

# Resin I: Synthesis and Characterization of 2,2'-Dihydroxybiphenyl-Urea-Formaldehyde Terpolymers

Manjusha M. Jadhao,<sup>1</sup> L. J. Paliwal,<sup>2</sup> N. S. Bhavé<sup>1</sup>

<sup>1</sup>Department of Chemistry, Nagpur University Campus, Nagpur 440033, India

<sup>2</sup>Department of Chemistry, Hislop College, Nagpur 440001, India

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**ABSTRACT:** Terpolymer resins (BPhUF) were synthesized by the condensation of 2,2'-dihydroxybiphenyl [BPh] and urea [U] with formaldehyde [F] in the presence of an 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 medium. Visco-

metric measurements in dimethyl formamide have been carried out with a view to ascertain the characteristic functions and constants. UV-VIS, IR, and NMR spectra were studied to elucidate the structure. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1605–1610, 2005

**Key words:** IR; NMR; structure; degree of polymerization

## INTRODUCTION

Much research work has been carried out on the synthesis and characterization of urea containing terpolymers. A literature survey reveals that terpolymer derived from substituted hydroxy or dihydroxy-urea-formaldehyde resin shows improved ion exchange properties, thermal resistance properties, coordinating properties, and good storage stability, etc.<sup>1–6</sup> Terpolymer resins prepared from *m*-phenylenediamine, *O*-anisidine, and 2,3-xylidine in aqueous HCl by chemical oxidative polymerization have been studied by Li et al.<sup>7</sup> Terpolymers derived from itaconic acid-acrylamide-2-acrylamido-2-methylpropanesulfonic acid by free radical polymerization have been reported in the literature.<sup>8</sup> Cyclohexanone-formaldehyde and acetophenone-formaldehyde resin modified by incorporation of phenol, biphenols, and substituted acetophenone have been reported in the literature.<sup>9</sup> The effect of annealing on structural changes in liquid crystalline copolyester based on 6-hydroxy-2-naphthoic acid-*p*-hydroxybenzoic acid-terephthalic acid-4,4'-biphenyldiol copolymer was investigated by Yoon et al.<sup>10</sup> Oxyethylene copolymers with 4,4'-biphenyl and phenyl structural units in their backbone have been studied.<sup>11</sup> Thermal behavior of some aromatic polyethers containing azobenzene and 4,4'-dihydroxy biphenyl moieties were studied by Otillia et al.<sup>12</sup> Extensive studies on the synthesis and characterization of various ter-

polymers derived from substituted hydroxy compounds-diamide-formaldehyde and their properties such as thermal and electrical conductivity, ion-exchange, and coordinating behavior have been undertaken in our research laboratory.<sup>13–18</sup> The present article describes the synthesis and characterization of terpolymers derived from 2,2'-dihydroxybiphenyl, urea, and formaldehyde.

## EXPERIMENTAL

### Materials

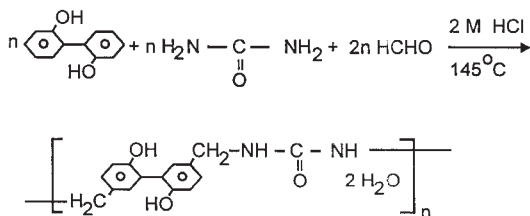
The chemicals used were all of A.R. or chemically pure grade.

### Preparation of BPhUF terpolymer resin [BPhUF-1]

A mixture of 2,2'-dihydroxybiphenyl [9.5 g, 0.05 mol], urea [3.1 g, 0.05 mol], and formaldehyde [8.6 mL of 35% solution, 0.1 mol] in the presence of 2 M HCl was heated in an oil bath at  $145 \pm 2^\circ\text{C}$  for 5 h with occasional shaking.<sup>19,2</sup> The separated resinous product [BPhUF-1] was washed with hot water to remove unreacted monomers. The resin was purified by dissolution in 8% NaOH and reprecipitated by dropwise addition of 1:1 (v/v) HCl with constant stirring. The precipitated resin product was filtered off, washed with hot water until it was free from chloride ions, dried, and ground to a powder. The yield of these terpolymer resins was found to be 69–87%. The reaction taking place is as shown in Scheme 1.

