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Synthesis and Characterization of Narrow Molecular Weight Distribution Fractions of Poly(aryl ether ether ketone)†

Jacques Roovers,* J. David Cooney, and Paul M. Toporowski

Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A OR9. Received April 26, 1989; Revised Manuscript Received July 31, 1989

ABSTRACT: Narrow molecular weight distribution fractions of poly(aryl ether ether ketone) have been prepared by hydrolysis of fractions of poly(aryl ether ether ketimine) prepolymer. The molecular weights of the prepolymer and the poly(ether ether ketone) fractions have been measured. Comparison of the molecular weight measurements indicates that the hydrolysis does not affect the backbone of the polymer. It is shown that poly(ether ether ketone) is probably protonated in methanesulfonic acid. *p*-Chlorophenol/*o*-dichlorobenzene is a good solvent mixture for poly(ether ether ketone), probably with preferential solvation by *p*-chlorophenol. The Stockmayer–Fixman treatment of the intrinsic viscosity data indicate that in the unperturbed state poly(ether ether ketone) has the dimensions of a freely rotating flexible chain. The thermal properties of the poly(ether ether ketone) fractions resembles those of commercial PEEK samples.

Introduction

Poly(aryl ether ketones) have been introduced commercially as a new class of high-temperature thermoplastics for engineering applications. Consequently, these polymers have become the subject of study in many laboratories. The most prominent member of the poly(aryl ether ketones) is poly(oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4-phenylene) in short PEEK. Research is usually performed on PEEK samples provided directly by the producer or after transformation by a processor. PEEK is commercially produced by nucleophilic subsitution polycondensation in diphenyl sulfone above 335 °C.[1] These severe reaction conditions, the use of additives, and different heat treatments may result in a large variability of the properties of the samples. At best these samples are identified by their grade code and sometimes by a batch number. Rarely is a molecular weight provided. Molecular characterization is not routinely performed because the semicrystalline PEEK is insoluble in common solvents. It is soluble only in strong acids or in high-boiling solvents above the melting point of the polymer ($\approx$350 °C). Two studies on PEEK samples dissolved in H_2SO_4 have provided molecular characterization.[2,3] Unfortunately, PEEK is sulfonated to various extents in H_2SO_4.[4]

Recently, Mohanty et al.[5] and Kelsey et al.[6] have developed methods to produce amorphous precursor polymers for poly(aryl ether ketones). In both cases the precursor polymer is produced at lower temperature and converted to the poly(aryl ether ketone) by hydrolysis. Kelsey et al. secured solubility by converting 4,4′-dihydroxybenzophenone monomer to the corresponding 1,3-dioxolane.[4] In this study we have used the ketimine precursor method of Mohanty[5] to synthesize an amorphous soluble precursor polymer, which we call poly(ether ether ketimine). This polymer has been fractionated, and the fractions have been characterized by various dilute solution techniques. The poly(ether ether ketimine) fractions have subsequently been converted to poly(ether ether ketone), a polymer that is chemically equivalent to commercial PEEK. The poly(ether ether ketone) fractions are characterized by light-scattering and intrinsic viscosity measurements in methanesulfonic acid. Intrinsic viscosities have also been measured in some mixed solvents at room temperature. A number of bulk characteristics of the poly(ether ether ketone) fractions have been determined and are compared with those of commercial PEEK.

Experimental Section

Synthesis of Ketimine Monomer.[5] 4,4′-Difluorobenzophenone (Aldrich) was recrystallized from diethyl ether (mp 112.2 °C). Aniline was dried over CaH_2 overnight and distilled at reduced pressure under N_2. It was immediately used. Toluene was refluxed over CaH_2 and distilled. Molecular sieves (Aldrich, 3 Å) were used as received. 4,4′-Difluorobenzophenone (0.1 mol) was reacted with aniline (0.11 mol) in 150 mL of refluxing toluene for 24 h in the presence of 150-g molecular sieves. The 4,4′-difluorobenzophenone *N*-phenylimine (I), in Figure 1, was twice crystallized from toluene (mp 115.2 ± 0.2 °C). Yield: 60–70%.

Synthesis of Poly(ether ether ketimine).[5] Hydroquinone (Anachemia) was crystallized three times from acetone under N_2 until the saturated solution was colorless. The crystals (mp 177 °C dec) were stored under vacuum and used within 1 week. 4-Fluorobenzophenone (Aldrich) was twice crystallized from diethyl ether (mp 49.1 °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 [bp 55 °C (8 mmHg)]. Hydroquinone (0.05 mol), I (0.05 mol), 175 mL of NMP, and 85 mL of toluene were charged together with 10 g of K_2CO_3 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 slowly to 143 °C, when the toluene–azeotrope began to reflux, and then to 170 °C over a 4-h period to remove all water. The polycondensation was performed at 175 ● 2 °C for 8–18 h. The increase in the molecular weight was monitored by size-exclusion chromatography (SEC). The reaction was terminated with excess 4-fluorobenzophenone and cooled to room temperature. The mixture was diluted with 200 mL of THF, and 5 mL of glacial acetic acid were added. The mixture was filtered and the polymer precipitated in CH_3OH containing 10% H_2O. Reactions were also performed with 0.1 mol of the reagents in the same volume of solvent.

Fractionation of Poly(ether ether ketimine). A 1% or less solution of poly(ether ether ketimine) in benzene was fractionally precipitated with *n*-hexane between 20 and 35 °C. Fractionation was monitored with SEC. The fractions were diluted with THF and precipitated in hexane–isopropyl alcohol (1/1). The precipitate was washed with CH_3OH and dried in vacuo at room temperature.

