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Synthesis of a series of metallophthalocyanine end-capped poly(aryl ether sulfone)s from a dicyanoarylene group containing biphenol

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Abstract

A novel biphenol monomer, 1,4-bis(4-hydroxy-phenyl)-2,3-dicyanonaphthlene was prepared in high yield in a two-step reaction from reduced phenolphthalein containing a hydro cyanic group by an improved method. A series of uncapped copolymers were synthesized using this bisphenol. In addition, a series of thermally stable poly(arylene ether)s having covalently bound metal (II) naphthalocyanine units were synthesized by the reaction of dicyanoarylene containing poly(aryl ether)s with excess amounts of 1,2-dicyanobenzene and the corresponding metal salt in quinoline. The copolymers synthesized had high glass transition temperature and exhibited good thermal stability. Also, these polymers were found to have good solubility and capable of forming tough films. These colored polymers showed visible absorption maxima in the range of 538–715 nm.

Keywords: Polyaromatics; 1,2-dicynobenzene; Metallophthalocyanine polymer

1. Introduction

Since the synthesis of phthalocyanines [1] in the early 1930s, a rich and varied chemistry and technology has developed around these interesting materials. There are literally thousands of publications and patents related to phthalocyanine and its analogs [2,3]. Owing to their application in optical data processing, recently, there has been renewed interest in phthalocyanine compounds [4–7]. Phthalocyanine compounds have high thermal, hydrolytic, and oxidative stability. They show high absorption intensities at longer wavelengths. This latter property is even more significant, since one of the goals of contemporary optical storage device design is to use solid semiconductor lasers for writing purposes. These solid-state lasers emit at wavelengths greater than 800 nm, i.e. in the near infrared (IR) region. However, naphthalocyanine compounds absorb in the near-IR or in the IR region, depending on the complexed metal ions or constituents on the naphthalocyanine rings. It was reported that the metallophthalocyanine end-capped poly(aryl ether sulfone)s were synthesized from the *o*-phthalonitrile end-capped polymers [8–10]. These polymers had high T_g and were soluble in common organic solvents. Copper and iron were used as the metals in the above preparation. It is always advantageous to synthesize amorphous polymers having high glass transition temperatures and excellent thermo-oxidative stability, as they are soluble in common organic solvents, and allow for easy solution processing and chemical modification. In this direction, Strukelj and Hay [11] prepared amorphous poly(aryl ether ketone)s. These can also be converted into soluble poly(aryl ether phthalazine)s [12]. Yang et al. [13] synthesized poly(aryl ether sulfone)s and poly(aryl ether ketone)s by the reaction of the imidobiphenols with activated dihalide. The imidobiphenols were prepared from phenolphthalein in three steps [11]. The polymers synthesized from them were amorphous and had very high glass-transition temperatures. The properties of the monomers and the resulting polymers could be tailored by changing the substituent attached to the imide nitrogen.

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In this paper, we aim at the synthesis of a new 1,2-dicyanobenzene containing bisphenol. By a two-step synthetic procedure, we have prepared the new bisphenol in high yield. Because of the new naphthalene moiety containing bisphenol, the polymers derived from it may possess good solubility and consequently be soluble to allow solution processing. This will facilitate the application of these polymers. Moreover, the incorporation of some metals with catalytic activity, such as Ni, Zn, Co, and Cr, into these polymers, may create a new category of soluble catalysts. We report herein the synthesis of uncapped copolymers and metal containing end-capped copolymers using the new bisphenol and their characterization using GPC, IR and UV–visible spectroscopy, TGA, and DSC techniques.

2. Experimental

2.1. Materials

Phenolphthalein, 4,4′-Isopropylidenediphenol (BPA) (Aldrich Chemicals Inc.), 1,2-dicyanobenzene (ACROS); fumaronitrile (TOKYO KASEI KOG CO, LTD), bis(4-chlorophenyl)sulfone, dimethylacetamide (DMAc), quinoline, toluene, chloroform, methanol, and acetic acid were obtained from commercial sources and used as received.

