

Synthesis and Physicochemical Characterization of Poly(azomethine)esters Containing Aliphatic/Aromatic Moieties: Electrical Studies Complemented by DFT Calculation

Asghari Gul,¹ Zareen Akhter,² Muhammad Siddiq,² Rumana Qureshi,² Arshad S. Bhatti¹

¹Department of Physics, COMSATS IIT, Islamabad, Pakistan

²Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan

Correspondence to: Z. Akhter (E-mail: zareenakhter@yahoo.com)

ABSTRACT: A conducting poly(azomethine)ester was prepared by solution phase polycondensation of a preformed Schiff base, 4-((4-(4-hydroxybenzylideneamino) phenoxy)phenylimino)methyl)phenol and isophthaloyl chloride (I). Different aliphatic/aromatic moieties were incorporated for examining their effect on the electronic properties of material. The resulting polymers (10^{-4} to 25 S cm^{-1}) were doped with silver (10^{-6} to $10^{-2} \text{ S cm}^{-1}$) and blended with polyaniline (10^{-1} to 13.4 S cm^{-1}) to enhance their electrical conductivity. Polymer/polyaniline blends had superior conductivity even at low polyaniline concentration relative to the silver-doped chains. The data obtained experimentally were complemented by density function theory at the 6–31G/B3LYP level. The results showed that ΔE along with lowest unoccupied molecular orbital and highest occupied molecular orbital electron density accounts for the electrical properties. Spectroscopic (¹HNMR, FTIR) and elemental analysis were used for structural elucidation. Structure–property relation in term of WXR, SEM-EDX, atomic force microscope, LLS, and thermal behavior was studied. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40698.

KEYWORDS: conducting polymers; polycondensation; poly(azomethine)ester; properties and characterization

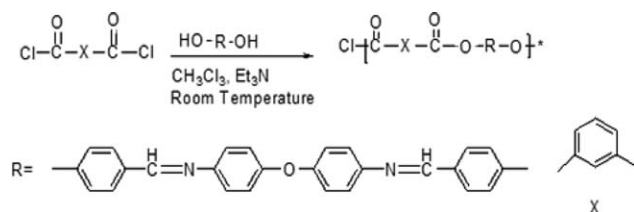
Received 9 December 2013; accepted 7 March 2014

DOI: 10.1002/app.40698

INTRODUCTION

The construction of poly(Schiff-base)s, a class of material comprises of Schiff base, via solution polycondensation is an area of extensive research in material chemistry. The resulting material offers exceptional properties such as high molecular weights, thermal stability, and high melting temperatures yet possess a disadvantage that they are insoluble in most of the common organic solvents owing to their strong chain–chain interaction.^{1–4} To overcome the problem of insolubility, different approaches are used like introduction of flexible aliphatic spacers in the main chain, pendent alkyl groups along the backbone, the copolymerization of different soft groups (aliphatic, alkyl, or siloxanes), and composite formation.^{5–8} The other approach is supramolecular modifications/dopant engineering of material. In this perspective, the dopants used are organic sulfonic acids, organic esters of phosphoric acids, sulfophthalic acid, or various substituted phenols, even though inorganic acids can also be used.⁹ This creates wide possibilities for the modification of properties of materials. These polymers have wide variety of applications in electronics and optoelectronics to synthesize organic batteries, electrode material, microelectronic devices, and electrochemical displays.^{9–11}

Moreover, poly(Schiff-base)s (esters, sulfones, imines, etc.) have ability to conduct electricity and, hence, are termed as semiconducting objects. Their ability to conduct electricity is slightly greater than those of normal organic compounds. The electrical conductivity of the polymer depends on the degree of conjugation as well as on the physical structure of the macromolecules. The conductivity of these organic compounds increases with the increase in the number of π -electron in the molecules which can be done by introducing electron donating molecules in the main chain. The conductivity can be introduced in the chain by the introduction of flexible spacers (methylene, silyl, etc) that favor denser packing.^{11–14} In addition, introducing the suitable dopant having compatibility with the host matrix adds electrons to the otherwise unfilled band. However, the introduction of such atoms which can engage free electrons or interrupt conjugation can decrease conductivity by increasing activation energy required for conduction. Silver having good conductivity when incorporated within a polymeric matrix can enhance its electrical conductivity drastically. Similarly, polyaniline (PANI) blends have attracted considerable scientific interest as lesser amount of PANI is required to enhance the conductivity of material.^{14–16} The geometric structure of the material is directly related to their



Scheme 1. Synthesis of the Poly(azomethine)ester (P).

functions. Therefore, studying the structure is very important as it allows to save a lot of time and money for various designs such as organic light-emitting diodes (OLEDs) and photovoltaic. However, only a handful of literature regarding density function theory (DFT) calculations for polymers is available whereas no such study for poly(azomethine)ester has been found so far.

The aim of the present study was to synthesize series of conjugated poly(azomethine)esters and their terpolymers having different aromatic, aliphatic, organic, and inorganic moieties and also to study and correlate the electrical behavior of the macrochains experimentally and theoretically (G03W, visualizing the geometry, electron density). In this context, DFT calculation of the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), and ΔE was carried out. In addition, structure–property relation in terms of solubility, surface morphology, thermal studies, and electrical behavior is discussed.