Hydrolysis of Poly(ether ether ketimine). Methanesulfonic acid (99%; Aldrich; MSA) was distilled under N_2 at reduced

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Table I
Molecular Characteristics of Poly(ether ether ketimine) Fractions

sample	d*n*/d*c*, mL/g 546	d*n*/d*c*, mL/g 633	M_w 546	M_w 633	$A_2 \times 10^4$, mL/g^2	M_w/M_n
PREKA001A22	0.269	0.258		68 200	6.5[a]	1.6
PREK001B	0.277	0.269	38 900	39 400	7.4	1.5
PREK001C		0.264		17 800	8.8	1.5
PREK002C	0.272	0.259	22 600	22 800	12.5	1.2_5
PREK002D			10 700	10 200	12.0	1.2
PREK002E	0.276		5 800		16.9	1.2
PREK004D			100 200		8.5[b]	1.3
PREK004E			49 400		8.5[c]	1.3

[a] $\langle R_G{}^2\rangle_z = 322$ nm^2. [b] $\langle R_G{}^2\rangle_z = 310$ nm^2. [c] $\langle R_G{}^2\rangle_z = 165$ nm^2

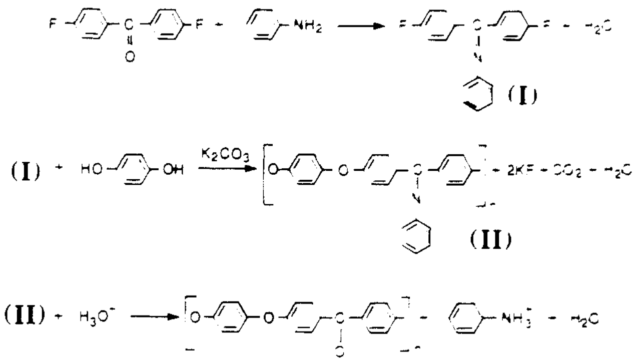

Figure 1. Reaction scheme for the synthesis of poly(ether ether ketone).

pressure (bp <140 °C). The colorless distilled acid was assayed 99.5% pure. Finely divided powder of poly(ether ether ketimine) was hydrolyzed in refluxing water containing 10% MSA (bp 115 °C) for 24 h. The high concentration of MSA ensured wetting of the polymer. The color of the powder changed from pale yellow to white. The poly(ether ether ketone) was washed three times with large amounts of boiling water to pH = 5. Alternatively, to very dilute solutions of poly(ether ether ketimine) in THF, 10% by volume of an aqueous solution containing 20% MSA was added under vigorous stirring. At first a bright yellow precipitate formed, which completely redissolved. Then, suddenly a white precipitate appears. The latter was stirred for 24 h. The polymer was filtered and washed with boiling water. If hydrolysis was not complete, the polymer was dissolved in MSA (1% w/v) and reprecipitated in 9-fold ice water under vigorous stirring. This mixture was then treated as in the heterogeneous hydrolysis described previously.

Analysis of Poly(ether ether ketone). Pyrolysis of the samples (2–8 mg) was performed for 10 s at 1500 °C under helium flow using a Chemical Data Systems Inc. 120 Pyroprobe. The pyrolysis vapors passed through a GC system with a 30-m Durabond fused silica capillary column (DB-5 column from J. and W. Scientific). A Hewlett-Packard 5970 series mass selective detector (MSD) was used to measure phenol ($m/z = 94$), aniline ($m/z = 93$), and benzonitrile ($m/z = 103$). Aniline and benzonitrile are decomposition products of the ketimine group in the polymer. The relative abundances of aniline to phenol or benzonitrile to phenol at the peak maxima were used to estimate the ketimine content. The method was calibrated with the poly(ether ether ketimine) precursor.

The thermal stability of the samples (12 mg) was determined using a Du Pont 951 thermogravimetric analyzer/2100 thermal analysis system at a heating rate of 10 °C/min in either air or nitrogen flowing at 50 mL/min.

Characterization of Poly(ether ether ketimine). The whole polymer and the fractions were routinely characterized by SEC. THF at 1 mL/min is the effluent. Five microstyragel columns of nominal pore size, 10^6, 10^5, 10^4, 10^3, and 500, were held at 35 °C. Intrinsic viscosities of the fractions were determined in THF at 25 °C using Ubbelohde semimicroviscometers with electronically measured flow times in excess of 150 s. The weight average molecular weights of all fractions were measured by Rayleigh light scattering in THF at 25 °C using vertically polarized light with $\lambda_0 = 546.1$ or 632.8 nm. The molecular weights are based on the Rayleigh ratio of benzene $R_{90,u} = 16.3 \times 10^{-6}$ (546) and 8.51×10^{-6} cm^{-1} (633).[7] The depolarization ratio $\rho_v = 0.42$ was used. The Rayleigh ratio at 633 is in good agreement with two other literature values: $R_{90,u} = 8.76 \times 10^{-6}$ [8] and $R_{90,u} = 8.35 \times 10^{-6}$.[9] The refractive index of poly(ether ether ketimine) in THF was measured with a Brice-Phoenix differential refractometer. Average values of d*n*/d*c* are 0.275 (546) and 0.264 (633) (mL/g). Experimental values of d*n*/d*c* are given in Table I.

Characterization of Poly(ether ether ketone) Fractions. Weight average molecular weights were determined by light scattering with a Fica 50 photogoniometer in distilled MSA at 30 °C. Solutions were made by weight. The density of MSA is 1.481 g/cm^3. Solutions were clarified by filtration through porous glass filters with 0.9–1.4-μm nominal pore size. For poly(ether ether ketone) fractions in MSA d*n*/d*c* = 0.376 ($\lambda_0 = 633$ nm) and 0.451 ($\lambda_0 = 546$ nm). High values of d*n*/d*c* have also been observed for PEEK in H_2SO_4.[2,3] The large dispersion of d*n*/d*c* is due to the absorption of light by the PEEK solutions.[3] Measurements were routinely made with 633-nm light and as a check with 546-nm light. Since poly(ether ether ketone) solutions in MSA have an absorption maximum at 420 nm and the absorption extends into the red, the observed scattered light intensities have been corrected for absorption according to[10]

$$I = I_{\text{measd}} \times 10^{\epsilon c l} \tag{1}$$

where l is the path length of the light in the cylindrical light scattering cell ($l = 2.5$ cm), ϵ is the extinction coefficient (mL/g·cm), and c the polymer concentration (g/mL) of each solution. This correction is applied before subtracting the scattering intensity of the pure solvent and corrections for photomultiplier sensitivity variations and goniometer misalignment.[11] After the light-scattering measurements the absorbance of each polymer solution was measured in ground-glass stoppered 1-cm square quartz cells with a Cary 210 spectrophotometer. The absorbance was used to verify that no polymer was retained by filtration and to calculate ϵ for use in eq 1. By means of optical filters, it was confirmed that fluorescence does not contribute to the measured light intensity at 633 nm. For experiments with 546-nm light an optical filter was placed in front of the photomultiplier. The molecular weight is then determined from the excess light scattered by the solution extrapolated to zero concentration and zero scattering angle, θ, according to

$$1/M_w = K(c/I)_{c=0/\theta=0} \tag{2}$$

where K is an instrument constant containing also $R_{90,u}$ of benzene and the d*n*/d*c* of the polymer.

