*Polymer* Vol. 37 No. 14, pp. 3111-3116, 1996
Copyright © 1996 Published by Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/96/$15.00+0.00

# Polymerization of poly(*p*-phenylene sulfide) from a cyclic precursor

**Dean A. Zimmerman, Jack L. Koenig and Hatsuo Ishida***
*Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106-7202, USA*

*(Received 4 January 1995; revised 9 May 1995)*

Melt-state polymerization of synthesized cyclic phenylene sulfides is reported. Fourier transform infra-red (*FT* i.r.) spectroscopy is used to follow the crystallization as a function of time. Optical microscopy is used to examine the morphology during polymerization. The resulting polymer is compared with commercial poly(phenylene sulfide) using differential scanning calorimetry (d.s.c.), (*FT* i.r.) spectroscopy, density measurements and optical microscopy. The glass transition temperature and crystallization parameters as a function of the reaction temperature are obtained by (d.s.c.) and related to the degree of polymerization. The effect of thermal treatment with and without carbon fibres is also examined. Curing of the cyclic phenylene sulfides is also examined at various temperatures. Densities of the polymer and cyclics are compared. Copyright © 1996 Published by Elsevier Science Ltd.

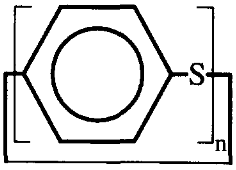
**(Keywords: poly(phenylene sulfide); cyclic precursor; polymerization)**

## INTRODUCTION

Cyclic compounds are often used as polymeric precursors. A majority of these cyclic oligomers have aliphatic main chains. However, there have recently been reported several cyclic compounds with phenyl rings in the main chain that have been used to obtain polymers: carbonates[1,2], ethers[3], bisphenol-A sulfone[4] and 1,4-xylylene[5]. In addition, it has been reported that the cyclic hexamer of phenylene sulfide has been polymerized[6-8] by solution, thermal and mechanochemical methods. However, little information is given about the polymerization, and any application of these materials could not afford to use an isolated cyclic. Therefore, a study on the polymerization of a mixture of cyclic phenylene sulfides (CPS) was undertaken.

There are many potential benefits of using cyclic oligomers for the production of poly(phenylene sulfide)s (PPS). The polymerization of PPS from cyclic compounds would result in a pure polymer, with no by-products or impurities such as halogenated oligomers and thiols that are found in commercial PPS. Low-molecular-weight PPS typically has up to 3% soluble impurities. This increased purity could be an important benefit for PPS in electronic applications. Impurities can also lead to a reduction in solvent resistance and have additionally been shown to decrease mechanical properties[6]. Furthermore, the use the cyclic oligomers would allow for reactive processing of PPS. In particular, *in situ* polymerization would be expected to have a beneficial effect on adhesion in PPS composites. Cyclics are known to have a lower viscosity than the corresponding polymer[3], which is beneficial for processing.

CPS were first identified by Kaplan and Reents[9] as an impurity in commercial PPS using mass spectrometry.



They are a by-product of the commercial PPS process of the reaction between dichlorobenzene and sodium sulfide in *N*-methyl pyrrolidone (NMP). CPS occur in about 1% yield in low-molecular-weight PPS (i.e. Phillips V-1) and are virtually absent in higher molecular weight PPS. They have been reported[8-12] from $n = 4$ to $n = 10$, with the most prevalent CPS being the hexamer. CPS from $n = 4$ to 8 have been isolated and characterized[9-12]. Directed synthesis of CPS was first done by Sergeev *et al.*[11], who obtained 73% yield for the hexamer with only 4% polymer by using brominated trimers under dilute reaction conditions with the cyclic-to-polymer ratio being highly dependent on the concentration of the reactants. Synthesis of CPS from copper bromothiophenolate has also been reported[13].

## EXPERIMENTAL

Synthesis of the CPS was done by adding dichlorobenzene over a 12 h period to 300 ml of NMP at an initial sodium sulfide concentration of 0.1 M (ref. 11). The mixture was added to 500 ml of deionized water (pH = 4), and the solid was filtered. The solid was extracted with tetrahydrofuran (THF). The THF was removed yielding an off-white solid. The resulting solid

---

[*] To whom correspondence should be addressed

was extracted with acetone yielding a white powder. Low-molecular-weight PPS (L–PPS) (Ryton V-1, Phillips) and high-molecular-weight linear PPS (H-PPS) (Ryton PR28, Phillips) are used for comparison with the PPS from cyclic oligomers (CO-PPS). The carbon fibers (Amoco Thornel) were unsized and were poly(acrylonitrile) (PAN) (T650/42) and pitch-based (P25).