EXPERIMENTAL

Experimental Section

Materials. Isophthaloyl chloride (m.p. = 43–44°C), 4-hydroxybenzaldehyde (m.p. = 112–114°C), 4,4'-oxydianiline (m.p. = 188–192°C) *p*-toluene sulfonic acid (monohydrated, m.p. = 98–102°C, Fluka), 1,3-propan-diol (211–217°C, Sigma Aldrich), 1,6-hexan-diol (250°C, Sigma Aldrich), poly(dimethyl-siloxane), hydroxyl-terminated ($n = 550$) (Sigma Aldrich), (1,1,1,3,3,3-hexafluoro)bisphenol propane (160–163°C, Sigma Aldrich), and bisphenol A (158–159°C, Sigma Aldrich) were used as received. The solvents dichloromethane, ethanol (Sigma Aldrich), and dimethyl sulfoxide (Sigma Aldrich) used were purified according to the standard reported methods.¹⁷ G03W was used for DFT calculations at the 6–31G/B3LYP level to evaluate the energies of HOMO, LUMO and band gaps.

Equipment. Melting point was determined on a Mel-Temp. (Mitamura Riken Rogyo, Inc.) by using open capillary tubes. FTIR spectra in KBR pellets were recorded on a Perkin Elmer 1600 series FTIR spectrophotometer. Nuclear magnetic resonance was carried out by using Bruker Avance 300 digital NMR in DMSO- d_6 as solvent and tetramethylsilane as an internal standard. Elemental analyses were obtained on a Vaio-EL instrument. A commercial light-scattering spectrometer (BI-APD equipped with a BI9000AT digital Auto correlator) was used along with a He-Ne laser (output power ~ 400 mW at $\lambda = 638$ nm) as a light source. Relevant measurements were carried out at $25 \pm 0.1^\circ\text{C}$. The software used was BI-ISTW. X-ray diffraction was carried out on a Philip X-Pert PRO 3040/60 diffractometer equipped with Cu K α radiation source ($\lambda = 1.54$ Å) operated to

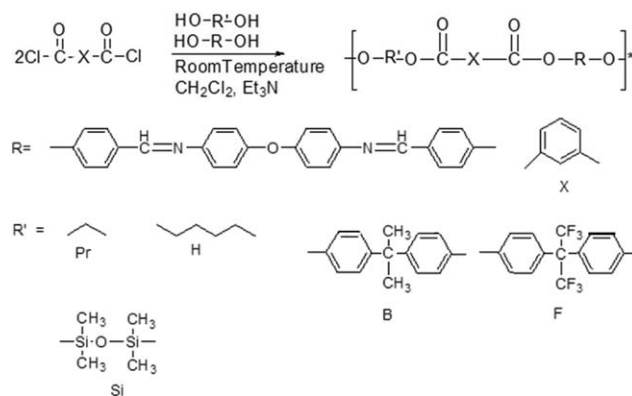
characterize the solid samples. Atomic force microscope (AFM) was performed by using an instrument of model Pco Scan having Si tip coated with Al in a tapPng mode. Tip size used was of 100 Å diameter, along with attachment of 200 micron long Cantilever. SEM-EDX studies were carried out by using model JSM 6460, EDX OXFORD model 7573. Thermal behavior of the polymers was studied in air using MettlerToledo, model thermogravimetric analysis (TGA)/SDTA 851e DSC 823e with a heating rate of $10^\circ\text{C min}^{-1}$ in nitrogen atmosphere. Electrical conductivity was measured by Keithley 2400 at room temperature pressure.

Methods. Synthesis of monomer, 4-((4-(4-(4-hydroxybenzylideneamino) phenoxy) phenylimino)methylphenol. The dihydroxy-terminated Schiff base monomer (SB), 4-((4-(4-(4-hydroxybenzylideneamino) phenoxy)phenylimino)methylphenol was synthesized and characterized following a previously reported method.¹⁸

Synthesis of polymer: (P). The polymer was prepared by the solution polycondensation of SB and isophthaloyl chloride (I) in a three-necked round-bottom flask fitted with reflux condenser, hot plate, magnetic stirrer, and ice bath under inert atmosphere (N_2). The SB and diacid chloride (I) were taken in 250 mL round-bottom flask in 50 mL dried dichloromethane in the ratio 1:1 at 0°C . It was followed by the addition of 3–4 mL triethyl amine with constant stirring. The reaction mixture was stirred for 24 h at room temperature and then refluxed for 1 h. Yellow colored precipitates of polymer were filtered, washed several times with water followed by ethanol, dried in air and then weighed,¹⁸ Scheme 1.

IP: 538, yellow powder, 86%, FTIR (cm^{-1} , KBr) 3122 (arom-CH), 1734 (C=O), 1106 (—O—), 1629 (—N=CH—). ¹HNMR [(DMSO- d_6) δ (ppm), deuterated dimethyl sulfoxide (protonated): 8.4 (2H, s, azomethine), 7.48–6.9 (aromatic), 2.4 (3H, s, methyl), 2 (1H, s, alcohol), Elemental analysis, calcd; (C 75.01, H 4.45, N 5.43), found;(C 75.84, H 4.09, N 5.20).

Synthesis of terpolymers: (PPr, PH, PB, PF, PSi). The terpolymers were produced via solution polycondensation in a 100 mL round-bottom flask fitted with a reflux condenser and hot plate. Monomers, SB, and the diol (Pr, H, Si, B, or F) were added in flask in dried dichloromethane. The stream of dried N_2 gas was purged into the reaction flask from the gas inlet. The reaction



Scheme 2. Synthesis of the terpolymers (PPr, PH, PB, PF, PSi).

was carried out at 0°C in an ice bath. 4–5 mL triethyl amine was added drop wise to the flask followed by the addition of diacid chloride (isophthaloyl chloride, I). The ratio of the reactants, SB, diol (HOROH, where R is defined in the Scheme 2) and the diacid (I) taken was 1:1:2. The reaction mixture was stirred for 24 h and then refluxed for 1 h. Yellow colored precipitates of the polymer were filtered and washed several times with water to remove diethyl ammonium chloride and then with ethanol to eliminate impurities,¹⁸ Scheme 2.

