

Extension of the concept of chemical nucleation to poly(ether ketones)

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(Received 19 July 1989; revised 13 October 1989; accepted 19 October 1989)

Fast-crystallizing poly(ether ether ketone) (PEEK) and poly(ether ketone) (PEK) samples have been prepared by substitution of the F chain ends, leading to alkaline sulphonate groups. Ionic chain-end associations act as seeds for nucleation. The concept of chemical nucleation already demonstrated with poly(ethylene terephthalate) is shown to apply to PEEK and PEK.

(Keywords: poly(ether ketones); crystallization kinetics; nucleation; ionic polymers)

INTRODUCTION

Poly(ether ether ketone) (PEEK) is a crystallizable polymer and the processing conditions deeply influence the morphology and consequently the physical properties. A key factor controlling processing is the crystallization rate. Publications dealing with PEEK crystallization report overall kinetics¹⁻³, morphology⁴⁻⁷ and melting behaviour^{8,9} but few papers have discussed the nucleation step.

In previous papers¹⁰⁻¹³ we reported that the nucleation density of poly(ethylene terephthalate) (PET) can be artificially controlled by a mechanism called 'chemical nucleation'. It has been demonstrated that the presence of ionic chain ends in the polymer melt leads to ionic associations acting as seeds upon cooling.

The purpose of this paper is to investigate the application of a similar mechanism in PEEK and poly(ether ketone) (PEK). This work has been performed on PEEK and PEK samples synthesized by nucleophilic substitution of fluorinated benzophenones. In these samples all the chain ends are fluorine atoms^{14,15}; therefore a method¹⁶ was developed to substitute the F atoms by ionic groups ($-\text{SO}_3\text{X}$).

In this paper, we report the results dealing with the crystalline behaviour of the modified polymers.

EXPERIMENTAL METHODS

Gel permeation chromatography

The g.p.c. method for PEEK molecular-weight measurements has already been published¹⁴. The chromatograph is a Waters 150 C high-temperature equipment connected with a Trivector Data Station. Two Shodex (mixed bed) columns from Showa Denko (ref. AD-80M/S) are used in series. The working temperature is 115°C and the solvent is a 50/50 mixture of phenol and 1,2,4-trichlorobenzene. The flow is 1 ml min⁻¹ and the sample concentration is 2 g l⁻¹.

¹⁹F n.m.r. spectroscopy

In a previous paper¹⁵ it has been shown that PEEK chain ends are F atoms and that an accurate measurement of fluorine concentration leads to M_n values. In this work, we used the same technique to follow the F chain-end concentrations of various samples. The measurements were performed in 99–100% sulphuric acid using a Bruker WM 250 spectrometer working at 235.34 MHz.

Differential scanning calorimetry

The d.s.c. experiments were carried out under nitrogen using a Perkin-Elmer DSC-2 differential scanning calorimeter coupled with a TADS Data Station. The size of the samples varied between 5 and 10 mg. The d.s.c. instrument was calibrated with metal standards (indium and lead).

Before the d.s.c. runs all the samples were previously melted at 420°C for 2 min. For the T_{cc} determinations (crystallization temperature on cooling) the molten samples were cooled at 10°C min⁻¹. For T_{ch} determinations (crystallization temperature on heating) the molten samples were quenched at room temperature in acetone–solid CO₂ before heating at 10°C min⁻¹. The isothermal crystallization data at 298°C were obtained by cooling the molten samples at 320°C min⁻¹ to the pre-determined crystallization temperature. The isothermal crystallization data at 160°C were obtained with molten samples quenched in acetone at room temperature and then reheated rapidly (80°C min⁻¹) up to the crystallization temperature.

Optical microscopy

Optical microscopic observations were carried out with a Leitz Orthoplan–Pol microscope equipped with a Stanton Redcroft hot stage.

Melt viscosity

The melt viscosities were measured with a Davenport capillary rheometer working at 400°C at a shear rate of 1000 s⁻¹.

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PRODUCTS

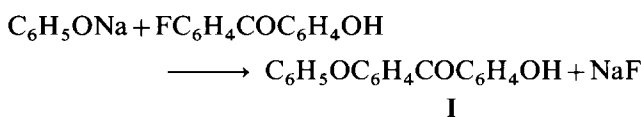
Polymers

The different PEEK and PEK samples used throughout this work were supplied by ICI. Their number-average molecular weights were ranging between 6500 and 17 000.

