

Resins IV: Preparation and Characterization of Terpolymer Resins Prepared from Biphenol, Thiourea and Formaldehyde

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ABSTRACT: Terpolymer resins (BPhThF) were synthesized by the condensation of 2,2'-dihydroxybiphenyl [BPh] and thiourea [Th] with formaldehyde [F] in the presence of acid catalyst and using varied molar ratios of reacting monomers. Terpolymer resin compositions have been determined on the basis of their elemental analysis, and the number average molecular weights of these resins were determined by conductometric titration in nonaqueous me-

dium. Viscometric measurements in dimethyl formamide (DMF) have been carried out with a view to ascertain the characteristic functions and constants. UV-vis, FTIR, and NMR spectra were studied to elucidate the structure. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1245–1251, 2010

Key words: resins; terpolymer; FTIR; NMR; degree of polymerization; viscosity

INTRODUCTION

Various modified phenol formaldehyde resins and their renowned applications are reported in literature.^{1–3} With the development of phenolic resins, which were of dark colors necessity was felt to produce a colorless product. This requirement was satisfied by introduction of amino resins. This resin also got commercial success. Hence, keeping in view of advanced properties of these copolymers, a new material having combined property of these resins have attracted the attention of many research workers, especially terpolymer. Perusal of literature survey reveals that many terpolymers are derived from different monomers.^{4–10} These terpolymers can be used as ion exchangers,^{5,11} high temperature resistance material,^{12–15} semiconductors,^{16,17} antioxidants,¹⁸ optical storage data,¹⁹ moulding materials,^{3,20} etc. From the literature data, it has been noted that thiol/mercapto and amine group possessing resin used as a chelating resin^{21–23} and biphenol containing resin exhibits thermosetting, electrical insulating property²⁴ and in many other electronic device application.¹⁹ In continuation to our earlier communication,^{25–27} in this article, synthesis and characterization of terpolymer resins prepared from biphenol, thiourea, and formaldehyde are incorporated.

EXPERIMENTAL

Materials

The chemicals used were all of AR or chemically pure grade. DMF and DMSO were used HPLC grade. 2,2'-Dihydroxybiphenyl (Lancaster, >99%); formaldehyde solution (Merck, 35%), and thiourea (Merck, 99%).

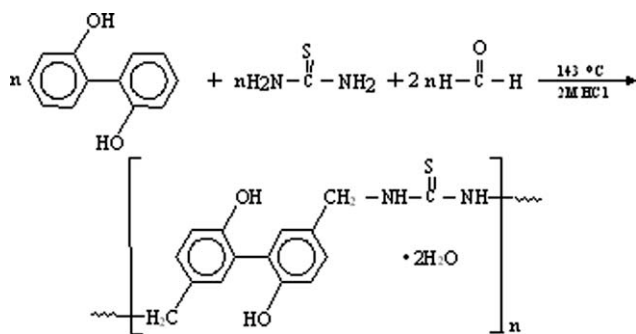
Preparation of BPhThF terpolymer resin [BPhThF-1]

A mixture of BPh (9.3 g, 0.05 mol), Th (3.8 g, 0.05 mol), and F (8.6 mL of 35% solution, 0.1 mol) in the presence of 100 mL 2M HCl as a catalyst was taken in 250-mL round bottom flask fitted with water condenser and heated in an electrically operated oil bath at $143 \pm 2^\circ\text{C}$ for 5 h with occasional shaking.²⁸ The temperature of the oil bath was controlled with the help of dimmer stat. The resinous was immediately removed from the flask as soon as reaction period was over. The separated resinous product (BPhThF-1) was purified as follows:

Purification of resin

The solid product was repeatedly washed with hot water followed by methanol to remove unreacted monomers. The resinous product was air dried and powdered. The powder was washed many times with ether in order to remove biphenol formaldehyde copolymer which may exist with the terpolymer. The product so obtained was further purified by reprecipitation technique. The terpolymer was dissolved in

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Scheme 1 Reaction scheme for BPhThF-1 terpolymer resin.

8% aqueous NaOH, filtered, and reprecipitated by drop wise addition of ice cold 1 : 1 (v/v) conc. HCl / distilled water with constant stirring. The precipitated resin product was filtered off, washed with hot water until it was free from chloride ions, dried, and powdered. The purified polymer sample was dried in vacuum at room temperature. The finely ground resin was pass through a 300 mesh size sieve. The yield of terpolymer resin was found to be 83%. The reaction taking place is shown in Scheme 1.