Intrinsic viscosities of the poly(ether ether ketone) fractions were measured in MSA at 30 °C. The solvent flow time was about 213 s. The poly(ether ether ketone) solutions in MSA are stable for up to 1 week in ground-glass stoppered flasks. Concentrations resulting from dilutions performed in the viscometer were measured by their visible light absorbance. Flow times of polymer solutions in the viscometer were reproducible for up to 1 h.

Intrinsic viscosities of poly(ether ether ketone) fractions were also measured in mixtures of *p*-chlorophenol and *o*-dichlorobenzene at 35 °C. *p*-Chlorophenol (Aldrich) was distilled under

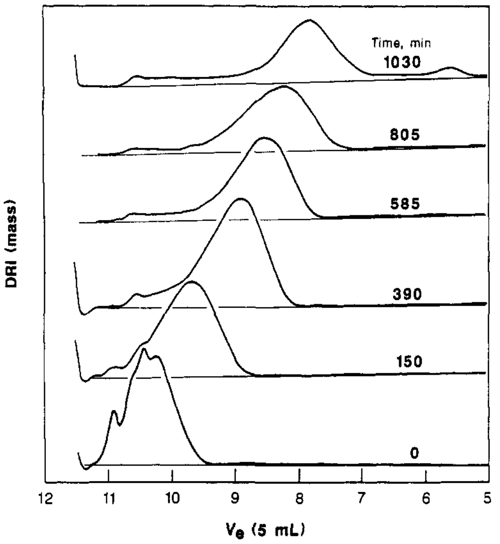

Figure 2. Size-exclusion chromatograms obtained during the synthesis of poly(ether ether ketimine).

reduced N_2 pressure before use.[12] *o*-Dichlorobenzene (Aldrich; filtered HPLC grade) was used as received. Solutions were made by weight. The polymers were first swollen overnight in a 60/40 (w/w) mixture of the two solvents and then heated for 3–5 min at 160 °C to complete dissolution. If necessary, other solvent compositions were then made by adding *o*-dichlorobenzene to the 60/40 (w/w) solution.

Results and Discussion

Synthesis and Characterization of Poly(ether ether ketimine). The three-step synthesis of poly(ether ether ketone) is given in Figure 1.[5]

A typical set of SEC patterns of the poly(ether ether ketimine) obtained at various stages of the synthesis is shown in Figure 2. The final SEC trace (1030 min) has a main peak at $V_e = 7.8$ and a $M_w/M_n \approx 2.0$ as expected for a step-growth polymer. Beside the main peak there is a small fraction of low MW material ($V_e > 9.0$). The low MW material can also be seen in Figure 6 of ref 5. Hergenrother ascribes it to cyclic oligomers.[13] Indeed, addition of 4-fluorobenzophenone at the start of the reaction reduced the importance of the low MW fraction. At very long times of reaction a very high molecular weight material is also observed. The V_e (5–6 counts) of this fraction indicates that it is not retained by the column set that has been used. It can be removed in the first fraction of the fractional precipitation. It is suspected that it is highly branched or cross-linked polymeric material. It has been hydrolyzed and characterized as poly(ether ether ketone) by its crystallization and melting behavior in DSC. The possibility that a side reaction produces branched and/or cross-linked high molecular weight material during polymerization at 175 °C should be kept in mind. Generally, this material is not found when lower MW poly(ether ether ketimine) polymers are prepared. A very sensitive UV detector set at 254 nm was also used to check qualitatively for the absence of this material in the poly(ether ether ketimine) fractions studied.

In Figure 3 the SEC profiles of the poly(ether ether ketimine) fractions retained for further study are collected. These were used to calculate the M_w/M_n ratios that are given in Table I. No correction for zone spreading has been applied.

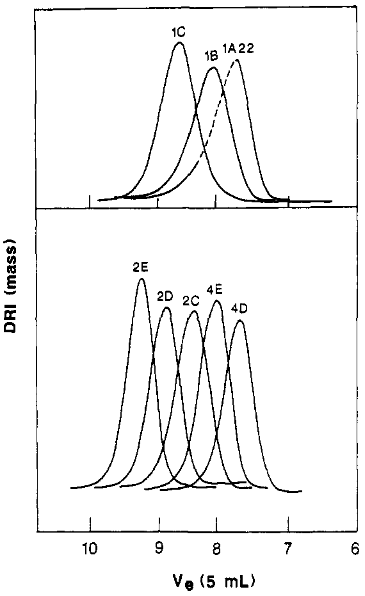

Figure 3. Size-exclusion chromatograms of poly(ether ether ketimine) fractions. The fractions at the top have M_w/M_n = 1.5–1.6. The fractions at the bottom have M_w/M_n = 1.2–1.3.

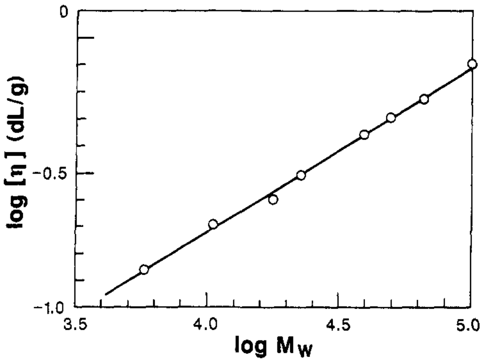

Figure 4. Double logarithmic plot of the intrinsic viscosity against molecular weight for poly(ether ether ketimine) fractions in THF at 25 °C.