PF; 742, yellow powder, 87%, FTIR (cm⁻¹, KBr): 3100 (arom-CH), 1750, 1765 (C=O), 1030, 1040 (—O—), 1640, 1647(—N=CH—). ¹HNMR [(DMSO-d₆) δ(ppm), deuterated dimethyl sulfoxide (protonated): 8.78 (2H, s, azomethine), 7.88–7.3 (aromatic, m), 2.6 (3H, s, methyl), 2.1 (1H, s, alcohol). Elemental analysis, calcd; (C 79.24, H 4.04, N 3.65), found; (C 79.10, H 4.10, N 3.65)

PB; 748, yellow powder, 88%, FTIR (cm⁻¹, KBr): 3130 (arom-CH), 1750, 1765 (C=O), 1020, 1015 (—O—), 1625, 1629 (—N=CH—). ¹HNMR [(DMSO-d₆) δ(ppm), deuterated dimethyl sulfoxide (protonated): 8.46 (2H, s, azomethine), 7.43–7.1 (aromatic, m), 2.33 (6H, s, methyl), 2.6 (3H, s, methyl), 2.1 (1H, s, alcohol). Elemental analysis, calcd; (C 79.61, H 4.80, N 3.74), found;(C 79.87, H 5.01, N 3.83)

PH; 638, yellow powder, 87%, FTIR (cm⁻¹, KBr): 3120 (arom-CH), 2020 (aliphatic-CH), 1705, 1710 (C=O), 1030, 1050 (—O—), 1650, 1653 (—N=CH—). ¹HNMR [(DMSO-d₆) δ(ppm), deuterated dimethyl sulfoxide (protonated): 8.23 (2H, s, azomethine), 7.5–6.8 (aromatic, m), 2.6–2.1 (12H, m, methylene) 2.6 (3H, s, methyl), 2.2 (1H, s, alcohol). Elemental analysis; (C 75.23, H 5.33, N 4.42), found; (C 75.48, H 5.74, N 4.42)

PPr; 596, yellow powder, 89%, FTIR (cm⁻¹, KBr): 3120 (arom-CH), 2910 (aliphatic-CH), 1710, 1710 (C=O), 1020, 1090 (—O—), 1670, 1674 (—N=CH—). ¹HNMR [δ, deuterated dimethyl sulfoxide (DMSO-d₆)] δ (ppm) (protonated). ¹HNMR [(DMSO-d₆) δ(ppm), deuterated dimethyl sulfoxide (protonated): 8.3 (2H, s, azomethine), 7.5–7.0 (aromatic, m), 2.4–2.0 (6H, m, methylene), 2.1 (3H, s, methyl), 2.0 (1H, s, alcohol). Elemental analysis, calcd; (C 74.5, H 4.70, N 4.70), found; (C 74.87, H 4.83, N 4.91)

PSi: yellow powder, 86%, FTIR (cm⁻¹, KBr): 3150 (arom-CH), 2990 (aliphatic-CH), 1700, 1708 (C=O), 1010, 1025 (—O—), 1640, 1643 (—N=CH—). ¹HNMR [(DMSO-d₆) δ(ppm), deuterated dimethyl sulfoxide (protonated): 8.4 (2H, s, azomethine), 7.2–6.7 (aromatic, m), 2.1–1.6 (m, methyl) 2.6 (3H, s, methyl), 1.9 (1H, s, alcohol).

Silver Doping. The atomic silver was incorporated (by wt %) into the matrix of poly(azomethine)esters and their terpolymers. The polymer was weighed and suspended in DMF in a beaker. A 1:1 molar solution of silver nitrate and formaldehyde was added to the mixture with continuous stirring in a dark room. The mixture was stirred for an hour and then left in the dark for 24 h.¹⁹ It was filtered, washed several times with water, dried in air and then in an oven at 40°C for 6 h. EDX analysis was carried out to check the silver contents incorporated in the

polymer matrix. The doped material was compressed into pellets under a 5-ton load for conductivity measurements.

Synthesis of PANI. PANI was prepared according to the reported method.^{15,16}

PANI Blending. PANI/poly(azomethine)ester were taken in the weight ratio percentage 1:9. The powder was ground/blended properly in a crucible for homogenous mixing, dried in an oven at 40°C for 6 h. The blended material was compressed into pellets under a 5-ton load for conductivity measurements.¹⁶

RESULTS AND DISCUSSION

The SB-containing terminal diol was prepared based on previously published procedure given in supporting information.¹⁴ Poly(azomethine)ester (P) was synthesized in good yield using low temperature solution condensation polymerization (in dichloromethane, without catalyst) of monomers isophthaloyl chloride and 4-((4-(4-(4-hydroxybenzylideneamino)phenoxy)-phenylimino)methyl)phenol (SB). After that a series of terpolymers was synthesized by adding different fragments of diols in the macrochain using one-pot three-reactant reaction in an *in situ* process for comparison and to study the electrical properties of material. The material was solubilized by protonating with *p*-sulfonic acid. The low reflux temperature was used to prevent unwanted reaction and to assure reaction by dissolving diols completely in the solvent.²⁰ The FTIR and NMR techniques were used to confirm the functionalities present in the synthesized monomer (SB), polymer (P), and their terpolymers (PE, PB, PH, PPr, PSi). Significant changes were observed in the spectral properties of initial compounds and product as some of the signals disappeared and some new appeared.

