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SYNTHESIS OF POLY(ETHER SULFONE)S END-CAPPED WITH METAL CONTAINING PHTHALOCYANINES

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Key Words: Poly(ether sulfone)s, End-Capped, Metallophthalocyanines, Stacking, Aggregation

ABSTRACT

A series of low molecular weight poly(aryl ether sulfone)s with metallophthalocyanine (PcM) end groups were synthesized by reacting o-phthalonitrile end-capped poly(aryl ether sulfone)s with excess phthalonitrile and metal salts/metals in high boiling solvents. The metals selected for this study were copper and iron. The polymers were soluble in common organic solvents. They were characterized by ^{1}H NMR, IR, GPC and UV-VIS spectroscopy. Appearance of an absorption band at around 700 nm confirmed the presence of phthalocyanine moieties in these polymers. The possibility of occurrence of any stacking phenomenon of the PcM rings was studied by annealing the polymers in a Thermo-Gravimetric/Differential Thermal Analysis (TG/DTA) instrument. An increase in T_g was observed for the PcM containing polymers perhaps indicating the aggregation of the terminal Pc rings in the solid state.

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INTRODUCTION

Phthalocyanines are used as dyestuffs in inks and also in the clothing industry [1]. In recent years, there has been an upsurge in research activities centered around phthalocyanine chemistry because of the recognition of its many interesting properties which find applications in the polymer and materials science arenas. To name a few, they are applied as photoconductors in xerography [2], as non-linear optical materials [3-6], and also in liquid crystal displays [7] and molecular electronic devices [1]. Another important use of phthalocyanines is their applicability as sensitizers in photodynamic cancer therapy [8].

In the early 1930s, Linstead and co-workers reported the synthesis of various phthalocyanines [9-12]. One of the inherent processing problems associated with phthalocyanines is their insolubility in organic solvents [1-13]. Improvements in solubility have been made by attaching flexible organic groups to phthalocyanines [1]. Incorporating the phthalocyanines into polymers also improves their solubility. Phthalo-cyanines have been incorporated into the polymer backbone in a variety of ways. Sometimes the ligand or the central metal atom forms part of the polymer chain [1]. The metal phthalocyanines have also been bound to the polymer chain by covalent bonds or the central metals are sometimes co-ordinatively bound to a donor ligand on the polymer chain. Synthesis of covalently bound phthalocyanines or its analogs to the polymer chain has previously been reported by our group [14]. Our objective, in this paper, is to demonstrate the synthesis of thermally stable polymers end-capped with metal-phthalocyanine rings.

Synthesis of phthalonitrile end-capped polymers as thermosetting resins has been described by Keller [15-17]. In a similar fashion, we synthesized o-phthalonitrile end-capped poly(aryl ether sulfone)s by reacting the corresponding oligomeric bisphenoxy salts with 4-nitrophthalonitrile. The o-phthalonitrile end-capped poly(aryl ether sulfone)s were then reacted with excess phthalonitrile in the presence of a metal or metal salt in a high boiling solvent to obtain phthalocyanine end-capped poly(aryl ether sulfone)s.

It has been reported that the electronic conductivitiy of phthalocyanines arises from their tendency to stack in the solid state [18]. We have prepared a series of relatively low molecular weight PcM (M=Cu, Fe) end-capped poly (aryl ether sulfone)s and the aggregation phenomenon of the PcM rings was studied. A potential advantage of end-capping poly(aryl ether sulfone)s with PcM moieties is that the properties of high molecular weight polymers could possibly be obtained from the corresponding low molecular weight polymers, presumably because of the stacking of the phthalocyanine rings in the solid state. In the melt they might behave as low molecular weight species, thereby easing the processability of these polymers. In addition, if there is stacking of the PcM rings in the solid state, the polymers possessing the PcM rings might have some electronic conductivity. Furthermore, because of the high thermal stabilities of the poly(aryl ether sulfone)s and the PcM rings, these polymers could be used in high temperature applications.