2.2. Instrumentation

The glass transition temperatures (T_g) were determined using modulated TA DSC instrument (model 2910) at a heating rate of 20 °C/min under nitrogen flow of 100 ml/min. The reported T_g values were recorded from the second scan after first heating and quenching. The ^{1}H NMR spectra were recorded on a DRX-400 instrument using dimethysulfoxide-d_6 (DMSO-d_6) and chloroform ($CDCl_3$), as solvents. IR spectra were recorded using KBr pellet method using Analect RFX-65A FTIR spectrophotometer. UV–visible spectra were recorded on SHIMADZU UV-2550 spectrophotometer. Gel permeation chromatograph (GPC) analysis was carried using a Waters 410 HPLC instrument equipped with Ultrastyragel (10,000 Å) arranged in series with THF (tetrahydrofuran) as solvent and a UV detector at 254 nm. Thermo gravimetric analysis was carried out employing a Seiko thermo gravimetric analyzer (TGA/DTA; model SSC-5200) under a protective helium or nitrogen atmosphere (100 ml/min) at a heating rate of 20 °C/min.

2.3. Preparation of 1,4-bis(4-hydroxyphenyl)-2,3-dicyanonaphthlene

To a dry 25 ml round-bottom flask equipped with a mechanical stirrer, 2 g (6.24 mmol) of dry, finely powdered reduced phenolphthalein (**1**) was added. The flask was immersed in an ice-acetone bath for 10 min and then concentrated sulfuric acid (6.5 ml, also cooled to 0 °C) was poured into the flask. The mixture was vigorously stirred for 2–3 min to dissolve the solids. The mixture was then stirred for another 7–8 min at this temperature. The resulting yellow-brown slurry (isobenzofuran, coded as **2**) was quickly poured into a 500 ml beaker containing 120 ml of ice-water. The solids (**2**) were separated by filtration, and washed with 20 ml cold water (0 °C) and dried on the filter paper for 5–15 min before being used directly in the following Diels–Alder reaction.

To a 50 ml round-bottom flask containing 2.0 g (20.41 mmol) of fumaronitrile in 13 ml of acetic acid the compound **2** was added. The mixture was quickly heated to the temperature of reflux. After 15–20 min, a yellow product, 1,4-bis-(4-hydroxy-phenyl)-naphtha-2,3-dicarbonitrilen coded as **3** precipitated out from the reaction mixture. The reaction was continued at this temperature for another 2 h to complete the reaction. The product was isolated by filtration and washed twice with a minimum amount of acetic acid. The final product powder **3** was obtained in 64% yield as light gray powder.

2.4. General procedure for synthesis of polymers

The procedure for the synthesis of a series of uncapped copolymers (coded as **6**) is as follows. To a 25 ml three-neck round-bottom flask equipped with a magnetic stirrer, a Dean-Stark trap and condenser, and a nitrogen inlet, the monomer **3** (0.0801 g, 0.25 mmol), BPA (0.5136 g, 2.25 mmol) **6** (0.7179 g, 2.5 mmol), DMAc (7.1 ml), K_2CO_3 (0.4837 g), and toluene (7.1 ml) were added. Under an atmosphere of nitrogen, the solution was heated to 140 °C and maintained at that temperature for 2 h to remove all water by means of a Dean-Stark trap using toluene. The polycondensation was continued for 1–3 h at 180 °C (oil bath temperature). When the reaction mixture became too viscous, 2–3 ml of DMAc was added into the reactor. The reaction mixture was diluted three more times with DMAc, and then the viscous solution was slowly poured into 100 ml of methanol with little hydrochloric acid and stirred vigorously. The uncapped copolymer **6** precipitated out as a lengthy fiber, and the material was dissolved in 50 ml of chloroform followed by filtration through a thin layer of celite. The filtrate was slowly poured into 200 ml of methanol with stirring, and then the resulting polymer was separated by filtration. The purification product, a white fiber, was dried at 110 °C under vacuum for 24 h. The copolymers were prepared with varying mole fractions of **3**(m) and BPA (**4**)(n). The copolymers with different m/n ratio viz. 5/95, 10/90, 20/80, and 30/70 were prepared and designated as **6a**, **6b**, **6c**, and **6d**, respectively.

