

Synthesis and Properties of Composites of Oligoazomethine with Char

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ABSTRACT: Conjugated aromatic oligo(azomethine) derivatives (oligo-AMs) were prepared by the condensation of terephthaldehyde 4,4'-diformylbiphenyl bis(4-formylphenyl) ether and *p*-phenylene diacrolein with 1,4-diaminobenzene at room temperature. The structures of the synthesized oligomers were characterized by FTIR, ¹H-NMR, TGA-DTG, UV-vis absorption spectra, and elemental analyses. Additionally, in this study, the oligomer com-

posites were obtained using the carbon material (char) derived from the 450°C pyrolysis of waste polyethylene terephthalates. The conductivity measurements of the produced composites were determined at 24-h periods by doping with iodine vapor. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 815–823, 2012

Key words: oligo(azomethine); char; conductivity; composites

INTRODUCTION

The first poly(azomethines) were prepared by Adams et al.¹ from terephthaldehyde and benzidine in 1923. The basic aromatic-conjugated poly(azomethine) is poly(1,4-phenylene methylidene-1,4-phenylene nitromethylidene) (PPI). In the past, there were also many studies performed on the synthesis of different polyazomethines.^{2–17}

Poly(azomethine)s (PAMs) with aromatic backbones are attractive high-performance conductive polymers with high thermal stability and excellent mechanical strength. In the recent years, the application of PAMs in organic electronics has been explored for light-emitting diodes, pH sensors, metal-collecting sites, etc.

However, their insolubility in common organic solvents limits their processability and characterization.

Therefore, the targeted PAMs often bear large alkyl, alkoxy, or aryloxy groups to improve solubility and lower their glass transition temperatures (T_g s) and thermal stability. Over the past 25 years, different methods have been adopted to produce processable PAMs by introducing various substituted benzene rings into the main chain.^{5,9–11}

In this study, the carbon material (raw char) was obtained by the pyrolysis of waste polyethylene terephthalate (PET) at 450°C, and the (oligoAM-char) composites were synthesized from oligomers that include phenylene, oxygen, and methylene in the main chain. The structures of the synthesized oligomers were clarified using FTIR and ¹H-NMR techniques. In this context, this work presents the results of an experimental study on the variations of electrical conductivity in oligoAM composites that use char mixtures (pyrolysis product) within the oligomer matrix.

EXPERIMENTAL

Terephthaldehyde (tfa), 4-fluorobenzaldehyde, NiCl₂, chlorobenzene, acetaldehyde, triphenyl phosphine, Zn, NaOH, DMSO, and DMF were obtained from Aldrich, while 4-hydroxybenzaldehyde and *p*-diaminobenzene were obtained from Merck and TCI Japan, respectively.

Synthesis of aldehydes

Apart from the tfa, the aldehydes used for oligomerization were synthesized according to the existing literature.^{18–20} Yellow, white, cream, and red-colored DAs are terephthaldehyde, 4,4'-diformylbiphenyl, bis(4-formylphenyl) ether, and *p*-phenylene diacrolein, respectively. ¹H-NMR spectrums of TFA and db aldehydes are shown in Figures 1 and 2.

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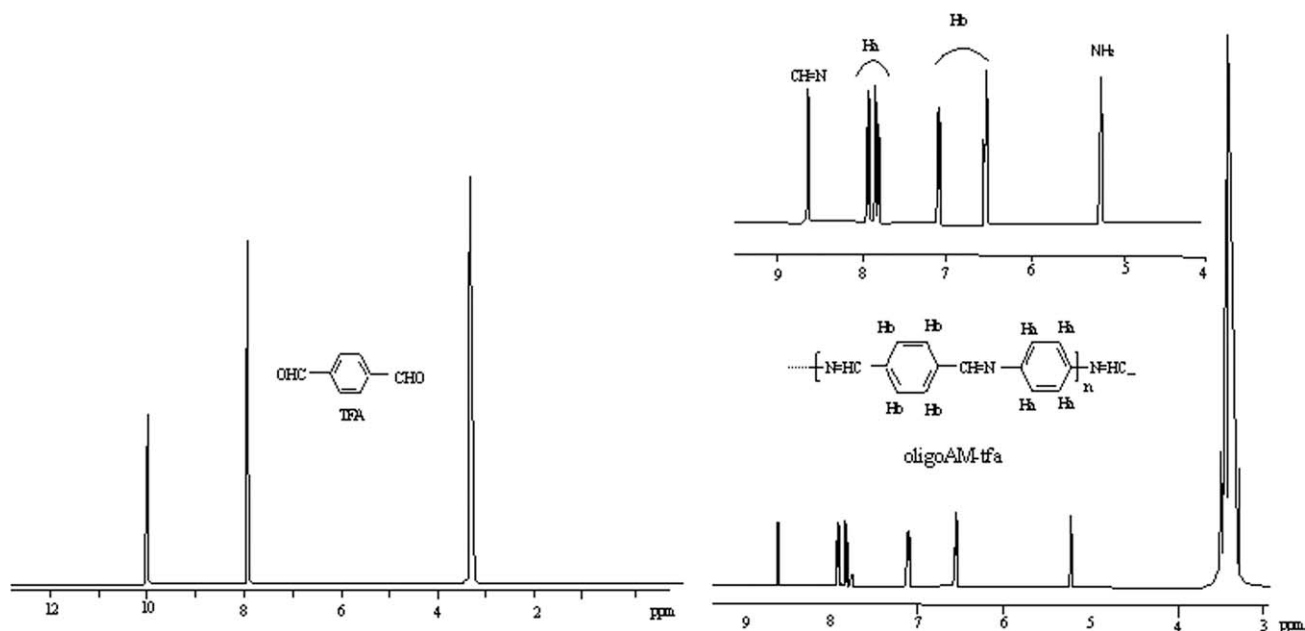


