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Perfectly alternating poly(arylene ether ketone sulfone)'s

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Summary

In this study, the synthesis of perfectly alternating poly(arylene ether ketone sulfone)'s (PAEKS) via their soluble poly(arylene ether ketimine sulfone) (PAEKetS) intermediates was described. In the first stage of this procedure a new bishalide monomer, 1,1'-bis(4-fluoro(n-benzohydroxylidene aniline)) sulfone (FBHAS) was synthesized. In the second stage, the polymerization of this monomer with various aromatic bisphenols to form the amorphous PAEKetS's and then the hydrolysis of the ketimine groups on the PAEKetS's backbones to ketones in mild acidic conditions in order to obtain perfectly alternating PAEKS's was conducted.

Introduction

The necessity of using heat-resistant materials in the aerospace and electronic industries has become an important driving force for researches on high performance poly(arylene ether ketone)'s (PAEK) and pol(arylene ether sulfone)'s (PAES) with target applications. However, high melt and/or softening temperatures and limited solubility of PAEK's, due to their rigid chain structures, cause problems during their processing. A common method to solve these problems is to introduce flexible linkages such as ether, sulfone and a bulky pendant group into the polymer chain. Incorporation of sulfone groups into the main chain will also generates interesting properties such as higher decomposition temperature and liquid crystallinity due to strong interactions between sulfone groups (1-7).

Introduction of both sulfone and carbonyl linkages into the aromatic poly(arylene ether) structure are desirable and it can be achieved by nucleophilic and electrophilic reactions in commercial scales. One of the important goals in the synthesis of such polymers is to introduce perfectly alternating bridging groups into the polymer backbone with the expectation of interesting properties. Introducing of thermally stable and flexible ether and carbonyl groups on the polymer backbone hoped to effect the tractability of the polymers positively. It is known that most of the commercially available PAES's do not crystallize and have amorphous structure but PAEK's are semicrystalline and can crystallize readly by cooling from its molten state (6). On the other hand, there is limited literature on the physical and thermal properties of homopolymers having carbonyl, sulfonyl and ether linkages on the backbone in a regular sequence. Investigations on the characterization of perfectly alternating PAEKS and comparison with their randomly sequenced homologes and PAEK-PAES block copolymers are much more limited (6,7).

Nucleophilic aromatic substitution reaction was the most widely used and well established method for the synthesis of PAEK and PAES. The electron withdrawing ability of the sulfone group is much stronger than the carbonyl group. Therefore it is almost impossible to synthesize high molecular weight perfectly alternating PAEKS by aromatic nucleophilic

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polycondensation reaction because of electronegativity differences of sulfone and carbonyl groups on the aryl bishalogen. In fact, Staniland and coworkers have made an attempt to synthesize perfectly alternating PAEKS but they obtained low molecular weight polymers. They attributed the low molecular weights to the consumption of phenate anions by the sulphinic groups which were produced by the cleavage of sulfone linkages with nucleophilic reagents in the presence of electron withdrawing groups in a ring containing both sulfone and ketone functional groups (6).

In addition, it is known that crystallizability or rigid rod structure, strongly affects the solubility of polymers causing precipitation of oligomers at the early stages of polymerization, thus preventing to achieve the desired high molecular weights. Our early attempts to synthesize perfectly alternating PAEKS directly from 4,4'-bis(4-fluorobenzoyl)diphenyl sulfone (FBDPS) with bisphenol A and 6F- bisphenol A, yielded very low molecular weight products due to early precipitation, probably caused by the rigid rod structure of the polymer. In the first stage of the presented work, in order to overcome the solubility problem and to keep the growing polymer chains in solution, FBDPS was derivatized through carbonyl groups with aniline to obtain FBHAS and the resulting ketimine functional monomer was then polymerized with bisphenols via aromatic nucleophilic substitution. In the second stage, the soluble ketimine derivatives were completely hydrolysed by dilute HCl solutions to convert the ketimines to ketone groups in the polymer backbone and to obtain the perfectly alternating PAEKetS's.