2.5. Procedure for synthesis of metal containing end-capped copolymers 7

For the synthesis of the metal containing copolymers, the

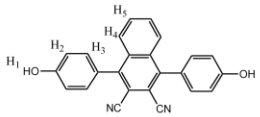
copolymers **6b** and **6c** were selected. To a 25 ml three-neck flask equipped with a condenser and nitrogen gas inlet, the copolymer **6b** (0.1 g), 1,2-dicyanobenzene (0.1 g, 0.7805 mmol), the corresponding metal chloride (0.06 g), and 15 ml of quinoline were added. Under an atmosphere of nitrogen, the mixture was heated to 220–240 °C for 6–8 h, and after this period; the reaction mixture became dark blue. The mixture was poured into a liquid mixture of 30 ml methanol and 2 ml of hydrochloric acid (36%), with vigorous stirring. The precipitated deep green to blue particles were washed with acetone, water, dilute hydrochloric acid, and finally by water and ethanol. The precipitate was collected by filtration and extracted by chloroform, using a Soxhlet extractor. The chloroform solution was concentrated and precipitated into methanol. The dark blue fibrous material was produced and dried at 110 °C for 24 h. In the present work, magnesium, zinc, chromium, cobalt, and nickel chloride were used. The above procedure was repeated for the copolymer **6c**. When the copolymer **6b** was employed, the resulting metal containing copolymers with Zn, Ni, Co, Cr, and Mg were designated as **7a**, **7b**, **7c**, **7d**, and **7e**, respectively. Similarly, when the copolymer **6c** was employed, the resulting metal containing copolymers with Zn, Co, and Mg were designated as **7f**, **7g**, and **7h**, respectively.

3. Results and discussion

3.1. Synthesis of 1,4-bis(4-hydroxyphenyl)-2,3-dicyanonaphthlene

The reaction mechanism for the preparation of the monomer is presented in Scheme 1.

The monomer **3** prepared as shown in above scheme was characterized by its melting point (mp > 350 °C), ^{1}H NMR (DMSO-d_6) spectra (Fig. 1): δ 9.988 (s, 2H of –OH group);



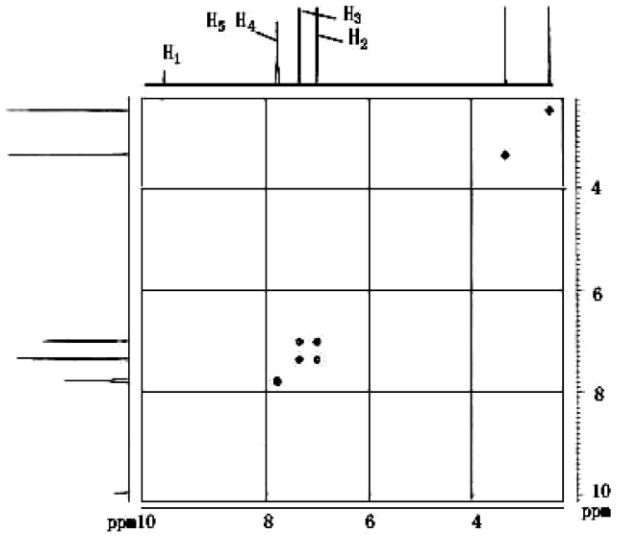
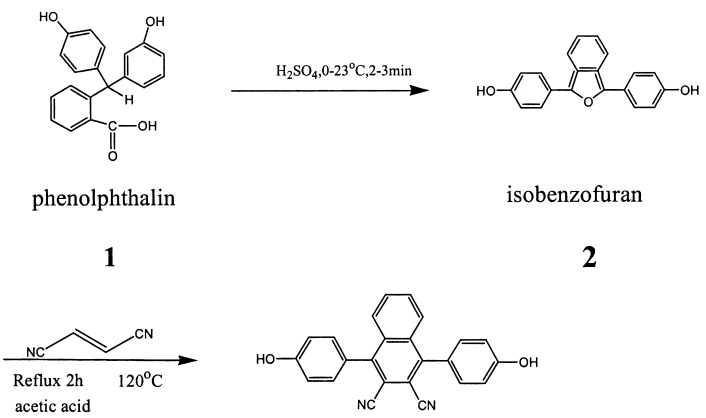


Fig. 1. COSY 2D ^{1}H NMR spectrum of the monomer **3**.