Similarly, other terpolymer resins viz, BPhThF-2, BPhThF-3, and BPhThF-4 were synthesized by varying the molar proportion of the starting materials, i.e., BPh, Th, and F in ratio 1 : 2 : 4, 1 : 3 : 5, and 1 : 4 : 6 (Table I).

Characterization of terpolymer

These terpolymer resins were subject to microanalysis for C, H, N, and S on Perkin Elmer 2400 series II CHNS/O analyzer at Sophisticated Instrumentation Centre for Applied Research and Testing (Sicart), Vallabh Vidyanagar, Gujarat, India. The number average molecular weights (\overline{M}_n) were determined by conductometric titration in DMF using KOH in 50% (v/v) DMF/Alcohol mixture as the titrant using Equip-Tronics conductivity meter within built magnetic stirrer (model No EQ-664). The viscosity were determined using a Tuan-Fuoss viscometer at six different concentrations ranging from 0.5 to 3.0% of

terpolymer in DMF at 33°C. The intrinsic viscosity $[\eta]$ was calculated by the Huggins equation (1) and Krammer equation (2).

$$\eta_{sp}/C = [\eta] + k_1[\eta]^2 C \quad (1)$$

$$\ln \eta_{rel}/C = [\eta] - k_2[\eta]^2 C \quad (2)$$

Electronic absorption spectra of all synthesized terpolymer resins were recorded at Cintra 10e UV-visible spectrometer, GBC Instrument 3170, Australia having range of 280 nm to 900 nm at Department of Chemistry, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur. Infrared spectra of BPhThF terpolymer resins were recorded in Nicolet Magna 550 IR spectrophotometer in KBr pellets in the number region of 4000–400 cm^{-1} . Proton NMR spectra of BPhThF terpolymer were recorded on Varian - VXR - 300S, 300 MHz Proton NMR spectrophotometer using DMSO - d_6 as a solvent at Regional Sophisticated Instrumentation Centre, IIT, Powai, Mumbai.

RESULTS AND DISCUSSION

All the terpolymer resins are found to be amorphous and pale yellow in color. These purified resins are found to be soluble in DMF, DMSO, aqueous NaOH, and KOH solution. The BPhThF terpolymer resins were analyzed for the percentage of carbon, hydrogen, nitrogen, and sulphur. The results are incorporated in Table II. The resins synthesized do not show sharp melting point but undergo decomposition above 200°C.

The \overline{M}_n of the terpolymer resins were determined by nonaqueous conductometric titration in DMF against KOH in 50% (v/v) DMF-Alcohol mixture using 100 mg of resin sample. A plot of specific conductance against the [meq] of potassium hydroxide required for neutralization of 100 g of terpolymer was made. Inspection of such a plot revealed that there are many breaks in plot. From this plot, the first break and the last break were noted. The calculation of (\overline{M}_n) by this method is based on the following considerations²⁵: (1) The first break corresponds to neutralization of the more acidic phenolic

TABLE I
Experimental Details of BPhThF Terpolymer Resins

Resin Abbreviation (Decomp Temp) (°C)	Reactants			Molar ratio	Catalyst 2M HCL (mL)	Reflux Temp ± 2K (K)	Yield (%)	Time (h)
	2,2'-dihydroxy biphenyl BPh (mol)	Thiourea Th (mol)	CH ₂ O F (mol)					
BPhThF-1 (above 400)	0.05	0.05	0.1	1:1:2	100	416	85	6
BPhThF-2 (above 200)	0.025	0.05	0.1	1:2:4	100	378	83	5
BPhThF-3 (above 200)	0.02	0.06	0.1	1:3:5	100	378	80	5
BPhThF-4 (above 200)	0.02	0.08	0.12	1:4:6	100	379	78	5

TABLE II
Elemental Analysis, Empirical Formula, Molecular Weight, and Intrinsic Viscosity Data of BPhThF Terpolymer Resins