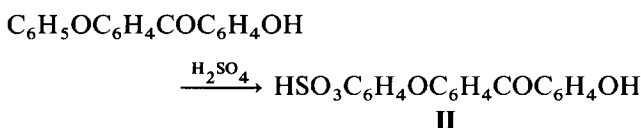
Salts

$\text{NaOC}_6\text{H}_4\text{SO}_3\text{Na}$. This salt has been obtained by neutralization of the corresponding phenol (4-hydroxybenzenesulphonic acid sodium salt supplied by Aldrich) in a 1 M sodium hydroxide solution. After neutralization the phenate-sulphonate sodium salt was dried overnight at 120°C under vacuum.

Na, Li and K salts of $\text{HOC}_6\text{H}_4\text{COC}_6\text{H}_4\text{OC}_6\text{H}_4\text{SO}_3\text{H}$. In a first step, sodium phenate is reacted with 4-fluoro-4'-hydroxybenzophenone (Aldrich) in dimethylformamide at 140°C for 6 h. The product I is then precipitated in iced water and dried at 60°C under vacuum. The purity is verified by ^{19}F n.m.r. and i.r. spectroscopy:



In a second step I was dissolved in concentrated sulphuric acid (99%). After 24 h at room temperature the sulphonated product is precipitated in water, washed with a 80/20 $\text{H}_2\text{O}/\text{HCl}$ solution and dried under vacuum at room temperature:



Finally, both sulphuric and phenol end groups of the product II were neutralized using a 1 M sodium hydroxide solution. After reaction, the salt is washed with water and dried overnight at 100°C under vacuum.

Sample preparation

PEEK or PEK salt systems. The fluorine end-groups of PEEK or PEK were reacted with the salts in benzophenone at 300°C for different times. The polymer and the salt were previously mixed in methanol (slurry method). After reaction the modified polymer was precipitated in acetone, washed with methanol and dried overnight at 80°C under vacuum. Polymer/salt reactions were also performed in a Brabender Plastograph at 400°C under nitrogen. Before mixing the salt was dispersed in the polymer powder by the slurry method.

RESULTS

Crystallization of PEEK and PEK

PEEK samples of $M_n = 10\,000$ were measured by d.s.c. on cooling at $20^\circ\text{C min}^{-1}$. As already mentioned for T_{ch} measurements the sample has been quenched in acetone before heating. In Table 1 are reported the values measured by d.s.c. on PEEK ($M_n = 10\,000$) and PEK ($M_n = 6500$). It was observed that PEK cannot be quenched in the amorphous state and therefore no crystallization peak on heating could be measured. The degree of undercooling ($T_m - T_{cc}$) of PEEK is 52°C while the corresponding value of PEK is only 35°C . These

Table 1 D.s.c. results obtained on a PEEK sample $M_n = 10\,000$ and on a PEK sample of $M_n = 6500$

	T_g (°C)	T_m (°C)	T_{cc} (°C)	T_{ch} (°C)	$T_m - T_{cc}$ (°C)	H_c (J g^{-1})
PEEK	140	348	296	173	52	58
PEK	155	365	338	—	35	71

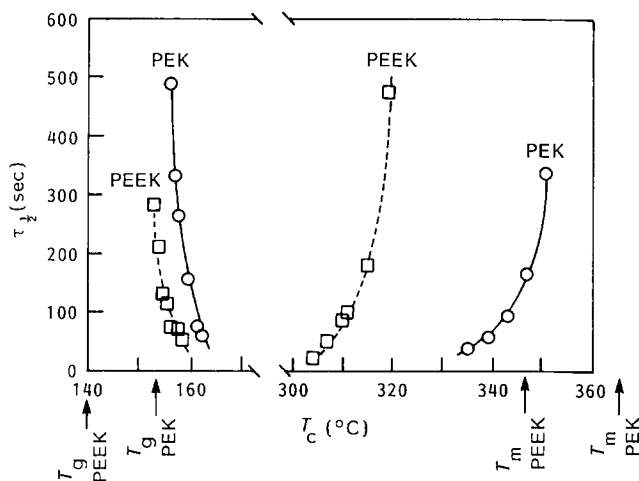


Figure 1 Isothermal crystallization kinetics of PEEK ($M_n = 10\,000$) and of PEK ($M_n = 6500$)

results seems to corroborate the fact that PEK crystallizes more rapidly than PEEK as observed in Figure 1.