7.782 (m, 4H, H5, 6,7,8 of naphthalene ring); 7.37 (d, 4H, H3, 5 of 4-hydroxyphenyl ring,); 7.014 (d, 4H, H2, 6 of 4-hydroxyphenyl ring), and IR spectrum (Fig. 2). The yield for this monomer was 64%.

3.2. Synthesis of the metal containing end-capped copolymers 7

The reaction mechanism for the preparation of the copolymers **6** and metal containing end-capped copolymers **7** is presented in Scheme 2.



Scheme 1.

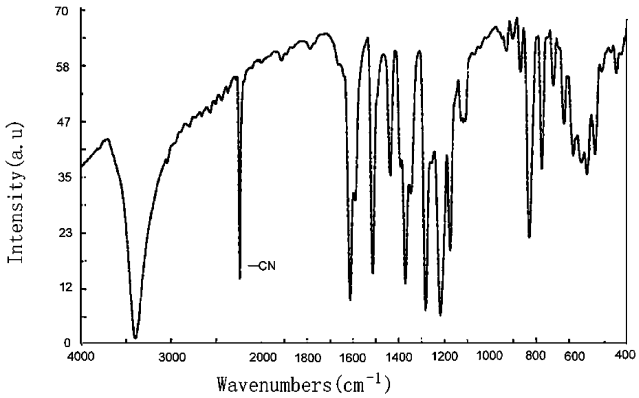


Fig. 2. IR spectrum of monomer **3**.

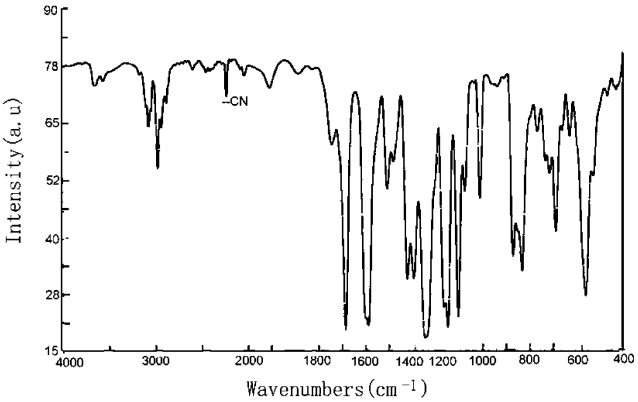


Fig. 4. IR spectrum of copolymer **6d**.

The copolymers prepared as shown in the above scheme were characterized by the GPC, DSC, IR, TGA, and optical spectroscopic techniques. The yield was found to be about 55%. The IR spectra for the copolymers **6b** and **6d** are presented in Figs. 3 and 4, respectively. From the spectra, it is clearly evident that the intensity of the –CN band at 2229 cm^{-1} is more for **6d** when compared to **6b**. It is as expected that the mole fraction of the –CN containing monomer is more in **6d** than in **6b**. The IR spectrum for the sample **7c** is presented in Fig. 5. From this spectrum, it is clear that the peak at 2229 cm^{-1} is missing indicating the completion reaction at this site. The ^{1}H NMR spectrum of polymer **7c** is shown in Fig. 6, and the signals of protons a and b appear at 9.28 and 8.50 ppm, respectively, as broad peaks. Because protons a and b are not very close to the core of large metal-complex ring, the downfield shift effects of the metal-complex ring on the chemical shift of protons a and b are not significant. The signal intensities of protons a and b are weak because the metal-complex units is about 7.1 mol% as estimated from NMR characterization. This value indicates that 71% dicyanobenzene groups are converted and incorporated into the polymer **7c**. The properties of the copolymers **6a**, **6b**, **6c**, and **6d** are listed in Table 1. From this table, it is evident that the number average and weight average molecular weights of the copolymers varied from 19,571 to 57,299 and 30,763 to 101,098, respectively. The polydipersity varied from 1.57 to 1.76. The glass transition temperatures (T_gs) of the copolymers varied from 195 to 209 °C. It is also evident from this table that the T_g of the copolymers is increasing with the content of **3**. However, the T_gs of these copolymers are close to or slightly higher than that of BPA-type polysulfone (Udel). This is because the backbone of the synthesized copolymers is same as that of Udel polysulfone with exception of small amount of metallophthalocyanine end-capped groups. The 5 wt% weight loss temperatures of these copolymers varied from 487 to 498 °C indicating that these copolymers exhibited thermal stability.