Experimental

Materials

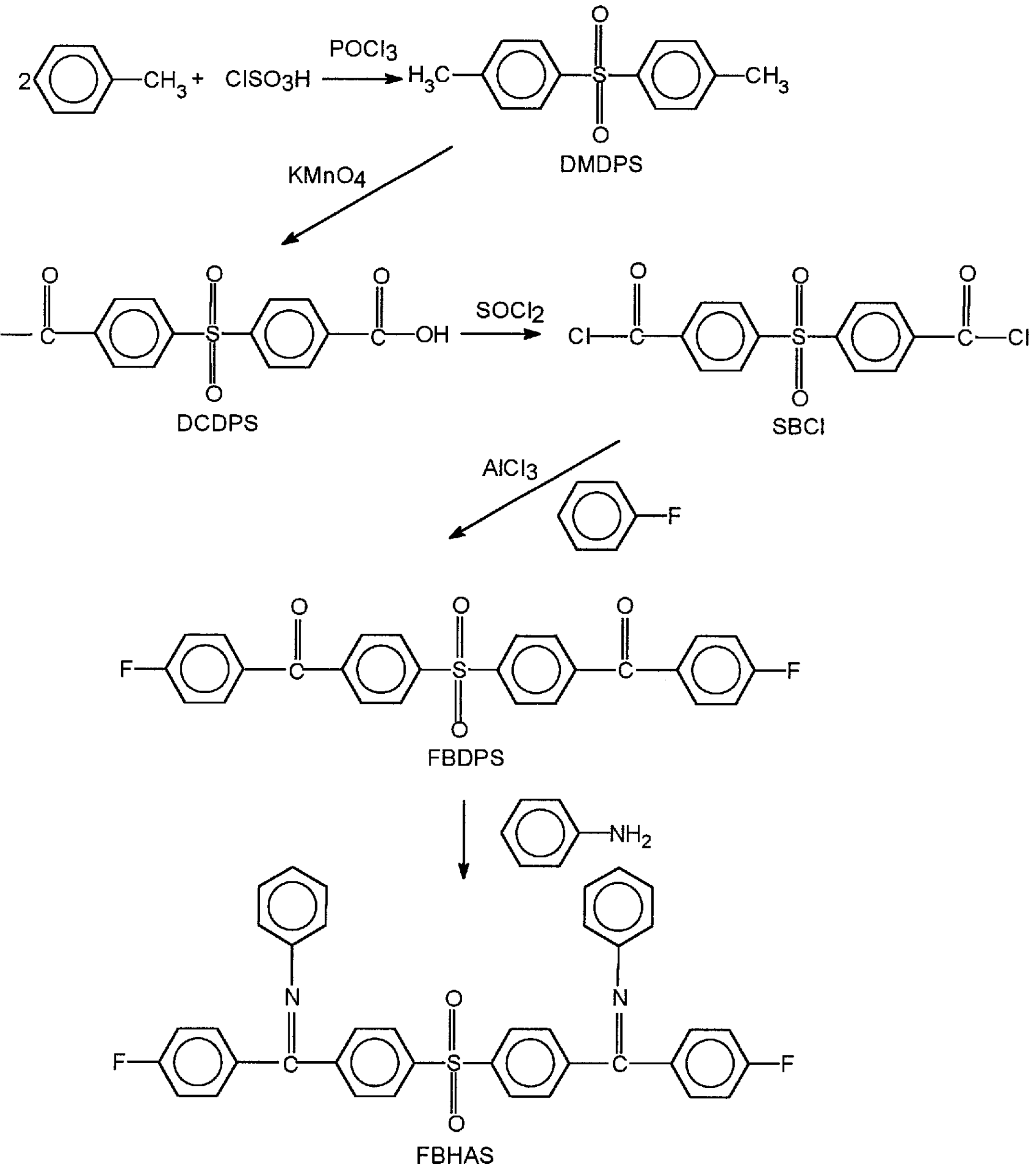
Chlorosulfonic acid, phosphorous oxychloride, thionyl chloride (Merck) and potassium permanganate (Fluka) were used without further purification. Fluorobenzene (Mallincrot), aniline (Merck) and o-dichlorobenzene (Merck) were dried over 3A° molecular sieve. Toluene (Merck) distilled over sodium, 1-Methyl-2-pyrrolidinone (BASF) distilled over phosphorous pentoxide under reduced pressure. Anhydrous potassium carbonate (Aldrich) was kept at 170°C for 3h before use. Hydroquinone (Merck) was recrystallized from acetone, 4,4'-Biphenol and 6F Bisphenol A (Aldrich) were purified by sublimation. Bisphenol A (Dow) was purified by crystallization from toluene. 4,4'-Thiodiphenol (Aldrich) was used without further purification.