Figure 1 $^1\text{H-NMR}$ spectra of tfa and oligoAM-tfa.

Bis(4-formylphenyl)ether (o): (mp: 69°C , yield: 90%). $^1\text{H-NMR}$ (DMSO): δ 9.94 (d, 2H, $J = 7.1$ Hz), 7.97 hydrogen adjacent to formyl group (d, 4H, $J = 4.76$ Hz), 7.27 hydrogen adjacent to phenoxy group (d, 4H, $J = 5.01$ Hz). Anal. Calcd. for $\text{C}_{14}\text{H}_{10}\text{O}_3$ (%): C: 74.34, H: 4.42. Found: C: 74.68, H: 4.40.

4,4'-Diformylbiphenyl (db): (mp: 145°C , yield: 60%). $^1\text{H-NMR}$ (DMSO): δ 10.10 (m, 2H), 8.04 (q, 8H, $J = 7.01$ Hz). Anal. Calcd for $\text{C}_{14}\text{H}_{10}\text{O}_2$ (%): C: 80.00 H: 4.76 found: C: 79.72, H: 4.70.

β,β' -*p*-Phenylen-diacrolein (ppda): (mp: 164°C , yield: 52%) $^1\text{H-NMR}$ (DMSO): δ 10.0739 (d, 2H),

7.6511 (s, 4H, $J = 10.90$ Hz), 7.4804 (d, 2H, $J = 5.98$ Hz), 6.7962 (q, 2H, $J = 8.46$ Hz). Anal. Calcd for $\text{C}_{14}\text{H}_{10}\text{O}_2$ (%): C: 77.42 H: 5.38, O: 17.20 found: C: 77.45, H: 5.05, O: 17.24.

Oligomerization

A 50-mL flask rounded from the bottom was equipped with nitrogen inlet, dialdehyde (0.1 mol), and anhydrous ethanol (10 mL). The mixture was heated to dissolve the dialdehyde before an equivalent weight of 1,4-phenylene diamine was added slowly to the

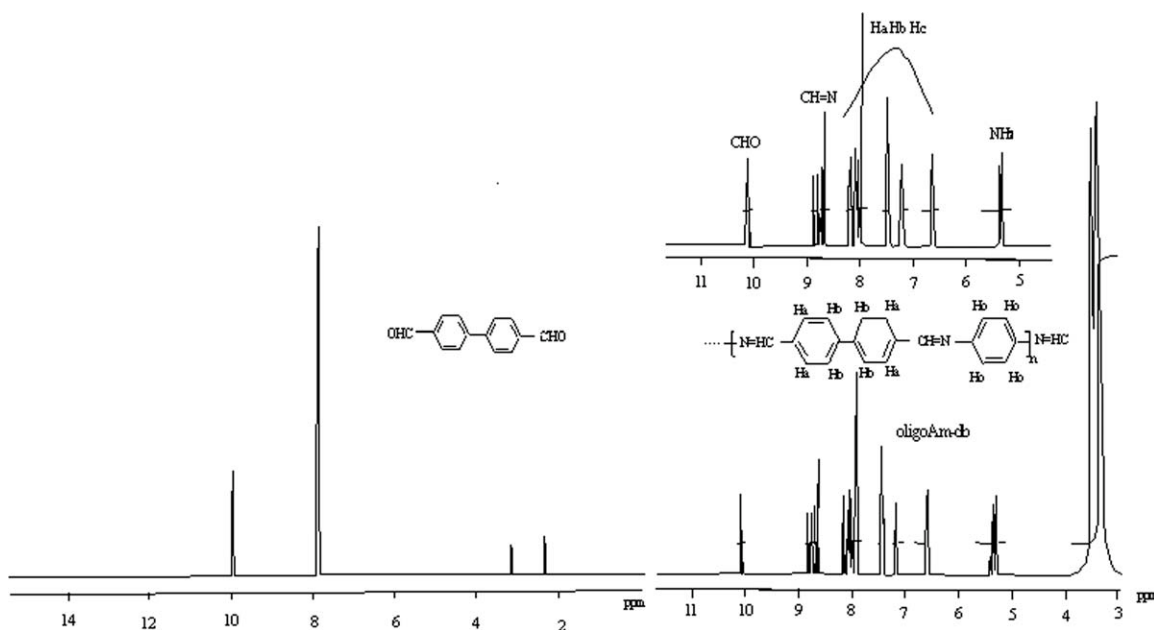
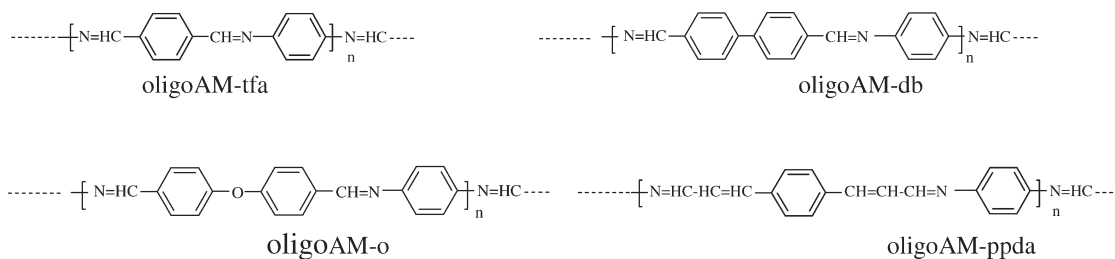