The properties of the metal containing end-capped copolymers **7a**–**e** are presented in Table 2. It can be seen that the polydispersity varied from 1.51 to 3.23, which is larger than that of copolymers **6**. As depicted in Scheme 2, the metal-complex ring can be formed by either intermolecular or intramolecular. The former would cause the cross-linking and insolubilization of resulting polymers **7**. The behavior can be avoided by using an excess 1,2-dicyanobenzene followed by extracting with chloroform as described in experimental section. Presumably, the larger polydispersity of polymers **7** comes from the GPC measurements because the incorporation of the very bulky metal containing ring pendants. Generally, the increase in the rigidity of polymer backbone leads to the increase in its

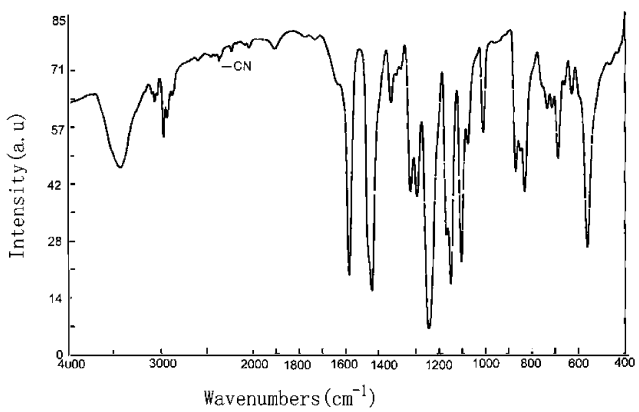


Fig. 3. IR spectrum of copolymer **6b**.

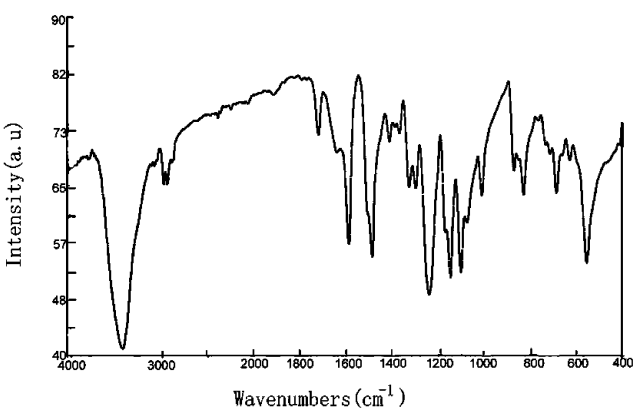
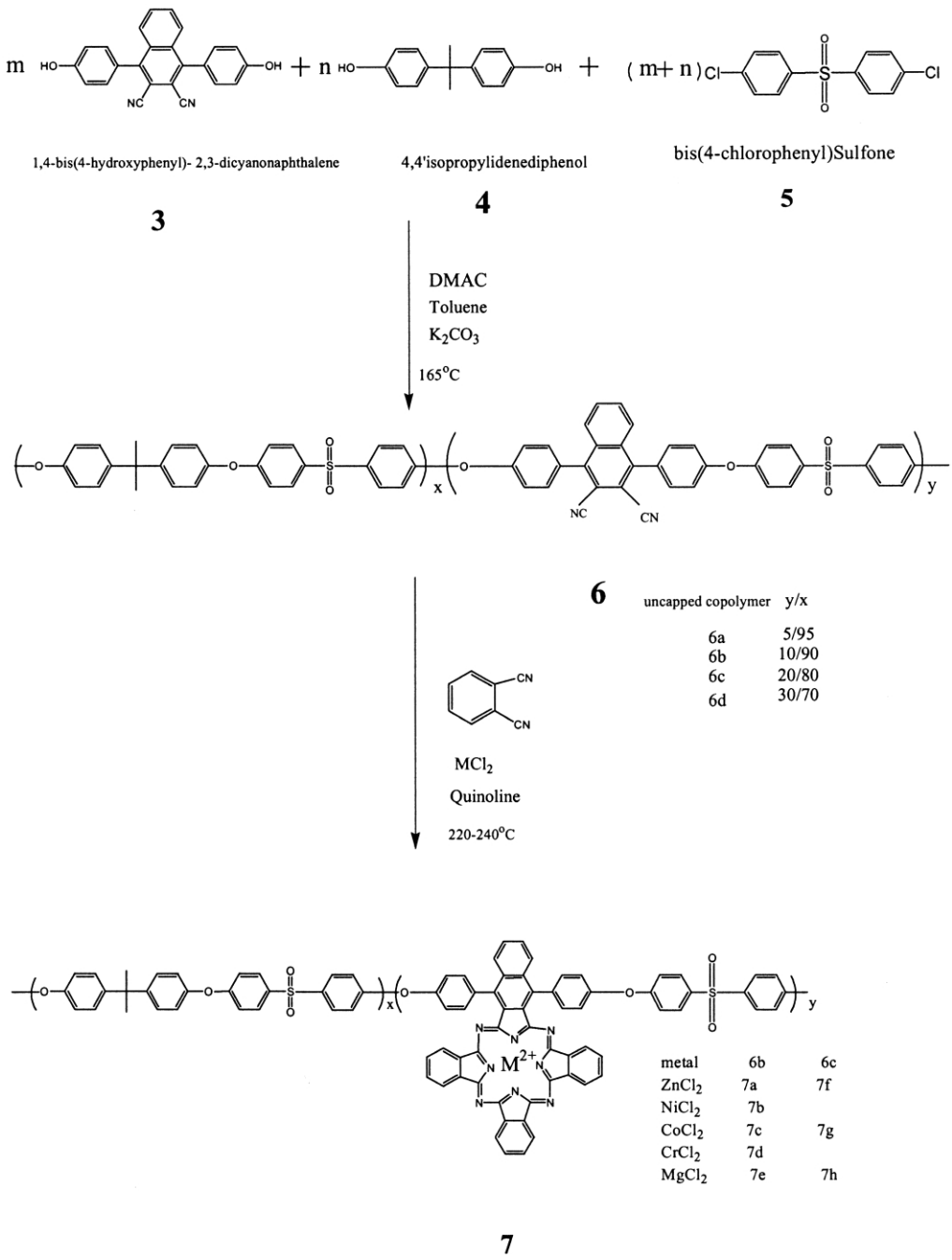