Characterization Methods

Thermal properties of the polymers were determined by Differential Scanning Calorimetry (DSC) and Thermogravimetric analysis (TGA) by DuPont Instruments model 910 and 951 respectively. ^{1}H-NMR spectra in $CDCl_3$ solution were obtained using a Bruker AC 200 L spectrometer. FTIR spectra of monomers and polymers were recorded using a Nicolet 510 P spectrometer. Mass spectra were recorded by double focusing Magnetic Sector, VG ZabSpec, equipped with the standart electron impact source. Gel Permeation Chromatography (GPC) was used to determine molecular weight of polymers with a Waters Instrument. Polystyrene standards were used for calibration. Wide angle X-ray diffractograms were obtained by a Philips PW 1050/25 X-ray diffractometer.

Monomer Synthesis

4,4'-Dimethyldiphenyl sulfone (DMDPS) was prepared from toluene, chlorosulfonic acid and phosphorous oxychloride according to literature (8). ^{1}H-NMR: δ 7.81-7.27 (s, 8H, arom.), δ 2.38 (s, 6H, CH_3). FTIR (cm^{-1}): 1400-1450 (CH_3 bend.), 1317-1155 (SO_2 strech.). MS (EI^{+}) m/z: 246.3 (M^{+}). Calcd. for $C_{14}H_{14}O_2S$:C, 68.21%; H, 5.73%. Found: C, 68.20%; H, 5.71%.



Scheme 1: Synthesis of FBHAS

4,4'-Dicarboxydiphenyl sulfone (DCDPS) was synthesized by the oxidation of DMDPS according to literature (8). ^{1}H-NMR: δ 13.43 (1H,s,COOH), δ 8.15 (d,2H,arom.), δ 8.08 (d,2H,arom.). FTIR (cm^{1}): 1331-1161 (SO_2 strech.), 1695 (C=O strech.), 1425 (C-OH bend.). MS (EI^{+}) m/z: 306.3 (M^{+}). Calcd. for $C_{14}H_{10}O_6S$:C, 54.90%; H, 3.29%. Found: C, 54.88%; H, 3.25%.

4,4'-Sulfonyl bis(benzoyl chloride) (SBCl) was prepared from DCDPS and thionyl chloride. It was used without further purification.

4,4'-bis (4-fluorobenzoyl) diphenylsulfone (FBDPS) was synthesized via Friedel Crafts reaction of SBCl with fluorobenzene. ^{1}H-NMR: δ7.2 (4H,m), δ7.9 (8H,m), δ8.1 (d,4H). FTIR (cm^{-1}): 1300-1150 (SO_2 strech.), 1658 (C=O strech.), 1230 (C-F strech.). MS (EI$^+$) m/z: 462 (M$^+$). Calcd. for $C_{26}H_{16}O_4F_2S$:C, 67.53%; H, 3.49%. Found: C, 67.50%; H, 3.48%.

