×10^5	3.1	−0.73	−0.16
FW147B4	38 150[c]	2.23×10^5	150.6	$3.7_5 \times 10^5$	3.1 ± 0.1	−0.32	0.16
FW58B5	58 800		152.4		3.3 ± 0.1	-0.07_5	0.52
FW147B3	59 900[c]		152.6		3.25 ± 0.1	+0.33	0.90
FW58B4	85 500		153.0		3.2 ± 0.2	+0.88	1.52

[a] At T_g + 40 °C. [b] $J_e^0 = 1.51 \times 10^{-7}$ cm²/dyn. [c] From [η] in NMP and eq 2.

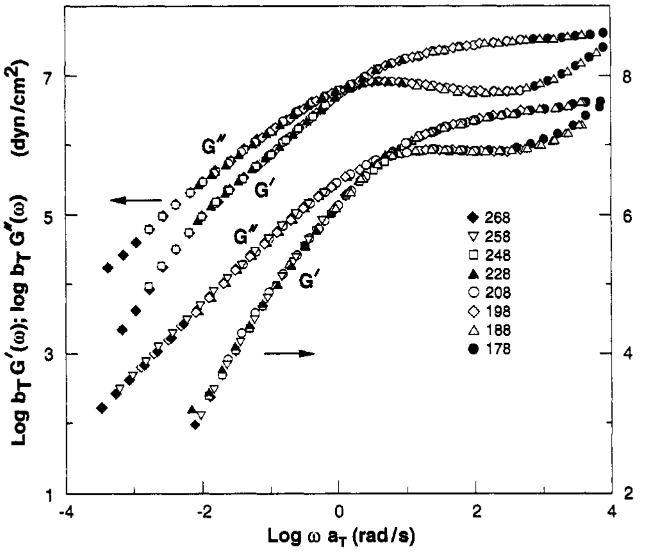

Figure 8. Master curves of G'' and G' against frequency for FW58B6 (top cruves, left axis) and FW59B2 (bottom curves, right axis). The temperatures are the temperature setting on the instrument, which differ slightly from the true calibrated temperatures of the sample.

All samples listed in Table V show the viscoelastic characteristics of entangled linear polymers with a crossover of values of G' and G'' at low frequencies. When no crystallization occurs, the frequency–temperature superposition used to construct master curves is quite satisfactory (see Figure 8).

The horizontal shift factors obey

$$\log a_T = B/(T - T_\infty)$$

with $T_\infty = T_g - 42$ °C. The average value of $B = 428 \pm 30$ K, and the free volume expansion coefficient $\alpha_f = (2.303B)^{-1} \approx 1 \times 10^{-3}$ K^{-1}. The thermorheological complexity previously observed for Radel-R fractions[13] was not found in this study, probably because the transition zone has not been studied to the same depth.

The zero-shear viscosities, determined from

$$\eta_0 = \lim_{\omega \to 0} (G''/\omega)$$

at 250 °C are shown in Table V. For the low molecular weight fractions $\eta_0 \propto M_w^{4.5}$. A similar relation has been observed for Radel-R fractions,[13] and for poly(EEKK) polymers based on bisphenol-A.[28]

The high exponent for the molecular weight dependence of the zero-shear viscosity is due to the omission of correction to iso-free volume (or iso-friction) conditions. Values of η_0 at T_g + 90 °C are also given in Table V. In that case $\eta_0 \propto M_w^{3.7}$ in reasonable agreement with the relation expected for a linear polymer.

High molecular weight fractions FW58B4, FW58B5, FW58B6, and FW14B3 contain different amounts of a (branched?) high molecular weight material. The values of η_0 for these fractions are therefore higher than expected and difficult to determine accurately. Low shear rate measurements are very sensitive to traces of high molecular weight impurities that are difficult to detect in the dilute solution characterization of the samples.

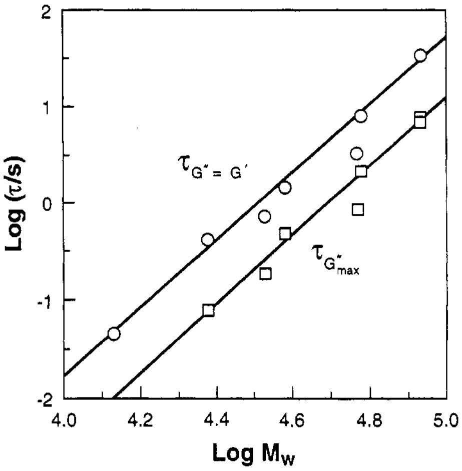

Figure 9. log τ against molecular weight for MePEEK fractions.