EXPERIMENTAL

Materials

4,4'-Isopropylidenebiphenol(BPA) (Aldrich; 99+%), bis(4-fluorophenyl)-sulfone (Aldrich; 99%), 4-nitrophthalonitrile (Aldrich; 99%), phthalonitrile (Aldrich; 98%), copper chloride (Lancaster; 97%), iron powder (Aldrich; 99.99%) were used as received. The solvents were used as received from Lancaster.

Characterization Techniques

NMR spectra were recorded on a Varian Unity 500 spectrometer. The GPC analyses were carried out on a Waters 510 HPLC using four phenogel 5μ m columns arranged in series. Chloroform was used as eluent and the UV detector was set at 254 nm. Infrared spectra were taken using an Analect FT-IR AQS-20 spectrometer. UV-VIS spectra were recorded on a Hewlett Packard 8452A diode array spectrophotometer. A Seiko 220 DSC and a 220 TG/DTA instrument were used for the thermal analyses of the polymers under nitrogen atmosphere. The heating rate in both cases was 20°C/min.

General Procedure for the Synthesis of o-Phthalonitrile End-Capped Poly(aryl Ether Sulfone)s

To a 50 mL three-necked round-bottomed flask equipped with a Dean-Stark trap, condenser, thermometer, and nitrogen inlet , were added BPA (2.3970 g, 10.5 mmol), bis (4-fluorophenyl)sulfone (2.5425 g, 10 mmol), anhydrous potassium carbonate (1.9 g, 13.75 mmol), 22 mL of N, N-dimethylacetamide (DMAc), and 11 mL of toluene. The reaction flask was purged with nitrogen for about fifteen minutes. The flask was then heated to 140°C under nitrogen atmosphere and maintained at this temperature for two and a half hours in order to azeotropically remove all the water from the reaction mixture. The temperature of the reaction mixture was then increased to 160°C and held at this temperature for 4 hours. The reaction mixture was then cooled down to room temperature. At this juncture, 4-nitrophthalonitrile (1.73 g, 10 mmol) was added to the reaction flask and the temperature was raised to 120°C. The reaction flask was maintained at this temperature for another 4 hours and then cooled down. The mixture was diluted with more DMAc and then precipitated into a 2/1 mixture of methanol and water. The pale yellow polymer was redissolved in chloroform and filtered hot through a bed of celite in order to remove inorganic salts. The chloroform solution was concentrated and reprecipitated again into a mixture of 400 mL of methanol and 200 mL of water. The final polymer was dried *in vacuo* at 120°C for 48 hours. The yield of the polymer was 96%.

General Procedure for the Synthesis of Metallophthalocyanine End-Capped Poly(aryl Ether Sulfone)s