Differential scanning calorimetry (d.s.c.) was done on a TA DSC 2910 at a heating rate of 20°C $\mathrm{min}^{-1}$. Fourier transform infra-red (*FT* i.r.) spectroscopy was performed on a Bomem Michelson MB spectrometer with a liquid nitrogen cooled mercury–cadmium–telluride (MCT) detector at a resolution of 2 $\mathrm{cm}^{-1}$. The specific detectivity, $D^*$, of the MCT detector was $1 \times 10^{10}$ cm $\mathrm{Hz}^{1/2}\,\mathrm{W}^{-1}$. Far infra-red spectra containing wavenumbers below 480 $\mathrm{cm}^{-1}$ were obtained with a Biorad FTS-60A spectrometer at 2 $\mathrm{cm}^{-1}$ with a deuterated tryglycine sulfate (DTGS) detector. Spectral analysis was performed on a Sun SPARC station 2 using the Spect Ir (New Methods Research) software package.

Density of the polymer was measured by preparing solutions of water and potassium carbonate of the approximate density. The density was slowly changed until the PPS did not sink or float for 5 min, and the density of the solution was measured using a pycnometer. For the reaction of the cyclic mixture, the sample was ground with a small amount of KBr and heated for the desired time. The sample was removed and more KBr added, and the pellet was formed. The polymer samples were studied as a thin film cast from $\alpha$-chloronaphthalene solution. For fibre samples, the powder was dispersed onto the fibres using an acetone slurry.

## RESULTS AND DISCUSSION

### *Isolation of cyclics*

The crude PPS product was extracted with THF to obtain cyclic oligomers and some linear impurities. The dilution of the reaction resulted in a theoretical yield of 21% PPS and 30% THF-soluble fraction. Higher dilution would increase the per cent yield but decrease the amount of material, so a concentration of 0.1 M was chosen. Polymerization of the crude mixture is possible, however the resulting polymer is very brittle due to the presence of impurities. The THF-soluble fraction was therefore extracted with acetone to remove the low-molecular-weight linear materials, notably thiols, which were detected by the odour in the crude mixture but not in the purified material. The yield of the purified material was 22% of the crude mixture. The *FT*i.r. spectrum of the purified CPS mixture is shown in *Figure 1* along with that of the pure cyclic hexamer of phenylene sulfide (CHPS). There are differences due to the different crystal arrangement, however there are no new peaks, which would be indicative of non-cyclic material. For example, monosubstituted benzene can be identified by a peak at 1450 $\mathrm{cm}^{-1}$, which is not seen, or thiols would show bands at 2570 and 905 $\mathrm{cm}^{-1}$. Size exclusion chromatography (s.e.c.) shows four components, which correspond to the pentamer, hexamer, heptamer and octamer.

### *Polymerization*

The d.s.c. scan in *Figure 2* of the cyclic mixture shows four melting points. The melting points are all considerably below the melting points of the different crystalline cyclics[9,10] due to their imperfect crystalline state. The lower melting point allows for polymerization at lower temperatures. Polymerization of well-grown crystal needles of the hexamer had to be performed at 335°C, while polymerization of the mixture has been observed to occur above 280°C. The d.s.c. sample of *Figure 2* was heated at 325°C for 1 h after the initial ramping, however no reaction peak was observed. The reaction is expected to be nearly thermoneutral due to the small degree of strain and size of the ring. No melting peak is observed above the reaction temperature of 320°C if the scan temperature is increased to 350°C.

The broad band at 280°C may be polymerization of the lower melting point cyclics or a crystal transition. A transition is observed using optical microscopy at 280°C as the crystal needles become distorted hexagons about 40 $\mu$m in diameter. The crystals melt before assuming the new ordered state. Optical microscopy using cross-polarized light shows the original starting material to contain needles (*Figure 3a*). There is also some material which appears to be poorly crystalline. After heating at 300°C for 15 min and cooling, the distorted hexagon along with the presence of small spherulites (indicative of PPS) are observed (*Figure 3b*). Also, polymerization as