Synthesis of 1, 1'-bis(4-fluoro(n-benzohydroxylidene aniline)) sulfone (FBHAS): A mixture of 29.88 g (0.0646 mol) FBDPS and 19 ml (0.2080 mol) aniline was charged into a three necked reaction flask equipped with a nitrogen inlet, a Dean Stark trap, a condenser and a mechanical stirrer. Then 120 ml toluene and 72 g molecular sieve 3 A° were added to the reaction mixture. The reaction temperature was set to 130 °C and refluxed until all the carbonyl groups of FBDPS were converted to ketimine groups which were monitored by FTIR and ^{1}H-NMR. Toluene and excess aniline were distilled away under reduced pressure. After three successive crystallization from methanol, yellow crystalline material was obtained with a yield of 92%. Mp: 150°C. ^{1}H-NMR: δ 6.6 (4H,m), δ 7 (14H,m), δ 7.9 (m,8H). FTIR (cm^{-1}): 1304-1153 (SO_2 strech.), 1620 (Ar-C=N), 1228 (C-F). MS (EI$^+$) m/z: 612 (M$^+$). Calcd. for $C_{38}H_{26}O_2F_2N_2S$:C, 74.49%; H, 4.28%; N, 4.57%. Found: C, 74.47%; H, 4.27%; N, 4.56%. (Scheme 1)

Synthesis of PAEKetS's

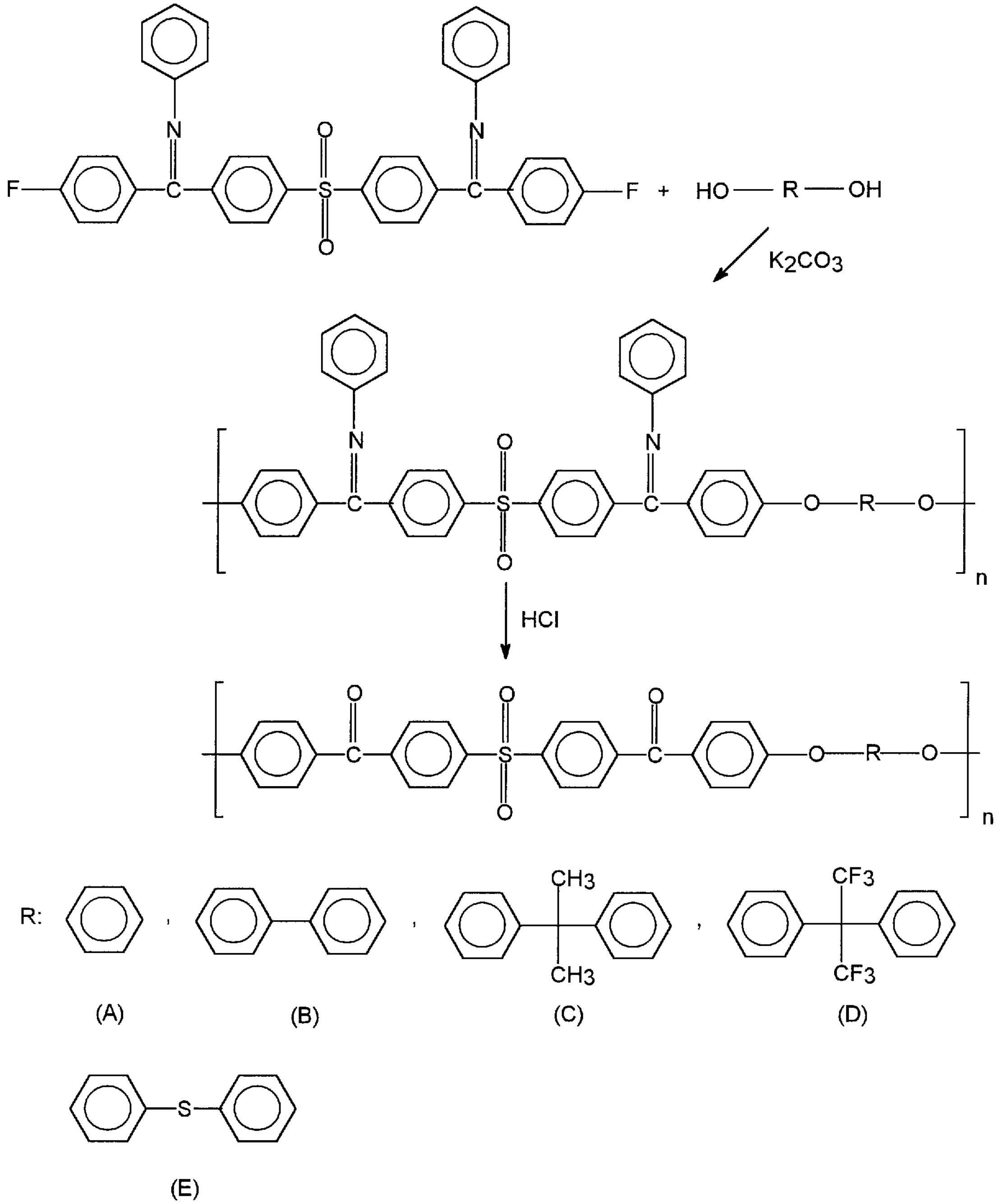
PAEKetS's were prepared by the condensation of FBHAS and aromatic bisphenols via aromatic substitution reaction (Scheme 2). Stoichiometric amounts of FBHAS, bisphenol and K_2CO_3 were charged into the reaction flask equipped with an inverse Dean Stark trap, a condenser, a thermometer, a mechanical stirrer and N_2 inlet. Reactions were carried out in NMP at 180°C for 8h and o-dichlorobenzene was used as the azeotropic agent. After removal of o-dichlorobenzene, polymers were precipitated from methanol/water mixture. Light colored polymer was washed with water and dried at 105°C for 12 hours under vacuum.

