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STRUCTURE AND THERMAL CHARACTERISATION OF POLY(ARYLENE ETHER SULPHONE)S[*]

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Abstract

Structurally different poly(arylene ether sulphone) (PES) copolymers were synthesized by reacting stoichiometric amount of dichlorodiphenyl sulphone (DCDPS) with bisphenols. The molar ratio of bisphenol-A and phenolphthalein (ESP)/hydroquinone (ESH)/resorcinol (ESR) was varied to prepare nine copolymer samples. Structural characterization was done by FT-IR and ^{1}H-NMR studies. The initial decomposition temperature as well as temperature of maximum rate of mass loss in ESR and ESH copolymers were similar and a marginal decrease in these decomposition temperatures were observed by increasing the isopropylidine units in the backbone. High char residue at 800°C was observed in polymers having high content of phthalein units.

Keywords: bisphenol, char yield, oligomers, poly(arylene ether sulphone), thermal stability

Introduction

Several aromatic poly(arylene ether sulphone)s (PES) have been commercialized in the past three decades because these thermoplastics possess unique combination of useful chemical and physical properties, such as high hydrolytic, thermal and oxidation stability [1, 2], low inflammability, high T_g and good transparency. Backbone modification of PES has been reported in the past to improve its thermal stability, fire resistance, mechanical properties, solubility behaviour and increasing its potential application areas [3, 4]. Copolymers such as PES-amides, PES-imides [5], poly(arylene ether phenyl phosphine oxide-co-PES) [6, 7], poly(oxy-1,4-phenylene sulphonyl-4,4-biphenylene-4-sulphonyl-1,4-phenylene) [8], poly(ether-sulphone-ketone) [9, 10] have been reported. Random oligomers synthesized by reacting 4,4'-dichlorodiphenyl sulphone with varying mole proportion of bisphenol-A and sulphonyl diphenol using sulpholane as solvent and anhydrous K_2CO_3 have also been investigated [11]. Segmented poly(aryl ether sulphone)s with various end groups have been extensively reported by McGrath *et al*. [12–14]. Some of these co-

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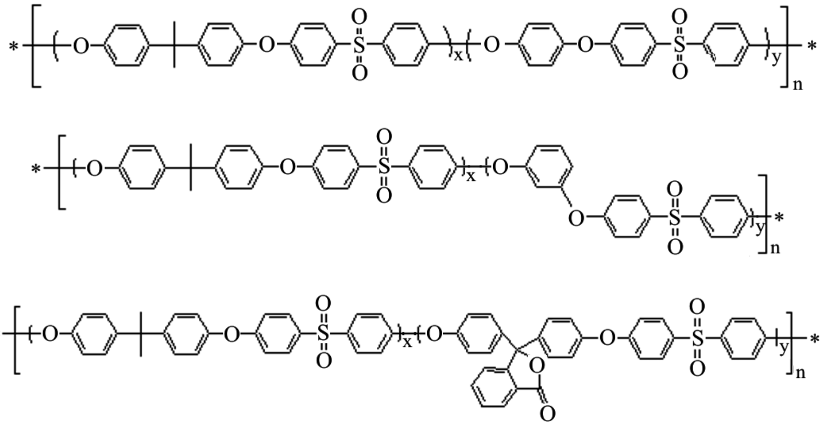
polymers have been investigated as precursors for ion exchange membrane with good thermal stability and adsorption capacity for metal ions [12].

Although considerable work has been done on synthesis of copolymers, but very few systematic studies have been reported dealing with effect of structure on thermal stability of PES [15, 16]. We now report the synthesis, characterization and thermal behaviour of PES copolymers. Such studies are important for correlation of structure with thermal behaviour [17, 18]. Recently the degradation mechanism of some low molecular mass aromatic polyethers containing flexible spacers has been investigated by using TG-MS technique [19]. Homopolymers as well as copolymers of several bisphenols i.e. 4, 4'- dihydroxy diphenyl, 4, 4'- dihydroxyazobenzene and bisphenol-A were synthesized using bis (2-chloroethyl)-ether or 1,6-dichlorohexane as flexible spacers. A degradation mechanism based on chain transfer reaction has been proposed.