Similarly, other terpolymer resins, viz. BPhUF-2, BPhUF-3, and BPhUF-4, were synthesized by varying

Correspondence to: N. S. Bhavé (manju\_poly@yahoo.com).



Scheme 1

the molar proportion of the starting materials, i.e., 2,2'-dihydroxybiphenyl, urea, and formaldehyde in a ratio of 1:2:4, 1:3:5, and 1:4:6 (Table I).

### Characterization of terpolymer

The terpolymer resins were subjected to microanalysis for C, H, and N on a Perkin-Elmer C, H, N, S analyzer. The number average molecular weights ( $M_n$ ) were determined by conductometric titration in DMF using KOH in a 50% (v/v) DMF/alcohol mixture as a titrant. The viscosities were determined using a Tuan-Fuoss viscometer at six different concentrations ranging from 3.0 to 0.5 wt % of resin in DMF at 33°C. The intrinsic viscosity  $\eta$  was calculated using the Huggins equation (1) and the Kramer 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 the terpolymers in DMF were also recorded on a Shimadzu double-beam spectrophotometer in the range of 190–700 nm. Infrared spectra of BPhUF terpolymer resins were recorded using a Nicolet Magna 550 IR spectrophotometer in KBr pellets in the number region of 4000–400  $\text{cm}^{-1}$ . Proton NMR spectra of BPhUF terpolymers were recorded on a Varian VXR 300S 300-MHz proton NMR spectrophotometer using DMSO- $d_6$  as a solvent at Regional Sophisticated Instrumentation Centre (IIT, Powai, Mumbai, India).

## RESULTS AND DISCUSSION

The resin samples were cream in color, except for BPhUF-2, which is white, and insoluble in commonly used organic solvents but were partly soluble in DMF and DMSO. These resins were analyzed for carbon, hydrogen, and nitrogen content. The resins synthesized do not show a sharp melting point but undergo decomposition above 220°C (Table I).

The molecular weight ( $\bar{M}_n$ ) of the terpolymer resin was determined by nonaqueous conductometric titration in DMF against KOH in a 50% (v/v) DMF/alcohol mixture using 100 mg of resin sample. A plot of specific conductance against the milliequivalents 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 the plot. From this plot the first and the last break were noted. The calculation of ( $\bar{M}_n$ ) by this method is based on the following considerations.<sup>19,20</sup>

(1) The first break corresponds to neutralization of the more acidic phenolic hydroxy group of all of the repeating units; and (2) the break in the plot beyond which a continuous increase in conductance is observed represents the stage at which the phenolic hydroxy group of all repeating units is neutralized. The average degree of polymerization ( $D_p$ ) is given by the relation

$$D_p = \frac{\text{Total meq of base required for complete neutralization i.e. last break}}{\text{Meq of base required for smallest interval i.e. first break}}$$

The number average molecular weight ( $M_n$ ) could be obtained by multiplying the  $D_p$  by the formula weight of the repeating unit.<sup>21</sup> The results are shown in Table II.

Viscometric measurements were carried out in DMF at 33°C. All resins showed normal behavior. The intrinsic viscosity was determined by the Huggins<sup>22</sup> equation

