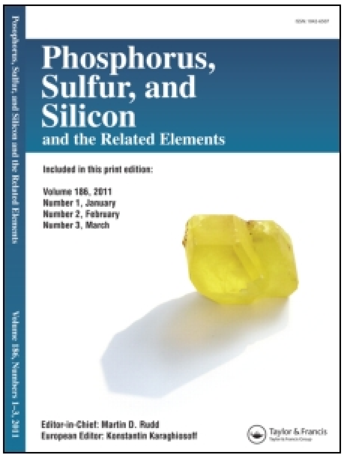

**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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**To cite this Article** Patel, R. T. , Patel, R. D. , Patel, R. G. and Patel, V. S.(1994) 'Hydroxy Terminated Aryl Ether-Sulfone Oligomers as Curing Agents for Epoxy Resins-Synthesis, Characterization and Thermal Study', Phosphorus, Sulfur, and Silicon and the Related Elements, 89: 1, 113 — 117

**To link to this Article: DOI:** 10.1080/10426509408020440

**URL:** http://dx.doi.org/10.1080/10426509408020440

*Phosphorus, Sulfur, and Silicon*, 1994, Vol. 89, pp. 113–117
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# HYDROXY TERMINATED ARYL ETHER-SULFONE OLIGOMERS AS CURING AGENTS FOR EPOXY RESINS-SYNTHESIS, CHARACTERIZATION AND THERMAL STUDY

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*(Received September 1, 1993; in final form March 28, 1994)*

Oligomeric aryl ether sulfones were prepared by aromatic nucleophilic substitution reactions of 4,4′-dichlorodiphenyl sulfone with 4,4′-isopropylidenediphenol and 4,4′-(1,1-cyclohexylidene)diphenol. The resultant products were characterized by elemental analysis, IR spectral data, gel permeation chromatography and thermogravimetry. These low molecular weight oligomers were used as curing agents for epoxy resins. The curing kinetic study was made by differential scanning calorimetry. The cured epoxy resins were observed to possess better heat resistance compared to the resins cured with the traditional curing agents (4,4-diamino diphenyl sulfone or phthalic anhydride).

*Key words:* Oligo aryl ether sulfone; epoxy resin; bisphenol-A; bisphenol-C; curing kinetics.

## INTRODUCTION

Polyaryl ethersulfone is an engineering thermoplastic material[1] exhibiting useful properties like excellent solvent and heat resistance. However, the use of such a polymer is very limited because of its insolubility in common solvents and high processing temperature. Recently, a method was reported for preparing a low molecular weight polyether sulfone (PES) by the condensation of 4,4′-dichlorodiphenyl sulfone (DCPS) with bisphenol.[2] In the present paper the modified method is reported to prepare still lower molecular weight hydroxy terminated oligomers. Thus the present work comprises the synthesis, characterization and application of a reactive oligo aryl ether-sulfones as curing agents for epoxy resins which are well known for their high performance applications in glass fiber and carbon fiber reinforced composites.[3–8]

## EXPERIMENTAL

*Materials*: Bisphenols viz. 4,4′-isopropylidene diphenol (bisphenol-A) and 4,4′-cyclohexylidene diphenol (bisphenol-C) were prepared by reaction of phenol with acetone and cyclohexanone, respectively, using hydrochloric acid as catalyst. 4,4′-Dichlorodiphenyl sulfone (DCPS) was prepared (~85%) by Friedel-Crafts reaction of chlorobenzene with chlorobenzenesulphonylchloride which was obtained by treating chlorobenzene with chlorosulfonic acid.[9]

*Synthesis of oligomers*: All the oligo arylethersulfones were prepared by the nucleophilic substitution reactions of DCPS with bisphenols in the presence of NaOH as per the following procedure.

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TABLE I

Synthesis and characterization of oligo ether sulfones (PES)