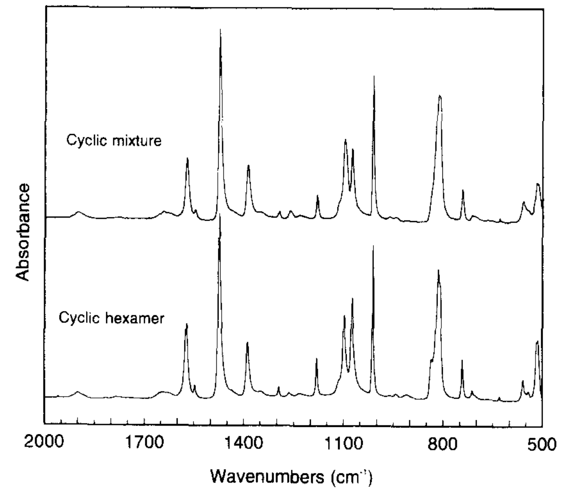


**Figure 1** *FT*.i.r. spectrum of mixture compared with that of the pure cyclic hexamer of phenylene sulfide

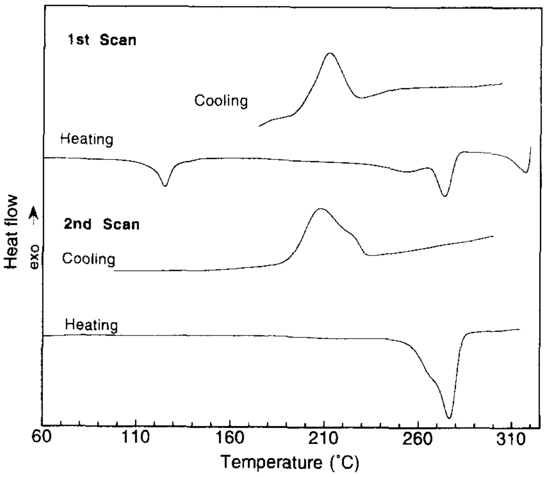


**Figure 2** D.s.c. scan of purified cyclic mixture at a heating rate of 20°C $\mathrm{min}^{-1}$. After first heating scan, the sample was held at 320°C for 1 h

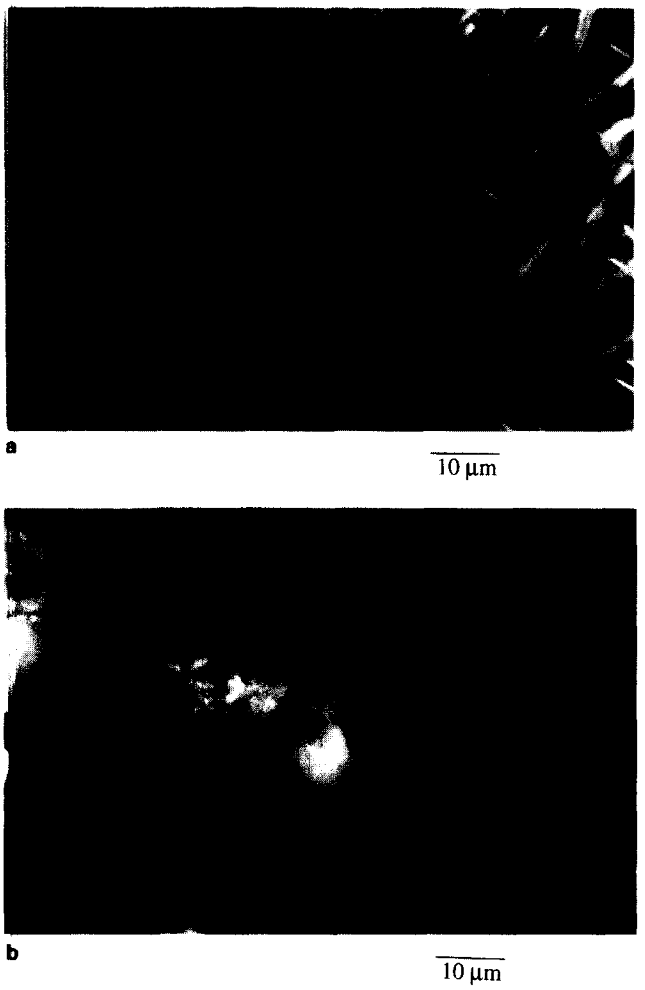


**Figure 3** Optical micrographs of: (a) CPS; (b) CPS after heating at 300°C for 15 min

examined by *FT*i.r. is extremely slow at 280°C; therefore, this is further evidence that the band seen in the d.s.c. scan is likely to occur as a result of the crystal change.

Ring-opening polymerization of the cyclics occurs upon sufficient heating without the addition of any catalyst. Polymerization is known to occur as seen by the presence of spherulites, melting point, insolubility in THF, and changes in the *FT*i.r. spectrum. Polymerization has been observed to occur above the melting point of the polymer, which for a degree of polymerization of 50 has been determined to be 272°C[14]. The upper limit of the reaction is determined by the oxidation and curing of the polymer, which is known to occur above 315°C[15]. The *FT*i.r. spectrum of the polymer obtained after heating of the cyclic mixture (CO-PPS) at 320°C for 1 h is shown in *Figure 4* along with that of L–PPS. It has been reported[16] that there is a chain-length sensitive band at 1450 cm$^{-1}$, which is not present in the polymer from the cyclics. Therefore, there does not appear to be unpolymerized oligomer present. Spherulites measuring ~ 30 $\mu$m are observed after heating, which are about the same size as those in commercial PPS.