$$\eta_{sp} / c = [\eta] + k_1 [\eta]^2 c$$

TABLE I  
Synthesis and Physical Data of Terpolymers

Terpolymer	Reactants				Catalyst 2 M (HCl) aqueous (mL)	Reflux temp. $\pm 2$ K	$D_1$ (°C)	Time (h)	% Yield	Color	Elemental analysis (%)					
	2,2'- Dihydroxy biphenyl [BPh] (mol)	Urea [U] (mol)	Formal- dehyde [F] (mol)	Molar ratio							C		H		N	
											Calc.	Found	Calc.	Found	Calc.	Found
BPhUF-1	0.05	0.05	0.1	1:1:2	100	418	475	5	83	Cream	58.82	58.64	5.88	5.9	9.11	9.15
BPhUF-2	0.03	0.06	0.12	1:2:4	100	413	220	5	87	White	61.02	60.85	5.08	5.10	15.82	15.79
BPhUF-3	0.025	0.075	0.125	1:3:5	100	393	240	6	79	Cream	56.21	56.04	5.39	5.34	19.67	19.61
BPhUF-4	0.02	0.08	0.12	1:4:6	100	401	235	5	69	Cream	53.01	53.19	5.22	5.12	22.49	22.80

Note.  $D_1$ , decomposition temperature (°C).

TABLE II  
Molecular Weight Determination and Viscometric Data of Terpolymers

Terpolymer	Empirical formula of repeating unit	Empirical formula weight	$D_p$	$\bar{M}_n$	Intrinsic viscosity $[\eta]$ dl g <sup>-1</sup>	( $k_1$ ) Huggin's constant	( $k_2$ ) Kraemer constant	$k_1 + k_2$
BPhUF-1	C <sub>15</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> ·2H <sub>2</sub> O	306	53	16218	0.089	0.681	-0.095	0.586
BPhUF-2	C <sub>18</sub> H <sub>18</sub> N <sub>4</sub> O <sub>4</sub>	354	54	19116	0.0945	0.6851	-0.1045	0.581
BPhUF-3	C <sub>20</sub> H <sub>23</sub> N <sub>6</sub> O <sub>5</sub>	427	56	23856	0.1035	0.6363	-0.0944	0.5419
BPhUF-4	C <sub>22</sub> H <sub>26</sub> N <sub>8</sub> O <sub>6</sub>	498	54	26892	0.1182	0.6666	-0.1133	0.5533

and the Kraemers<sup>23</sup> equation:

$$\ln \eta_{rel} / c = [\eta] - k_2[\eta]^2c.$$

The viscometric plots are shown in Figure 1. In accordance with the above relations, the plots of  $\eta_{sp}/c$  and  $\eta_{rel}/c$  against  $c$  were found to be linear, giving slopes  $k_1$  and  $k_2$ , respectively. The intercept on the axis of viscosity function gave the  $[\eta]$  value in both plots. The calculated values of constants  $k_1$  and  $k_2$  (Table II) in