The use of T_{ch} or T_{cc} values for the evaluation of crystallization rates has been reported elsewhere^{10,11}. For different systems, higher T_{cc} values or lower T_{ch} values correspond to faster rates of crystallization. In this work we have used T_{cc} as the controlling rate parameter to measure the influence of high-temperature annealing on the crystallization kinetics of PEEK.

In Figure 2, data obtained after an annealing of 2 min at a temperature T_s ranging between 360 and 430°C are reported. These results clearly show that a minimum T_{cc} value is obtained in a T_s range from 390 to 420°C. The lower limit of this temperature range corresponds exactly to the T_m° value of 395°C determined by Blundell for PEEK⁴. We confirm that thermal annealing below 390°C does not destroy all the residual crystalline fragments acting as seeds for crystallization at lower temperature.

Above 420°C, T_{cc} increases with T_s , meaning an enhancement of the crystallization rate for higher annealing temperatures. This behaviour is related to the thermal instability of PEEK above 420°C^{17,18}. In this work, all d.s.c. runs were performed after an annealing of 2 min at 420°C.

In Figure 3, the values of T_m , T_{cc} , T_{ch} and T_g for PEEK samples of different molecular weights (M_n) are reported. A strong dependence on M_n of the four parameters is observed. On the same samples we have also measured the half crystallization time $t_{1/2}$ at high temperature (298°C) and at low temperature (167°C).

In Figure 4 are reported the relationships obtained between $t_{1/2}$ at 167°C and T_{ch} and between $t_{1/2}$ at 298°C and T_{cc} .

For two different samples of $M_n = 7500$ and $M_n = 15\,000$ it is observed in Figure 3 that T_{ch} changes from 165 to 175°C ($\Delta T_{ch} = 10^\circ\text{C}$) while T_{cc} changes from 308 to 294°C ($\Delta T_{cc} = 14^\circ\text{C}$). This corresponds to a six-fold increase of