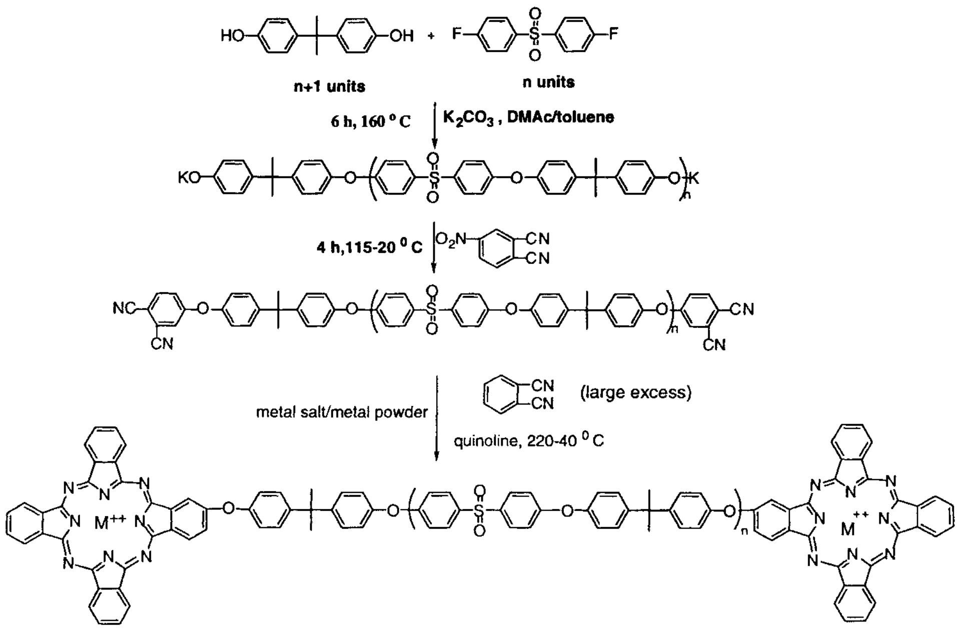
To a 50 mL three-necked round-bottom flask equipped with a reflux condenser and a nitrogen inlet were added o-phthalonitrile end-capped polymer (0.8 g), phthalonitrile (0.6 g, 30 equiv. based on the polymer), copper (II) chloride (0.3 g, 15 equiv based on the polymer) and 15 mL of quinoline. The reaction mixture was heated at 220-230°C under nitrogen atmosphere for about 3 hours during which time it turned dark blue. Some insoluble dark blue solids were observed, due to the formation of free copper-phthalocyanine in the reaction mixture. The solution was cooled down at the end of the reaction and precipitated into 500 mL of methanol. The dark blue polymer was washed with acetone and ethanol and then soxhlet extracted with chloroform to separate it from metal-phthalocyanine impurities. The concentrated chloroform solution of the polymer was precipitated again into 500 mL of methanol. The blue fibrous polymer was then dried *in vacuo* at 120°C for 24 hours. The final yield of the polymer was 40%.

The above procedure was repeated for iron-phthalocyanine end-capped poly(aryl ether sulfone)s except in this case iron powder was used instead of copper (II) chloride. The isolated yield of the polymer was again about 40%.

RESULTS AND DISCUSSION

Synthesis and Characterization of Metallophthalocyanine End-Capped Polymers

Poly(aryl ether sulfone)s end-capped with o-phthalonitrile groups were synthesized as precursors to phthalocyanine end-capped polymers following procedures described by Keller [17]. In the first step, a low molecular weight poly(aryl ether sulfone) was synthesized by reaction of bis(4-fluorophenyl)sulfone with an excess of BPA in a DMAc/toluene solvent system. The temperature of the reaction flask was maintained at 135°C for 2-3 hours in order to remove all the



Scheme 1

water azeotropically with toluene from the reaction mixture. The flask temperature was then increased to 160°C and the reaction mixture stirred at this temperature for another 3 hours to obtain polymers with phenoxide end-groups. At this juncture, the temperature of the flask was lowered to 50°C and excess 4-nitrophthalonitrile was added. The reaction temperature was raised to 115-20°C after the addition and maintained at this temperature for 4 hours according to a procedure described by Keller . This is described in Scheme 1. Polymers of different average molecular weights were synthesized by following this procedure.

Metallophthalocyanine end-capped poly(aryl ether sulfone)s were synthesized from the o-phthalonitrile end-capped polymers by reacting them with excess phthalonitrile and metal salt/metal in quinoline at high temperatures (Scheme 1). A large excess of phthalonitrile was used in order to achieve as complete conversion as possible of phthalonitrile end-groups to phthalocyanines and to reduce the extent of chain extension or crosslinking caused by having phthalocyanine moieties attached to different polymer chains.

The ^1H NMR spectrum of a poly(aryl ether sulfone) with DP = 20 is shown in Figure 1. This is similar to the spectrum observed by McGrath *et al.* [19]