Polymer (P) and its terpolymers containing different spacers were found to be insoluble in all organic and inorganic solvents owing to the presence of rigid, bulky aromatic groups in the main chain.⁹ The lone pair of electrons on the nitrogen atom, in the azomethine linkage has strong affinity for electrophiles. These receptor and substrate type of interactions help to modify the properties of polymers by forming branched/comb-like structures in which side chains have the ability to interact electrostatically with their surroundings. The dopant used in this case to dissolve poly(azomethine)esters was *p*-toluene sulfonic acid.⁹ The material becomes completely soluble in DMSO and sparingly in THF, ethanol, and methanol.

The structure of synthesized poly(azomethine)esters were confirmed by the presence of characteristic absorption peaks in their respective areas. Absorption peaks for (C=O) and (C—O) in range 1720–1750(s) cm⁻¹ and 1101–1200(s) cm⁻¹, respectively, confirmed the presence of ester linkage in the poly(azomethine)ester, P. The additional peak in the region 1600–1645(s) cm⁻¹ confirmed the existence of azomethine linkage in the macrochain. The absence of a broad peak in the region 3400 cm⁻¹ along with the presence of C—Cl peak around 780–540 cm⁻¹ confirmed the presence of diacid groups at the terminals of the macrochain.

Two symmetric peaks present in the ester and azomethine region in each terpolymer confirm the successful incorporation

Table I. Laser Light-Scattering Results of Poly(azomethine)ester and Its Terpolymers in DMSO at 25°C

Polymer	M_w (g mol ⁻¹)	$\langle R_g \rangle$ (nm)	$A_2 \cdot 10^{-4}$ (cm ³ mol g ⁻²)	$\langle R_h \rangle$ (nm)	$\langle R_g \rangle / \langle R_h \rangle$
P	2.30×10^5	260	6.0	140	1.80
PH	1.85×10^5	211	7.10	200	1.0
PB	1.10×10^5	25	-	-	-
PSi	3.00×10^4	190	2.0	112	1.70
PF	1.25×10^5	86	2.21	-	-
PPr	1.52×10^5	188	6.50	90	2.0

*The specific refractive index increment, $dn/dc = 0.097$ mL g⁻¹ for all the polymers.

M_w Weight average Molecular Weight of the Polymers.

$\langle R_g \rangle$ Radius of gyration.

A_2 Second virial Coefficient. The relative errors are: dn/dc , $\pm 1\%$, M_w , $\pm 5\%$, $\langle R_g \rangle$ & A_2 , $\pm 10\%$.

of diols in the parent chain. The FTIR spectra showed specific peaks related to added diols in addition to the peaks common to all spectra. The aliphatic absorption band (C—H aliphatic) appeared around 3000–2900 cm⁻¹ in the spectra of PH and PPr. The characteristic FTIR absorption peaks for (Si—O—Si) group present in PSi appeared as doublet around 1020 cm⁻¹ and 2900 cm⁻¹. The presence of aromatic C—H in polymers PF and PB, was confirmed by the presence of peak around 3100 cm⁻¹ indicating successful incorporation of diols in the parent chain. Occurrence of C—Cl absorption band in the range 780–540 cm⁻¹ along with the disappearance of hydroxyl group peak in all poly(azomethine)ester and its condensation terpolymers revealed that they have acid chloride group at the terminal.¹⁹

Structural analysis of poly(azomethine)ester (P) and their terpolymers was carried out using ¹H NMR spectroscopy. The study was carried out after protonation of samples with *p*-toluene sulfonic acid, in solvent DMSO, using TMS as internal reference to confirm their structures. ¹H NMR showed the presence of all types of proton expected for the proposed structures. Signals in the range 8.3–8.7 ppm, common to all spectra, were attributed to the presence of HC=N proton, whereas the resonance that appeared in the range 6.9–7.9 ppm confirmed the presence of aromatic protons. In addition to these signals which were common to all the spectra, the polymers having aliphatic diol-derived moieties (Pr, H) showed multiplet signal in the range 0.7–2.3 ppm (aliphatic —CH). The polymer (PB) showed additional signals in the range 7.0–8.0 ppm (additional aromatic rings of added diols) and 2.3 ppm (—CH₃ present in bisphenol A). PF showed resonance around 7.4–8.1 (aromatic

rings), slightly deshielded owing to the presence of electronegative F (CF₃) in the diol added. PSi exhibited additional resonance peaks at 1.9–2.1 (CH₃ attached to Si). The signal present in the range 2–2.5 (—CH₃) and 2–2.2 (OH) confirms the protonation in the main chain. The OH group appeared at the lower field owing to the magnetic anisotropy of the aromatic ring present in the *p*-toluene sulfonic acid group.^{9,19}

Elemental analysis was carried out to confirm the stoichiometry of the polymeric material. The calculations were made on the basis of structure of repeat units present in the polymer chain.²¹ The data for C, H, and N content in polymers were found to be in relatively good agreement with the presumed structure for the condensation terpolymer. The Si in the copolymers having poly(dimethylsiloxane), hydroxyl-terminated ($n = 550$) reacts with C at high temperature to make ceramic material. Therefore, their elemental analysis was not possible^{6,14} and such polymers are currently investigated as precursor to ceramic materials.