Fig. 5. IR spectrum of metal containing copolymer **7c**.



Scheme 2.

Table 1
Properties of copolymers **6a–d**

Polymer	Yield%	BPA%	T_g (°C)	TGA-5% (°C)	$\bar{M}_n$	$\bar{M}_w$	Polydipersity
6a	95	95	195.26	496	57,299	101,098	1.76
6b	92	90	196.88	493	52,967	87,181	1.65
6c	85	80	203.19	498.5	20,287	36,809	1.81
6d	81	70	209.63	487.4	19,571	30,763	1.57

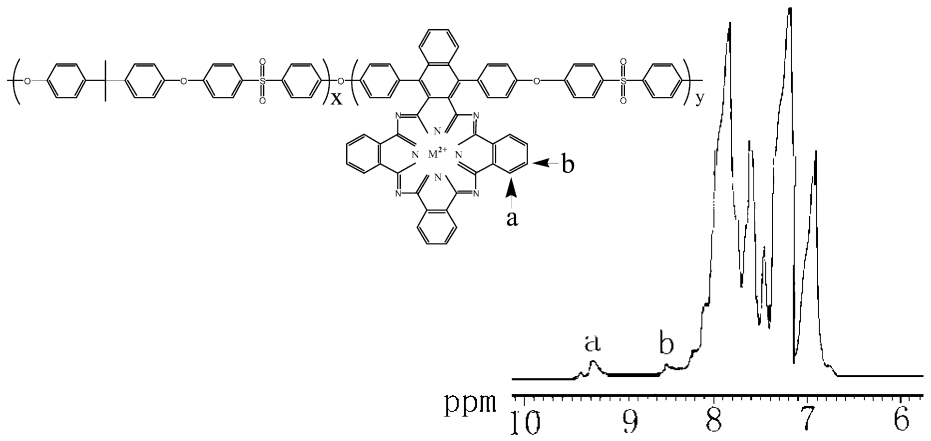


Fig. 6. ^{1}H NMR spectrum for copolymer **7a** (obtained at 90 °C in DMSO).