Terpolymer resin	%C obs (Cal)	%H Obs (Cal)	%N obs (Cal)	%S obs (Cal)	Empirical formula of repeating Unit	Empirical formula weight	D_p	M_n	k_1	k_2	k_1+k_2	η (dL/g)
BPhThF-1	56.00 (55.90)	56.10 (55.9)	99.50 (99.4)	86.8 (87)	$C_{15}H_{14}N_2SO_2 \cdot 2H_2O$	322	35	11,270	0.6452	-0.0800	0.5652	0.078
BPhThF-2	50.99 (51.19)	51.60 (52.1)	15.20 (15.17)	13.47 (13.27)	$C_{18}H_{18}N_4S_2O_2 \cdot 2H_2O$	422	33	13,926	0.6152	-0.0840	0.5314	0.084
BPhThF-3	45.28 (45.37)	54.8 (54.8)	15.84 (15.88)	18.13 (18.15)	$C_{20}H_{23}N_6S_3O_2 \cdot 3H_2O$	529	28	14,812	0.6520	-0.0909	0.5611	0.094
BPhThF-4	46.89 (46.97)	46.5 (46.3)	22.74 (22.78)	19.89 (19.93)	$C_{22}H_{26}N_8S_4O_2$	562	27	15,174	0.6878	-0.1200	0.5668	0.111

Obs, observed; cal, calculated; \overline{D}_p , degree of polymerization; k_1 , Huggin's constant; k_2 , Kraemer constant.

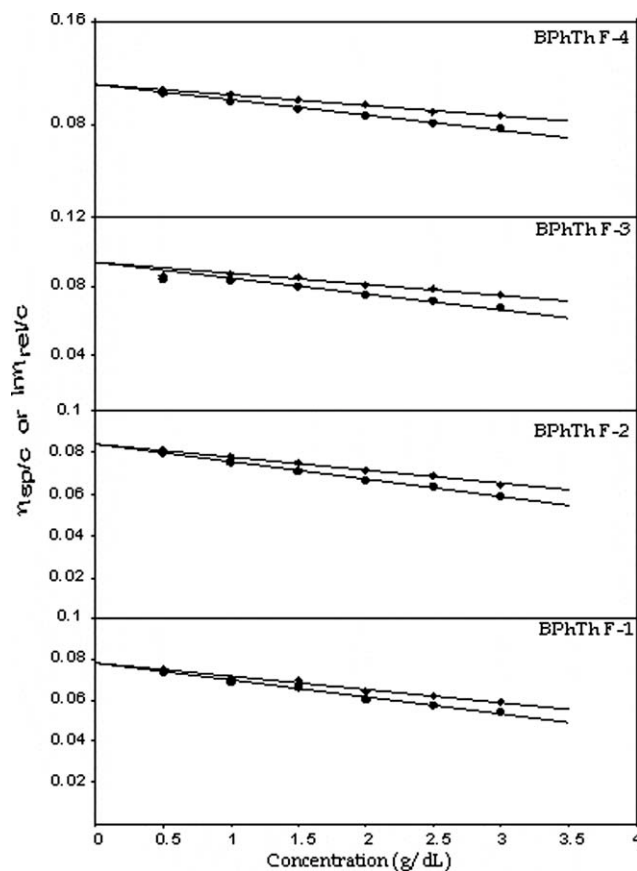


Figure 1 Viscometric plots of BPhThF terpolymer resins.

hydroxy group of all the repeating units, and (2) the break in the plot beyond which a continuous increase in conductance is observed represents the stage at which phenolic hydroxy group of all repeating units are neutralized. The degree of polymerization (\overline{D}_p) is given by the following relation:

$$\overline{D}_p = \frac{\text{Total meq. of base required for complete neutralization}}{\text{meq. of base required for smallest interval}}$$

On the basis of degree of polymerization (\overline{D}_p), the average number molecular weight (\overline{M}_n) is calculated by multiplying the (\overline{D}_p) by the formula weight of the repeating unit.²⁴ The results are incorporated in Table II.