Figure 2 $^1\text{H-NMR}$ spectra of db and oligoAM-db.

TABLE I
Structures, Inherent Viscosity Values, Number-Average Molecular Weights (\bar{M}_n), and UV-vis Maxima of Synthesized Oligomers

Compounds	Yield (%)	Color	Inherent viscosity in H ₂ SO ₄ at 30°C (dL/g)	m.p. (°C)	(\bar{M}_n) DMF/MeOH eluent polystyrene standards	UV-vis, Maxima (nm)
oligoAM-tfa	72	Yellowish green	0.15	>300	860	290, 419
oligoAM-db	77	Light brown	0.17	>300	950	309, 396
oligoAM-o	68	Light brown	–	>300	–	–
oligoAM-ppda	84	Brown	–	>300	–	–



solution at 50°C temperature, and the mixture was stirred under N₂ atmosphere conditions for 2 h. After, the mixture was stirred for 3 h, the yellow oligomers were filtered, washed with water and methanol in turn, and dried at 100°C under vacuum through the night. The oligomers of lower molecular weight were removed by washing with water and lukewarm methanol. The viscosity measurements of obtained oligomers were carried out only for two oligomers until the final possible dissolution was provided. The melting points and ¹H-NMR spectrums of the oligomers differ from the aldehyde structures from which they were synthesized. The structures of the synthesized oligomers are shown in Table I.

Synthesis of OligoAMs-char composites

The char obtained by the pyrolysis of PET has weak acidic character. Over 300–400°C temperature range,

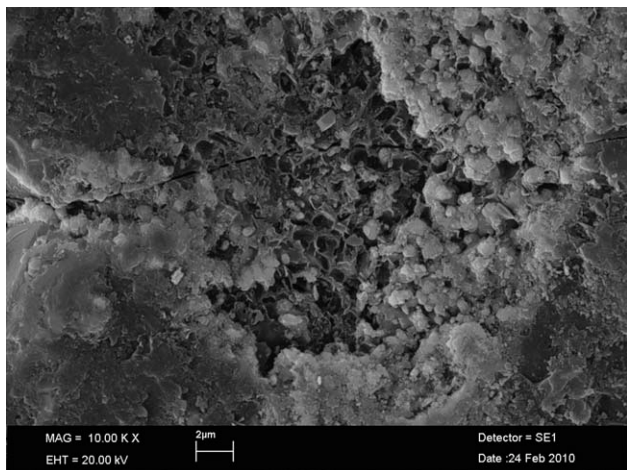


Figure 3 Scanning electron microscope image (SEM) of the carbon material (raw char) derived from the 450°C pyrolysis of waste PETs (polyethylene terephthalate).

the PET changes into a highly crosslinked polymer of terephthalic acid.²¹ The presence of terephthalic acid in char was detected by observing the weak peaks of 1709 and 3200 cm⁻¹ for –COOH group. FTIR spectrums data and the elemental analyses results of raw char are given in Table III.

Char was ground to obtain char powder before being mixed with oligoAMs, which was then placed into the molten matrix to result in a highly dense mixture. The obtained composite samples were allowed to cool inside the molds. The scanning electron microscope image of the carbon material (raw char) is given in Figure 3.

Measurements

The infrared spectra were measured with the Perkin-Elmer 1605 spectrum and FTIR system. The synthesized compounds were characterized by elemental analyses performed in the laboratories of the Scientific and Technical Research Council of Turkey (TUBITAK) for carbon, hydrogen, nitrogen, and sulfide. ¹H-NMR (Bruker Avance DPX-400) spectrums were recorded at 25°C by using DMSO as solvent and TMS as the internal standard. Thermal data were obtained using a Setaram SETSYS Evolution-1750 thermal analysis instrument. LC-MS analyses of oligomers were performed in the laboratories of the Ankara Test and Analysis Laboratory (ATAL/TUBITAK). The DTG-TGA measurements were performed between 20 and 900°C (in Ar, rate 10°C/min). M_n , M_w , and PDI were determined by SEC (Shimadzu Co. Japan) with a Macherey-Nagel GmbH and Co. (Germany; 100 Å and 7 nm diameter loading material) 7.7 mm i.d. × 300 mm columns, DMF/MeOH eluent (0.4 mL min⁻¹, v/v, 4/1), polystyrene standards, and a refractive index detector.