The surface imaging was done by Pco Plus AFM in tapping mode using Si cantilevers coated with Al under ambient conditions. Multiple scans were made for each sample covering different areas both from right to left and left to right. The surface of P sample is composed of granular-like planar macrostructure, with a difference of 0 ± 18 nm in heights. The rms value of surface roughness of P obtained from images is approximately 17 nm, whereas that of the terpolymer, Psi, is 53 nm. The difference in the rms of the parent polymer and their terpolymers

Table II. Thermal Analysis Data for PAMEs

Polymers	T_{10} (°C)	T_{50} (°C)	T_F (°C)	Residue C (%)	T_g (°C)
P	360	512	710	11	249
PPr	251	446	675	5	210
PH	170	410	640	8	203
PSi	168	270	790	3	57
PF	298	543	731	12	255
PB	310	530	723	10	277

Table III. Conductivity Measurements (S cm⁻¹) of Poly(azomethine)esters

Polymer	Neat (S cm ⁻¹)	Silver-doped (S cm ⁻¹)	PANI/PAME (S cm ⁻¹)
P	3×10^{-12}	2.4×10^{-4}	1.3×10^{-1}
PSi	5×10^{-13}	4.1×10^{-5}	3.1×10^{-4}
PPr	6×10^{-14}	7.4×10^{-5}	5.4×10^{-5}
PH	4×10^{-14}	5.3×10^{-6}	5.3×10^{-5}
PB	1.7×10^{-11}	2.3×10^{-2}	13.4
PF	4×10^{-12}	3.3×10^{-2}	3.3×10^{-1}

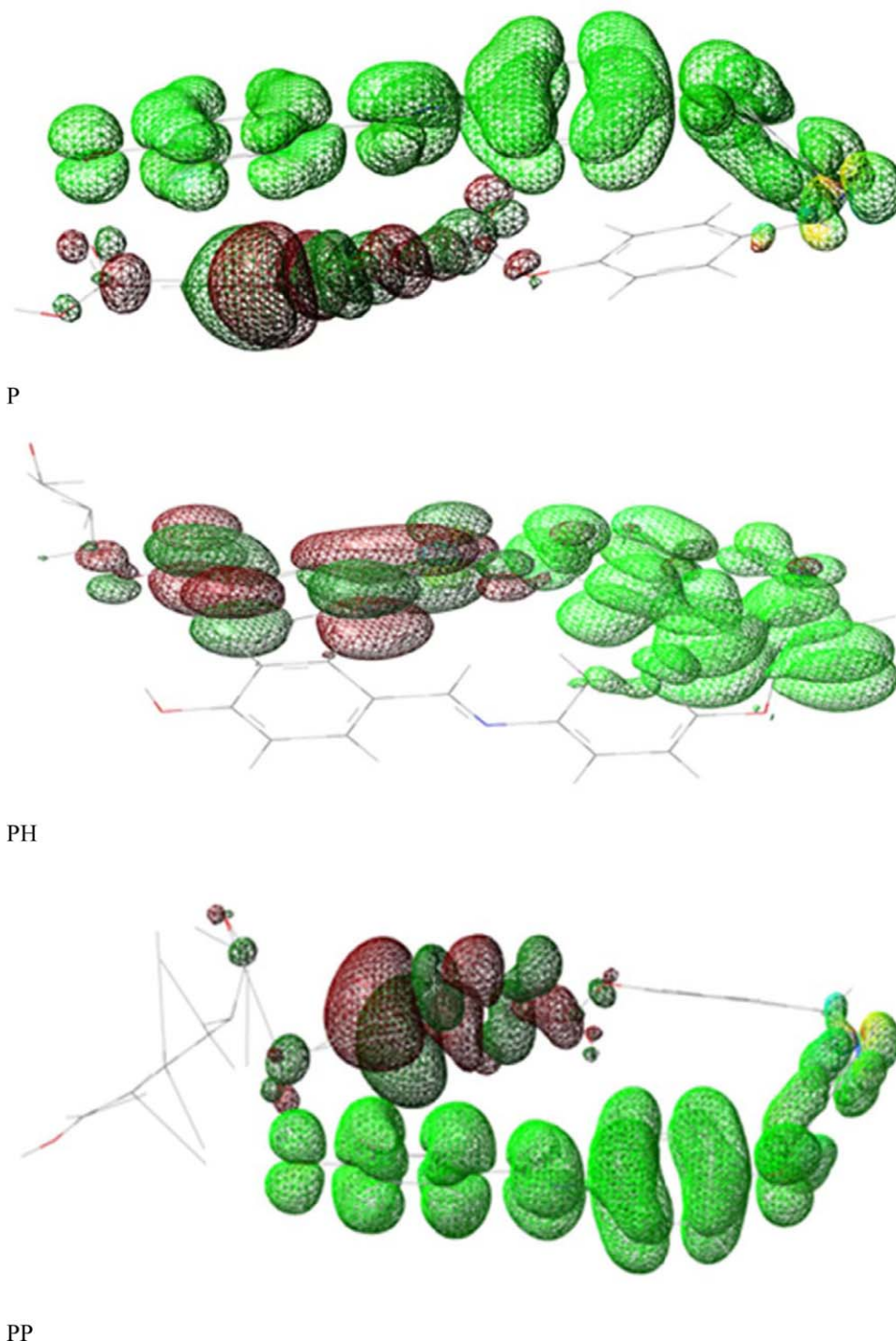


Figure 1. LUMO and HOMO orbitals of P and respective terpolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

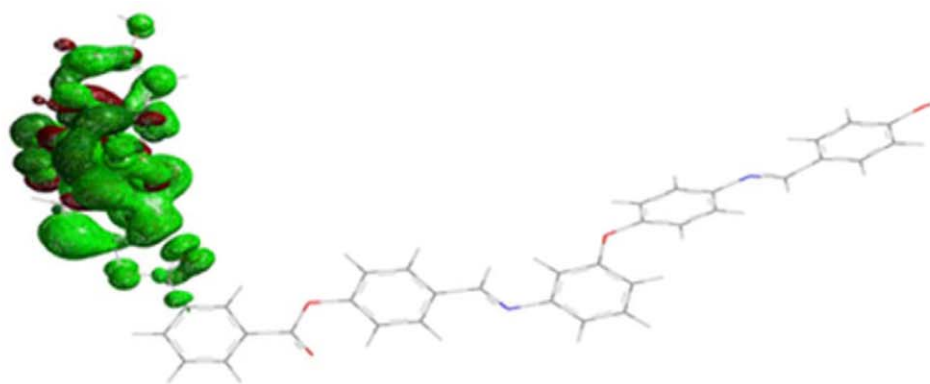
showed successful incorporation of diols in the parent polymer chain. Also the rms of terpolymer was different from other indicating their effect on the surface modification of the polymers.