Table II
Dilute Solution Properties of Poly(ether ether ketimine) Fractions

sample	M_w	$[\eta]_{THF}^{25°}$, dL/g	k_H	$[\eta]_{benz}^{35°}$, dL/g	k_H
PREK001A22	68 200	0.59_4	0.44		
PREK001B	39 200	0.43_8	0.41	0.41_8	0.54
PREK001C	17 800	0.250_5	0.45	0.25_0	0.48
PREK002C	22 700	0.31_0	0.42		
PREK002D	10 500	0.20_2	0.42		
PREK002E	5 800	0.139	0.40		
PREK004D	100 200	0.79_5	0.40		
PREK004E	49 400	0.51_0	0.46		

The weight average molecular weight for the eight poly(ether ether ketimine) fractions obtained in THF are given in Table I. They are usually based on $\theta = 90°$ measurements. Extrapolation to $\theta = 0°$ is performed when $M_w > 50\,000$. The values of the radius of gyration, $\langle R_G^2 \rangle_z$, in Table I are only given as an estimate since they are generally too low for accurate measurement with 546- or 633-nm light. The values of the second virial coefficient obtained from $(c/I)^{1/2}$ vs c plots are also given in Table I. $A_2 \propto M_w^{-0.23}$, in agreement with the dependence expected for a random-coil polymer in a good solvent.

The intrinsic viscosities of the poly(ether ether ketimine) fractions in THF at 25 °C are given in Table II and plotted double logarithmically against the weight average molecular weight in Figure 4. The Mark–Houwink–

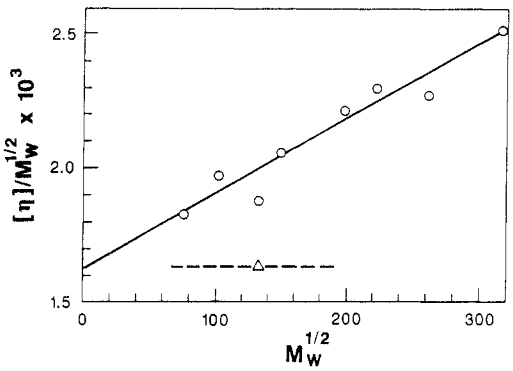

Figure 5. Stockmayer–Fixman plot for poly(ether ether ketimine): ○, intrinsic viscosities in THF; Δ, intrinsic viscosity in toluene.

Sakurada relation is

$$[\eta] = 6.3_4 \times 10^{-4} M^{0.61_7} \tag{3}$$

Some intrinsic viscosities were also determined in benzene at 35 °C. The data are given in Table II. It appears that benzene is only a slightly poorer solvent than THF for poly(ether ether ketimine). Only low MW fractions are soluble in toluene at 35 °C. For PREK001C, $[\eta]$ = 0.19 and k_H = 0.66. Toluene at 35 °C is therefore close to a Θ-solvent for poly(ether ether ketimine). This is confirmed by a Stockmayer–Fixman analysis of the intrinsic viscosity data in THF. Accordingly[14]

$$[\eta]/M_w^{1/2} = K_\theta + 0.51\phi_0 B M_w^{1/2} \tag{4}$$

where K_Θ is the Mark–Houwink–Sakurada constant for the Θ condition. B is related to the polymer–solvent interaction parameter, and ϕ_0 is the Flory constant relating the Θ-condition intrinsic viscosity of a polymer to its unperturbed end-to-end distance, $\langle r^2\rangle_0$, according to

$$K_\Theta = \phi_0(\langle r^2\rangle_0/M)^{3/2} \tag{5}$$

The results are shown in Figure 5. From $K_\Theta = 1.62 \times 10^{-3}$ one finds, with $\phi_0 = 2.5 \times 10^{21}$ (cgs units), $\langle r^2\rangle_0/M = 0.758$ Å^2. The poor precision of the $[\eta]$ and M_w measurement does not justify the small correction for polydispersity in the fractions.

The principle of universal calibration[15] of the SEC based on the hydrodynamic volume, $M_w[\eta]$, is applicable to poly(ether ether ketimine) fractions as shown in Figure 6. The calibration is based on narrow molecular weight anionic polystyrenes.[16,17] The values of $[\eta]$ for polystyrene are based on the equation of Benoit,[18] $[\eta] = 1.41 \times 10^{-4} M_w^{0.70}$, as recommended by Wagner.[19]

Synthesis and Characterization of Poly(ether ether ketone) Fractions. It has been found that the heterogeneous hydrolysis is best performed on a very fine powder of poly(ether ether ketimine) suspended in H_2O–MSA. None but the thinnest films of poly(ether ether ketimine) could be hydrolyzed, and they tended to break up in the boiling mixture. For its convenience we now prefer the hydrolysis of poly(ether ether ketimine) in the THF solution. The polymer yield on hydrolysis was typically 80.0% (theoretically 79.3%). After hydrolysis the N_2 content is less than (0.1 ± 0.1)% by elemental analysis. Both methods indicate that hydrolysis is at least 96% complete.

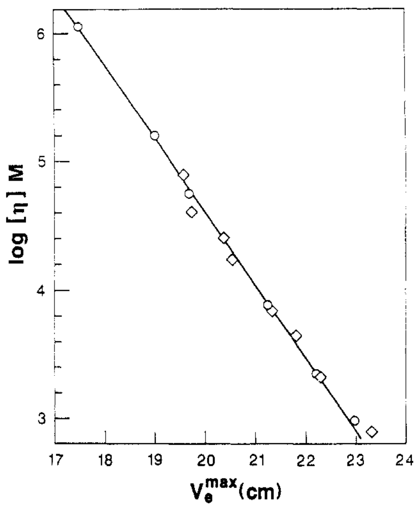

Figure 6. Universal calibration plot for SEC data obtained in THF: ○, narrow MW distribution polystyrene standards; ◇, poly(ether ether ketimine) fractions.