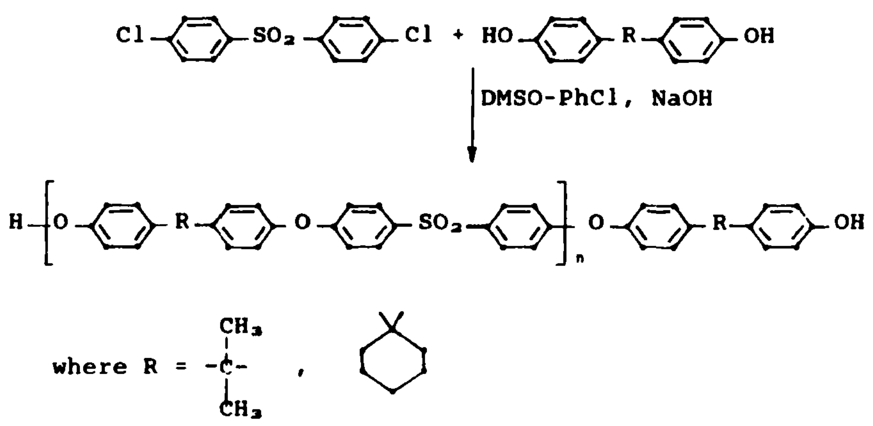
| Sample | Molar ratio DCPS-Bisphenol | Reaction conditions Temp. (°C) | Time (h) | % S Calc. | Obsd. | Softening range (°C) | [η] dl/g. | Mol.wt. $\bar{M}_n$ | $\bar{M}_w$ |
|---|---|---|---|---|---|---|---|---|---|
| PES(BPA[a])-1 | 1:1 | 160-165 | 3.0 | 5.7 | 5.0 | 240-270 | 0.18 | 6000 | 15000 |
| PES(BPA[a])-2 | 1:0.75 | 155-160 | 3.0 | 5.7 | 5.8 | 190-195 | - | - | - |
| PES(BPA[a])-3 | 1:2 | 130-140 | 5.0 | 5.9 | 5.8 | 125-135 | 0.030 | 452 | 1120 |
| PES(BPC[b]) | 1:2 | 195-200 | 2.5 | 5.2 | 5.0 | 140-155 | 0.036 | 467 | 960 |

[a]BPA = bisphenol-A, [b]BPC = bisphenol-C

Bisphenol (0.045 mol), DCPS (0.0225 mol), and NaOH (0.05 mol) were charged in a three-necked flask equipped with mechanical stirrer, condenser and thermometer. To this added was 1:1 dimethyl sulfoxide-chlorobenzene (25 ml). The reaction mixture was heated with stirring at the specified temperature for a specified time. After the completion of the reaction, the resultant viscous solution was filtered to remove salt, and then the oligomers were precipitated with methanol. The products were then filtered, washed with hot methanol, washed once with 10% aq. acetic acid and then with water and then dried at 60°C in vacuum.

The details of the reaction parameters are described in Table I.

**REACTION SCHEME**



*Characterization of the oligomers*

Sulfur content in the oligomers was estimated by the Carius method. IR spectra were recorded on Perkin Elmer 983 spectrophotometer using KBr pellets. Viscosity measurements were made by Ubbelhode suspended type viscometer in chloroform at 35°C. Molecular weights were determined by Waters gel permeation chromatograph using styragel columns in toluene. Thermogravimetric analyses were performed on a Du Pont 951 TGA unit in air at a heating rate of 10°C/min. Curing studies were made using a Du Pont 9900 differential scanning calorimeter as per the method reported in our earlier publications.[10,11]

## RESULTS AND DISCUSSION

All the oligomeric products obtained were soluble in solvents like toluene, chlorobenzene, tetrahydrofuran, dimethyl sulfoxide, dimethyl formamide and chloroform. The values of the sulfur content were well in agreement with the theoretical values. The softening point and molecular weight (Table I) of these oligomers depend upon the molar ratio and reaction parameters.

The IR spectra described in Table II reveals that the spectra of all the oligomers were almost similar, except some differences in certain characteristic absorption peaks. The main differences in the IR spectra of PES(BPA) and PES(BPC) were the absence of a sharp peak at 1370 $cm^{-1}$ and higher intensity at 2870 $cm^{-1}$ in spectrum of the latter. The major differences in the IR spectral data (listed in Table II) of the epoxy resin and the resin cured with synthesized oligomers PES(BPA)-3 and PES(BPC) were the disappearance of the bands at 920 $cm^{-1}$ and 860 $cm^{-1}$, characteristic frequencies of oxiran oxygen of DGEBA and appearance of new bands at 1290 $cm^{-1}$ and 1145 $cm^{-1}$, symmetric and asymmetric stretching vibrations due to $—SO_2—$ of oligoether-sulfone involved in crosslinked structure; in the spectra of latter.