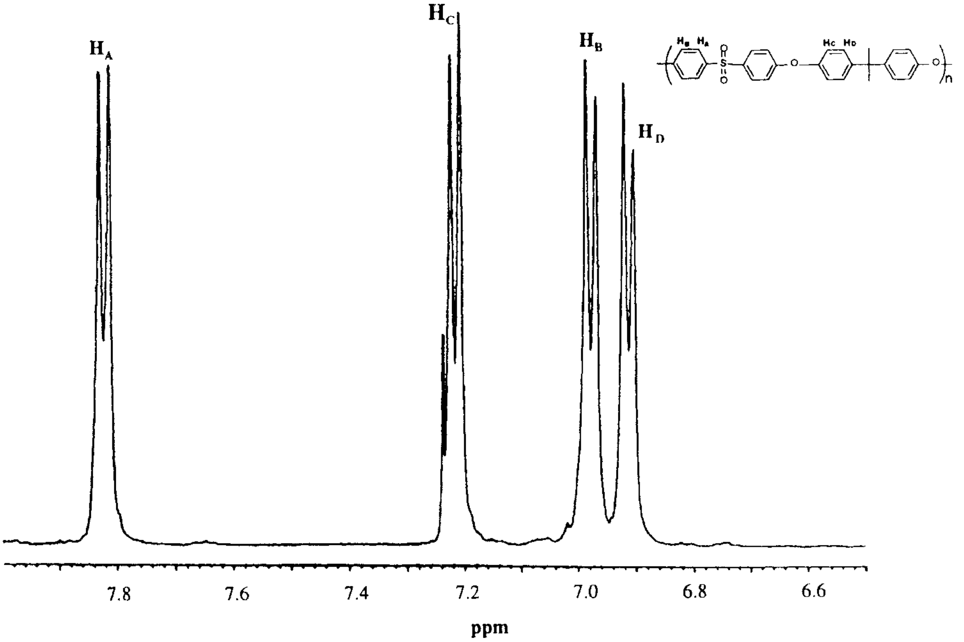


Figure 1. ^{1}H NMR spectrum of poly(aryl ether sulfone)s (DP=20).

previously. There is no signal observed between 7.35 and 7.75 ppm in this spectrum. Figure 2 represents the ^{1}H NMR spectrum of the o-phthalonitrile end-capped poly(aryl ether sulfone) with DP=20. Proton H_B which is in the vicinity of a -CN group appears as a doublet at 7.72 ppm whereas proton H_A appears as a doublet of doublet around 7.39 ppm because of meta coupling with the H_C proton. The H_C proton, in turn, appears as a doublet at around 7.48 ppm. From the NMR integration, it is estimated that the end-capping of the polymer chains by phthalonitrile groups is quantitative. The presence of -CN groups in the polymer is further confirmed by a strong absorption band at 2240 cm^{-1} (Figure 3) in the IR spectrum. The conversion of o-phthalonitrile end groups to metallophthalocyanine groups is confirmed by the disappearance of the -CN absorption band in the PcM end-capped polymers as shown in Figure 3. The appearance of an absorption maximum at 674 nm (Figure 4) is more evidence of the presence of PcM moieties in the CuPc end-capped poly(aryl ether sulfone)s. Similarly, FePc end-capped poly(aryl ether sulfone)s showed an absorption maximum at 656 nm in the UV-VIS spectrum (Figure 5).