Both static and dynamic laser light-scattering analysis was carried out to determine molecular parameters, Table I. The PAMEs were found to have high molecular weight of order 10^5 (g mol^{-1}). The results obtained showed that there is no regular variation in the

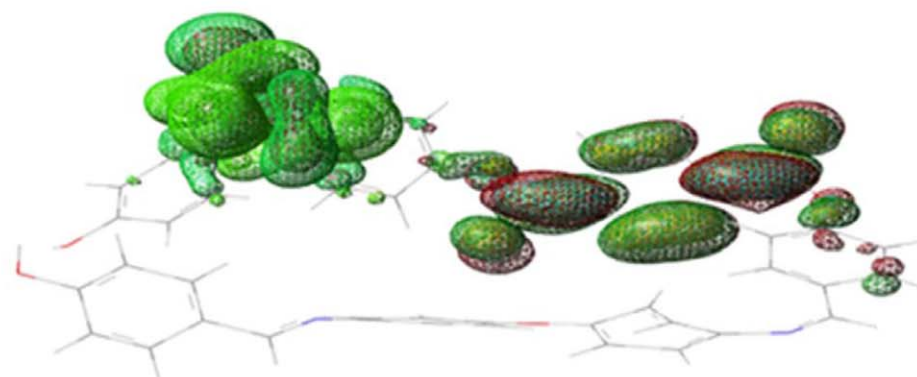
hydrodynamic radii for various polymers with molecular weight. The ratio of $\langle R_g \rangle / \langle R_h \rangle \sim 1.0\text{--}2.0$ indicates that the polymers have a coil chain conformation in the solvent used.^{22–25}

Thermal Studies (TGA and DSC)

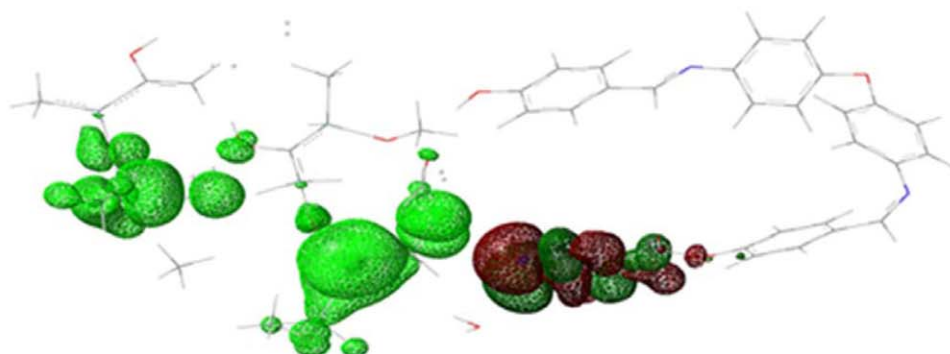
The thermal stability of P and its respective terpolymers was studied using TGA. TG curves of the material were recorded and the results are summarized in Table II. The stability was



PF



PB



PSi

Figure 1. Continued

evaluated with 10% and 50% weight loss under N_2 atmosphere; range found was 168–360°C and 270–543°C, respectively. Also it can also be seen that the value of T_{10} temperature increases with the increase in hardness of the chain.

The diols added to the parent chains showed their influence on the decomposition pattern. The chains having bulky aromatic groups are more stable and less susceptible to the foreign impact. However, one having methylene and silyl spacers are less stable and more prone to the foreign impact.^{26–28} The polymer having

diol, bisphenol A was more stable as compared to their parent chain (P) owing to the presence of stable isopropylidene group in the terpolymer (PB). The analogue (PF) based on (1,1,1,3,3,3-hexafluoro)bisphenol propane was less stable as highly oxidizable hexafluoroisopropylidene is present in the main chain. Among the other three terpolymers, the material having 1,3-propan-diol (Pr) is more stable than the one based on 1,6-hexan-diol and the least stable is poly(dimethylsiloxane), hydroxyl-terminated ($n = 550$) based polymer chain. The

Table IV. ΔE and HOMO/LUMO Coefficients

Polymer (S cm ⁻¹)	Energy (eV)	LUMO Coefficients
P	HOMO = -0.12020 LUMO = -0.00980 $\Delta E = 0.1104$	0.00565, 0.00019, 0.00101, 0.00468, 0.00050, 0.05072, 0.07971, 1.4034, 0.24253, 0.32555, 0.17396, 0.08983, 0.11218, 0.04771, 0.06159, 0.11396, 0.6913, 0.09007, Holes 41
PSi	HOMO = 0.00135 LUMO = 0.00823 $\Delta E = 0.007$	0.02713, 0.00551, 0.00008, 0.00145, 0.00491, 0.00041, 0.05723, 0.11183, 0.03075, 0.17736, 0.09457, 0.34907, 0.00608, 0.04103, 0.11639, 0.05764, 0.05451, Holes 94
PPr	HOMO = -0.07116 LUMO = -0.06022 $\Delta E = -0.01094$	Holes 54
PH	HOMO = -0.18816 LUMO = -0.09643 $\Delta E = -0.09173$	0.01675, 0.00141, 0.00136, 0.00569, 0.00056, 0.35640, 0.13401, 0.40809, 0.24041, 1.27886, 0.3104, 0.76343, 0.03409, 0.15691, 0.05944, 0.07742, 0.08968, 0.13134, 0.10697, Holes 73
PB	HOMO = -0.08514 LUMO = -0.07504 $\Delta E = 0.0101$	1.623, 76343, 0.03409, 0.15691, 0.21846, Holes 83
PF	HOMO = -0.22249 LUMO = 0.01536 $\Delta E = -0.20713$	0.03198, 0.88295, 0.18016, 0.04488, 0.06884, 0.05776, 0.04672, 0.15046, 0.49585, 0.0717, 0.21846, 0.06387