Two of the above oligomers, viz. PES(BPA)-3 and PES(BPC), were utilized for curing of epoxy resin, diglycidyl ether of bisphenol-A, with the expectation that these oligomers could yield a cured product with good thermal stability. In order to investigate the curing reaction, the DSC technique was adopted. DSC thermograms of the resin-curing agent compositions scanned at a heating rate of 10°C/min showed the exotherm in the range 260–350°C, but no exotherms were detected in the DSC scans of a resin only or in the scans of the cured resin, indicating that the exotherms are due to exothermic curing reactions. The curing of DGEBA-PES(BPC) started at 260°C and completed at 350°C with a peak maximum temperature ($T_p$) of 320°C, while the curing of DGEBA-PES(BPA) commenced at 255°C and completed at 340°C with a $T_p$ of 310°C. The activation energies for the curing[11,12] of DGEBA-PES(BPC) and DGEBA-PES(BPA) are 105.8 and 97.2 KJ/mol, respectively, with an order of reaction[12] as ~1.0. These differences in characteristic temperatures and activation energies are attributed to basic differences in the structures of the curing agents.

The thermal behaviour of the two selected oligomers, one after aging at 100°C for 6 months and one cured epoxy resin, DGEBA-PES(BPC) are summarized in Table III. All the thermograms were similar in general shape, and the degradation occurred in a single step. However, the characteristic temperatures varied widely depending upon the sample. From the data listed in Table III, it is evident that

TABLE II

IR spectral data ($cm^{-1}$) of oligoether sulfones and epoxy resins

| Assignment | PES(BPA) | PES(BPC) | DGEBA | DGEBA-PES(BPA) | DGEBA-PES(BPC) |
|---|---|---|---|---|---|
| -OH stretching | 3600-3250 (br) | 3600-3250 (br) | - | 3600-3100 (br) | 3600-3100 (br) |
| -CH stretching ($-CH_2$, -CH) | 2960<br>2870 | 2960<br>2870 | 2950<br>2860 | 2960<br>2870 | 2960<br>2870 |
| -C=C stretching | 1590<br>1490<br>1405 | 1590<br>1490<br>1405 | 1590<br>1490<br>1405 | 1590<br>1490<br>1405 | 1590<br>1490<br>1405 |
| $-SO_2$ assymetric stretching | 1300 | 1300 | - | 1290 | 1290 |
| $-SO_2$ symmetric stretching | 1150 | 1150 | - | 1145 | 1145 |
| -C-O-C stretching | 1240 | 1240 | 1240 | 1230 | 1230 |
|  stretching | - | - | 920<br>860 | - | - |

TABLE III

Thermal behaviour of the oligomers and cured epoxy resins

| Sample | $T_i^a$ | $T_{max}^b$ | $T_f^c$ | % Residue | Ea (±2) KJ/mol |
|---|---|---|---|---|---|
| PES(BPA)-3 | 400 | 575 | 700 | 31.5 | 138.7 |
| PES(BPA)-3[d] | 400 | 580 | 700 | 28.8 | 146.8 |
| PES(BPC) | 350 | 550 | 700 | 9.0 | 130.9 |
| DGEBA-PES(BPC)[e] | 375 | 475 | 700 | 5.0 | - |
| DGEBA-DDS[e] | 167 | 410 | 650 | 3.5 | 114.1 |
| DGEBA-PA[e,f] | 210 | 400 | 650 | 4.8 | 115.8 |

[a,b,c] Temperatures of starting, maximum rate of decomposition and leveling off of decomposition respectively.

[d] Sample PES(BPA)-3 kept at 100°C for 6 months.

[e] Curing agents were used in stoichiometric amount.

[f] Triethylamine (1%) was used as catalyst.

the oligomer PES(BPA)-3 is thermally more stable than the oligomer PES(BPC). This difference in thermal stability is due to the difference in the structure of the bisphenols used for the synthesis of oligomers. The sample PES(BPA)-3, after aging at 100° for 6 months, also showed remarkable thermal stability, having almost the same temperature characteristics as those of PES(BPA) without aging. The comparative study of the IR spectra of these two samples showed no change in the characteristic absorption peaks indicating that no easily identifiable change had occurred on aging.

The epoxy resin cured with PES(BPC) was analyzed by TGA, and the thermal characteristics were compared with those of two cured epoxy resin samples obtained using phthalic anhydride (PA) and 4,4′-diaminodiphenylsulfone (DDS). The resin cured with the synthesized oligomers yielded a cured product with a superior thermal stability to those obtained by curing with the traditional curing agents like PA or DDS.

The activation energies reported in Table II determined by the Broido method[14] were well within the range of those of cured epoxies obtained using diamines, anhydrides or dianhydrides as curing agents.[14–16]

## CONCLUSIONS

It is evident from the present study that the hydroxyl-terminated oligo(aryl ether sulfones), when used as curing agents, yield very good heat resistant epoxy systems. The study regarding the synthesis and application of some more oligomers in this series is in progress.

ACKNOWLEDGEMENT

The authors are thankful to Prof. M. N. Patel, Head, Department of Chemistry for providing research facilities.

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