Conversion of Ketimines to Ketones

The ketimine functionality of the polymer backbone was converted to ketone via acid hydrolysis (2). 2.16 g of dried polymer were dissolved in 42 ml of NMP, then 2 ml of water was added to the solution and mixed homogenously. In order to hydrolyse the polymer, HCl/NMP mixture (3 ml of 12.1 N aqueous HCl in 27 ml NMP) was added to the polymer solution. The hydrolysed polymer was precipitated from methanol, washed with water and dried at 160°C under vacuum for 12 h. The conversion was monitored by FTIR spectroscopy technique (Scheme 2).

Results and Discussion

The polymerization of FBDPS with hydroquinone to form a thermoplastic polymer which contains both sulfone and carbonyl groups in a regular sequence was reported by Staniland and co-workers (6). They reported that it is difficult to obtain perfectly alternating polymers in the presence of strong electron withdrawing sulfone and ketone groups, which activates the cleavage of the ether linkages in the polymer chain consequently inducing transetherification reactions which disturb the perfect sequence of the groups. Also they put strong emphasis on the work of Livingston at al. and Loudon et al (9, 10) in which it was started that sulphinic groups produced by the cleavage of sulfone linkages caused the dissappearance of phenate anion in a nucleophilic polycondensation, preventing an increase in the molecular weight.



Scheme 2: Synthesis of PAEKetS and their conversion to PAEKS

In this work, to solubilize the polymer through out the polymerization and thus to obtain high molecular weight and additionally to reduce the electron withdrawing ability of the carbonyl groups that cause undesirable transetherification reactions which distrub the perfect sequence of the polymer chain, FBDPS was derivatized through carbonyl groups with aniline to obtain FBHAS. The resulting ketimine functional monomer was then polymerized with bisphenols via nucleophilic substitution. The soluble ketimine derivatives of the PAEKS were then completely hydrolyzed by dilute HCl solutions to convert the ketimine groups to ketone groups in the polymer backbone.

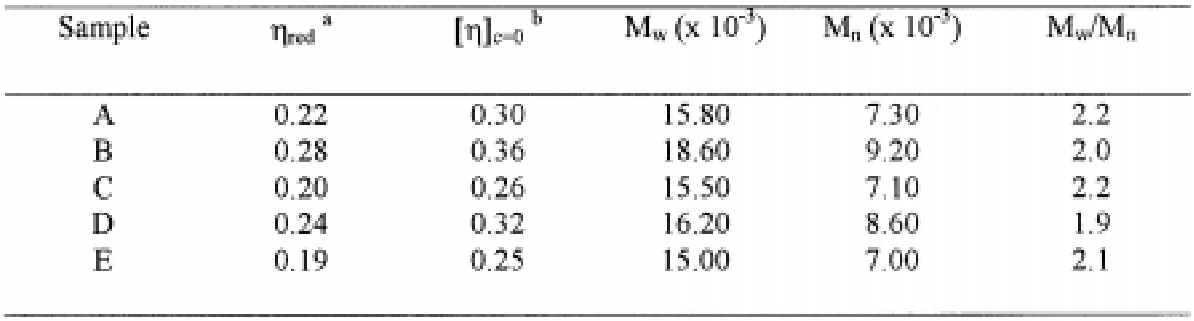
Table 1 summarizes the thermal data of the PAEKetS's (A-E). DSC measurements indicate that polymer (B) which contains biphenyl group in the polymer backbone have the highest T_g due to its rigidity. Polymer (E) having flexible -S- groups has the lowest T_g. Thermal stability behaviour of the polymers (A-E) are almost the same.