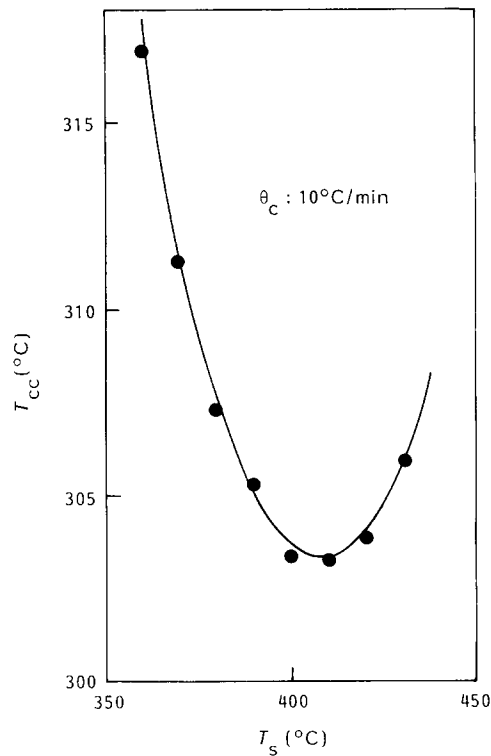


Figure 2 T_{cc} vs. T_s ($t_s = 2$ min) for PEEK of $\bar{M}_n = 10000$

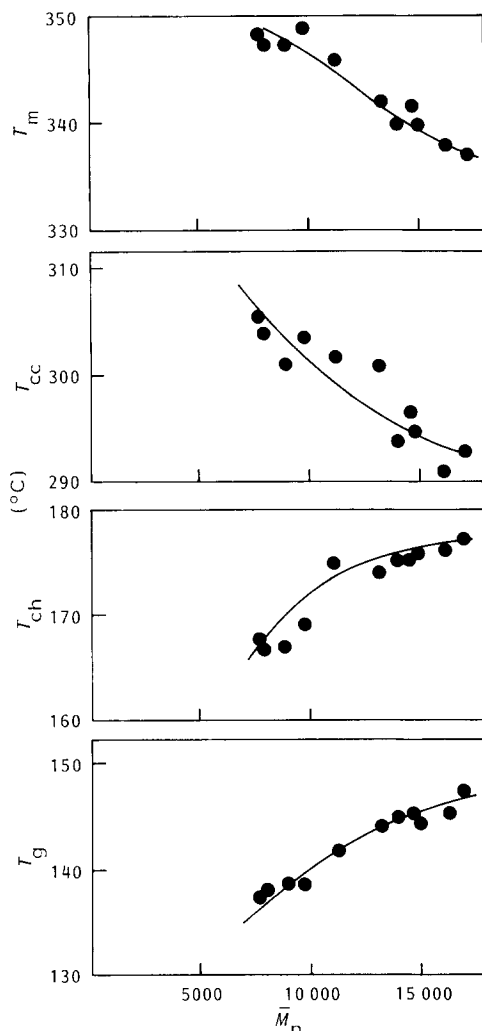


Figure 3 Thermal behaviour of PEEK as a function of \bar{M}_n

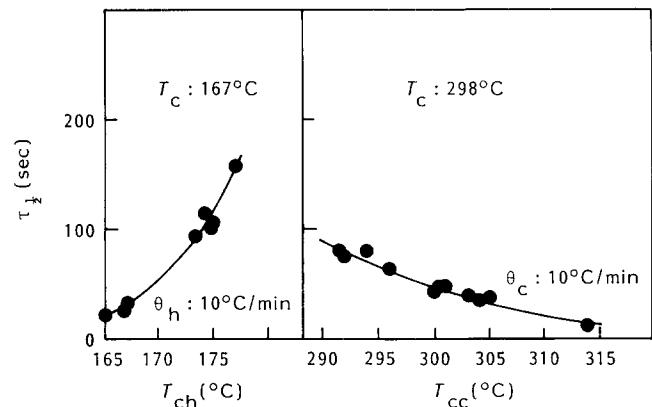


Figure 4 Relation between isothermal half crystallization times and crystallization temperature measured during dynamic d.s.c. runs ($10^\circ\text{C min}^{-1}$); PEEK samples of different \bar{M}_n

Table 2 ^{19}F n.m.r. and g.p.c. results for PEEK samples reacted with $\text{NaO}\phi\text{SO}_3\text{Na}$ (1.5%) at 300°C in benzophenone. [F] corresponds to the concentration of residual fluorine atoms while $[\text{F}]_s$ corresponds to the concentration of fluorine atoms that have reacted with the salt

Reaction time (min)	^{19}F n.m.r.		G.p.c.		
	[F] (ppm)	$[\text{F}]_s$ (ppm)	\bar{M}_n	\bar{M}_w	H
0	3900	0	9800	19 900	2.0
60	3850	50	9900	19 800	2.0
120	3890	10	9800	20 000	2.0
240	3680	220			
300	3710	190	9600	19 600	2.0

$t_{1/2}$ at 167°C and to a three-fold increase of $t_{1/2}$ at 298°C (Figure 4).

These results demonstrate the sensitivity of T_{ch} and T_{cc} to any modification of the crystallization rate at high or low temperature. The sensitivity of T_{cc} is even more important than that of T_{ch} .

For very fast crystallization rates, T_{ch} is no longer accurate because the samples cannot be completely quenched; this is why we will prefer to use T_{cc} later in this work.

It must also be pointed out that T_{ch} or T_{cc} depend on the d.s.c. rate of heating or cooling. For the sample of $\bar{M}_n = 10000$, the T_{ch} and T_{cc} values are 173 and 296°C for a rate of $20^\circ\text{C min}^{-1}$ (Table 1) while they are respectively 170 and 301°C for a rate of $10^\circ\text{C min}^{-1}$ (Figure 3). In this work, $10^\circ\text{C min}^{-1}$ has been chosen.

Crystallization of $-\text{SO}_3\text{Na}$ ended PEEK or PEK

Reaction with $\text{NaO}\phi\text{SO}_3\text{Na}$. Model compound studies¹⁶ have shown that the fluorine atoms carried by PEEK or PEK chain ends can be substituted using phenate salts. In Table 2, the ^{19}F n.m.r. and the g.p.c. results obtained on a PEEK sample ($\bar{M}_n = 10000$) after reaction with $\text{NaO}\phi\text{SO}_3\text{Na}$ (1.5%) in benzophenone at 300°C are given.