At low frequency, G'' and G' cross over and G'' goes through a maximum. Values of $\tau = \omega^{-1}$ (s) associated with these features are given in Table V. It can be seen from Table V that the ratio $\tau_{G''=G'}/\tau_{G''\max}$ is about 4.0. This is due to a large extent to the residual molecular weight distribution of the fractions.

Values of $\tau_{G''=G'}$ and $\tau_{G''\max}$ are closely related to the longest relaxation times of the sample,[29] but are less affected by the presence of traces of high molecular weight material than the melt viscosities. The molecular weight dependence of $\tau_{G''=G'}$ and $\tau_{G''\max}$ at T_g + 40 °C (iso-free volume condition) is given by $M_w^{3.2}$ as expected for the terminal relaxation time of a series of linear polymers (see Figure 9).

The plateau modulus of entangled polymer is derived from integration under the loss modulus peak according to[29]

$$G_N^0 = \frac{2}{\pi} \int_{-\infty}^{+\infty} [G''(\omega) - G_s''(\omega)] \, d \ln \omega \qquad (8)$$

where contributions from the transition zone $G_s''(\omega)$ are subtracted, as shown in Figure 10. Experimental values of G_N^0 at 190 °C are given in Table V. Application of the theory of rubber elasticity to the temporary network formed by entangling polymers is used to calculate the molecular weight between entanglements according to

$$M_e = \rho \frac{RT}{G_N^0} \qquad (9)$$

where R is the gas constant, T the absolute temperature, and ρ the density. From $G_N^0 = 3.3 \times 10^7$ dyn/cm², M_e = 1450 at 190 °C is obtained, with ρ estimated to be 1.16.[30]

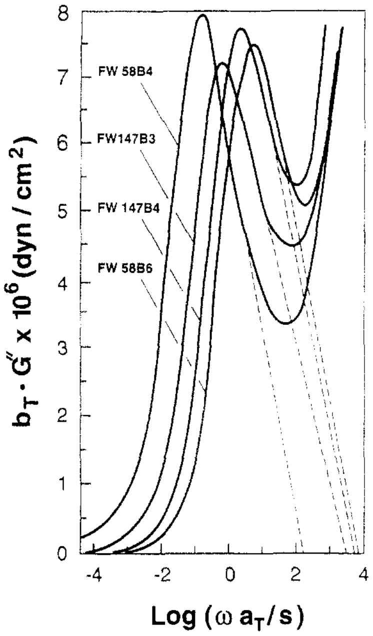

Figure 10. Loss moduli master curves against the logarithm of the frequency for the calculation of $G_N{}^0$.

This value of M_e can be compared to $M_e = 1300$ of PEEK at 350 °C, which was calculated by applying the Graessley–Edwards molecular description of chain entanglements.[13]

The results of the present study allow us to check the Graessley–Edwards molecular model for chain entanglement. They proposed that

$$\frac{G_N{}^0 l^3}{kT} \propto (\nu L l^2)^a \qquad (10)$$

where $l = l_0 C_\infty$ ($l_0 = 5.58$ Å and $C_\infty = 2.44$), $\nu = \rho N_A/M$, $L = Ml_0/m_0$, and $a = 2$–2.25. With $G_N{}^0 = 3.3 \times 10^7$ and $\rho = 1.16$ g/cm^3 for MePEEK at 190 °C, the left-hand side of relation 10 yields 1.32 and the right-hand side yields 7.48. These values place MePEEK slightly above the line drawn in Figure 9 of ref 13, in the neighborhood of Radel-R and bisphenol-A polycarbonate.

It is worth noting that the conclusions drawn from the study of MePEEK can only be applied directly to PEEK when it is assumed that the methyl substitution introduces a minor perturbance in the backbone conformation. It should also be stressed that we have assumed that the unperturbed dimension of MePEEK is identical under the θ-solvent condition and in the melt. In particular, the possible temperature dependence of the unperturbed dimension of MePEEK is unknown. Caution is required in the interpretation of the result. In the case of amorphous bisphenol-A polycarbonate, it has been reported that the value of $(\langle R_G{}^2\rangle/M_w)^{1/2}$ is 20% larger in the solid state [31,32] than under the θ-condition.[33] After this paper was written, a paper by Herrmann-Schönherr et al.[34] came to our attention. These authors calculated $C_\infty = 2.45$ for PEEK in good agreement with our results. Their estimate of $M_e = 2100$ for PEEK, obtained by applying the method of Wu,[35] is outside the limits of error of our experimental determination.