Table III
GC-MSD Analysis of Fractions of Poly(ether ether ketone)

sample	M_w	% ketimine groups
PREK001A22/1	54 100	
PREK001B/1	31 100	3.3
PREK001B/1′		<0.3
PREK001C/1	14 100	
PREK002C/1	18 000	0.9
PREK002D/1	8 300	0.9
PREK004D/1	79 500	0.7
PREK004D/2		1.9
PREK004D/2′		<0.5
PREK004E/1	39 200	1.0
PREK004E/2		1.7
PREK004E/2′		<0.3
PREK005C/1″	7 800	<0.3
PREK005D/1″	4 600	<0.3

The GC-MSD analysis of the pyrolysis products of poly(ether ether ketone) samples is a more sensitive method to detect traces of ketimine in the polymer. The percentage of ketimine groups as measured by the presence of aniline in the decomposition products is given in Table III. Analysis of the benzonitrile evolved gives slightly higher percentages, but an ordering of the samples by both methods results in an identical listing. The lower limit of reproducible analysis is 1 aniline/350 phenols (Table III). The benzonitrile level is similarly low. The ketimine free samples are colorless while the other samples are very pale yellow. The GC-MSD analysis is considered semiquantitative because we were unable to check that the decomposition of the precursor poly(ether ether ketimine) follows exactly the same path as the decomposition of the poly(ether ether ketone) fractions. Further physical characterization of the poly(ether ether ketone) fractions will be given later in a comparison with commercial PEEK.

The molecular characterization was mainly performed in MSA at 30 °C. MSA has the advantage over concentrated H_2SO_4 that it does not sulfonate poly(ether ether ketone). Moreover, it can be distilled easily. An example of a Zimm plot of poly(ether ether ketone) in MSA before and after correction for light absorbed by the solution is shown in Figure 7.

The extinction coefficients, ϵ_{633}, used to correct for absorption are given in Table IV. As expected, the correction for absorption does not affect the intercept greatly (and therefore neither the molecular weight). However, the radii of gyration and especially the second virial coefficients are affected more strongly.[2] Molecular weights can also be determined from light-scattering measurements with 546-nm light, but the 5 times larger extinction coefficient at that wavelength results in substantial corrections to the measured light intensities (up to 100%).

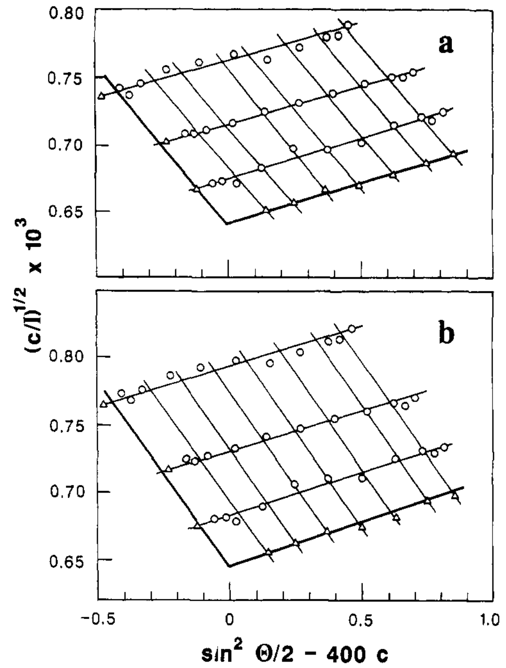

Figure 7. Zimm plot for PREK001A22/1. Light-scattering data obtained in methanesulfonic acid at 30 °C. (a) Data corrected for light absorbed by the solution. (b) Experimental data.

Table IV
Molecular Characteristics of Poly(ether ether ketone) Fractions

sample	M_{calc}[a]	M_w	ϵ_{633},[b] mL/g·cm	$\langle R_G^2 \rangle_z$ nm^2	$A_2 \times 10^3$, cm^3/g^2
PREK001A22/1	54 100	55 500[c]	32.3	645	6
PREK001B/1	31 100	32 200	28.4	380	10
PREK001C/1	14 100	13 500[d]	24.6	(100)	12
PREK002C/1	18 000				
PREK002D/1	8 300				
PREK002E/1	4 600				
PREK004D/1	79 500				
PREK004E/1	39 200				

[a] M_{calc} is the molecular weight of the precursor poly(ether ether ketimine) × (288.3/363.3). [b] Extinction coefficient at 633 nm in methanesulfonic acid. [c] M_w = 54 000 measured at 546 nm. [d] M_w = 13 000 measured at 546 nm.

Nevertheless, molecular weights determined at the two wavelengths agree remarkably well as shown in Table IV.

The experimental molecular weights of the poly(ether ether ketone) fractions are compared with those calculated from the precursor poly(ether ether ketimines), taking into account that the hydrolysis of the anilide group reduces the molecular weight by a factor of 0.793. Agreement between experimental and calculated molecular weights is excellent. See Table IV. These results indicate that hydrolysis proceeds without noticeable degradation of the backbone.

Table IV also includes values of the radius of gyration and the second virial coefficient for the poly(ether ether ketone) fractions in MSA. The experimental values of $\langle R_G^2 \rangle_z$ agree remarkably well with the radii of gyration measured by Bishop et al.[2] and Devaux et al.[3] (see Figure 8). Their data are for sulfonated PEEK samples in concentrated H_2SO_4. The comparison is made on the basis of their $(M_w)_u$, i.e., the molecular weight of the original or unsulfonated PEEK. The sulfonate group would shift their data by a factor of 1.28 or 0.107 log units along the molecular weight scale and make the agreement only slightly worse. The commercial PEEK samples have probably a wider MW distribution, and $\langle R_G^2 \rangle_z$ is therefore expected to be larger. One can therefore conclude that sulfonation does not seem to lead to a large expansion of PEEK over that observed for the poly(ether ether ketone) fractions in MSA. It should be noted that the line drawn in the log $\langle R_G^2 \rangle_z$ vs log M_w plot of Figure 8 has a slope of 1. In a good solvent this slope would be expected to be slightly larger (≤1.2). The small molecular weight range and experimental difficulties encountered with polymer solutions in strong acids preclude any definite conclusions on this point.

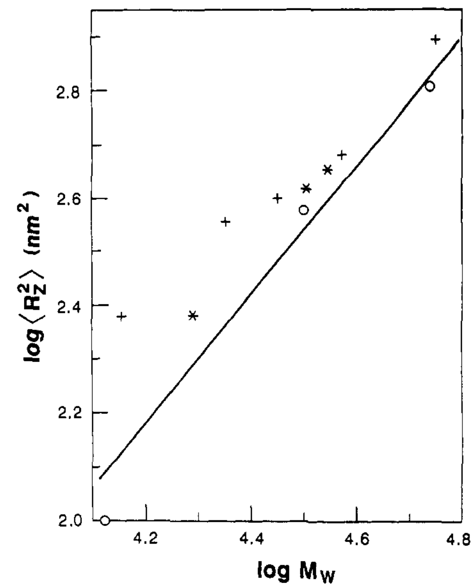

Figure 8. Double logarithmic plot of the mean-square radius of gyration against molecular weight for poly(ether ether ketone) fractions in MSA at 30 °C: ○, this work; +, data of ref 3 obtained on commercial PEEK samples in concentrated H_2SO_4; *, data of ref 2.