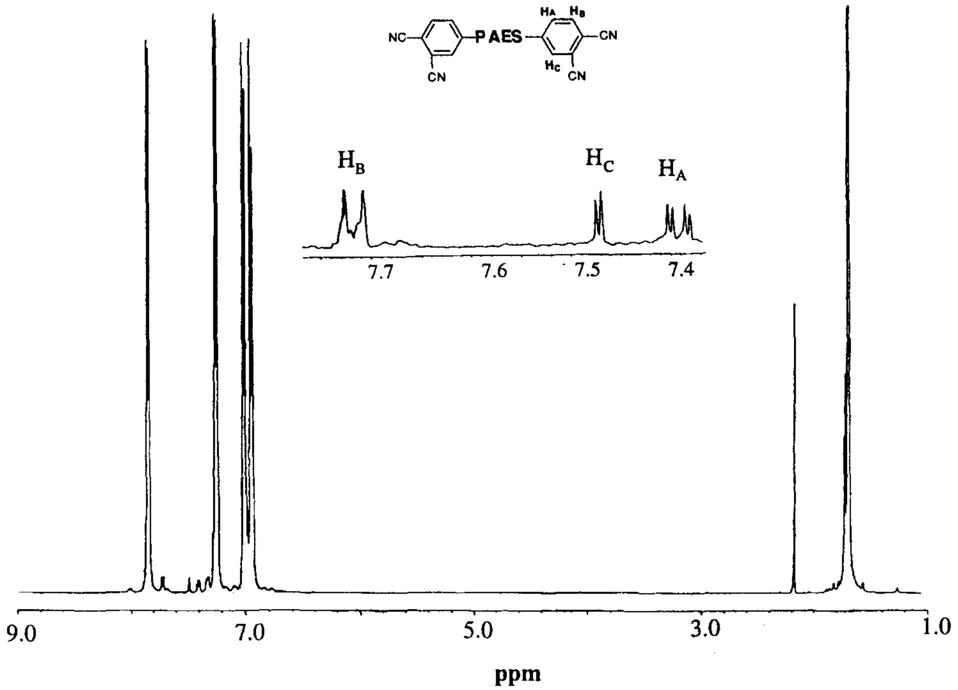


Figure 2. ^1H NMR spectrum of o-phthalonitrile end-capped poly(aryl ether sulfone)s (DP=20).

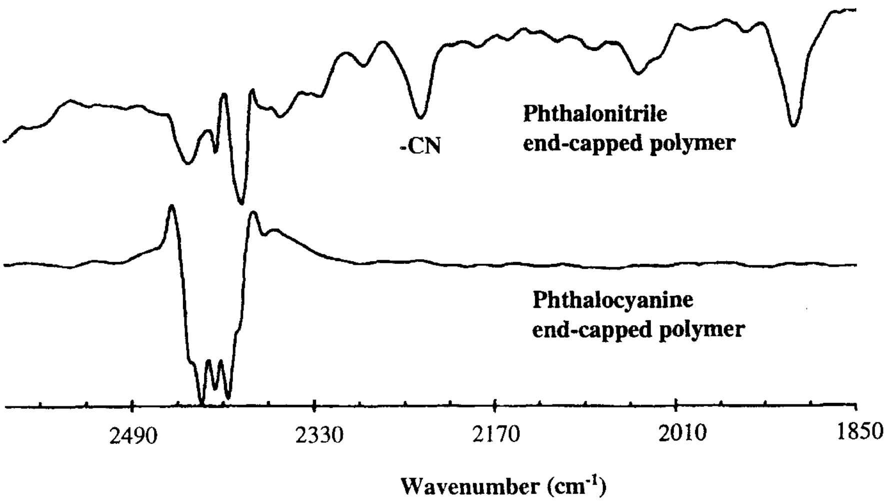


Figure 3. IR spectra of o-phthalonitrile and PcM end-capped poly(aryl ether sulfone)s.

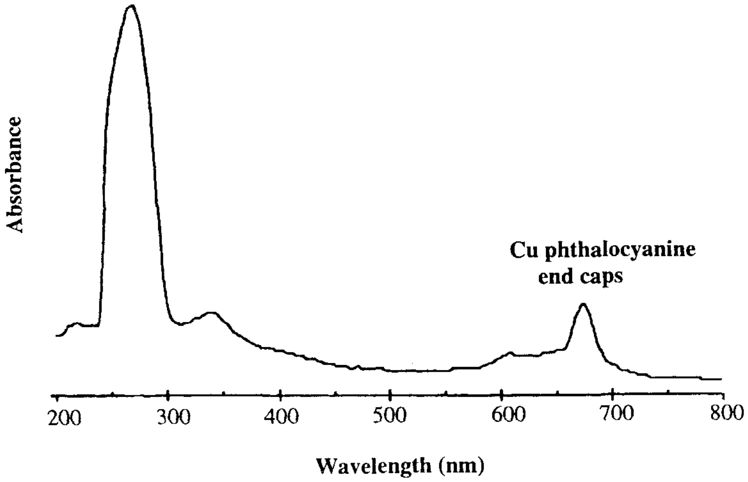


Figure 4. UV-VIS spectrum of CuPc end-capped poly(aryl ether sulfone)s.