Viscometric measurements were carried out in DMF at 33°C. All resins showed normal behavior. The $[\eta]$ was determined by the Huggin's equation (1) and Kraemer's equation (2). Viscometric plots are shown in Figure 1. In accordance with the aforementioned relations, the plots of η_{sp}/C and $\ln \eta_{rel}/C$ against C were found to linear giving as slopes k_1 and k_2 , respectively. Intercept on the axis of viscosity function gave the $[\eta]$ value in both the plots. The calculated values of constants k_1 and k_2 (Table II) in

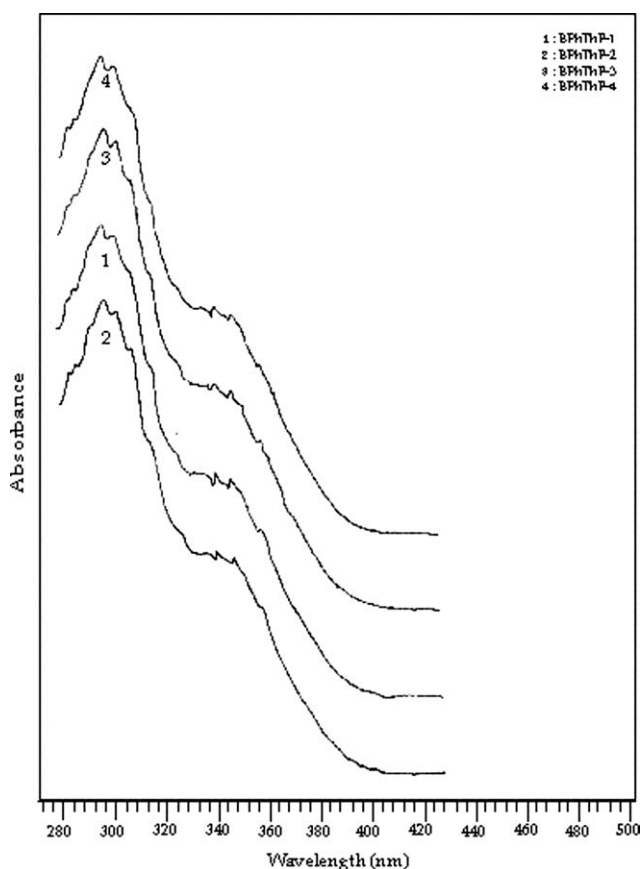


Figure 2 Electronic spectra of BPhThF terpolymer resins.

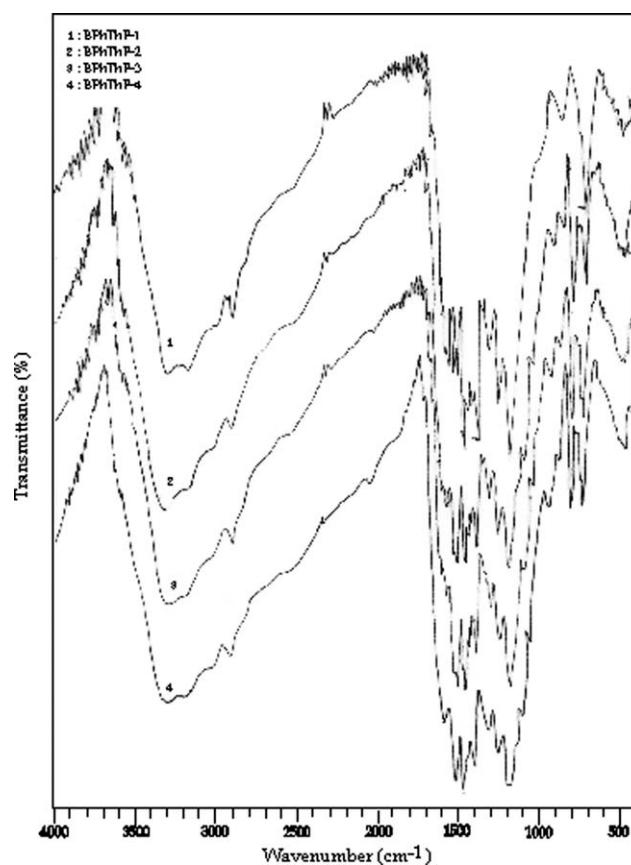


Figure 3 Infrared spectra of BPhThF terpolymer resins.

most of cases satisfy the relation $k_1 + k_2 = 0.5$ favorably.^{13,24} The values of $[\eta]$ obtained from eqs. (1) and (2) were in close agreement with each other. It

has been observed that the intrinsic viscosity increases with the increase in molecular weight of terpolymer.