The reaction does not modify the polymer molecular weight while it does change its fluorine content. After 300 min of reaction about 5% of the fluorine chain ends have been substituted by $-\text{SO}_3\text{Na}$ end-groups.

After reaction the polymer has been washed with methanol in order to remove all the salt residues. The thermal analysis of this system discloses a T_{cc} value

of 316°C instead of 303°C for pure PEEK. Using the Figure 4 data one calculates that the substituted polymer (5% substitution) crystallizes about four times faster than the starting polymer at 298°C.

The same behaviour can be observed with PEK samples ($M_n = 6500$) reacted with $\text{NaO}\phi\text{SO}_3\text{Na}$ in benzophenone at 300°C. When about 5% of fluorine atoms are substituted by sodium sulphonate groups one measures a T_{cc} value of 352°C instead of 335°C for the starting material.

In Table 3, it is shown that the reaction between the fluorine end-groups and the phenate salt is required to promote the crystallization rate. When the polymer is phenyl ended no reaction can occur and no T_{cc} changes are observed. As in both cases the polymers were not purified after the treatment in benzophenone, the systems analysed by d.s.c. still contained the phenate salt (2%). The results of Table 3 demonstrate that this salt is not by itself a nucleant of PEK.

We attribute the crystallization rate enhancement to the presence of SO_3Na chain ends in the matrix. Table 4 shows that when the ionic groups are acidified by HCl in solution, the rate of crystallization is decreased. T_{cc} changes from 316 to 297°C. The acid groups (SO_3H) can be reneutralized by sodium hydroxide or sodium acetate to restore the T_{cc} value of 316°C previously measured.

A PEEK sample containing 5% of $-\text{SO}_3\text{Na}$ chain ends has been studied by optical microscopy and compared with a pure PEEK sample. Figure 5 shows the micrographs taken at 315°C. One can observe the dramatic change of the nucleation density induced by the ionic chain ends.

Reaction with other phenate salts. Owing to the poor solubility of $\text{NaO}\phi\text{SO}_3\text{Na}$ in benzophenone, the substitution reaction of the fluorine atoms is slow. It takes 300 min at 300°C to convert only 5% of the chain ends.

Table 3 T_{cc} and [F] concentrations of [F] ended PEK and phenyl ended PEK after reaction with different phenate salts (2%) at 300°C in benzophenone

Polymer	Salt	D.s.c. T_{cc} (°C)	^{19}F n.m.r. [F] (ppm)
(PEK) _F	$\text{NaO}\phi\text{SO}_3\text{Na}$	338	5720
	$\text{NaO}\phi\text{CO}\phi\text{O}\phi\text{SO}_3\text{Na}$	351	—
	$\text{NaO}\phi\text{CO}\phi\text{O}\phi\text{SO}_3\text{Na}$	352	2980
(PEK) _φ	$\text{NaO}\phi\text{SO}_3\text{Na}$	340	0
	$\text{NaO}\phi\text{CO}\phi\text{O}\phi\text{SO}_3\text{Na}$	340	0

Table 4 T_{cc} values

Polymer	T_{cc} (°C)
PEEK ^a	303
PEEK/Na ^b	316
PEEK/Na/HCl ^c	297
PEEK/Na/HCl/NaOH ^d	316
PEEK/Na/HCl/AcNa ^e	317

^a Pure PEEK $\bar{M}_n = 10000$

^b Sample a after reaction with $\text{NaO}\phi\text{SO}_3\text{Na}$ for 300 min in benzophenone