The copolymers were prepared according to the procedure reported in the literature by taking the equimolar amounts of 4,4-dichlorodiphenyl sulphone and bisphenols i.e. bisphenol A: hydroquinone (ESH), bisphenol-A: resorcinol (ESR) and bisphenol-A: phenolphthalein (ESP). The molar ratio of these bisphenols was varied as 3:1, 1:1 and 1:3. The resulting copolymers were designated by writing 1, 2 or 3 after the letter designation of copolymers. For example ESH copolymers having 3:1, 1:1 and 1:3 molar ratio of bisphenol-A: hydroquinone have been designated as ESH-1, ESH-2, ESH-3 respectively. A decrease in bisphenol-A content in the copolymers (i.e. ESH-1 to ESH-3) will result in a decrease in thermally labile aliphatic moieties (isopropylidine units) in the backbone (Scheme 1).



Scheme 1 Structure of PES copolymers

Experimental

Materials

Bisphenol-A, resorcinol (RL), phenolphthalein (Ph), N,N-dimethylacetamide (DMAc) and toluene were purchased from CDH. Bis(4-chlorophenyl)sulfone (DCDPS), hydroquinone (HQ), NaOH, H_2SO_4, ethanol, chlorobenzene (all from Merck) and potassium carbonate (K_2CO_3), glacial acetic acid, chloroform (all from Qualigens) and methanol (Qualichems) were used as received.

Synthesis of PES oligomers

In a three necked round bottom flask, 0.033 moles of desired bisphenols (according to their molar ratio) and 0.033 DCDPS were dissolved in dimethyl acetamide (DMAc): toluene (70:30). Then 15 mol% excess of K_2CO_3 was added. Flask was fitted with condenser, nitrogen inlet and stirring was done by a magnetic stirrer. The contents were heated at 135°C for 4 h under reflux condition. Most toluene was then removed by distillation. Reaction temperature was increased to 160°C and maintained for 16 h. A viscous liquid was obtained. The contents of the flask were cooled to room temperature and diluted with DMAc. Subsequently glacial acetic acid was added to protonate any phenolate end groups.

The polymer was precipitated in methanol, filtered and dried in an air oven at 120°C for 8 h. The dried polymer was then dissolved in minimum quantity of chloroform, filtered and reprecipitated in methanol. The precipitate was filtered and dried in air oven at 150°C for 24 h. Nine copolymer samples were prepared by changing the ratios of bisphenols. The details of the initial monomer feed and designations of the copolymer samples are given in Table 1.

Table 1 Reaction conditions for synthesis of PES copolymers and their designation

Concentration of DCDPS	=0.033 mol
Concentration of bisphenols	=0.033 mol
K_2CO_3	=15 mol% excess of bisphenols
Solvent	=DMAc:Toluene (70:30)
Temperature	=135°C for 4 h, 160°C for 16 h

S.	bisphenols (molar concentration)				Sample
No.	bisphenol-A	hydroquinone	resorcinol	phenolphthalein	designation
1	0.0245	0.0085			ESH-1
2	0.0165	0.0165			ESH-2
3	0.0085	0.0245			ESH-3
4	0.0245		0.0085		ESR-1
5	0.0165		0.0165		ESR-2
6	0.0085		0.0245		ESR-3
7	0.0245			0.0085	ESP-1
8	0.0165			0.0165	ESP-2
9	0.0085			0.0245	ESP-3

Characterisation

Structural characterisation

FT-IR of powder polymer samples in KBr pellets was recorded using Nicolet FT-IR spectrometer or PerkinElmer 2000 FT-IR spectrometer.

^{1}H-NMR spectra were recorded using a Bruker Avance Spectrospin 300 MHz instrument and $CDCl_3$ as a solvent.

Thermal characterisation

TG analyses of polymer samples were done using a TA instrument 2100 thermal analyzer having a 951 TG module. TG studies were done in N_2 atmosphere in the temperature range of 50–850°C using a heating rate of 10°C min^{-1}. A sample mass of 10±2 mg was used.

Molecular mass determination

Molecular mass of few polymer samples (M_n and M_w), and molecular mass distribution (MWD), were determined by gel permeation chromatography (GPC).

Results

Preparation of PES

Initial colour of the reaction mixture containing bisphenol-A and hydroquinone was brown and after 2 h of the reaction at 135°C the colour changed to dark brown. The colour further deepened (chocolate) after 4 h of reaction at 160°C. The solution was highly viscous.