TABLE III
IR Spectral Data of BPhThF Terpolymer Resins

Observed band frequency (cm ⁻¹)				Assignment	Expected band frequency (cm ⁻¹)
BPhThF-1	BPhThF-2	BPhThF-3	BPhThF-4		
3343(b,St)	3369(b,St)	3338(b,St)	3338(b,St)	—OH phenolic intermolecular hydrogen bonding	3750–3200
2926(Sh,St)	2925(Sh,St)	2915(Sh,St)	2926(Sh,St)	—CH ₂ stretching	2800–3500
2540(w)	2550(w)	2555(w)	2565(w)	S—H stretching	2600–2550
1612(v)	1612(v)	1612(v)	1610(v)	>C=N stretch	1471–1690
1500(St)	1495(St)	1495(St)	1500(St)	N—H bending	1570–1490
517(b/m)	527(b/m)	508(b/m)	498(b/m)	N—H deformation out of plane	800–600
1546(b/m)	1551(b,m)	1556(b,m)	1556(b,m)	Aromatic ring (substituted)	1600–1500
1423(b/m)	1418(b/m)	1424(b/m)	1429(b/m)	—CH ₂ bending	1460
1347(Sh,m)	1347(Sh,m)	1347(Sh,m)	1347(Sh,m)	—CH ₂ wagging	1280–1370
1286(Sh,m)	1291(Sh,m)	1286(Sh,m)	1296(Sh,m)		
762(m)	751(m)	766(m)	761(m)	—CH ₂ — rocking / >C=S stretch	710–800/1563–700
1240(Sh,b)	1230(Sh,b)	1220(Sh,b)	1235(Sh,b)	>C—O stretch in phenol	1230
—	955(w)	958(w)	960(w)	1; 2; 3; 5 - substitution on aromatic ring	950
—	1017(w)	1067(w)	1058(w)		1058
—	1133(m)	1133(m)	1125(m)		1125
900–955(w)	900(w)	900(w)	900(w)	One isolated H-atom situated between two substitution	900
—	827(Sh)	828(Sh)	828(Sh)	Tetra substituted benzene ring	~830

Sh, Sharp; b, broad; st, strong; m, medium; v, variable; w, weak.