Polymerization can be observed by examining the structure-sensitive bands in the *FT*i.r. spectrum. The degree of crystallinity is expected to increase with molecular weight as the number of defect sites is reduced. Also, the cyclic has the appearance of an amorphous

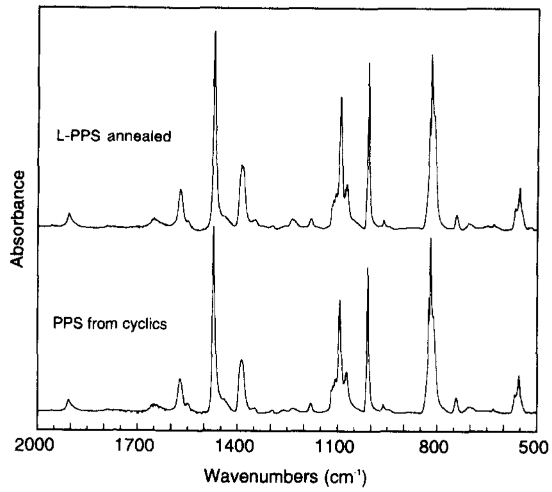


**Figure 4** *FT*i.r. spectrum of annealed CO-PPS compared with that of L-PPS

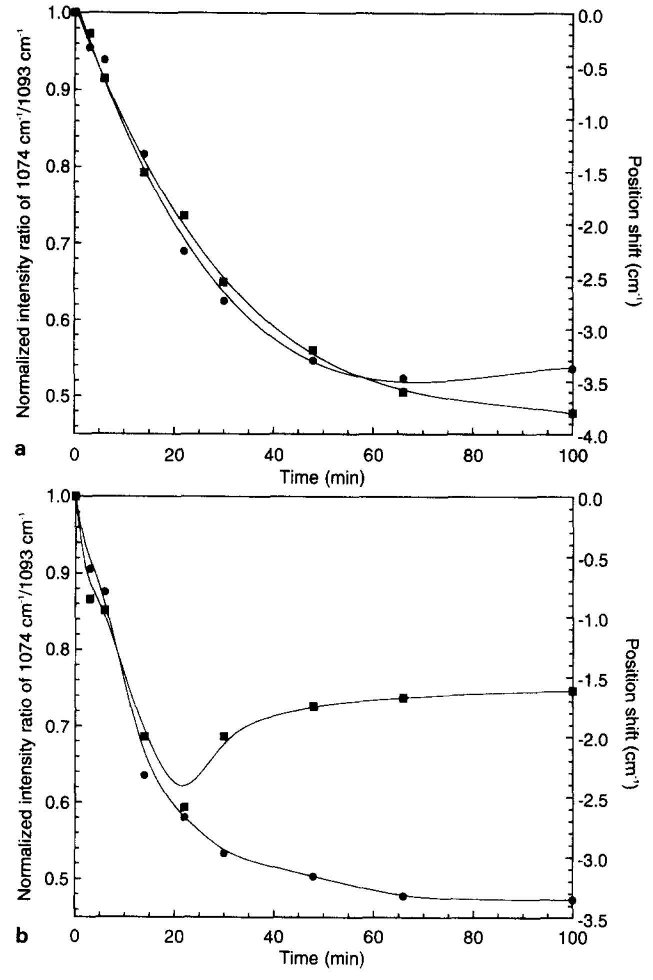


**Figure 5** *FT*i.r. results from the heating of CPS at: (a) 320°C; (b) 340°C showing (■) intensity ratio; and (●) band position shift of 1074 cm$^{-1}$ as a function of time

spectrum due to symmetry considerations[8]. Therefore, the intensity of the crystalline-sensitive bands can be used to examine the reaction. In addition, the 1074 cm$^{-1}$ band is known to change in position as a function of conformation and can be used to monitor the reaction. *Figure 5* shows the ratio of the bands at 1093 and

1074 cm$^{-1}$ and the band position change for 1074 cm$^{-1}$. From optical microscopy, it was observed that heating at 300°C resulted in incomplete polymerization as seen by the presence of non-spherulitic crystals; therefore 320 and 340°C were chosen. The samples were not annealed but were air-cooled. For 320°C, there is a gradual increase in crystallinity which closely follows the change in the band position. The minimum is reached after 50 min. However at 340°C, there is very different behaviour. The initial reaction is much quicker as expected, but after about 30 min a decrease in crystallinity is seen. This occurs due to the increased branching, which prohibits a high degree of crystallinity. Since the crystallization rate decreases as a function of molecular weight, the samples from the reaction at 340°C were annealed to ensure that the observed results were not due simply to increasing molecular weight, and they showed a similar trend.