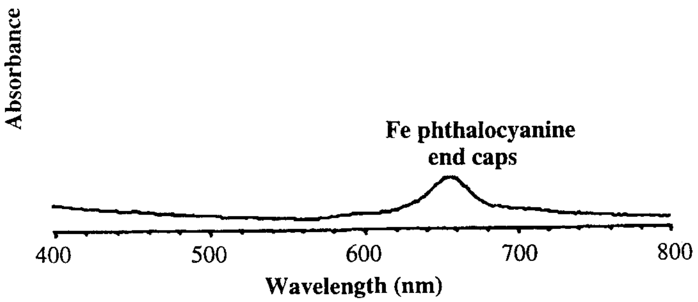


Figure 5. UV-VIS spectrum of FePc end-capped poly(aryl ether sulfone)s.

The GPC spectra of the o-phthalonitrile and CuPc end-capped poly(aryl ether sulfone)s are presented in Figure 6. In the case of PcM end-capped polymers, a shoulder in the higher molecular weight region is observed. This is presumably due to some chain extension caused by the reactions of phthalonitriles of different polymer chains to form phthalocyanines. A similar GPC pattern was observed earlier by Hay *et al.* [14] for poly(aryl ether)s containing tetrapyrazineporphyrazine units.

Properties of PcM End-Capped Polymers

Poly(aryl ether sulfone)s with PcM end groups were synthesized with different degrees of polymerization in order to evaluate the effect of PcM rings on

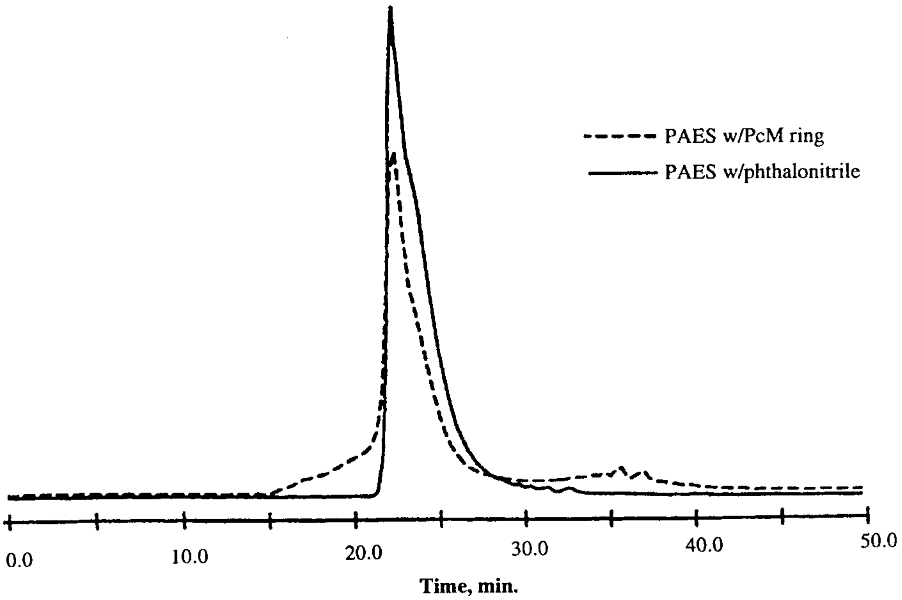


Figure 6. GPC spectra of o-phthalonitrile and CuPc end-capped poly(aryl ether sulfone)s.

the physical properties of polymers and also to probe if there is any stacking between the PcM rings in the solid state. Physical properties of CuPc end-capped polymers with DP=20 and DP=50 are presented in Table 1. The increase in M_w values for CuPc end-capped polymers is reminiscent of the chain extension which occurred in solution during the PcM ring formation as described earlier. An increase of 30°C in T_g for polymers (DP=20) with CuPc rings is perhaps due to a higher concentration of phthalocyanine rings in these polymers. In the solid state there is probably some aggregation of the PcM rings in these polymers which enhances the T_g. The higher the average molecular weight of the polymer, the lower the amount of Pc rings in the polymer with a resulting smaller effect on T_g. This is clearly noticeable in the case of polymers with DP=50. The increase in T_g for these Pc end-capped polymers compared to the o-phthalonitrile end-capped precursors is only 10°C which could be accounted for by a bulky end group with no stacking.