Table V
Molecular Characteristics of Poly(ether ether ketone) Fractions

sample	M_{calc}[a]	$[\eta]_{MSA}^{30°}$[b]	k_H	$[\eta]^{35°}$[c]	k_H
PREK001A22/1	54 100	1.87_5	0.425	1.24_5	0.41
PREK001B/1	31 100	1.15	0.44	0.86_5	0.33
PREK001C/1	14 100	0.54_8	0.42	0.45_2	0.42
PREK002C/1	18 000	0.65	0.30	0.55_5	0.37
PREK002D/1	8 300	0.36	0.49	0.33_8	0.40
PREK002E/1	4 600	0.18_1	0.30		
PREK004D/1	79 500	2.09	0.37	1.60_3	0.44
PREK004E/1	39 200	1.29_5	0.46	1.00	0.40

[a] M_{calc} is the molecular weight of the precursor poly(ether ether ketimine) × (288.3/363.3). [b] In dL/g. [c] Intrinsic viscosity (dL/g) in *p*-chlorophenol-*o*-dichlorobenzene (60/40 w/w).

Our values of A_2 are also given in Table IV. Agreement with the data of Bishop[2] and Devaux[3] is less satisfactory, however.

In Table V the intrinsic viscosities of the poly(ether ether ketone) fractions in MSA and in the mixed solvent consisting of *p*-chlorophenol-*o*-dichlorobenzene (60/40, w/w) are given. These data are shown in Figures 9 and 10. Figure 9 also includes the data of Bishop[2] and Devaux[3] obtained with commercial samples of PEEK in H_2SO_4. Figure 10 includes the data of Devaux in a 50/50 mixture of phenol and trichlorobenzene at 115 °C. In both cases the agreement is rather good. This corroborates the agreement obtained for the $\langle R_G^2 \rangle_z$ data, but, of course, the same caution should be applied in their interpretation. It was also observed that the intrinsic viscosities of the poly(ether ether ketone) fractions is little affected by the composition of the mixed solvent down to 25/75 (w/w) *p*-chlorophenol-*o*-dichlorobenzene.

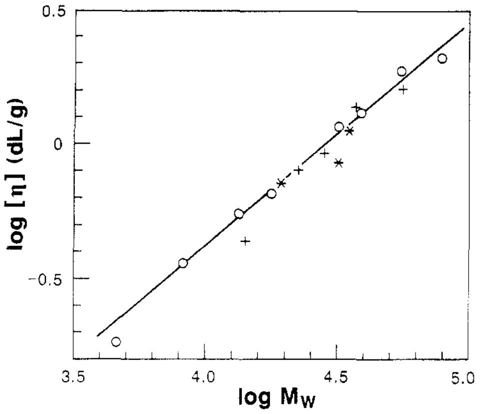

Figure 9. Double logarithmic plot of the intrinsic viscosity against molecular weight for poly(ether ether ketone) fraction in MSA. Symbols as in Figure 8.

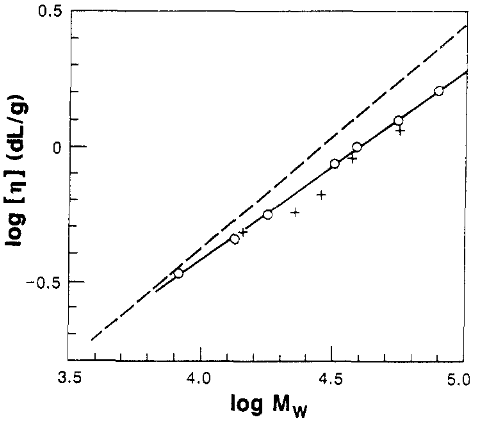

Figure 10. Double logarithmic plot of the intrinsic viscosity against molecular weight for poly(ether ether ketone) fractions in *p*-chlorophenol–*o*-dichlorobenzene (60/40, w/w). Symbols as in Figure 8. The dash line is for intrinsic viscosities in MSA from Figure 9.

The Mark–Houwink–Sakurada equation for poly(ether ether ketone) in MSA is

$$[\eta] = 2.26 \times 10^{-4} M^{0.81_8} \tag{6}$$

and in *p*-chlorophenol/*o*-dichlorobenzene

$$[\eta] = 5.86 \times 10^{-4} M^{0.70_2} \tag{7}$$

The difference in the solvent quality is immediately apparent from the exponents.

The UV–vis absorption spectra of poly(ether ether ketone) fractions in MSA and in the mixed solvent are compared in Figure 11. The poly(ether ether ketone) is strongly protonated in MSA with a maximum at 416 nm (ϵ = 48 000 L/mol·cm of repeat units). Note that the extinction coefficient is comparable to that of the diphenylcarbanion with λ_{max} = 470 nm and ϵ_{max} = 27 000,[20] suggesting that each ketone group is protonated. On the contrary, poly(ether ether ketone) in the mixed solvent shows a weak structureless spectrum, which seems to exclude the presence of specific protonation. The larger intrinsic viscosities in MSA can therefore be ascribed to chain expansion due to protonation. Of course the exponent in the mixed solvent (0.70_2) is characteristic of good polymer–solvent interaction, probably preferential interaction with the phenolic component.