TABLE II
The Solubility Test Results of the Synthesized Oligomers (0.01 g in 5 mL)

Compounds	DMSO	DMF	CHCl ₃	Acetone	CH ₃ OH	H ₂ SO ₄	Toluene	Hexane
oligoAM-tfa	+/-	+/-	-	-/-	-/-	+/+	-	-
oligoAM-db	+/-	+/-	-	-/-	-/-	+/+	-	-
oligoAM-o	-/-	-/-	-	-/-	-/-	+/+	-	-
oligoAM-ppda	+/-	+/-	-	-/-	-/-	+/+	-	-

+ / +, soluble at room temperature; - / +, soluble at heating; - / -, insoluble.

The viscometric measurements were performed at a constant temperature of $25 \pm 0.5^\circ\text{C}$ using Oswald viscometers, and a four-probe method was applied to measure the conductivity of the oligomer. The relationships between char percentage versus measured conductivity and doped time versus measured conductivity were evaluated using regression analysis. The comparison of means among treatments was made again using the regression test. The results were analyzed using the computer program of Minitab Statistical Analysis System (Minitab 1995).

LC-mass analysis of oligomers

The oligomers synthesized in this study had lower molecular masses that can be seen by looking at the polymerization level from the ¹H-NMR spectrum. Because the molecular masses of oligoAM-db and oligoAM-tfa oligomers were less than 1500 g/mol, the LC-mass spectra of them were examined. Therefore, the mass spectra of oligoAMs displayed signals at 824 (*m/z*), 825(*m/z*) for oligoAM-tfa, 946 (*m/z*), 947 (*m/z*) for oligoAM-db corresponding to their molecular, and (*M* + 1)⁺ ion peaks, respectively. These molecular masses verified the polymerization level of oligomers as utmost four, and the separation of CN-Ar and -NAr groups from the structures of oligomers resulted in the formation of Ar-CH⁺ cation signal at *m/z*:91 finally.

GPC analysis of oligomers

\bar{M}_n , \bar{M}_w and PDI were determined by SEC (Shimadzu Co. Japan) using DMF/MeOH eluent (0.4

mL min⁻¹, v/v, 4/1) and polystyrene standards. GPC analysis could be performed only for dissolved amounts of the oligoazomethine-tfa and oligoazomethine-db oligomers of four synthesized oligomers, while the other oligomers could not be subjected to the same analysis due to dissolubility difficulties. The average molecular weights (\bar{M}_w), the number-average molecular weights (\bar{M}_n), and the polydispersity indices of oligoAM-tfa and oligoAM-db were obtained as 1.058×10^3 and 1.126×10^3 , 860 and 950, 1.231 and 1.186, respectively.

oligoAM-tfa : $\bar{M}_n = 860$, $\bar{M}_w = 1058$, and PDI = 1.231

oligoAM-db : $\bar{M}_n = 950$, $\bar{M}_w = 1126$, and PDI = 1.186

Solubility of oligomers

Low solubility in available common organic solvents is the common feature of aromatic polyazomethines having rigid backbone chain structure. The solubility test results for the synthesized oligomers are presented in Table II, where oligoAM-o, oligoAM-ppda are insoluble, and oligoAM-tfa and oligoAM-db are slightly soluble in common organic solvents.^{22,23}

Elemental analysis and FTIR analysis of the oligomers

The strongest peaks of oligoAMs occurred at about 1588, 1589, 1608, and 1609 cm⁻¹. The strongest peak in the oligoAM spectrum was observed at 1608 and 1609 cm⁻¹, and small ones occurred at about 3461 cm⁻¹. The peaks attributable to C—O and C—O—C

TABLE III
FTIR Data and Elemental Analyses Results of the Synthesized Oligomers

Compound	Calculated (found)				FTIR (KBr, cm ⁻¹)				Terminal group
	C%	H%	N%	O%	(ArOAr)	(CH _{ar})	(CH=N)	(C=C _{ar})	
oligoAM-tfa	78.89 (63.05)	4.92 (6.672)	13.01 (12.79)	-	-	3420	1608	1485	3461
oligoAM-db	81.63 (80.783)	5.198 (6.448)	10.29 (7.140)	-	-	3445	1609	1499	1701 3462
oligoAM-o	78.32 (71.299)	4.818 (5.251)	8.95 (6.547)	-	1242	3400	1588	1498	-
oligoAM-ppda	78.13 (72.169)	5.505 (6.744)	10.53 (7.898)	-	-	3336	1589	1493	-
Char	(60.58)	(4.51)	(0.09)	(34.09)	-	-	(-C=O) 1708	-	(-OH) 3021