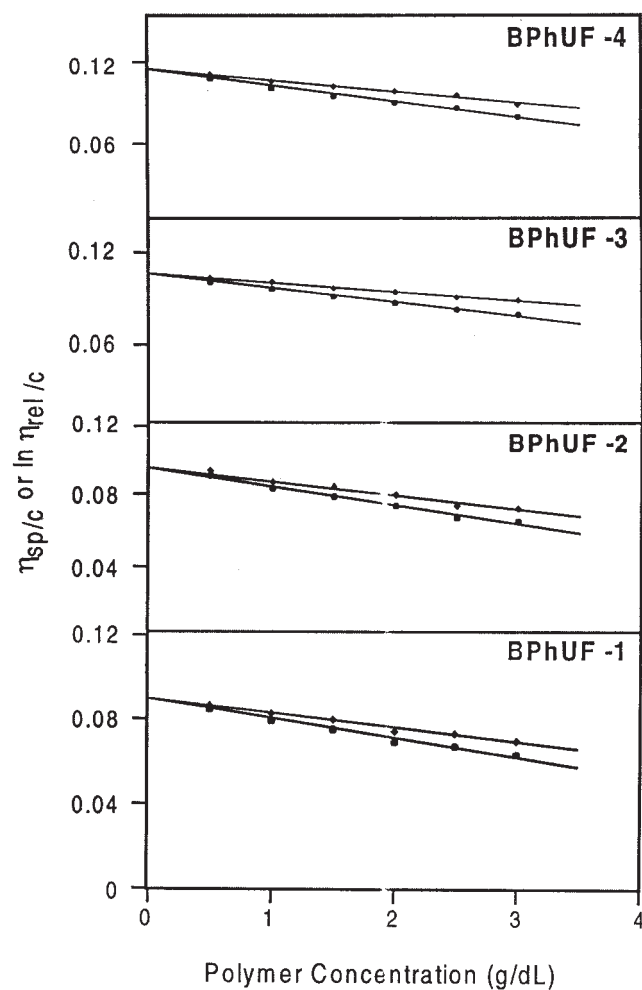


Figure 1 Viscometric plots of terpolymers.

most cases satisfy the relation  $k_1 + k_2 = 0.5$  favorably.<sup>24</sup> The values of  $[\eta]$  obtained from Eqs. (1) and (2) were in close agreement with each other. The intrinsic viscosity increases with an increase in molecular weight of the terpolymer.

The electronic spectra of all the BPhUF terpolymer resins give rise to a similar pattern and are depicted in Figure 2. The spectra of these terpolymers exhibit two absorption maxima in the region 280 to 300 and 310 to 350 nm. The intense band at 295 nm is due to the ( $\pi-\pi^*$ ) allowed transition of biphenyl moiety, which readily attains coplanarity and the shoulder merging (loss of fine structure) band at 330 nm may be due to ( $n-\pi^*$ ) forbidden transition in saturated aliphatic carbonyl compounds.<sup>25-29</sup> The bathochromic shift from the basic value, viz., 252 and 270 nm, respectively, may be due to the combined effect of conjugation and phenolic hydroxy group (auxochrome).<sup>26-29,30</sup>

The IR spectra of all four terpolymer resins are presented in Figure 3 and IR spectral data are shown in Table III. The IR spectra revealed that all of these resins give rise to a nearly similar pattern of spectra. A broad band appearing in the region 3750-3200 cm<sup>-1</sup> may be assigned to the stretching vibrations of phenolic hydroxy groups exhibiting intermolecular hydrogen bonding with the carbonyl group of a different polymeric chain, i.e., -OH phenolic intermolecular polymeric association.<sup>3,19,28,29,31,32</sup> The band at 1643-1680 cm<sup>-1</sup> may be due the stretching vibrations of the  $>C=O$  group of substituted urea or amide moi-

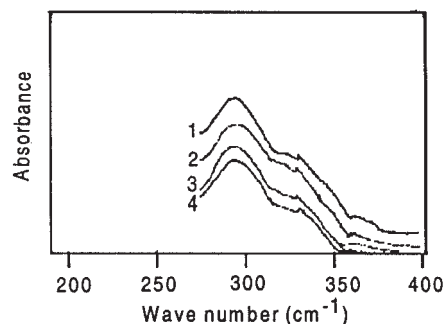
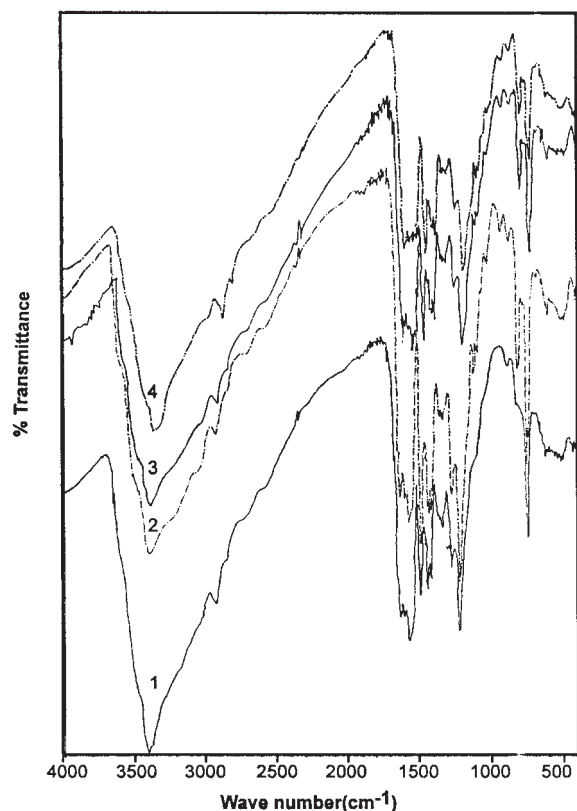


Figure 2 Electronic spectra of terpolymers. 1, BPhUF-1; 2, BPhUF-2; 3, BPhUF-3; 4, BPhUF-4.