Table 1. Thermal analysis results of PAEKetS's

Sample	Tg (°C)	5% weight loss (°C)	50% weight loss (°C)	95% weight loss (°C)	Char yield (%)
A	180	450	600	660	1
B	190	475	625	700	1.2
C	185	460	575	670	1
D	180	460	580	650	1.4
E	160	465	570	650	1.5

As seen from Table 2, the weight average molecular weights of PAEKetS's were in the range of 15 000-18 600 g/mol. All polymers have polydispersity index in the range of 1.85-2.11, which are within the reported values for many poly(arylene ether)'s.

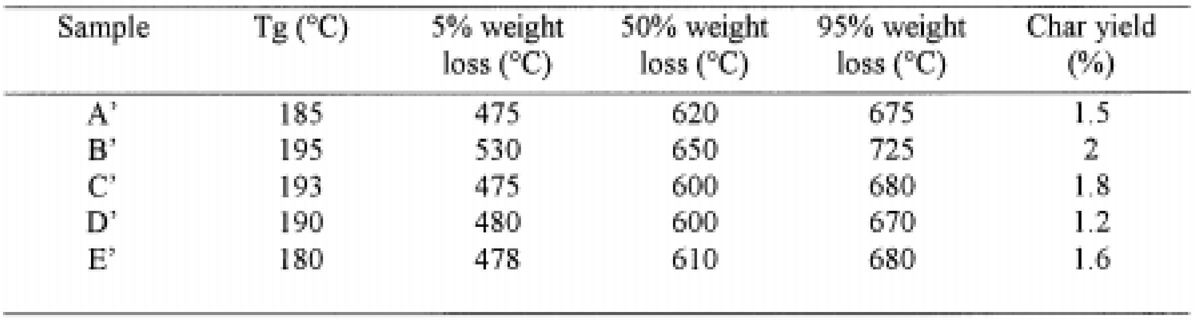
Table 2. GPC and solution viscosity results of PAEKetS's



Sample	η_{red} [a]	$[\eta]_{c=0}$ [b]	M_w (x 10^{-3})	M_n (x 10^{-3})	M_w/M_n
A	0.22	0.30	15.80	7.30	2.2
B	0.28	0.36	18.60	9.20	2.0
C	0.20	0.26	15.50	7.10	2.2
D	0.24	0.32	16.20	8.60	1.9
E	0.19	0.25	15.00	7.00	2.1

[a]: Reduced viscosity
[b]: Intrinsic viscosity

Table 3. Thermal analysis results of PAEKSs



Sample	Tg (°C)	5% weight loss (°C)	50% weight loss (°C)	95% weight loss (°C)	Char yield (%)
A'	185	475	620	675	1.5
B'	195	530	650	725	2
C'	193	475	600	680	1.8
D'	190	480	600	670	1.2
E'	180	478	610	680	1.6

Thermal analysis and GPC-solution viscosity values of perfectly alternating PAEKS's (A'-E') obtained after the hydrolysis of ketimine functionalized polymers are given in Table 3 and Table 4, respectively. As seen from Table 3, Tg values of PAEKS's (A'-E') are higher than their corresponding PAEKetS intermediates. By comparing TGA data, it seen that PAEKS's are much more thermooxidatively resistant.