In case of bisphenol-A and resorcinol, the solution was colorless initially and the colour changed to light yellow after 2 h at 135°C. The colour change observed after distilling off toluene and continuing the reaction for 4 h at 160°C was brick red. A reddish brown viscous solution was obtained after 16 h of reaction at 160°C.

In bisphenol-A and phenolphthalein, the initial reaction mixture was pink due to alkalinity of the medium. The colour changed to purple after 2 h of reaction at 135°C and darkened further after 4 h at 165°C. A light yellowish viscous solution was obtained after 16 h of reaction at 160°C.

Structural characterisation of oligomers

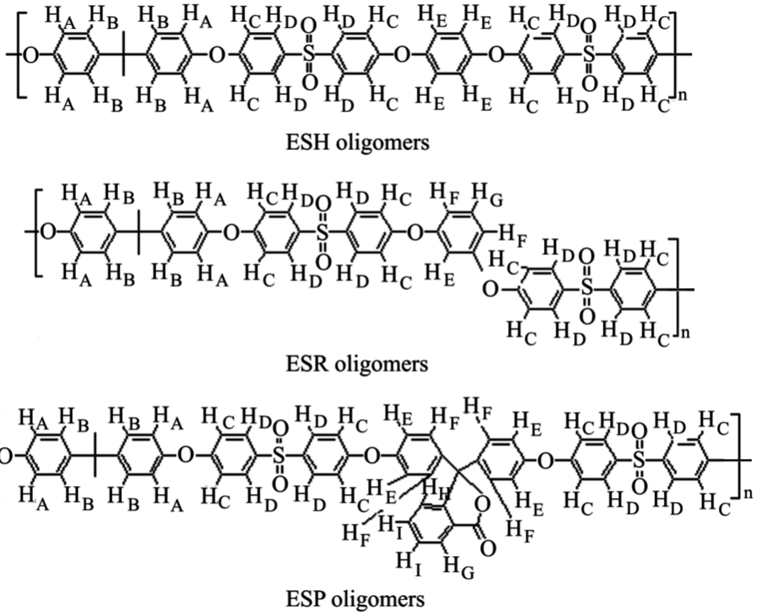
The number average molecular mass ($\overline{M}_n$) of copolymers, as determined by GPC, were in the range of 2000–6000 g mol^{-1}.

In the FT-IR spectra, the characteristic absorption peaks due to asymmetric (1324 and 1294 (doublet) cm^{-1}) and symmetric (1150 cm^{-1}) stretching vibration of sulphone group were observed in all the samples. The aromatic C–H stretching (3092, 3067 and 3036 cm^{-1}) and symmetric C–H stretching vibration due to methyl groups were at 2965 and 2872 cm^{-1}, aromatic skeletal vibrations at 1585–1505 cm^{-1} and characteristic band due to gem dimethyl doublet at 1409–1364 cm^{-1}, phenylene ether stretching vibration at 1243 cm^{-1}, ring vibration of *p*-substituted phenyl ethers (1011 cm^{-1}), out-of-plane C–H deformation characteristic of *p*-substituted phenyl (832 cm^{-1}), C–S stretching vibration (714, 686 and 634 cm^{-1}) were observed. Ring vibration of *m*-substituted aryl ethers in ESR copolymers was observed at 961 cm^{-1}, and its intensity increased with the concentration of resorcinol (ESR-1 to ESR-3). In case of ESP copolymers, the carbonyl stretching of phthalide was observed at 1773 cm^{-1} and its intensity increased with the concentration of phenolphthalein (ESP-1 to ESP-3) (Fig. 1).

^{1}H-NMR

The assignment of proton resonance signals observed in ^{1}H-NMR was made on the basis of published literature (Scheme 2).

In all the copolymers, H_A and H_C proton resonance signals were at 6.92–7.04 ppm, H_B protons around 7.22–7.26 ppm and the sulphone group causes a downfield shift in the chemical shift of H_D to exhibit peak positions at 7.82–7.86 ppm (Fig. 2). In case of ESR copolymers, H_E showed a singlet at 6.72 δ ppm. H_F displayed a doublet at 6.84, 6.86. H_G appeared as a triplet at 7.37 ppm which was of much lower intensity than the rest of the signals.