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References and Notes

(1) Rose, J. B. *NATO ASI Ser., Ser. C* **1987**, *215*, 207.
(2) Hergenrother, P. M.; Jensen, B. J.; Havens, S. J. *Polymer* **1988**, *29*, 358.
(3) Gardner, K. H.; Hsiao, B. S.; Matheson, R. R.; Wood, A. A. *Polymer* **1992**, *33*, 2483.
(4) Kricheldorf, H. R.; Delius, U.; Tonnes, K. U. *New Polym. Mater.* **1988**, *1*, 127.
(5) Kricheldorf, H. R.; Bier, G. *Polymer* **1984**, *25*, 1151.
(6) Mohanty, D. K.; Lin, T. S.; Ward, T. C.; McGrath, J. E. *SAMPE Symp.* **1986**, *31*, 945.
(7) Risse, W.; Sogah, D. Y. *Macromolecules* **1990**, *23*, 4029.
(8) Bennett, G. S.; Farris, R. J.; Thompson, S. A. *Polymer* **1991**, *32*, 1633.
(9) Roovers, J.; Cooney, J. D.; Toporowski, P. M. *Macromolecules* **1990**, *23*, 1611.
(10) Day, M.; Deslandes, Y.; Roovers, J.; Suprunchuk, T. *Polymer* **1991**, *32*, 1258.
(11) Deslandes, Y.; Sabir, F. N.; Roovers, J. *Polymer* **1991**, *32*, 1267.
(12) Bishop, M. T.; Karasz, F. E.; Russo, P. S.; Langley, K. H. *Macromolecules* **1985**, *18*, 86.
(13) Roovers, J.; Toporowski, P. M.; Ethier, R. *High Perform. Polym.* **1990**, *2*, 165.
(14) Mohanty, D. K.; Lowery, R. C.; Lyle, G. D.; McGrath, J. E. *SAMPE Symp.* **1987**, *32*, 408.
(15) Pretsch, E.; Clerc, T.; Seibl, J.; Simon, W. *Tables of Spectral Data for Structure Determination of Organic Compounds*; Biemann, K., Translator; Springer-Verlag: Berlin, 1983.
(16) Morris, G. A. In *Topics in ^{13}C NMR Spectroscopy*; Levy, G. C., Ed.; Wiley: New York, 1984; Vol. 4, pp 179–96.
(17) Abraham, R. J.; Haworth, I. S.; Bunn, A.; Hearmon, R. A. *Polymer* **1990**, *31*, 126.
(18) Stober, E. J.; Seferis, J. C.; Keenan, J. D. *Polymer* **1984**, *25*, 1845.
(19) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row: New York, 1971.
(20) Oono, Y. *J. Chem. Phys.* **1983**, *79*, 4629.
(21) Stockmayer, W. H.; Fixman, M. *J. Polym. Sci. C* **1963**, *1*, 137.
(22) Roovers, J.; Ethier, R.; Toporowski, P. M. *High Perform. Polym.* **1990**, *2*, 151.
(23) Dawson, P. C.; Blundell, D. J. *Polymer* **1980**, *21*, 577.
(24) Rueda, D. R.; Amia, F.; Richardson, A.; Ward, I. M.; Balta Calleja, F. J. *Polym. Commun.* **1983**, *24*, 258.
(25) Hay, J. N.; Kemmish, D. J.; Langford, J. I.; Rae, A. I. M. *Polym. Commun.* **1984**, *25*, 175.
(26) Grubisic, Z.; Rempp, P.; Benoit, H. *J. Polym. Sci. B* **1967**, *5*, 753.
(27) Handa, P.; Wang, F.; Roovers, J. Unpublished results.
(28) Hinkley, J. A.; Crook, R. A.; Davis, J. R. *J. High Perform. Polym.* **1989**, *1*, 61.
(29) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; J. Wiley & Son: New York, 1980.
(30) The density of MePEEK at 25 °C is 1.233 g/cm^3. The thermal expansion coefficient below T_g was found to be 3×10^{-4} K^{-1}, and the thermal expansion coefficient above T_g was found to be 1×10^{-3} K^{-1} from the rheological measurements.
(31) Garwrisch, W.; Brereton, M. G.; Fischer, E. M. *Polym. Bull.* **1981**, *4*, 687.
(32) Ballard, D. G. H.; Burgess, A. N.; Cheshire, P.; Janke, E. W.; Nevin, A.; Schelten, J. *Polymer* **1981**, *22*, 1353.
(33) Berry, G. C.; Nomura, H.; Mayhan, K. G. *J. Polym. Sci.; Part A-2* **1967**, *5*, 1.
(34) Herrmann-Schönherr, O.; Schneller, A.; Seifert, A. M.; Soliman, M.; Wendorff, J. H. *Makromol. Chem.* **1992**, *193*, 1955.
(35) Wu, S. *J. Polym. Sci.; Part B: Polym. Phys.* **1989**, *27*, 723.