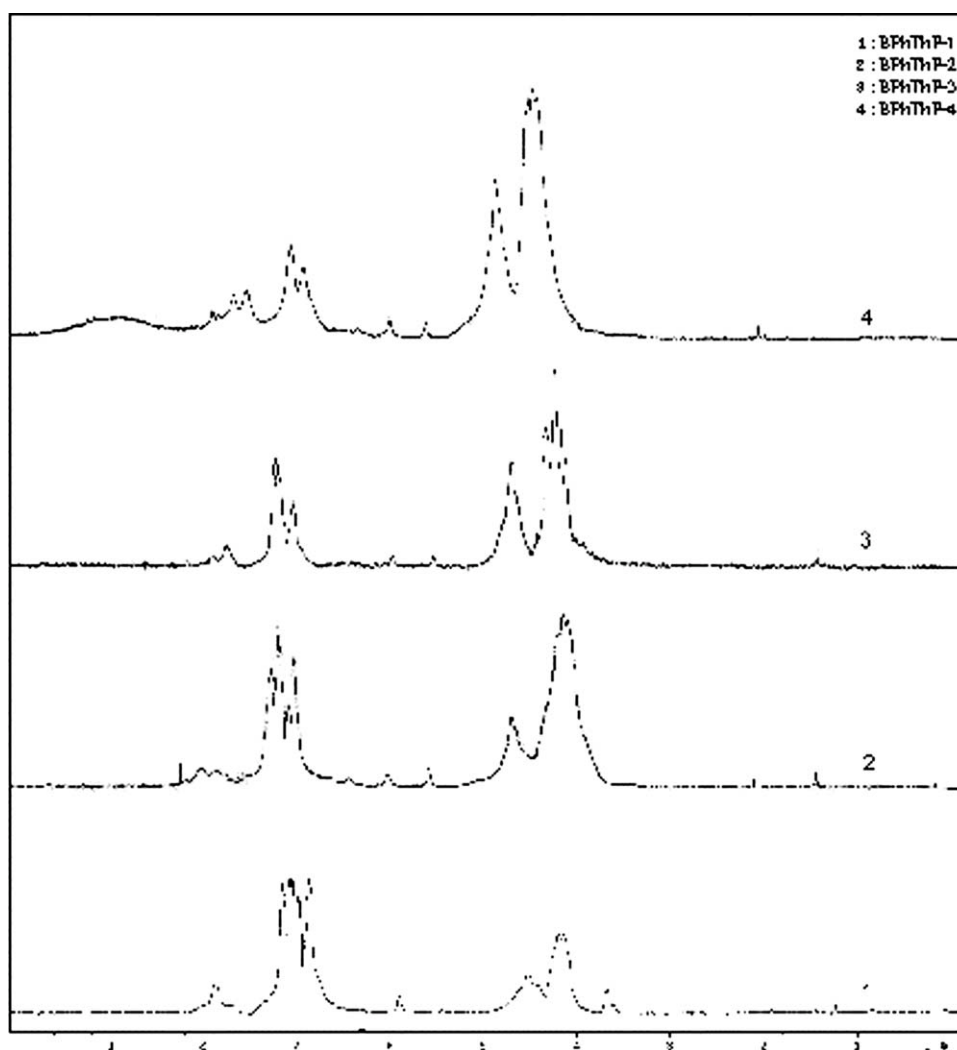


Figure 4 NMR spectra of BPhThF terpolymer resins.

The electronic spectra of all the BPhThF terpolymer resins give rise to similar pattern and are depicted in Figure 2. Electronic spectra of all BPhThF terpolymer resins were scanned in HPLC grade DMF. All the terpolymers exhibit two characteristic bands at 293–296 nm and 328–336 nm. The intense band at 293–296 nm may be due to ($\pi \rightarrow \pi^*$)

allowed transition of biphenyl ring, which readily attains coplanarity and shoulder merging (loss of fine structure) band at 328–336 nm may be due to ($n \rightarrow \pi^*$) forbidden transition in $>C=S$ or $>C=N$ group.²⁹ The bathochromic shift from the basic value viz: 250–320 ($\pi \rightarrow \pi^*$) and 291 ($>C=S$) or 270–300 nm ($>C=N$) may be due to combined effect of

TABLE IV
Proton NMR Spectral Data of BPhThF Terpolymer Resins

Observed chemical shift, δ (ppm)				Nature of proton assigned	Expected chemical shift, δ (ppm)
BPhThF-1	BPhThF-2	BPhThF-3	BPhThF-4		
4.0–4.4	4.0–4.4	4.0–4.4	4.0–4.4	Methylene proton of Ar–CH ₂ –NH– linkage	3.5–6.0
4.6	4.6	4.6	4.6	Protons of –NH– bridge	5.0–8.5
6.8–7.2	6.8–7.2	6.8–7.2	6.8–7.2	Aromatic protons (Ar–H)	6.2–8.5
7.8–8.0	7.8–8.0	7.8–8.0	7.8–8.0	Fast/intermediate proton exchange reaction of phenolic –OH group/–NH–CS– group or Ar–OH phenolic hydrogen bonded or hydrogen bonding of –NH–CS– group	8–12
1.2	1.2	1.2	1.2	S–H protons (aliphatic sulfhydryl protons)	1.2–1.6

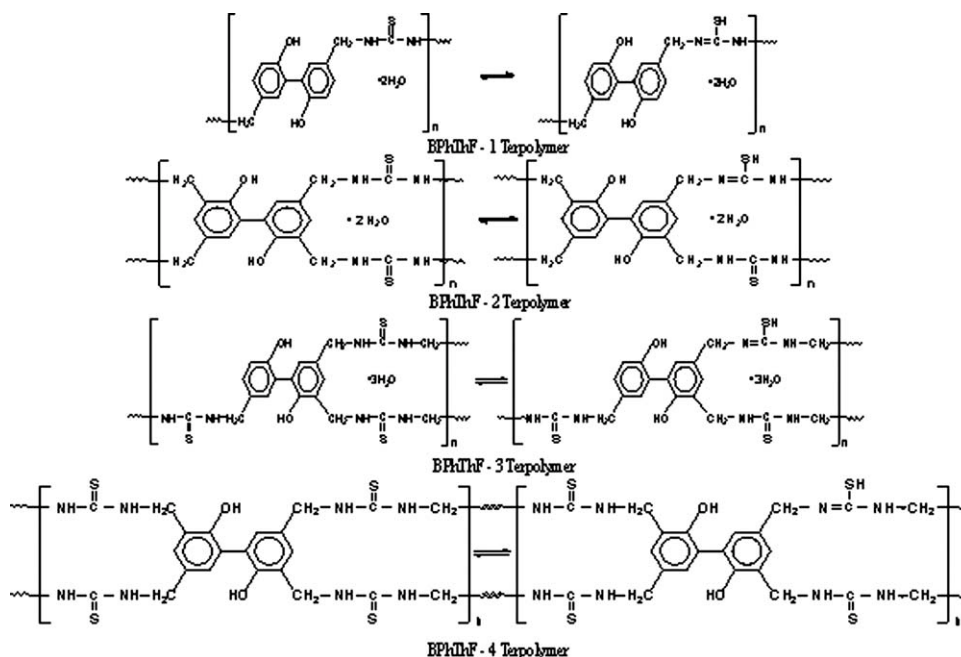


Figure 5 Suggested structures of BPhThF terpolymer resins.