Table 4. GPC and solution viscosity results of PAEKS's

Sample	η_{red} [a]	$[\eta]_{c=0}$ [b]	M_w (x 10^{-3})	M_n (x 10^{-3})	M_w/M_n
A'	0.25	0.34	12.3	5.6	2.2
B'*	-	-	-	-	-
C'	0.24	0.28	12.0	5.5	2.1
D'	0.27	0.36	13.5	7.1	1.9
E'	0.23	0.26	12.1	5.8	2.0

* Data could not obtained because the polymer was partially soluble.

The structural characterization of PAEKetS's and PAEKS's were made by X-ray methods. All polymers(A-E, A'-E') show semi-crystalline patterns, exhibiting crystalline peaks (2θ) appearing at round 15°-23°, as shown in Fig. 1 and 2, respectively.

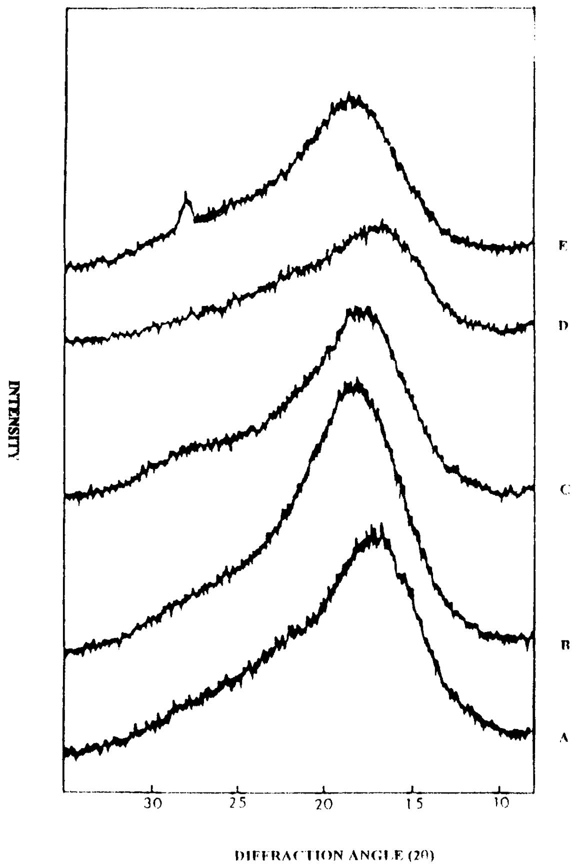


Figure 1: X-ray diffractograms of PAEKetS's

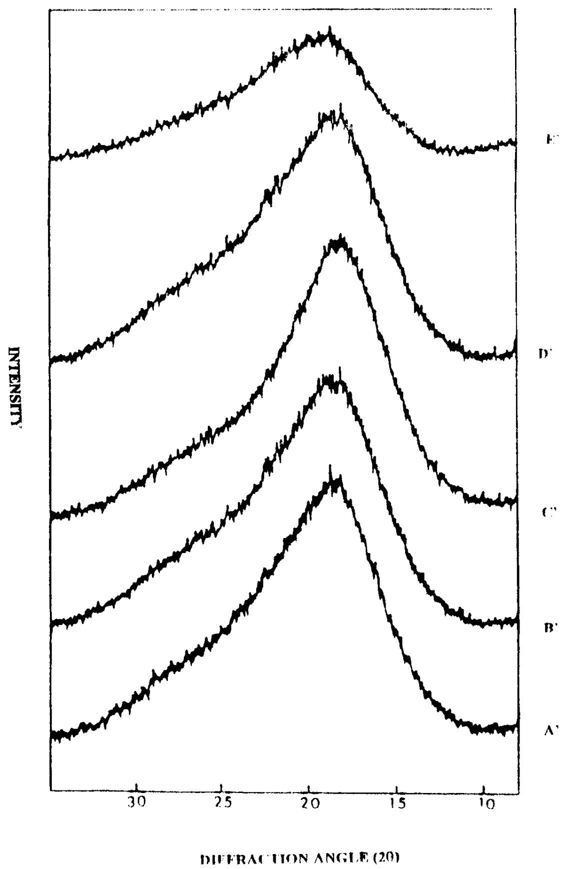


Figure 2: X-ray diffractograms of PAEKS's

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