Another region that can be used to observe the reaction is the C–H out-of-plane mode. *Figure 6* shows this region as a function of time for the reaction at 340°C. Initially each cyclic component has different bands. After 3 min, there is seen an increase in the number of bands due to the crystal transition. Annealing of the crystal also results in band width narrowing. Subsequently, the two polymer crystalline bands are observed at 825 cm$^{-1}$ and 820 cm$^{-1}$ along with the amorphous shoulder. These bands decrease with increased branching; and, after 48 min, it is difficult to distinguish the crystalline bands, which is consistent with the results in *Figure 5*. The other notable change upon polymerization is in the 600–475 cm$^{-1}$ region. This region shows bands that are sensitive to long-range motion. Upon heating, these bands show a significant reduction and the emergence of a new band at 480 cm$^{-1}$.

The effect of the reaction temperature on the molecular weight of the PPS was examined. The insolubility of PPS at temperatures below 200°C makes conventional techniques like s.e.c. very difficult. The crystallization temperatures and glass transition temperature have been shown to be a function of molecular weight[14,17-19]. Correlation of the degree of polymerization, $D_p$, with a series of iodine-terminated PPS has been performed by Fagerburg *et al.*[14]. In that study the $D_p$ was measured by end-group analysis. For PPS, the logarithm of the glass transition temperature, $T_g$, is directly proportional to the molecular weight up to a $D_p$ of 200. The amount of undercooling, defined as the melting temperature, $T_m$, minus the crystallization temperature upon cooling, $T_{cc}$, is also an indication of molecular weight. The difference between $T_{cc}$ and the crystallization temperature upon heating, $T_{ch}$, is indicative of the relative rate of crystallization and is also used.

Three reaction temperatures were chosen within the polymerization range: 300, 320 and 340°C. Initially, a reaction time of 1 h was chosen; however this did not seem to be a valid comparison since the 300°C sample does not polymerize completely and the 340°C sample undergoes branching. Therefore, the time to achieve maximum crystallization as measured by *FT*i.r. was used, which for 300, 320 and 340°C was 1.5, 1 and 0.5 h, respectively. At the end of the reaction time, the sample was quenched in the aluminium pan and scanned at 20°C min$^{-1}$, the same rate as that used by Fagerburg *et al.*[14]. *Tables 1* and *2* show the crystallization parameters for the different conditions and the corresponding degree of polymerization. The degree of polymerization for the CHPS is approximately 60. The samples from the cyclic mixture do not give the same value, although in each case

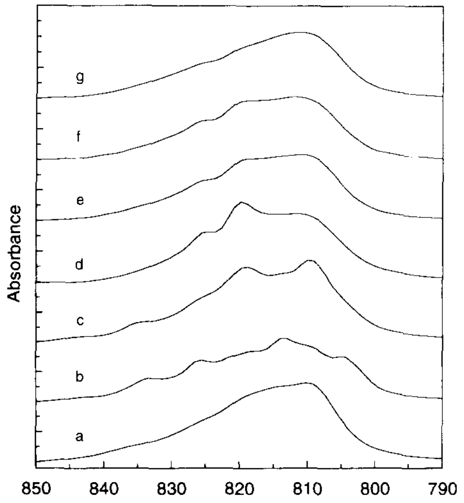


**Figure 6** *FT*i.r. spectra of C–H out-of-plane region as a function of time at 340°C: (a) initial; (b) 3 min; (c) 6 min; (d) 14 min; (e) 22 min; (f) 30 min; and (g) 48 min. Spectra were taken at room temperature

**Table 1** Crystallization parameters obtained from d.s.c. experiment of cyclic phenylene sulfides polymerized at different conditions

| Polymerization temperature (°C) | Time (h) | $T_g$ (°C) | $T_{ch}$ (°C) | $T_m$ (°C) | $T_{cc}$ (°C) |
|---|---|---|---|---|---|
| 300 | 1 | 70 | 116 | 264 | 222 |
| 320 | 1 | 80 | 122 | 278 | 215 |
| 340 | 1 | 80 | 125 | 277 | 200 |
| 320<br>250 | 1<br>12 | 70 | 107 | 263 | 212 |
| 320 (CHPS) | 1 | 86 | 141 | 278 | 220 |
| 320 (with fibres) | 1 | [a] | [a] | 272 | 243 |