poly(dimethylsiloxane), hydroxyl terminated ($n = 550$) in the chain give it a freedom of rotation, therefore, they have minimum stability. Based on literature, it is known that Si-CCO group is very sensitive toward both hydrolysis and alcoholysis occurring readily in the absence of acid/base catalysts. The fact was also evident from FTIR studies at different time. In case of Si-containing terpolymers, the reduction of bands assigned to the silyl ester group with times was a result of hydrolysis that occur the influence of humidity in the environment which resulted in the formation of their respective diacid and diols. Therefore, these polymers (PSi) were found biodegradable. The H-bonding present in the poly(azomethine)ester that had azomethine beside ester linkage gave stability to the chain. The TGA curves revealed a multistage process as reported earlier²³ which probably included pyrolytic cleavage of the (azomethine)ester.^{26,27,29} The DSC analysis was carried out at the heating rate of 10°C min⁻¹. The glass transition temperature (T_g) of PAME are listed in Table II. T_g values of the material varied from 277 to 57°C. It is of interest to note that the T_g s of the macrochains having hard segments are shifted to the higher temperature regions, whereas the presence of flexible segments result in a decrease in T_g . The thermograms revealed that the parent polymer chain, P exhibited T_g 249, owing to the presence of bulky aromatic aryl groups, however, its lower glass transition temperature as compared to PB was attributed to the presence of flexible aryl ether linkage. PB had glass transition temperatures T_g 277°C due to the presence of bulky isopropylidene groups in the main chain. PF having the oxidizable hexafluoroisopropylidene group had relatively lower T_g 255°C owing to the presence of six "F" in each unit. PH exhibiting six methylene units had T_g 203°C lower than PPr (210°C) having three methylene spacers. The increasing number of methylene spacers in the main chain decreased the stability of the chain and vice versa. The presence of Si and methyl groups in PSi reduces the value of T_g to 57°C which is minimum among all the spacers. It is known that Si has ability to increase the freedom of

rotation of the main chain. The addition of different groups in the main chain resulted in decreased thermal stability.^{26,27}

Electrical Properties

The material was compressed in the pellets of equal dimensions to study its conducting behavior at room temperature. The influence of the presence of different diols in the case of condensation terpolymers was also studied, Table III. It is known that the valence electrons in sp³ hybridized orbitals have low mobility and do not contribute to the electrical conductivity of the material. However, in conjugated materials, the situation is that they have backbones of connecting sp²-hybridized carbon centers having a valence electron on each center in a p_z orbital. The poly(azomethine)esters having continuous conjugation in the chain (P and PB) were more conducting as compare to PF due to the presence of highly electronegative hexafluoroisopropylidene group in the chain. The polymers incorporating methylene and silyl spacers exhibited the lowest conductivity. Based on literature, undoped polymers usually have energy gap > 2 eV, which is too great for conduction, therefore, they usually have low conductivity. Polymers were doped with silver and blended with PANI. The trend of conductivity was found same as was in neat material, however, the material blended with PANI were more conducting than the doped one³⁰⁻³² that lesser amount of PANI as compared to silver is required to increase the conductivity, Table III.

Despite intensive research, the relationship between morphology, chain structure, and conductivity is still poorly understood. It is assumed that conductivity should be higher for the higher degree of crystallinity and better alignment of the chains; however, this could not be confirmed for PANI, which is amorphous in nature.

DFT Calculations

To provide further insight into the electrical behavior, DFT calculations were carried out at 6-31G/B3LYP level, Figure 1 and Table IV. The calculations were carried out for a repeat unit

from each macrochain. It is known that the electrical conductivity of the polymer is correlated to the difference of energy (ΔE) between the HOMO and LUMO orbitals.

Also that, higher value of LUMO coefficient means greater electron density on excitation and, hence, more will be the ability of the material to conduct. Similarly, the HOMO coefficients of the atoms are examined to see the presence of intrinsic holes which also play important role in conduction. Electrical conductivity of P was $3 \times 10^{-12} \text{ S cm}^{-1}$, Table III. The theoretical calculations showed, P has low value of ΔE (0.1104 eV) and most of the connecting centers in the chain have significant LUMO electron densities and holes, therefore, has more conductivity as compared to other polymers (except PF). Despite having lower value of ΔE (0.007 eV) as compared to P, the conductivity for P*Si* ($4.9 \times 10^{-13} \text{ S cm}^{-1}$) was less owing to almost zero LUMO electron density at certain centres. The ΔE value for P*Pr* and P*H* was 0.01094 and 0.09173 eV, respectively, indicating easier excitation of electrons from HOMO to LUMO, still they have lower conductivity as compared to P, that is, (6×10^{-14} and $4 \times 10^{-14} \text{ S cm}^{-1}$) which is in accordance to the experimental results, Table III. The polymer P*B* had ΔE , 0.0101 eV, hole 83, and very high value of LUMO coefficient (1.623) and, hence, has highest conductivity amongst all. The polymer P*F* had a relatively greater ΔE and was less conductive than P*B*. It was concluded that difference of energy between HOMO/LUMO orbitals along with their coefficient account for the electrical behavior of the material also the theoretical results obtained were in good agreement with the experimental data.