conjugation (due to chromophore) and phenolic hydroxy group (auxochrome).³⁰

The IR spectra of all four terpolymer resins are depicted in Figure 3 and spectral data incorporated in Table III. The IR spectra revealed that all these resins give rise to nearly similar pattern of spectra. A broad band appeared in the region 3380–3370 cm^{-1} may be due to the stretching vibrations of phenolic hydroxy groups exhibiting intermolecular hydrogen bonding which exists between $-\text{OH}$ and $>\text{NH}$ group of different polymer chains.^{30,31} The presence of weak bands at 2540–2573 cm^{-1} and medium bands at 750–772 cm^{-1} are assigned to stretching modes of $\text{S}-\text{H}$ vibrations³⁰ and $>\text{C}=\text{S}$ vibrations,^{30,31} respectively. These bands indicate that the terpolymer exists in tautomeric forms. The bands observed at 2915–2926 cm^{-1} , 1418–1434 cm^{-1} , 1347 cm^{-1} , and 1280–1296 cm^{-1} suggest the presence of methylene bridges in polymeric chains. The medium broad band at 1546–1566 cm^{-1} may be ascribed to aromatic skeletal ring.^{29–31} The band at 1610–1642 cm^{-1} may be due to the stretching vibrations of $>\text{C}=\text{N}-$.²⁹ The bands appeared at 1495–1500 cm^{-1} and 498–527 cm^{-1} are due to $-\text{NH}-$ bending and deformation out of plane vibrations of the thiourea moiety in terpolymer resins respectively.^{30,31} The band at 1220–1240 cm^{-1} may be due to $>\text{C}-\text{O}$ stretch in phenol.^{30,31} The presence of band at 955–960 cm^{-1} , 1017–1058 cm^{-1} , and 1125–1133 cm^{-1} suggest that the aromatic ring is 1,2,3,5-substituted. This fact is further supported by presence of band at 823–833 cm^{-1} for tetra substituted benzene ring³¹ and band at 895–955 cm^{-1} for one isolated H-atom situated between two substituents.³¹

Proton NMR spectra of all four terpolymer resins are presented in Figure 4 and NMR spectral data are incorporated in Table IV. Peaks at 4–4.5 (δ) ppm may be due to the presence of methylene protons of $\text{Ar}-\text{CH}_2-\text{NH}-$ moiety.³⁰ The proton on $-\text{NH}-$ bridge can be identified from the peaks at 4.6 (δ) ppm.³⁰ Signals appeared at (δ) ppm values 6.8–7.2 can be assigned to aromatic protons.^{30,29} The protons of $\text{Ar}-\text{OH}$ group involved in proton exchange reaction gives peak at 7.8–8.0 (δ) ppm. From the NMR spectra it is revealed that BPhThF-2, BPhThF-3, BPhThF-4 exhibits doublet in region 7.8–8.0 (δ) ppm, may be due to intermediate proton exchange reaction, whereas in case BPhThF-1 it shows sharp singlet which is due to fast proton exchange reaction or hydrogen bonding exists between the



group. Smallest peak observed may be due to protons of $\text{S}-\text{H}$ group.

On the basis of the nature and reactive positions of the monomers, elemental analysis, electronic, IR, NMR spectra, and molecular weight, the most probable structures, have been proposed for terpolymer resins as shown in Figure 5.

CONCLUSION

1. The terpolymer resins prepared from biphenol, thiourea, and formaldehyde are cream in color and are found to be amorphous.

2. All the newly synthesized terpolymer resins are insoluble in common organic solvent but soluble in DMF, DMSO, aqueous NaOH, and KOH solutions
3. The polycondensation reaction of biphenol, thiourea, and formaldehyde is sensitive to stoichiometry of monomers in their preparation.

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