polydispersity. Also from the same table, we can see that the T_g values varied from 193 to 207 °C. These values are almost same as those of the corresponding copolymer **6b**. The 5 wt% weight loss temperatures varied from 420 to 537 °C, which are higher than that corresponding to the copolymer **6b**. These observations indicate that the metal present in the copolymers is responsible for the better thermal stability. In order to study the relationship between the thermal stability and the nature of the metal substituted, Fig. 7 is drawn between the 5 wt% weight loss temperatures of the transition metal containing copolymers and the corresponding atomic number. From this figure, it is evident that the thermal degradation is decreasing with the atomic number of the substituted transition metal with an exception of zinc. Similar observation was made by Horowitz and Perros [14] in the case of Mn(II), Co(II), Ni(II), and Zn(II) 5,5′[methylenebis(*p*-phenylenenitrilomethylidyne)]di-8-quinolinol coordination polymers. They observed that the variation of the ionic radii of the transition metals with their corresponding atomic numbers was found to be similar to that of the variation in the thermal stability. Basing on this observation, they concluded that the thermal stability of the metal coordinated polymers is proportional to the ionic radii of the metals in them. The present study also supports their view.

The properties of the metal containing copolymers **7f–h** are presented in Table 3. Here also, the polydispersity is found to be greater than those of the corresponding copolymer **6c**. The T_g and the thermal stability are found to be greater than for the polymer **6c**.

All the copolymers and metal containing copolymers were found to be non-birefrigent confirming their amorphous nature. These were found to be soluble in common solvents like DMSO, DMAc, NMP, and $CHCl_3$, etc. It was also found that the copolymers were capable of forming clear tough films by solution casting.

The UV–visible spectra of the copolymers **7a–f** are shown in Figs. 8 and 9, respectively. From these figures, it is clearly evident that strong absorption in the visible range existed for the copolymers **7b** and **7d**, whereas for other copolymers it was medium. The absorption maxim values of the copolymer **7a–g** are presented in Table 4. These metal

Table 2
Properties of copolymers **7a–e**

Polymer	Yield%	T_g (°C)	TGA-5% (°C)	$\bar{M}_n$	$\bar{M}_w$	Polydipersity	Metal
7a	72	202.1	276.54	57,012	123,013	2.16	$ZnCl_2$
7b	64	195.1	419.52	17,186	27,023	1.57	$NiCl_2$
7c	47	193.65	542.34	31,735	72,611	2.29	$CoCl_2$
7d	41	207.74	537.49	49,878	75,460	1.51	$CrCl_2$
7e	59	200.15	434.91	32,396	104,749	3.23	$MgCl_2$

Table 3
Properties of copolymers **7f–h**

Polymer	Yield%	T_g (°C)	TGA-5% (°C)	$\bar{M}_n$	$\bar{M}_w$	Polydipersity	Metal
7f	69	204.69	504.19	54,310	114,842	2.11	$ZnCl_2$
7g	52	201.49	506.75	14,449	27,591	1.91	$CoCl_2$
7h	70	203.67	536.42	16,358	30,000	1.83	$MgCl_2$

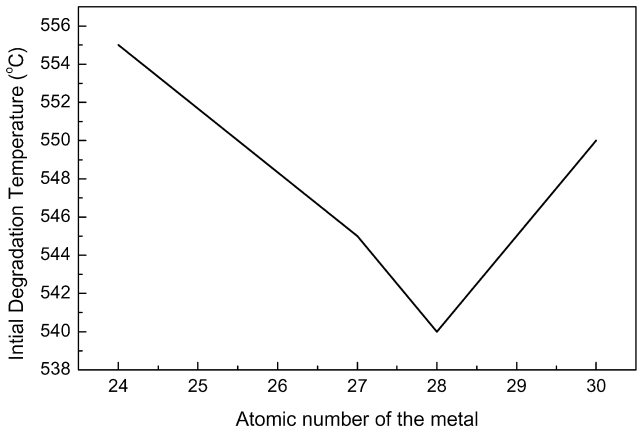


Fig. 7. The variation of the initial degradation temperature with atomic number of the metal in the metal containing polymer.