CONCLUSIONS

A low-temperature solution polycondensation technique was used to synthesize conjugated, thermally stable poly(azomethine)esters. Electrical behavior of the material was studied, and the effect of the presence of different sequences in the terpolymer was evaluated. It was found that the polymers with continuous conjugation and symmetric units in the chain were more conducting as compared to the others. The doped and blended material showed drastic increase in conductivity; however, a lesser amount of PANI is required to increase the conductivity of the material. Therefore, the study can help to design material with small band gaps, more electron density, and holes resulting in significant technological progress in next generation organic field effect transistor, OLEDs, and flexible photovoltaic material.

ACKNOWLEDGMENTS

The authors are grateful to Quaid-i-Azam University, Islamabad, Pakistan, for financial, technical, and laboratory facilities.

REFERENCES

1. Marin, L.; Cozan, V.; Bruma, M. *Polym. Adv. Technol.* **2006**, *17*, 664.
2. Gutch, P.; Banerjee, S.; Gupta, D. C.; Jaiswal, D. K. *J. Polym. Sci. Part A: Polym. Chem.* **2001**, *39*, 383.
3. Miyake, J.; Chujo, Y. *Macromolecules* **2008**, *41*, 5671.
4. Marin, L.; Cozan, V.; Bruma, M.; Grigoras, V. C. *Eur. Polym. J.* **2006**, *42*, 1173.
5. Wenz, G.; Steinbrunn, M. B.; Landfester, K. *Tetrahedron* **1997**, *53*, 15575.
6. Haraha, A. *Adv. Poly. Sci.* **1997**, *133*, 92.
7. Whang, D.; Kim, K. *J. Am. Chem. Soc.* **1997**, *119*, 451.
8. Grigoras, M.; Farcas, A. *J. Optoelectron. Adv. Mater.* **2000**, *2*, 525.
9. Iwan, A.; Sek, D. *Prog. Polym. Sci.* **2008**, *33*, 289.
10. Garrett, C. G. B. In *Semiconductors*; Hannay, N. B., Rheinhold, Eds.; Publishing Co: New York, **1959**; Chapter 15 p. 31.
11. Terenin, A. N. *Mendeleeva* **1960**, *5*, 498.
12. Terenin, A. N. *Proc. Chem. Soc.* **1961**, 321.
13. Terenin, A. N.; Kallman, H. M. In *Symposium on Electrical Conduction in Organic Solids*, U.S. Army Research Office (Durham), Eds.; Silver Durham, **1961**; p.39.
14. Lyons, L. E. *Physics and Chemistry of the Organic Solid State*; Interscience, New York, **1963**; p 745.
15. Kaya, I.; Koça, S. *Int. J. Polym. Mater.* **2007**, *56*, 197.
16. Kumar, L. R.; Sengodan, V.; Prasad, M. B.; Gopalakrishnan, K. *Mater. Lett.* **2002**, 167.
17. Armarego, W. L. F.; Chai, C. L. *Purification of Laboratory Chemicals*; Butterworth Heinemann: London, **2003**.
18. Gul, A.; Akhter, Z.; Bhatti, A. S.; Siddiq, M.; Khan, A.; Siddiqe, H. M.; Janjua, N. K.; Shaheen, A.; Sarfraz, S.; Mirza, B. *J. Organomet.Chem.* **2012**, *719*, 41.
19. Pavia, D. L.; Lampman, G. M.; Kriz, G. S. *Introduction to Spectroscopic*, 3rd ed.; Thomson Learning Inc.: New York, **2001**.
20. Zhang, G.; Wu, C. *Adv. Polym. Sci.* **2006**, *195*, 101.
21. Akhter, Z.; Khan, M. S.; Bashir, M. A. *Appl. Organometal. Chem.* **2005**, *19*, 848.
22. Zimm, B. H. *J. Chem. Phys.* **1948**, *16*, 1099.
23. Siddiq, M.; Wu, C.; Shuqin, B.; Chen, T. *Macromolecules* **1996**, *29*, 3157.
24. Schmidt, M.; Stockmayer, W. H. *Macromolecules* **1984**, *17*, 509.
25. Khan, A.; Farooqi, Z. H.; Siddiq, M. *J. Appl. Polym. Sci.* **2012**, *2*, 951.
26. De Souza, A. C.; Pres, A. T.; Soldi, V.; *J. Therm. Anal. Calorim.* **2002**, *70*, 405.
27. Eldes, Sajo, I. *High Perform. Polym.* **2002**, *14*, 397.
28. Tripathi, S.; Vasudev, I.; Ray, A. *J. Macromol. Sci. Phys.* **2011**, *50*, 1196.
29. Cazacu M, Racles M, Vlad A, Marcu M. *Eur. Polym. J.* **2007**, *37*, 2465.
30. Shukla, U.; Rao, K. V.; Rakshit, A. K. *J. Appl. Polym. Sci.* **2003**, *88*, 153.
31. Devi, U.; Sharma, A. K.; Rao, V. V. R. N. *Pure Appl. Chem.* **2002**, *74*, 857.
32. Kazakov, S. V.; Galaev, I. Y.; Mattiasson, B. *Int. J. Thermophys.* **2002**, *23*, 161.
33. Racles, C.; Cozan, V.; Sajo, I. *High Perform. Polym.* **2007**, *19*, 541.
34. Wong, B. M.; Cordaro, J. G. *J. Phys. Chem. C* **2011**, *115*, 18333.