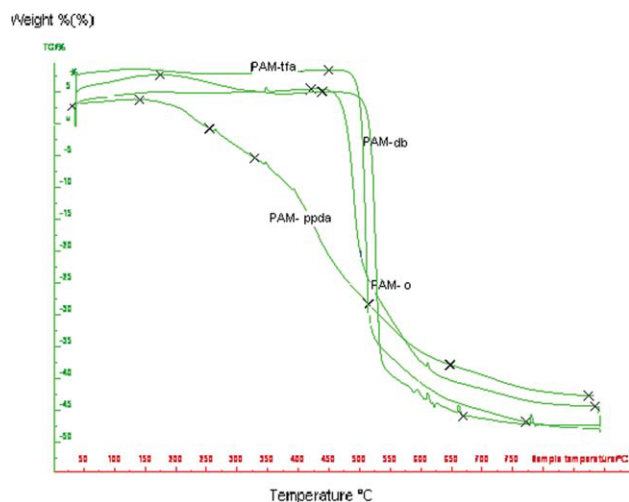


Figure 4 TGA of synthesized oligomers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

vibrations of ether groups occurred at about 1154 and 1242 cm^{-1} . These constitute oligoAM-o with benzene rings separated by an oxygen atom in each aldehyde-related fragment of the chain.²⁴ The presence of 1608, 1609, and 1588 cm^{-1} peaks became the confirmation of oligoazomethine $-\text{C}=\text{N}-$ double imine bonds formed by the condensation polymerization.^{25–27} About 1670, 1689, 1691, and 1701 cm^{-1} peaks were observed in the infrared spectrum of oligomers due to terminal aldehyde groups. The peaks at 1588 and 1589 cm^{-1} were related to benzene ring vibrations.^{11,24–27}

The weak absorption peak at 3461 cm^{-1} was observed for oligoAM-tfa due to the terminal amino

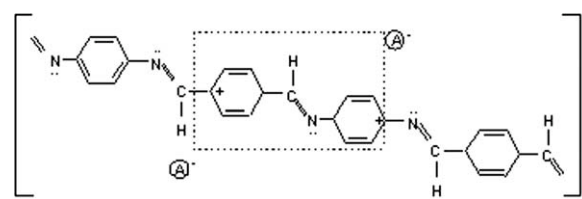


Figure 6 Positive polaron mechanism of (oligoAM)s.

group. Moreover, weak absorptions at 1701 and 3462 cm^{-1} were obtained in the FTIR spectrum of oligoAM-db due to terminal aldehyde group and terminal amino group, respectively. These results of FTIR spectrums for relevant oligomers were substantiated by the results of $^1\text{H-NMR}$ spectroscopies. The data of FTIR spectrums and the results of elemental analyses of the synthesized oligomers are shown in Table III.

UV-vis

The electronic (UV-vis) absorption spectra of these oligomers in DMF solution showed two maxima of 309 nm, 396 nm to the $\pi-\pi^*$ transitions for oligoAM-db, and 290 nm, 419 nm to the $n-\pi^*$ transitions for oligoAM-tfa.

$^1\text{H-NMR}$

$^1\text{H-NMR}$ values were observed in DMSO for the synthesized oligomers of oligoAM-tfa and oligoAM-db. However, because of solubility difficulties with the other oligomers, the $^1\text{H-NMR}$ values could not be examined.^{10,11,25,26} The $^1\text{H-NMR}$ peaks of tfa with

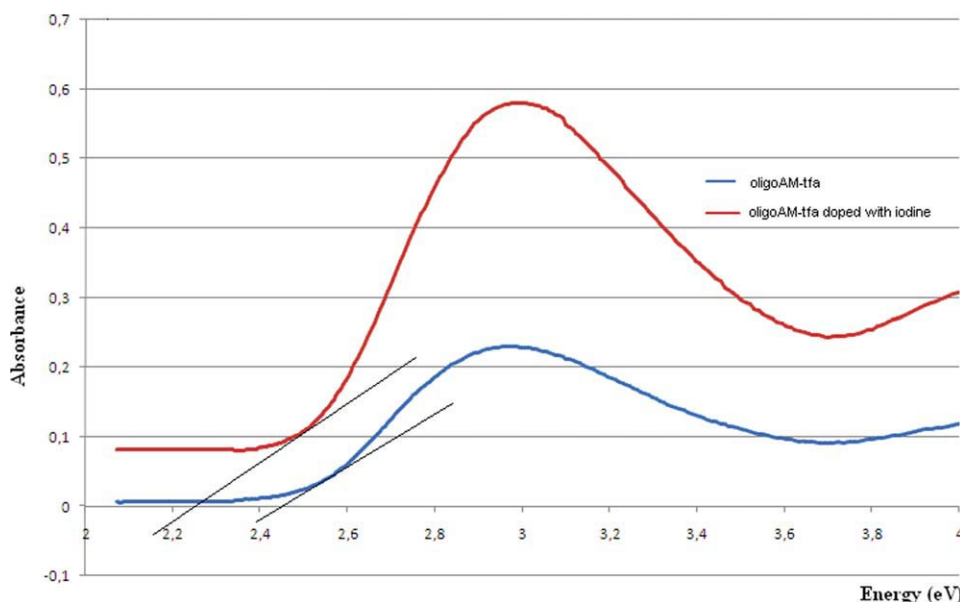


Figure 5 UV-vis absorption spectrum of the neutral (blue) and doped (red) forms of oligoAM-tfa. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