The Stockmayer–Fixman technique has been used to estimate the unperturbed dimensions of poly(ether ether ketone), as shown in Figure 12. Data of both solvents extrapolate almost to a common intercept. K_Θ = 2.3 × 10^{-3} and 2.6 × 10^{-3} from MSA and *p*-chlorophenol–*o*-dichlorobenzene, respectively. As described above for the poly(ether ether ketimine) fractions, this allows the calculation of $\langle r^2\rangle_0/M$ = (0.99 ± 0.04) Å^2 where $\langle r^2\rangle_0$ is the unperturbed mean-square end-to-end chain length. The characteristic ratio for poly(ether ether ketone) is then

$$C_\infty = \langle r^2\rangle_0/nl^2 = 3.04 \pm 0.12 \tag{8}$$

For the calculation of l^2, the mean-square main-chain bond length, the values quoted by Bishop[2] have been used as shown in Figure 13. This value of C_∞ is typical of a freely rotating chain with approximately 120° valence angles. It is worth pointing out that the mean-square step length $b^2 = (\langle r^2\rangle_0/M)m_0$, where m_0 is the molecular weight of

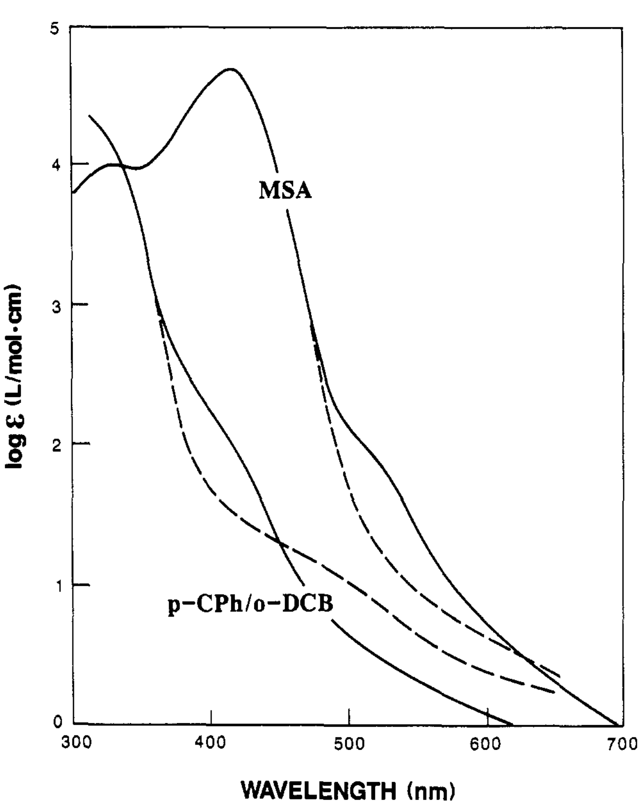

Figure 11. Logarithm of the molar extinction coefficient versus wavelength in methanesulfonic acid and in *p*-chlorophenol–*o*-dichlorobenzene (60/40, w/w): full line, PREK004E/1; dashed line, PREK005D/1″.

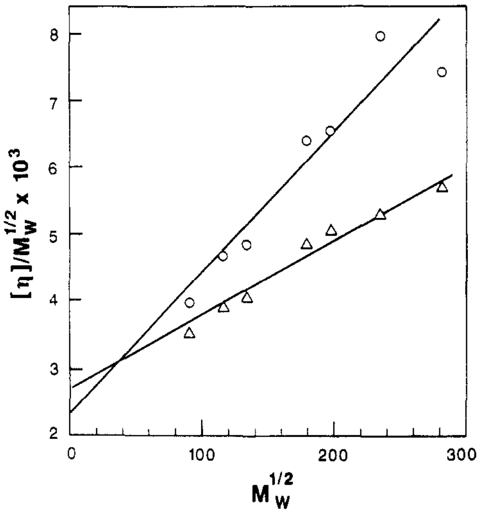

Figure 12. Stockmayer–Fixman plot for poly(ether ether ketone) fractions: ○, intrinsic viscosities in MSA; △, intrinsic viscosities in *p*-chlorophenol–*o*-dichlorobenzene.

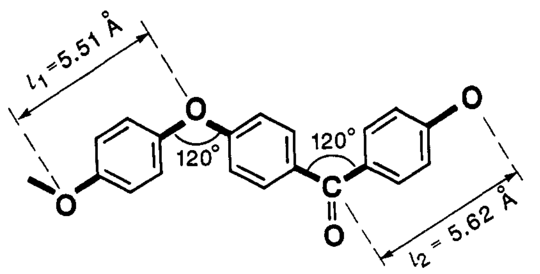

Figure 13. Molecular dimensions of the poly(ether ether ketone) repeat unit.[2]

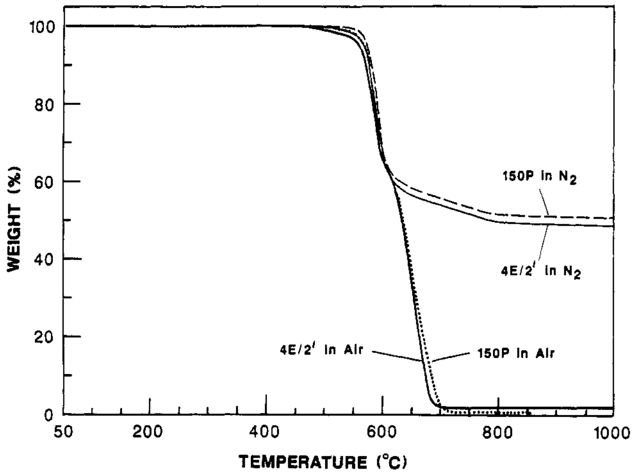

Figure 14. Thermogravimetry analysis traces of PREK004E/2′ and the commercial PEEK (150P). Obtained at 10 °C/min.

the repeat unit, is practically identical for poly(ether ether ketimine) and poly(ether ether ketone). This agrees, of course, with the identical backbone structure and similar bond angles in the two polymers.

At this point, it is worth returning to the UV-vis spectra of Figure 11. We never observed a shoulder or maximum at 550 nm in the absorption spectra measured in MSA. Attwood et al. ascribed this absorption to the triphenylcarbonium ion of a branch point.[1] However, we found a shoulder with somewhat variable absorbance around 500–510 nm for solution of poly(ether ether ketone) in MSA. In Figure 11 the absorption spectra of PREK004E/1 and PREK005D/1″ are compared. The absorbance at 500 nm correlates qualitatively with the residual anilide groups in the sample as measured by pyrolysis GC.