Scheme 2 Proton designations of PES copolymers

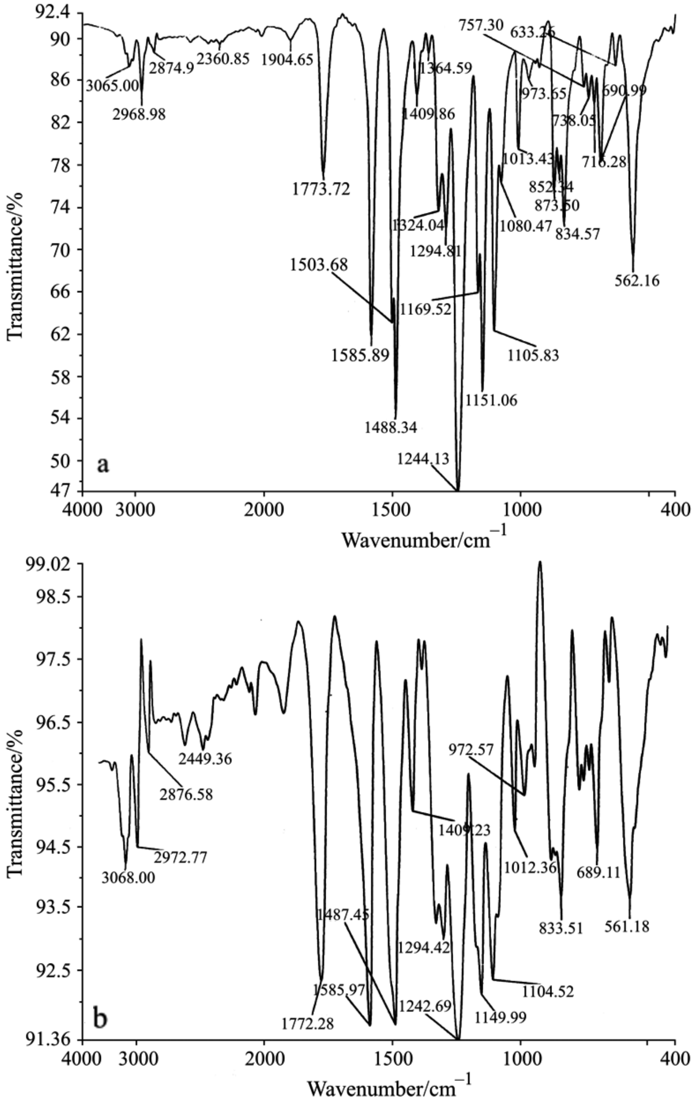


Fig. 1 IR spectra of ESP copolymers a – ESP-1 and b – ESP-3

In case of ESP copolymers, the doublet characterizing H_E overlaps with the proton resonance signal of H_B protons. The steric hindrance offered by the presence of the phenolphthalein ring shifts the doublet characterizing H_F downfield 7.33, 7.36 ppm. The anisotropic effect brought about by the carbonyl group in the proximity of proton H_G shifts the signal downfield than any other proton signal (7.95, 7.97). H_H shows a multiplet in the region 7.55–7.59.

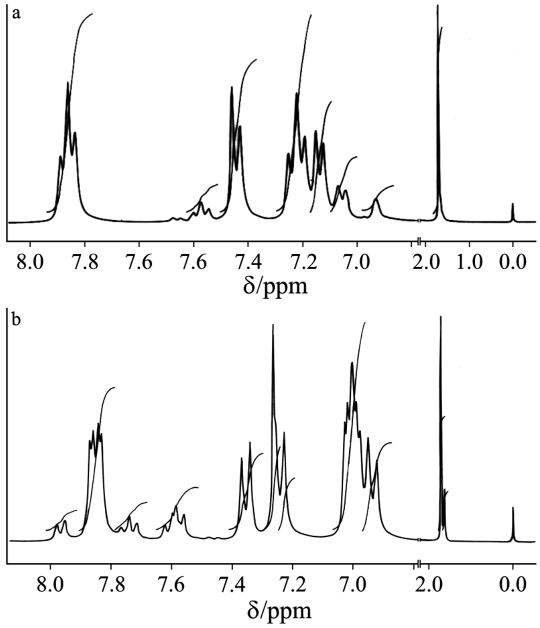


Fig. 2 ^{1}H-NMR spectra of a – ESR-1 and b – ESP-2

On the basis of FT-IR and ^{1}H-NMR spectral data, the structure of copolymer was confirmed.