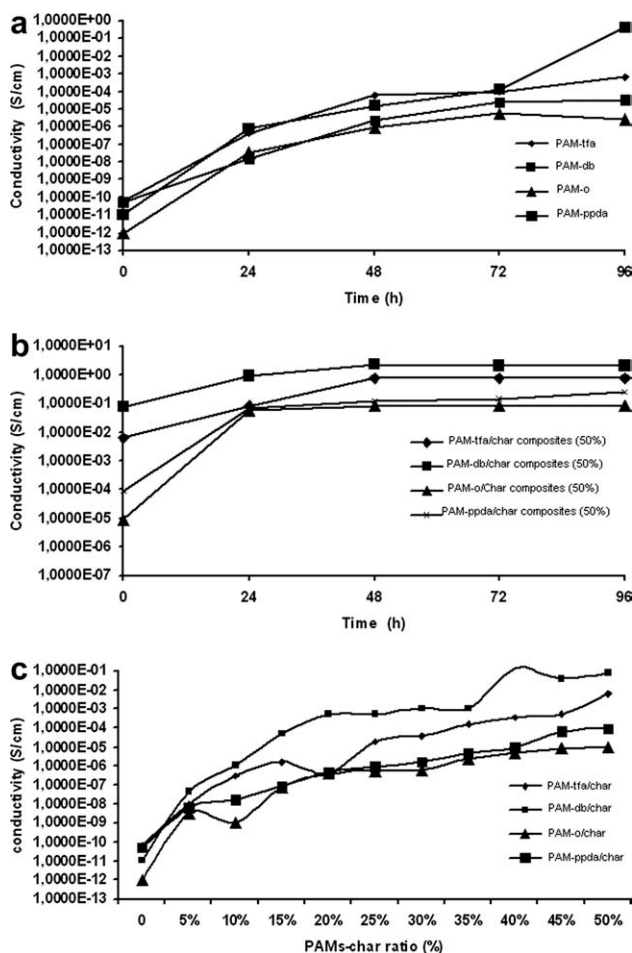


Figure 7 (a) Conductivity graphics of PAMs; (b) conductivity graphics of PAM-char (50%) composites; (c) conductivity graphics of PAM-char composites is not doped.

oligoAM-tfa and db with oligoAM-db are shown in Figures 1 and 2.

When Figures 1 and 2 are examined, the differences between the $^1\text{H-NMR}$ peaks of aldehydes and oligomers and the formation of new peaks for the oligomers due to condensation reaction at 8.63 and 8.605 are seen. In Figure 1, the singlet peak seen in $-\text{CHO}$ group of aldehyde at 10 ppm could not be observed by the formation of oligomer; however, the peak of $-\text{CH}=\text{N}$ group was determined at 8.63 due to the formation of azomethine, and the NH_2 group was observed in the same oligomer at 5.28 ppm. In Figure 2, the peak of azomethine group was observed at 8.605 ppm, while the peaks at 10.05 ppm and 5.25 ppm were, respectively, observed for CHO and NH_2 terminal groups.

We can easily estimate the degree of polymerization (DP) and the number-average molecular weight (\overline{M}_n) by calculating the ratio of terminal aldehyde signal area to the azomethine proton signal area appearing at around 8.605 ppm. The DP and \overline{M}_n of

TABLE IV
Regression Models of Oligomer-Char Composites

Regression equation of oligoAMs/char composites	
Time (h)	oligoAM-tfa
0	$\text{Log}(1/\text{conductivity}) = 9.433 - 0.2310(\text{char } \%) + 0.001929(\text{char } \%)^2; R^2: 0.95$
24	$\text{Log}(1/\text{conductivity}) = 5.68 - 0.00968(\text{char } \%); R^2: 0.922$
48	$\text{Log}(1/\text{conductivity}) = 3.566 - 0.03037(\text{char } \%) - 0.000868(\text{char } \%)^2; R^2: 0.889$
72	$\text{Log}(1/\text{conductivity}) = 3.69 - 0.0756(\text{char } \%); R^2: 0.96.7$
96	$\text{Log}(1/\text{conductivity}) = 3.23 - 0.0661(\text{char } \%); R^2: 0.973$
Time (h)	oligoAM-db
0	$\text{Log}(1/\text{conductivity}) = 9.851 - 0.3861(\text{char } \%) + 0.004399(\text{char } \%)^2; R^2: 0.939$
24	$\text{Log}(1/\text{conductivity}) = 4.789 - 0.1029(\text{char } \%); R^2: 0.841$
48	$\text{Log}(1/\text{conductivity}) = 4.353 - 0.1921(\% \text{ char}) + 0.001954(\text{char } \%)^2; R^2: 0.965$
72	$\text{Log}(1/\text{conductivity}) = 3.130 - 0.1481(\text{char } \%) + 0.001587(\text{char } \%)^2; R^2: 0.866$
96	$\text{Log}(1/\text{conductivity}) = 0.4551 + 0.2155(\text{char } \%) - 0.01187(\text{char } \%)^2 + 0.000146(\text{char } \%)^3; R^2: 0.888$
Time (h)	oligoAM-o
0	$\text{Log}(1/\text{conductivity}) = 11.04 - 0.2786(\text{char } \%) + 0.003290(\text{char } \%)^2; R^2: 0.922$
24	$\text{Log}(1/\text{conductivity}) = 6.218 - 0.1158(\text{char } \%) + 0.000591(\text{char } \%)^2; R^2: 0.823$
48	$\text{Log}(1/\text{conductivity}) = 5.176 - 0.1663(\text{char } \%) + 0.001805(\text{char } \%)^2; R^2: 0.888$
72	$\text{Log}(1/\text{conductivity}) = 4.177 - 0.1467(\text{char } \%) + 0.001788(\text{char } \%)^2; R^2: 0.792$
96	$\text{Log}(1/\text{conductivity}) = 4.356 - 0.168(\% \text{ char}) + 0.002045(\text{char } \%)^2; R^2: 0.766$
Time (h)	oligoAM-ppda
0	$\text{Log}(1/\text{conductivity}) = 9.090 - 0.1089(\text{char } \%); R^2: 0.929$
24	$\text{Log}(1/\text{conductivity}) = 6.420 - 0.1929(\text{char } \%) + 0.001881(\text{char } \%)^2; R^2: 0.847$
48	$\text{Log}(1/\text{conductivity}) = 5.117 - 0.09275(\text{char } \%); R^2: 0.946$
72	$\text{Log}(1/\text{conductivity}) = 4.152 - 0.1212(\text{char } \%) + 0.001141(\text{char } \%)^2; R^2: 0.95$
96	$\text{Log}(1/\text{conductivity}) = 4.013 - 0.1357(\text{char } \%) + 0.001460(\text{char } \%)^2; R^2: 0.946$