To further understand the effect of PcM rings on the polymer properties in the solid state, annealing studies were carried out on some of the polymers possessing higher concentrations of PcM moieties. In the annealing studies, the

TABLE 1. Property Changes in Poly(Ether Sulfone) Olifomers End-Capped with Phthalocyanine Groups

Number of repeat units	Molecular Weights	T_g (°C)
20	M_n=8, 000 M_w=18, 000	162
20 with phthalocyanine end caps	M_n=14, 000 M_w=39, 000	190
50	M_n=22, 000 M_w=33, 000	187
50 with phthalocyanine end caps	M_n=21, 000 M_w=61, 000	197

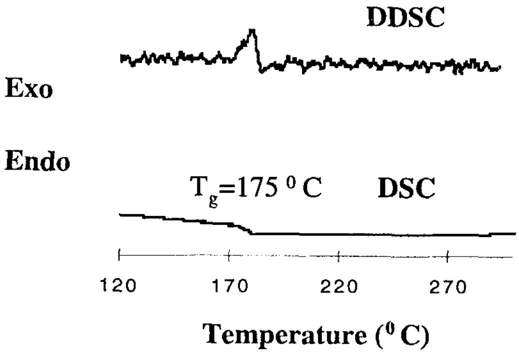


Figure 7. DSC chart of FePc end-capped poly(aryl ether sulfone)s before annealing.

polymer sample was continuously heated at a temperature approximately 50°C above its T_g, for 12 hours under nitrogen atmosphere. The thermal profiles of a poly(aryl ether sulfone) with FePc end groups (DP=20) before and after annealing, are presented in Figure 7 and Figure 8, respectively. The T_g of the FePc end-capped poly(aryl ether sulfone) before annealing is 175°C. It is evident from Figure 8 that

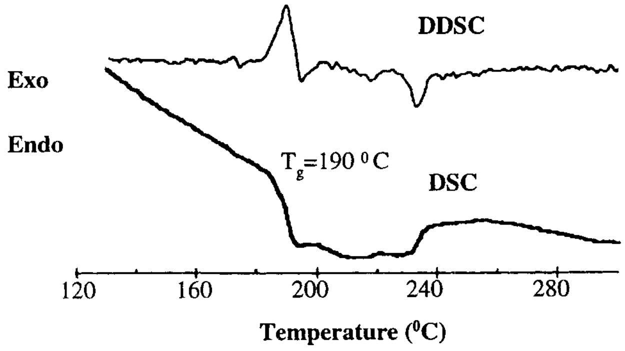


Figure 8. DSC chart of FePc end-capped poly(aryl ether sulfone)s after annealing.

after annealing there is a melting endotherm at around 240°C in addition to increased T_g at 190°C. In the melt state, because of the mobility of the polymer chains, there is a distinct possibility that the PcM rings would aggregate and stack because of the presence of weak intermolecular interactions. This would give rise to crystallization in the stacked domains of the polymer chains. The presence of a melting endotherm, therefore, may be indicative of some stacking of Pc end groups in these polymers. Also the increase in T_g in these polymers and in the polymers containing CuPc end-groups is most likely due to stacking of PcM rings in the solid state.

CONCLUSION

PcM end-capped poly(aryl ether sulfone)s were synthesized from the o-phthalonitrile end-capped polymers in reasonably good yield. The polymers were soluble in common organic solvents. PcM end-capped polymers showed increased T_g which perhaps indicates stacking of PcM moieties. A melting endotherm due to crystallization which may be caused by stacking of PcM rings, was observed after annealing.

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