**Figure 3** Infrared spectra of terpolymers. 1, BPhUF-1; 2, BPhUF-2; 3, BPhUF-3; 4, BPhUF-4.

ety.<sup>28,29,31,32</sup> The bands at 2925–2935  $\text{cm}^{-1}$ , which is merged in the -OH band, 1479–1500, and 634–693  $\text{cm}^{-1}$ , are assignable to -NH- stretching, bending, and

deformation out of plane vibrations of the urea moiety in terpolymers, respectively.<sup>1,28,29,31,32</sup> The band at 1560  $\text{cm}^{-1}$  may be ascribed to an aromatic skeletal ring.<sup>28,29,31,32</sup> The presence of methylene bridges (-CH<sub>2</sub>-) in the polymeric chain may be assigned to the presence of a band at 1420–1467, 1333–1350, and 751–766  $\text{cm}^{-1}$  [-CH<sub>2</sub>-rocking].<sup>28,29,31–33</sup> The band at 1230  $\text{cm}^{-1}$  may be due to >C—O stretch of the polymeric phenol.<sup>28,31</sup> The bands obtained at 950–939  $\text{cm}^{-1}$ , 1058, and 1133  $\text{cm}^{-1}$  suggest that the aromatic ring is 1, 2, 3, 5-substituted.<sup>19,21,28,29</sup> The 1, 2, 3,5-substitution of the benzene ring is also confirmed by the presence of a band at 900  $\text{cm}^{-1}$ <sup>29,31,4</sup> and 827  $\text{cm}^{-1}$  for a tetrasubstituted benzene ring.<sup>31,32</sup>

Proton NMR spectra of all four terpolymer resins are presented in Figure 4 and NMR spectra data are shown in Table IV. Proton NMR spectra of all terpolymer resins show a multiplet signal (asymmetrical pattern) in the region 6.9 to 7.99 ( $\delta$ ) ppm, which is due to aromatic protons.<sup>28,29</sup> A doublet signal appearing in the region 6.2–6.4 ( $\delta$ ) ppm can be assigned to the proton of the phenolic -OH group involved in hydrogen bonding.<sup>28,26,34</sup> A broad signal at 9.2 ( $\delta$ ) ppm shows intramolecular hydrogen bonding of the -NH-CO- group or intermediate proton exchange reaction of both phenolic -OH groups.<sup>27,28,34</sup> A weak signal at 5.8–5.9 ( $\delta$ ) ppm may be due to protons of the -NH- bridge.<sup>28,34,35</sup> A signal at 4.1 to 4.2 ( $\delta$ ) ppm may be assigned to methylenic protons of an Ar-CH<sub>2</sub>-NH-CO- moiety.<sup>28,34</sup> A very weak signal in the region of 3.8 to 3.9 ( $\delta$ ) ppm may be due to the presence of BPhF copolymer as an