Thermal characterization

A single step decomposition was observed in all the samples. From the TG traces, the initial decomposition temperature T_i, final decomposition temperature T_f and char yield (%) at 800°C were noted down. The temperature of maximum rate of mass loss (T_{max}) was determined from differential thermogravimetric trace (DTG).

Table 2 Results of TG analysis of PES copolymers in N_2 atmosphere

S. No	Sample designation	T_i/°C	T_{max}/°C	T_f/°C	Mass loss/%	Char yield/%
1	ESH-1	510	520	579	62.3	37.7
2	ESH-2	527	561	588	64.4	35.6
3	ESH-3	526	557	588	61.4	38.6
4	ESR-1	520	529	580	61.1	38.9
5	ESR-2	530	542	583	61.0	39.0
6	ESR-3	532	555	583	65.8	34.2
7	ESP-1	510	513	584	57.9	42.1
8	ESP-2	487	515	562	55.1	44.9
9	ESP-3	497	529	573	50.4	49.6

T_i values of ESH and ESR were similar but increased marginally by decreasing the isopropylidine content in the copolymers (ESH and ESR) while in ESP copolymers an opposite trend was observed. T_i values decreased in ESP copolymers with decrease in isopropylidine units in the backbone in all copolymers. T_{max} increased with a decrease in isopropylidine groups in the backbone in ESH, ESR and ESP copolymers. The T_{max} values were comparable in ESH and ESR while in ESP the values were lower. These results indicate that structural variation of the backbone by using

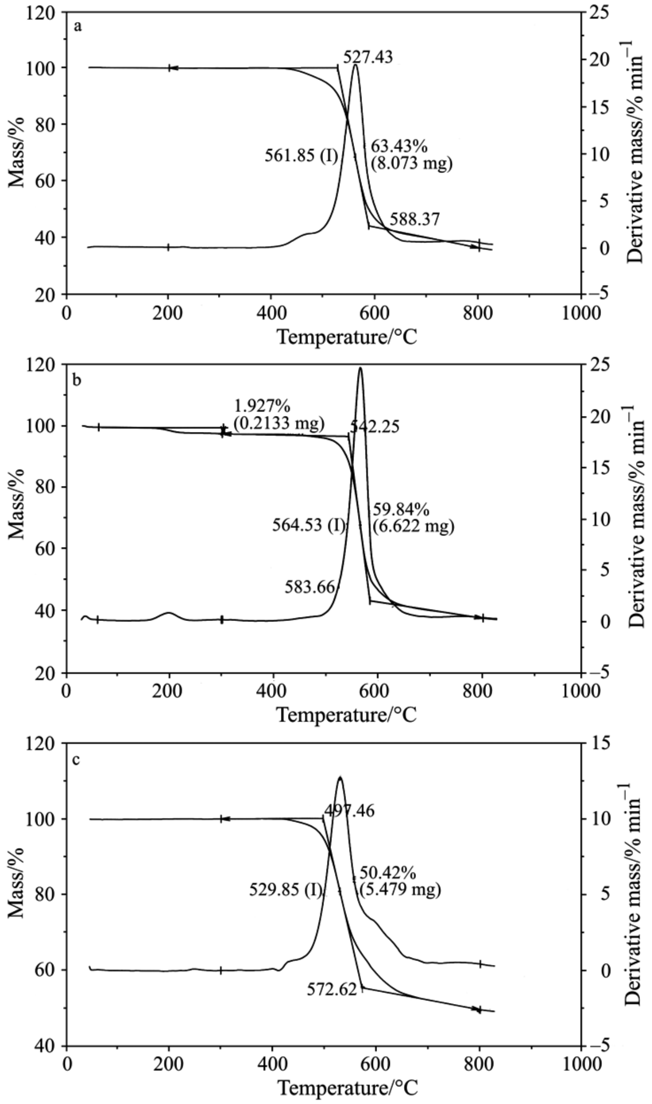


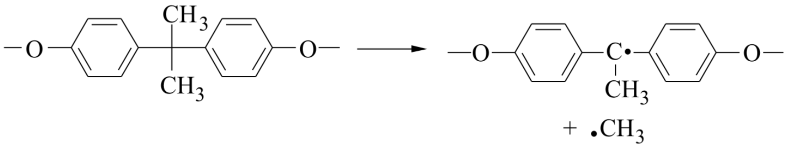
Fig. 3 TG traces of a – ESH-2, b – ESR-2 and c – ESP-3

m- or *p*-substituents (ESH or ESR) did not affect the onset of degradation or temperature of maximum rate of mass loss. The presence of phthalein units reduce the onset temperature of degradation as well as T_{max} values in ESP copolymers.