^c Sample b after acidification in HCl

^d Sample c neutralized by caustic soda

^e Sample c neutralized by sodium acetate

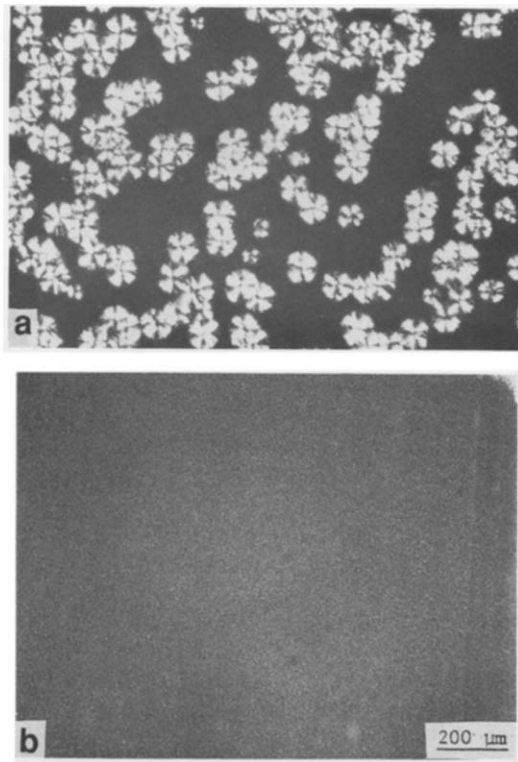


Figure 5 Optical micrographs (polarized light) of (a) pure PEEK and (b) PEEK reacted with a phenate salt (2.8%) for 90 min at 300°C in benzophenone. The two micrographs were taken at 315°C after 3 min. The samples were previously melted at 410°C for 2 min

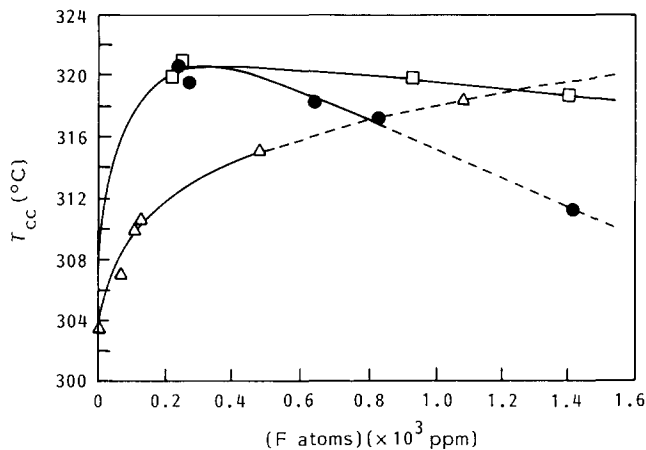


Figure 6 Evolution of T_{cc} of PEEK ($\bar{M}_n = 10000$) as a function of the concentration of fluorine atoms substituted by ionic groups (see Table 5)

This reaction can be accelerated by using longer phenate salts such as $\text{NaO}\phi\text{CO}\phi\text{O}\phi\text{SO}_3\text{Na}$. Table 5 reports the results obtained by reacting long phenate salts of Na, K and Li with F ended PEEK. It is shown that for the Na salt 5% of F end-group substitution is obtained after 15 min and a T_{cc} value of 320°C is recorded. For longer reaction times, the conversion of F atoms is increased, after 180 min of reaction 25% of the chain ends are $-\text{SO}_3\text{Na}$ groups. In Table 5 and Figure 6 no further increase of T_{cc} is observed between 5 and 25% conversion.

The method to perform the reaction between PEEK and phenate salts has been described in the experimental part of this paper. The first step consists of preparing a slurry of the polymer powder and the phenate salt to promote intimate contact between the reagents.

Table 5 T_{cc} , \bar{M}_n , \bar{M}_w and $[F]$ and $[F]_s$ of PEEK and PEK samples after reaction with 2.8% of $XO\phi CO\phi O\phi SO_3X$ ($X=Na, K, Li$) in benzophenone at 300°C. Results obtained by the slurry technique have also been reported

Polymer	Cation X	Reaction time (min)	$[F]$ (ppm)	$[F]_s$ (ppm)	\bar{M}_n	\bar{M}_w	T_{cc} (°C)	
PEEK	-	0	3900	0	9800	19 900	303	
		Na ⁺	15	3680	220	-	-	320
			30	3650	250	9900	19 000	321
	-	180	2970	930	9700	20 100	320	
		K ⁺	Slurry	2497	1403	-	-	318
			15	-	-	-	-	320
	-	30	3660	240	-	-	320	
		120	3630	270	-	-	320	
		224	3260	640	9800	20 000	318	
	-	300	3070	830	9800	19 500	317	
		Li ⁺	Slurry	2487	1413	-	-	311
			15	3830	70	-	-	307
	-	120	3790	110	9800	21 000	310	
		225	3770	130	-	-	310	
		300	3420	480	9900	20 000	315	
-	Slurry	2818	1082	-	-	318		
	Na ⁺	0	5860	0	6500	-	335	
		150	5400	460	6500	-	352	

By simply heating the slurry in the d.s.c. at $10^\circ\text{C min}^{-1}$ up to 420°C one observes in Table 5 that high degrees of conversion (25–30%) can be achieved for the three cations used.