**TABLE III**  
IR Spectral Data of BPhUF Terpolymers

Observed band frequency ( $\text{cm}^{-1}$ )				Assignment	Expected band frequency
BPhUF-1	BPhUF-2	BPhUF-3	BPhUF-4		
3389	3379	3363	3409 (b, St)	-OH phenolic intermolecular hydrogen bonding	3750–3200
2925	2926	2926	2931 (Sh, St)	> NH stretching	2800–3500
1640	1642	1637	1633 (Sh,m)	>C=O stretch of II <sup>ry</sup> amide	1630–1680
1495	1494	1479	1500 (m)	N-H bending of II <sup>ry</sup> amide	1570–1490
645	693	644	644 (w)	N-H deformation out of plane of II <sup>ry</sup> amide	600–800
1566	1566	1561	1560 (sh,b)	Aromatic ring	1600–1500
1467	1423	1420	1423 (m)	-CH <sub>2</sub> - bending	1460
1346	1350	1333	1333 (Sh, b)	-CH <sub>2</sub> - wagging	1280–1370
762	751	766	761 (m)	-CH <sub>2</sub> - rocking	710–800
1235	1230	1235	1230 (Sh,b)	>C—O stretch in phenol	1230
—	949	944	939 (w)	} 1, 2, 3, 5 - substitution	950, 1058, 1125
—	1053	1051	1042 (w)		
—	1133	1130	1133 (m)		
900	900	900	900 (w)		One isolated H-atom situated between two substitution [1,2,3,5-substitution]
—	833	828	828 (Sh)	Tetrasubstituted benzene ring	≈830

Sh, sharp; b, broad; St, strong; m, medium; w, weak.