**Table 2** Degree of polymerization obtained from crystallization parameters obtained from d.s.c. experiments using cyclic phenylene sulfides polymerized at different conditions. Molecular weight of repeat unit is 108 g mol$^{-1}$

| Polymerization temperature (°C) | Time (h) | Degree of polymerization at $T_g$ | $T_{ch}$ | $T_m - T_{cc}$ | $T_{cc} - T_{ch}$ |
|---|---|---|---|---|---|
| 300 | 1 | 25 | 27 | 20 | 42 |
| 320 | 1 | 42 | 31 | 72 | 58 |
| 340 | 1 | 42 | 34 | 100 | 70 |
| 320<br>260 | 1<br>12 | 25 | 21 | 40 | 40 |
| 320 (CHPS) | 1 | 52 | 44 | 48 | 60 |
| 320[a] (with fibres) | 1 | – | – | [b] | – |

[a] Unable to quench sample

the same trend is observed. The 340°C reaction temperature gives the highest molecular weight. Some of the discrepancy may be related to the fact that the Fagerburg experiment has large iodine end-groups which will cause a change in molecular mobility compared with the hydrogen end-groups in the current experiment, although this effect should become less pronounced at high molecular weights. The trend however is still valid, which shows that the molecular weight increases as a function of reaction temperature.

Crystallization parameters indicate that the PPS is low molecular weight. PPS is known to increase in molecular weight by thermal treatment below the melting point[17]. The CPS was therefore heated at 320°C for 55 min, cooled slowly (1 h) to 250°C, followed by annealing for 12 h. D.s.c. shows that branching has occurred, and crystallinity is actually decreased. Therefore, the thermal treatment should be at a lower temperature, since the melting point is lower. However, using a thermal treatment of 220°C does not show any change from the original material polymerized at 320°C.

The crystallization of PPS has been extensively studied and the appearance of a double melting peak is reported[18,20–23]. The second scan in *Figure 2* of the CO-PPS shows typical melting behaviour of PPS. A double melting peak is also observed for the different reaction temperatures.

Typically, extraction of the material would be of interest to examine the extent of impurities. However, since there was limited material, optical microscopy using cross-polarized light was utilized to see if material was soluble in THF. After immersion in THF, the sample shows no amorphous component unlike the appearance of the L-PPS, which has a readily observed amorphous component. The THF-soluble component in CO-PPS is therefore definitely less than the 3% observed for L-PPS and likely comparable to the 0.5% for the H-PPS. Upon observing the polymer after soaking, there is no pitting or surface irregularity.

Density was examined to verify that polymer was obtained and to examine the change upon polymerization. *Table 3* shows a summary of the densities obtained. The density of the cyclic mixture is difficult to obtain because of the different fractions that are present. The average density of the cyclic mixture was calculated based on the proportions of the different fractions given by Sergeev *et al.*[10]. The density of the CPS is very close to the density of the polymer crystal. Therefore, polymerization of the cyclic crystal to the annealed polymer results in slight expansion. Since shrinkage can potentially impose stresses on a composite, this could be a benefit for processing of these materials.

**Table 3** Density of cyclic phenylene sulfide oligomers and PPS

| Material | Density ($g cm^{-3}$) |
|---|---|
| Semicrystalline PPS | |
| Experimental | 1.35 |
| Literature[24] | 1.35 |
| PPS crystal[21] | 1.42 |
| PPS amorphous[21] | 1.32 |
| Cyclic hexamer of phenylene sulfide[10] | 1.43 |
| PPS from CHPS | 1.35 |
| Cyclic mixture of phenylene sulfides[a] | 1.39 |
| PPS from cyclic mixture | 1.35 |