TABLE V
Regression Models of oligoAMS and oligoAMs/Char (50%) as Function of Time

oligoAMs	Conductivity/dope time Regression Equation
oligoAM-tfa	$\text{Log}(1/\text{conductivity}) = 9.999 - 0.1622(h) + 0.000981(h)^2$; $R^2: 0.981$
oligoAM-tfa/char (50% composites)	$\text{Log}(1/\text{conductivity}) = 2.210 - 0.05901(h) + 0.000392(h)^2$; $R^2: 0.985$
oligoAM-db	$\text{Log}(1/\text{conductivity}) = 9.913 - 0.09730(h)$; $R^2: 0.924$
oligoAM-db/char (50% composites)	$\text{Log}(1/\text{conductivity}) = 1.048 - 0.04372(h) + 0.000315(h)^2$; $R^2: 0.964$
oligoAM-o	$\text{Log}(1/\text{conductivity}) = 11.77 - 0.1861(h) + 0.001285(h)^2$; $R^2: 0.984$
oligoAM-o/char (50% composites)	$\text{Log}(1/\text{conductivity}) = 4.990 - 0.2366(h) + 0.004182(h)^2 + 0.000022(h)^3$; $R^2: 0.987$
oligoAM-ppda	$\text{Log}(1/\text{conductivity}) = 10.37 - 0.1312(h) + 0.000724(h)^2$; $R^2: 0.998$
oligoAM-ppda/char (50% composites)	$\text{Log}(1/\text{conductivity}) = 3.730 - 0.09536(h) + 0.000680(h)^2$; $R^2: 0.895$

the reprecipitated oligomer oligoAM(db) were obtained as 3.15 and 933, respectively.

OligoAM-tfa: $^1\text{H-NMR}$ (DMSO- d_6) 8.63 ppm (s, 2H, azomethine protons), 7.9–6.61 ppm (four doubled peaks, aromatic protons 8H), and 5.28 (s, end amino group of oligomer backbone, 2H).

OligoAM-db: $^1\text{H-NMR}$ (DMSO- d_6) 10.05 ppm (m, CHO group end group of oligomer backbone, 1 proton), 8.605 ppm (m, 2H, azomethine group), 6.6–8.2 ppm aromatic protons, 12 H), and 5.25 ppm (end NH_2 group of oligomer backbone, 2H).

Thermal analyses of oligomers

To investigate the thermal stability, the DTG-TGA curves of the oligomers were measured in an Ar-Coeff atmosphere under a temperature range of 50–1000°C. The weight loss data obtained by TGA of the oligomers are shown in Figure 4. When the thermal resistances of the oligomers are considered, they can be listed in the order of oligoAM-tfa, oligoAM-db, oligoAM-o, and oligoAM-ppda. For oligoAM-ppda and oligoAM-db at 150°C, the groups of H_2O left the reaction container with a ratio of 0.9698–2.6317%. The mass loss of 50.94% at 512°C occurred at single step after the moisture loss in oligoAM-db. For oligoAM-ppda, five-step decomposition took place, and the maximum material loss of 20.97% was experienced at 393°C. About 48.42% decomposition at 472°C occurred for oligoAM-tfa at single step. A higher mass loss of 49.85% at 496°C was observed for oligoAM-O at single step. As a conclusion, all the oligomers except oligoAM-ppda showed $\sim 50\%$ weight loss in the temperature range of 472–531°C. At 850°C, oligomers decomposed by leaving no residue.^{10,27,28}

Conductivity of oligomers

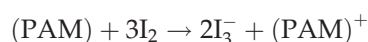
Conductivity measurements of the oligoAMs were carried out with an electrometer using a four-point probe technique. Although the conductivity values for all oligoazomethines were initially found to be between 10^{-12} and 10^{-9} S/cm, an increase was then observed

after iodine doping. Despite the fact that these molecules were similar to each other, oligoAM-db and oligoAM-tfa showed higher conductivity behavior than that of the others. The presence of ether group in aldehyde fragment of oligoAM-o causes energy gap increase and increase in amorphous properties.⁵ Therefore, the conductivity of oligoAM-o is observed lower than that of other oligomers.