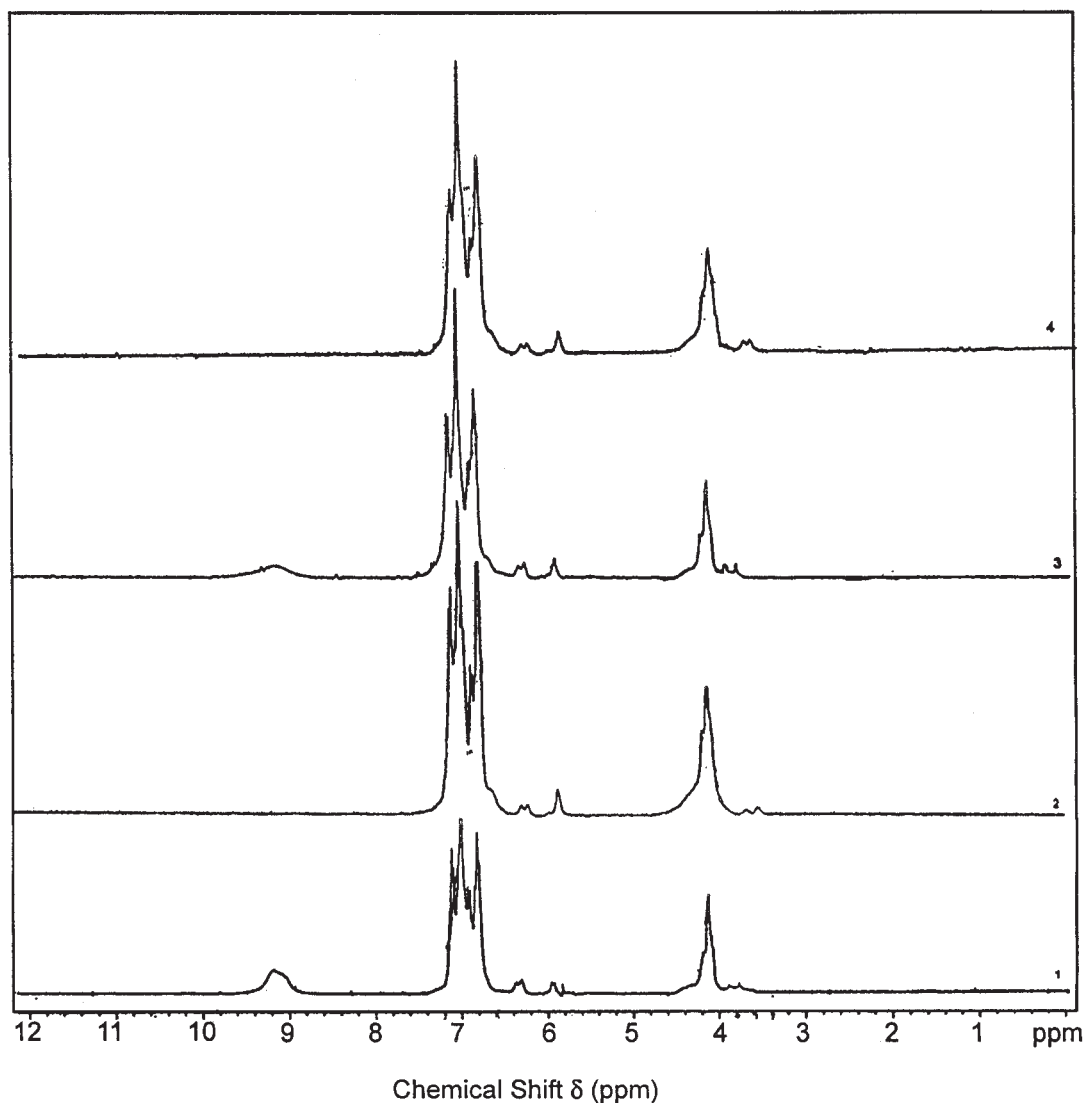


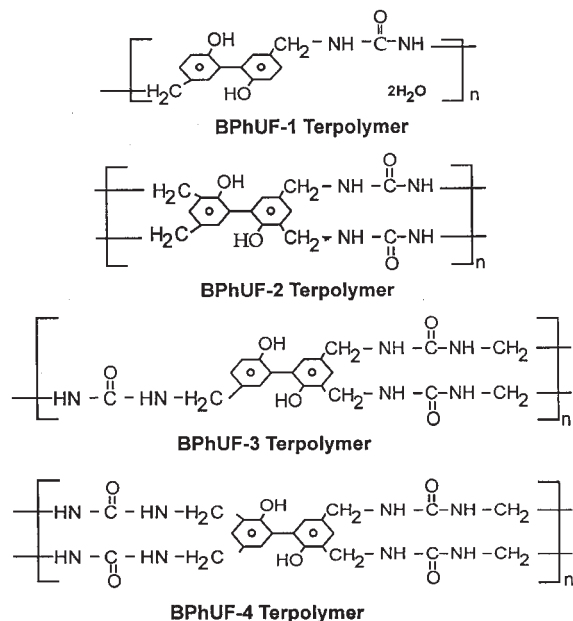
Figure 4 Proton NMR spectra of terpolymers. 1, BPhUF-1; 2, BPhUF-2; 3, BPhUF-3; 4, BPhUF-4.

impurity associated with terpolymer resins. On the basis of the nature and reactive positions of the monomers, elemental analysis, electronic, IR, and

NMR spectra, and molecular weight, the most probable structures have been proposed for terpolymer resins as shown in Figure 5.

TABLE IV  
Nuclear Magnetic Resonance Spectral Data of BPhUF Terpolymers

Observed chemical shift $\delta$ (ppm)				Nature of proton assigned	Expected chemical shift (ppm)
BPhUF-1	BPhUF-2	BPhUF-3	BPhUF-4		
4.1-4.2	4.1-4.2	4.1	4.1	Methylenic protons of Ar - CH <sub>2</sub> - NH - CO -	3.5-6
5.8-6.00	5.8-5.9	5.8-5.9	5.8-5.9	Protons of -NH - bridge	5.0-8.5
6.3-6.4	6.2-6.3	6.2-6.3	6.2-6.4	Ar-OH polymeric association or protons of phenolic -OH involved in hydrogen bonding (Intermediate Exchange)	4-7.7
7.99	6.99	6.99	6.9-7.2	Aromatic proton (Ar-H) (asymmetrical substitution pattern)	6.2-8.5
9.2 (b)	-	9.2 (b)	-	Intermediate proton exchange of phenolic -OH group or intramolecular hydrogen bonding of -NH - CO -	8-12



**Figure 5** Suggested structure of terpolymers.

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