In Figure 6, we report the evolution of T_{cc} as a function of the degree of conversion independently of the method used to prepare the sample. One can observe that a maximum value of T_{cc} equal to 320°C is observed for the three cations. This maximum value is reached rapidly with K and Na (5% conversion) while it requires 25% degree of conversion with the Li salt.

Above 5% conversion T_{cc} decreases more rapidly with potassium ionic chain ends than with sodium ones. For 25% conversion a value of only 311°C is recorded for $-\text{SO}_3\text{K}$ chain ends.

Melt viscosity

In Figure 7, we compare the melt viscosity at 400°C of PEEK ($\bar{M}_n=10\,000$) and of a modified PEEK containing 5% of $-\text{SO}_3\text{Na}$ chain ends. For a shear stress of 10^4 N m^{-2} , the viscosity of the modified polymer is 4 times higher than the viscosity of the starting material. This effect cannot be due to a molecular-weight increase as it has already been shown that the substitution of the F atoms of PEEK occurs at constant \bar{M}_n value. Therefore, we attribute this viscosity enhancement to ionic chain-end associations in the melt.

EXAFS

A PEEK sample has been reacted with $\text{CsO}\phi\text{SO}_3\text{Cs}$ in benzophenone. A degree of conversion of $\approx 10\%$ has been achieved. EXAFS measurements at the synchrotron at Darlington show that each caesium atom is surrounded by six oxygen atoms at a distance of 3.1 \AA . A model for a crystallographic arrangement of the $-\text{SO}_3\text{Cs}$ groups has been proposed. In Figure 8, we represent different views of the model.

DISCUSSION AND CONCLUSIONS

It is shown in this work that phenate salts react with the F atoms carried by the chain ends of pure PEEK and

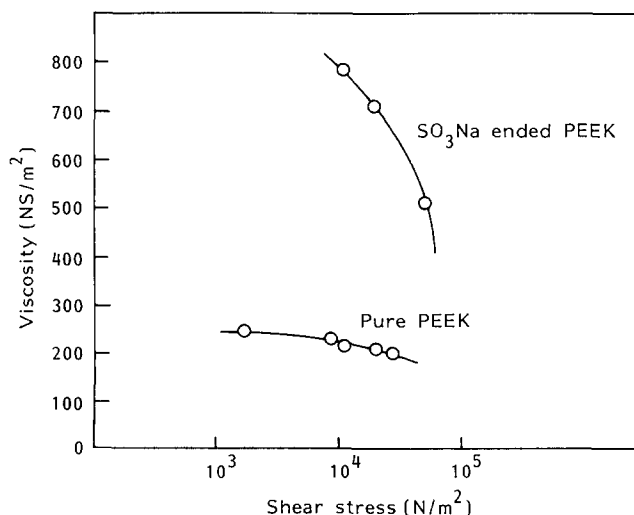


Figure 7 Melt viscosity of pure PEEK and PEEK reacted with $\text{NaO}\phi\text{SO}_3\text{Na}$ as a function of shear stress

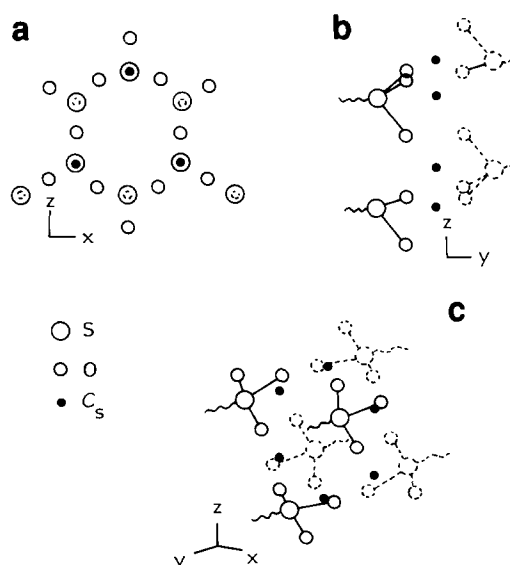


Figure 8 Crystallographic arrangement of $-\text{SO}_3\text{Cs}$ in PEK as deduced from EXAFS measurement