[a] Calculated based on the distribution of each fraction given in ref. 11

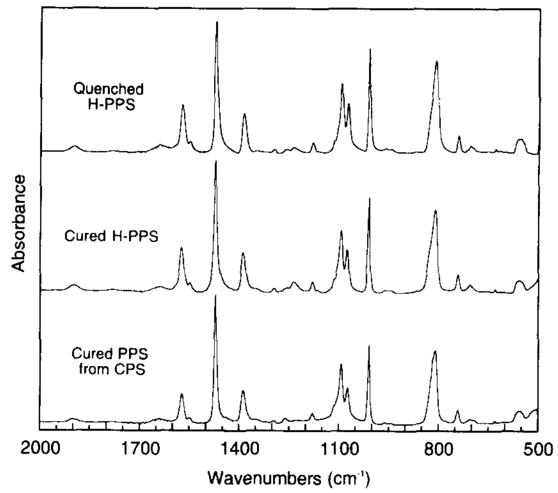


**Figure 7** *FT*i.r. spectra of quenched H-PPS, cured H-PPS and polymerization of CPS at 350°C for 2 h

*Curing*

Besides a semicrystalline polymer, it is also possible to produce cured films, which, with the high purity, could be ideal for coatings. *Figure 7* compared the *FT*i.r. spectrum of the quenched H-PPS with those of the cured H-PPS and the cured PPS from the cyclic – both having been heated at 350°C for 2 h. The spectrum is essentially that of amorphous PPS, although there is still some degree of order based on the shape of the band at 800 $cm^{-1}$. Also, the band at 1240 $cm^{-1}$ is the strongest in the cured H-PPS. This indicates that there is a greater amount of phenyl–O linkages in the cured H-PPS than in the cured CO-PPS. The only molecular difference between the samples is that branch chains will be considerably longer in the PPS from the cyclics. There is a very weak band observed at 1440 $cm^{-1}$, which is a sign of degradation. There is likely a small oligomeric fraction that degrades at the curing temperature.

*Effect of fibres*

CPS were applied to fibres that had been extracted with acetone for 24 h. The coating was not thicker than 200 $\mu m$ using an acetone slurry. The fibres were unsized, and both PAN and pitch-based fibres were used. The fibres were heated at 320°C for 1 h and annealed at 250°C for 12 h. For the polymer without fibres, this was shown to lead to a decrease in the crystallization upon thermal treatment. The polymer was extracted from the fibres with $\alpha$-chloronaphthalene, and the spectrum is shown in *Figure 8*. The degree of crystallinity that is obtained after annealing these samples is very high. It is estimated to be 68%, compared with 64% in the H-PPS, from the ratio of the bands at 1093 and 1074 $cm^{-1}$ (ref. 25). Typically, higher molecular weight PPS is expected to have higher crystallinity; however this does not occur in this case. It is believed that the fibre somehow prevents extensive curing/branching from occurring, possibly by limiting the mobility of the chains. Also there are no end groups to interfere with crystallization. The morphology does differ from the H-PPS. There are no spherulites observed; rather small crystalline domains of the order of 0.5 $\mu m$ are observed. This morphology has been reported to be beneficial for composites[26].

The d.s.c. scan of the CO-PPS from the carbon fibre is

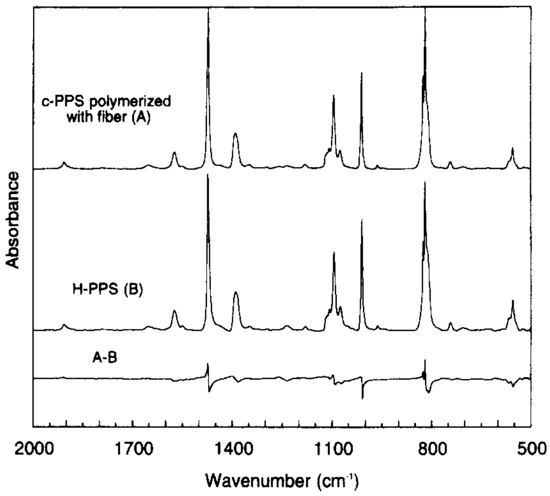


**Figure 8** *FT*i.r. spectrum of polymer obtained by heating CPS on PAN-based carbon fibres at 320°C for 1 h followed by annealing at 250°C for 12 h and extracting with $\alpha$-chloronaphthalene. Spectral subtraction of the H-PPS is shown

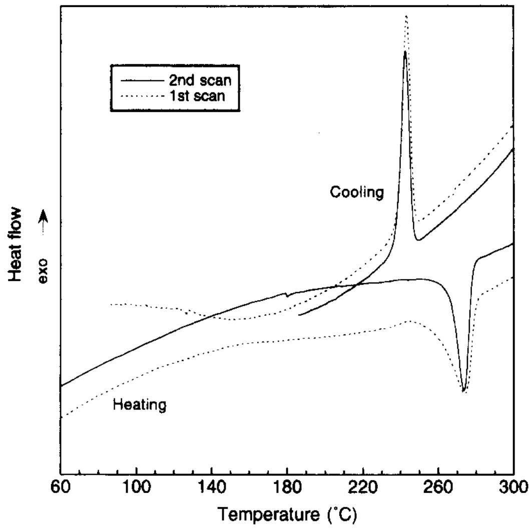


**Figure 9** D.s.c. scan of polymer obtained by heating CPS on PAN-based carbon fibres at 320°C for 1 h followed by annealing at 250°C for 12 h and extracting with $\alpha$-chloronaphthalene

shown in *Figure 9*; it shows rapid recrystallization upon cooling at 240°C which is higher than that typically observed for PPS[21]. Every attempt was made to ensure that no particles were present that could induce crystallization. The polymer was extracted from continuous fibres and the solution was filtered using a glass frit at 210°C. Using optical microscopy, the same effect was observed. At the same cooling time as in d.s.c., crystallization on the fibre was seen to occur at 247°C while bulk nucleation occurred at 238°C. In the composite, the fibre acts as a nucleating agent, and the higher crystallization temperature is expected. However, if the effect seen in the d.s.c. is due to the presence of a fibre particle, the temperature should be close to 247°C; therefore it appears to be solely due to molecular considerations.