In Figure 11 the spectra of the same samples in the *p*-chlorophenol-*o*-dichlorobenzene (60/40) mixture are also shown. The sample containing a small percent of anilide group has a shoulder at 400 nm, but the anilide free sample (PREK005D/1″) has a longer tail with a shoulder at 500 nm. We found that the spectral details are somewhat sensitive to the details of the dissolution process as described in the Experimental Section. The color of the solutions in the 60/40 mixtures decreased reversibly with increasing temperature. No quantitative measurements on this phenomenon have been made. It suggests, however, that there is a definite interaction between two chemical groups, e.g., between the *p*-chlorophenol and the ketone. This phenomenon requires further study.

The possible effect of traces of anilide groups in the poly(ether ether ketone) fractions on the dilute solution properties described in this work has been checked by measuring intrinsic viscosities of the same fraction with different anilide contents. No effect has been found. This is consistent with the low levels of anilide shown in Table III.

Thermal Properties of Poly(ether ether ketone) Fractions. The thermal stability of poly(ether ether ketone) fractions has been compared to that of commercial PEEK (ICI grade 150 P) by thermogravimetry. In Figure 14 thermogravimetric curves of PREK004E/2′, heated in air and in nitrogen, are compared with those obtained on the PEEK sample.[21] The initial temperature of weight loss for both samples occurred at 470 °C in air and at 520 °C in nitrogen. In nitrogen there is 49% char at 1000 °C. Little residue was left in air after heating to 1000 °C. Of course, weight loss is a rather crude measure of thermal stability that gives no insight into the molecular transformations that may occur at lower temperature and/or over longer times.

Conclusions

Poly(ether ether ketimine) polymers have been prepared and fractionated. By hydrolysis, these fractions have been converted to poly(ether ether ketone) fractions with relatively narrow molecular weight distribution ($1.2 \leq M_w/M_n \leq 1.5$). A special effort has been made to reduce and quantify the residual anilide groups in the poly(ether ether ketone) fractions. The molecular weight of the poly(ether ether ketone) fractions compare well with those calculated from the parent poly(ether ether ketimine). Intrinsic viscosities of the poly(ether ether ketone) fractions have been measured in methanesulfonic acid and in a 60/40 mixture of *p*-chlorophenol and *o*-dichlorobenzene. A Stockmayer–Fixman treatment yields K_Θ, from which a characteristic ratio $C_\infty = 3$ is calculated for poly(ether ether ketone). This ratio is consistent with that of a freely rotating flexible chain with 120 °C valence angles.

Preliminary measurements of the thermal stability of the poly(ether ether ketone) fractions indicate that they are comparable to those of commercial PEEK. The study of T_g, T_c, and T_f under various conditions also supports the concept that these fractions are good models for commercial PEEK.[22] This work will be described in another report.

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Particle Formation and Catalyzed Agglomeration in Emulsion Polymerization

Herbert Schlueter

Research and Development, Dispersions Department, Hüls AG,
4370 Marl, Federal Republic of Germany.
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ABSTRACT: Catalyzed agglomeration, restricted to the particle formation phase of emulsion polymerization, can be used to distinguish experimentally whether or not a homogeneous nucleation mechanism is operative in a given persulfate-initiated emulsion polymerization system. The agglomeration catalyst used had a mode of action disclosed in earlier work, which proves that a homogeneous and not the generally accepted micellar nucleation mechanism is effective in a persulfate-initiated polymerization system even for monomers of low water solubility, such as styrene and butadiene, and emulsifier concentrations > cmc. Using catalyzed agglomeration, particle size and the monodispersity coefficient as well as the particle formation time were investigated as a function of monovalent cation concentration, emulsifier concentration and polymerization temperature. All correlations found either were consistent with homogeneous nucleation or completely excluded micellar nucleation. This means that poor water solubility of monomers like styrene and butadiene can no longer be a criterion for micellar nucleation. Homogeneous primary particle formation followed by agglomeration, which may be more or less pronounced or—in a few cases—does not occur at all, is most applicable and seems to be the particle formation mechanism generally valid for persulfate-initiated emulsion polymerization.

Introduction

Emulsion polymerization is one of the most important processes for manufacturing polymers. However, many mechanistic aspects of emulsion polymerization remain unclear despite its industrial importance. This applies especially to the initial stage of emulsion polymerization, the particle formation phase. Many mechanisms have been proposed for particle formation in emulsion polymerization systems. The most important are micellar nucleation,[1-3] homogeneous nucleation,[4-8] and coagulative nucleation.[9-11] In this paper, an attempt will be made to use catalyzed agglomeration as a means of deciding experimentally whether or not a homogeneous nucleation is operative in a specific polymerization system using in particular styrene and butadiene as monomers.

According to the micellar nucleation mechanism, radicals generated in the aqueous phase enter monomer-swollen soap micelles and initiate polymerization to form monomer-swollen polymer particles. Only one of every 100–1000 micelles captures a radical and becomes a polymer particle: the others disband, giving off monomer and soap molecules to neighboring micelles that have captured a radical.

According to the homogeneous nucleation mechanism, the radicals generated in the aqueous phase add monomer molecules until the oligomer radicals have exceeded their solubility limit and precipitate. The precipitated oligomer radicals form spherical particles that adsorb emulsifier molecules and absorb monomer molecules, thus becoming primary particles. These primary particles may be stable or may be stabilized by agglomeration.

In view of the questions raised in this paper, it is advisable to particularly emphasize three characteristic differences between micellar and homogeneous nucleation:

(1) When initiation is in the micelles, the end of the particle formation phase is characterized by complete disappearance of the micelles. When initiation is in the aqueous phase, particle nucleation continues during the course of polymerization but is moderated by capture of precipitated oligomer radicals and by agglomeration of primary and secondary particles. Consequently, the rate of particle formation (dN/dt) is only initially the same as the rate of radical formation (R_i). Within a short period of time, a steady state is reached between initiation and capture of precipitating oligomer radicals (R_c) and agglomeration of primary and secondary particles (R_a):[5]

$$dN/dt = R_i - R_c - R_a$$

Therefore the number of particles remains unchanged if

$$R_c + R_a = R_i$$

(2) A fundamental difference between micellar and homogeneous nucleation is the different action of monomer droplets and soap micelles. For initiation in micelles, monomer droplets serve as reservoirs providing the micelles with monomers via the aqueous phase, whereas for initiation in the aqueous phase the micelles provide the emul-