After being kept under iodine vapor during 2 h, the UV-vis absorption spectrum of oligoAM-tfa thin film was taken. As the spectra taken for the neutral (blue) and doped (red) forms of oligoAM-tfa are shown in Figure 5, the band gaps (E_g) of the neutral and doped oligoAM-tfa were, respectively, estimated at 2.25 and 2.45 eV by considering the characteristic step absorption edges.²⁹ It is clear from the absorption spectra that the red shift due to iodine doping is ~ 0.1 eV.

Nitrogen is an electronegative molecule, and Diaz et al.³⁰ suggested a conductivity mechanism of imine ($-\text{CH}=\text{N}-$) polymers when they were doped with iodine.

The formation reaction of positive polaron can be briefly expressed as



In previous studies, the type of I_2 doping mechanism was determined as *p*-type for oligoAM-tfa polymer doped with iodine.^{30,31} Additionally, the existence of a positive polaron mechanism was mentioned in the literature as shown in Figure 6.

The conductivities of the synthesized oligomer composites produced with char using definite ratios (5–50%) were also recorded, after being doped with iodine vapor up to 96 h under room temperature conditions. Although the conductivity of synthesized oligoAM-char composites reached to the 10^{-2} S/cm level in a short period of time, as seen by the measurements, the conductivity level of oligoAMs composites produced by only iodine vapor was about 10^{-4} S/cm after a very long time period according to some of the literature references.^{27,32} The conductivity of the oligomers and carbon black-(oligoAM) composites is shown in Figure 7.

DISCUSSION OF RESULTS AND CONCLUSION

Dialdehyde molecules (DAs) were synthesized according to previously published procedures.^{18–20} The results of the ¹H-NMR, melting point, and elemental analyses of the synthesized aldehydes were determined as compatible with those obtained in the literature.^{12,13,18}

Aromatic oligo(azomethine)s were prepared by polycondensation of terephthaldehyde, 4,4'-diformylbiphenyl, and bis(4-formylphenyl) ether with 1,4-diaminobenzene at room temperature. The structures of the synthesized oligomers were clarified, and the results of the analyses were determined in accordance with the results of the literature.^{27,9–11} In contrast to literature, no catalyzation was required for the synthesis of these oligomers.

The conductivity values of the oligomers were observed between the values of 10⁻¹¹ and 10⁻¹² S/cm. A conductivity level of 10⁻⁴ S/cm was reached after 72 h, when the oligomers were doped with iodine, although 10⁻⁷ – 10⁻⁵ S/cm conductivity values were observed after 96 h or more when oligoAMs were doped with iodine.^{11,27,32} In the literature, the conductivity values of 10⁻⁵ – 10⁻⁴ S/cm were obtained for the oligomers doped with iodine in a shorter period of time when compared with the oligomers of this study.²⁷ The UV–vis absorption spectrum of neutral and doped forms of oligoAM-tfa clearly explains that a red shift was observed by iodine doping.

The weak acid effect due to terephthalic acid in the char structure contributes to the alteration of load balance in the possible oligomer matrix and the increase in the conductivity. At the same time, the electrical contacts in the oligomer matrix can be activated by the formation of additional conduction bridges through the char particles.³³ The effects of both weak acid and conduction bridges may cause to have higher red shift at the band gaps (E_g) of oligoazomethines-char composites than the oligoazomethines. And then, the oligomer composites were prepared using definite char ratios (5–50%).

Using raw char (pyrolysis waste) obtained in a study of the composite formation of oligomers meant that the study cost less in comparison with the state of carbon fiber use. The conductivities of the composites (oligoazomethin-char) doped with iodine were measured at 24-h intervals. The increase in conductivity after the first 24 h was 10⁻⁵ S/cm for all the oligomers except oligoAM-ppda and between a 10⁻² and 10⁻³ S/cm level of conductivity was observed after 72 h. When the conductivities of oligomers and oligoAM-char composites were measured in definite time intervals by doping them with iodine vapor, the composite oligo(azomethine)s produced with char showed higher conductivity in a shorter period of time.

According to the statistical analyst, the conductivity values presented differences among the treatments. Because a significant relation between conductivity, char %, and doping time was obtained by the regression analysis, the conductivity can be modeled associated with char % and doped time. The regression models are given in Tables IV and V. The conductivity values can be estimated by using these models for each oligoAM, every char % levels, and definite time durations, besides the conductivity values that can be also estimated as the function of time for every oligoAM at 0 and 50% char levels.

When conductivity measurements are examined, it is clear that the conductivity values of the composites increased with the increasing char ratios. The composite oligo(azomethine)s formed with varying char percentages reached to a conductivity level of 10⁻¹ S/cm in a short period of time.

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