## CONCLUSIONS

Polymerization of PPS from a mixture of cyclic oligomers has been achieved. The product is free from impurities and shows melting behaviour of PPS polymer upon heating. Maximum crystallization exceeds that of commercial PPS. A reaction temperature of 320°C is recommended to avoid incomplete polymerization and extensive branching of the material. The cyclic crystal and polymer crystal have nearly the same density, resulting in slight expansion upon polymerization. Degradation occurs between 450 and 500°C. In the melt state, crosslinking of the cyclic mixture is shown to occur in the range 350–400°C.

Polymerization onto a fibre surface can result in a polymer with high crystallinity and rapid nucleation characteristics. The crystal size is less than 0.5 $\mu$m, which does not permit transcrystallization, a condition believed beneficial for composites. The fibre has been shown to alter the morphology of the CO-PPS that has been polymerized onto it at high temperatures.

## ACKNOWLEDGEMENTS

The authors would like to acknowledge the partial financial support of the Office of Naval Research. The carbon fibres were provided by Amoco Performance Products. PPS was supplied by Phillips Petroleum Company.

## REFERENCES

1 Brunelle, D. and Shannon, T. *Macromolecules* 1991, **24,** 3035
2 Brunelle, D. *Makromol. Chem., Macromol. Symp.* 1992, **64,** 65
3 Mullins, M., Woo, E., Murray, D. and Bishop, M. *Chemtech* Aug. 1993, 25
4 Ganguly, S. and Gibson, H. *Macromolecules* 1993, **26,** 2408
5 Surendran, G., Gazicki, M., James, W. and Yasuda, H. *J. Polym. Sci., Polym. Chem.* 1987, **25,** 1481
6 Nedel'kin, V., Zhorin, V., Astankov, A., Sergeev, V. and Enikolopov, N. *Polym. Sci.* 1993, **35,** 1282
7 Nedel'kin, V., Astankov, A. and Sergeev, V. *Dokl. Phys. Chem.* 1992, **326,** 496
8 Zimmerman, D., Koenig, J. and Ishida, H. *J. Polym. Sci., Polym. Phys.* submitted
9 Kaplan, M. and Reents, W. *Tetrahedon Lett.* 1982, **23,** 373
10 Sergeev, V., Nedel'kin, V., Astankov, A., Yunnikov, V. and Erzh, B. *Dokl. Phys. Chem.* 1989, **304,** 114
11 Sergeev, V., Nedel'kin. V., Astankov, A., Nikiforov, A., Alov, E. and Moskvichev, Yu. *Bull. Acad. Sci. USSR* 1990, **39,** 763
12 Reents, W. and Kaplan, M. *Polymer* 1982, **22,** 310
13 Franke, J. and Vögtle, F. *Tetrahedon Lett.* 1984, **25,** 3445
14 Fagerburg, D., Watkins, J. and Lawrence, P. *Macromolecules* 1993, **26,** 114
15 Bulakh, N., Jog, J. and Nadkarni, V. *J. Macromol. Sci., Phys.* 1993, **B32,** 275
16 Piaggio, P., Cuniberti, C., Dellepiane, G., Campani, E., Gorini, G., Masetti, G., Novi, M. and Petrillo, G. *Spectrochim. Acta* 1989, **45A,** 347
17 Zeng, H. and Ho, G. *Makromol. Chem.* 1984, **127,** 103
18 Menczel, J. and Collins, G. *Polym. Eng. Sci.* 1992, **32,** 1264
19 Song. S., White, J. and Cakmak, M. *Polym. Eng. Sci.* 1990, **30,** 947
20 Budgell, D. and Day, M. *Polym. Eng. Sci.* 1991, **31,** 1271
21 Cebe, P. and Chung, S. *Polym. Compos.* 1990, **11,** 265
22 López, L. and Wilkes, G. *Polymer* 1988, **29,** 106
23 Huo, P., Chung, J. and Cebe, P. *Polym. Compos.* 1992, **13,** 346
24 'Modern Plastics Encyclopedia', McGraw-Hill, New York, 1994, Vol. **71,** p. B189
25 Cole, K., Noël, D. and Hechler, J. *J. Appl. Polym. Sci.* 1990, **39,** 1887
26 Spoo, K., Hagenson, R. and Söules, D. *36th Int. SAMPE Symp.* 1991, 2082