PEK. The substitution of the F atoms by $-\text{SO}_3\text{X}$ end-groups enhances the crystallization rate of both polymers. Phenate salts in the presence of phenyl ended polymers cannot react and no change in the crystallization rate is observed. This experience shows also that the phenate salts as such are not efficient nucleants of PEEK or PEK.

The reaction between F atoms and a phenate salt occurs without any modification of the molecular weight of the polymer. The enhancement of the crystallization rate cannot be explained by a M_n decrease as it is observed in the first part of the paper. A degree of substitution of 5% between F atoms and $-\text{SO}_3\text{Na}$ groups induces an increase of T_{cc} from 303 to 320°C for PEEK of $M_n=10000$. This ΔT_{cc} shift will correspond to a decrease of M_n from 10000 to 5000, which was not observed, it corresponds also to a reduction of the half-crystallization time at 297°C by a factor of 5 (from ≈ 40 to ≈ 8 s). This behaviour is also observed for PEK.

Microscopic observations at 300°C show also that the nucleation density is considerably enhanced. In Figure 5, a calculation of the number of spherulites per surface unit allows one to estimate that the number of seeds (N_0) in the modified system is about 100–150 times the number accounted for in the plain polymer. For those systems, the rate of crystallization ($t_{1/2}$) has changed by a factor of 5.

Based on the Avrami model for spherulitic growth and instantaneous nucleation one can calculate that $N_0 G^3 t_{1/2}^3 = N'_0 G'^3 t'_{1/2}{}^3$ with N_0 , G , $t_{1/2}$ concerning the plain polymer and N'_0 , G' , $t'_{1/2}$ concerning the nucleated system. If one assumes a constant value for G for both systems it is verified that a reduction of $t_{1/2}$ by a factor of 5 corresponds well to an increase of N_0 by a factor 125. This value corroborates well with what has been measured by optical microscopy.

Up to now, we have not investigated the influence of the presence of ionic chain ends on the growth rate of the spherulites. In the calculation of N_0 , G is assumed to remain unchanged. As we have proved that the substitution reaction occurs without any molecular degradation, an increase of G is not expected.

On the contrary, melt flow measurements show a strong increase of the viscosity in the melt at 400°C. This can lead to a reduction but certainly not to an increase. If G were reduced by the presence of $-\text{SO}_3\text{Na}$ chain ends, the increase of N_0 would have been expected to be higher.

Melt viscosity shows also that $-\text{SO}_3\text{Na}$ chain ends are strongly associated in the melt at 400°C. This behaviour is similar to what is observed in ionomers¹⁹. However, in our case those ionic associations exhibit a crystallographic structure which has been identified by EXAFS. We believe that those associations act as seeds during

crystallization. Similar behaviour has already been described for PET–COONa chain ends and this peculiar nucleation mechanism was called 'chemical nucleation'.

It is also shown in this paper that $-\text{SO}_3\text{Na}$ is not the only ionic group that enhances the nucleation density of PEEK or PEK. Other cations such as K or Li can also be used. However, $-\text{SO}_3\text{K}$ end-groups are active as nucleant only for a degree of substitution of 5% while it requires a substitution of 25% for $-\text{SO}_3\text{Li}$. For $-\text{SO}_3\text{H}$ chain ends, no nucleation effect is observed. We attribute this behaviour to the differences in ionic strength of those different cations, which lead to stronger associations for K and Na than for Li and H. It confirms also that previous associations of the chain ends in the melt are required to promote the nucleation step.

In the near future we intend to publish other results concerning this mechanism of nucleation, especially the relationship existing between the lamellar thickness of the crystals and the ionic associations.

ACKNOWLEDGEMENTS

The authors would like to thank Mrs A. Halin for her critical assistance during the elaboration of this work.

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