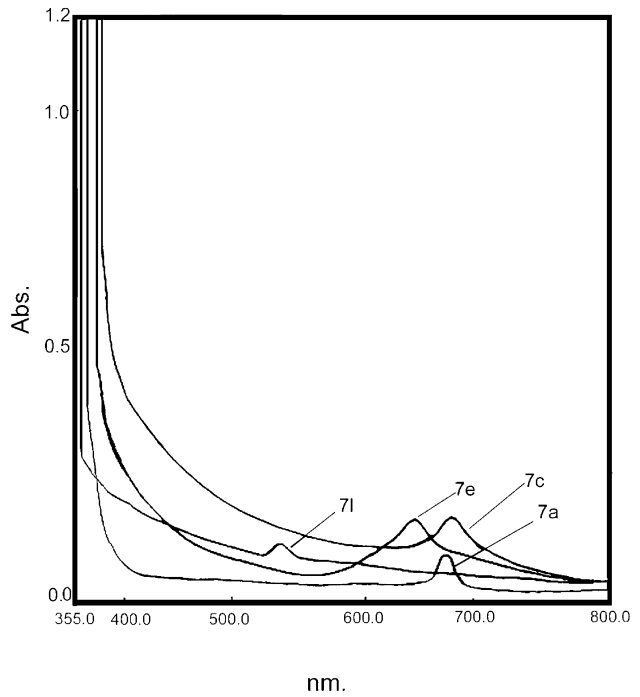


Fig. 8. Optical absorption maxima of the copolymers **7a**, **7c**, **7e**, **7g** in chloroform.

Table 4
Optical absorption maxima of the metal containing copolymers in chloroform

Polymer	λ_{max} (nm)	Color in the chloroform
7a	665	Light yellow
7b	664	Dark green
7c	667	Gray
7d	715	Dark green
7e	642	Gray green
7g	538	Light green

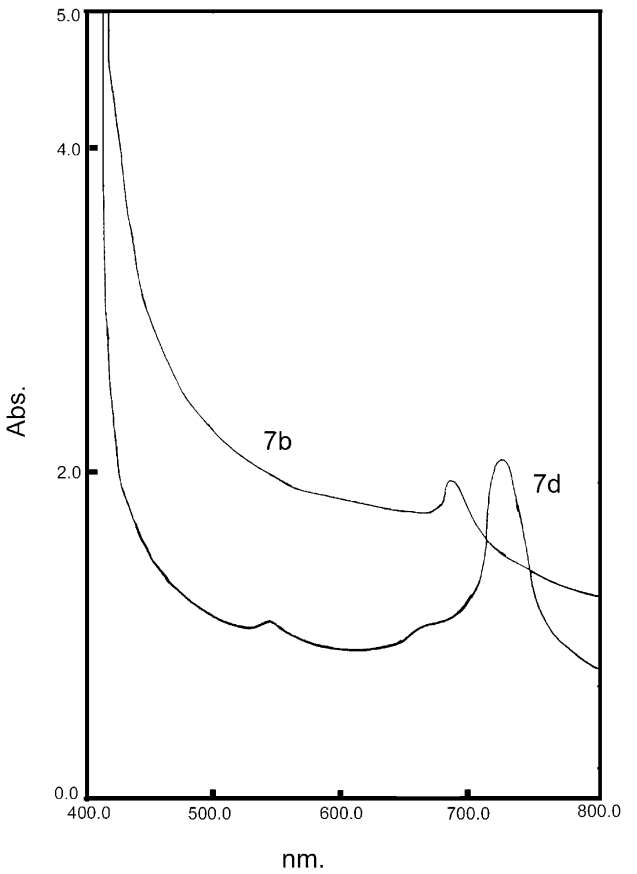


Fig. 9. Optical absorption maxima of the copolymers **7b**, **7d** in chloroform.

containing copolymers were found to be colored as expected.

4. Conclusions

The novel bisphenol 1,4-bis-(4-hydroxy-phenyl)-naphthale-2,3-dicarbonitrilen was prepared in a two-step reaction. Using this bisphenol some uncapped and metal containing end-capped copolymers were synthesized. These copolymers were found to have high glass transition temperatures and thermal stability. These copolymers exhibited amorphous structure and therefore were soluble in common solvents. Clear tough films could be cast from these copolymer solutions. These copolymers showed strong optical absorption in the visible region.

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