The char yield of copolymers having similar content of bisphenol-A units was in the order (Table 2) ESP>ESH~ESR (Fig. 3). The char yield of copolymer having phthalein units was highest. This may be attributed to fused aromatic rings present in these copolymers.

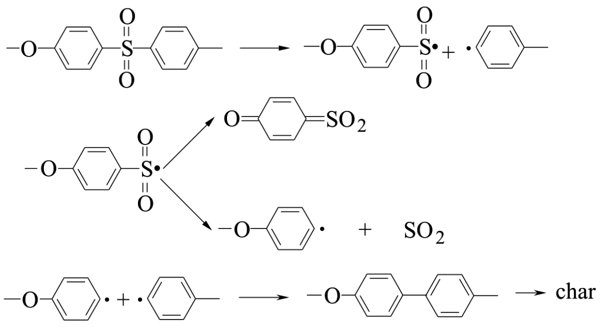
Discussions

The one stage pyrolysis in PES polymer has been reported to proceed by random chain scission and carbonization [15, 16]. In PES, ether and sulphone groups show similar thermal stability. However, the bond dissociation energy of C–CH_3 and C–SO_2 groups which undergo cleavage at initial stages is reported as 250 and 270 kJ mol^{-1} by Rao *et al*. [11]. This indicates that C–CH_3 groups are more susceptible for initiation of degradation. We have observed a decrease in T_i values with an increase in isopropylidine

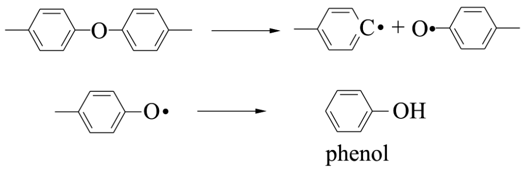


*Further reaction of radicals may lead to carbonisation

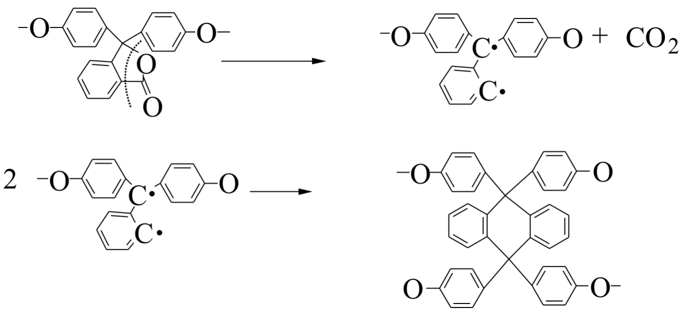
Scheme 3 Thermal cleavage of isopropylidine units in PES



Thermal cleavage of SO_2 units in PES copolymers



Scheme 4 Random chain scisson of PES leading to evolution of SO_2 and phenol



Scheme 5 Thermal degradation of ESP copolymers

units in the backbone. For example, sample ESH-1 and ESR-1 had highest content of isopropylidine units in the backbone and their T_i values were 510 and 520°C. On the other hand, ESH-3 and ESR-3 with lowest isopropylidine content had T_i values of 526 and 530°C, respectively. Scheme 3 depicts the mechanism of degradation.

The volatile products evolved during degradation above 500°C have been identified as SO_2, phenol, etc. (Scheme 4).

A decrease in T_i and T_{max} temperatures and an increase in char yield were observed in copolymers containing phthalein units. The loss of CO_2 from PES containing phthalein has been reported in earlier studies also [15]. The increase in char residue may be attributed to combination of radicals after loss of CO_2 in accordance with Scheme 5.

Conclusions

Poly(arylene ether sulphone) oligomers based on different bisphenols could be successfully prepared by reacting stoichiometric amounts of 4,4-dichlorodiphenyl sulphone and bisphenol-A in presence of a weak base K_2CO_3. An increase in isopropylidine units in the backbone resulted in a decrease in initial decomposition temperature and temperature of maximum rate of mass loss. The *m*- or *p*- linkages in the backbone (ESH and ESR) copolymers did not affect thermal stability. An increase in phthalein units in the backbone resulted in a decrease in T_i and T_{max} values and an increase in char residue observed at 800°C. A mechanism has been proposed to account for these observations.

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