

ISMET KAYA ^{*)}, SÜLEYMAN ÇULHAOĞLU

Çanakkale Onsekiz Mart University
Faculty of Sciences and Arts
Department of Chemistry
Çanakkale TR-17020, Turkey

Syntheses, structures and properties of novel oligo(azomethine ether)s containing or not chlorine atoms in the main chain

Summary — New oligoazomethines were synthesized *via* polycondensation of aromatic diamines with one of two dialdehydes. Both dialdehydes, namely 4-((2-[(4-formylphenoxy)methyl]benzyl)oxy)benzaldehyde (2-FPMBB), and 4-((4-[(4-formylphenoxy)methyl]benzyl)oxy)benzaldehyde (4-FPMBB) were prepared from *p*-hydroxybenzaldehyde with *o*-xylenedibromide or *p*-xylenedibromide, respectively. Dialdehydes and oligomers were characterized by FT-IR, ¹H NMR and ¹³C NMR methods. Size exclusion chromatography (SEC) technique was used to determine molecular weights and molecular weight distributions of synthesized oligomers. The thermal stability of oligomers was conducted by thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The weight losses of oligoazomethines (O1, O2, O3 and O4) at 1000 °C were found to be 54.74, 46.27, 54.85 and 53.10 % respectively. In all cases, the imine (-HC=N-) linkage is the first breaking group due to the high temperature. It can be seen from TGA that oligo(azomethine ether)s containing chlorine atoms have higher thermal stability at 1000 °C than O1 and O3 oligomers.

Key words: oligoazomethines, dialdehyde monomers, molecular weight distribution, thermal stability.

OTRZYMYWANIE, STRUKTURA I WŁAŚCIWOŚCI NOWYCH OLIGO(ETERÓW AZOMETINOWYCH) ZAWIERAJĄCYCH LUB NIE ATOMY CHLORU W ŁAŃCUCZU GŁÓWNYM

Streszczenie — Zsyntetyzowano dwa monomery dialdehydowe tj.: 4-((2-[(4-formylofenoksy)metylo]benzyl)oksy)benzaldehyd (2-FPMBB) i 4-((4-[(4-formylofenoksy)metylo]benzyl)oksy)benzaldehyd (4-FPMBB) (Schemat A). Metodą polikondensacji aromatycznych diamin z jednym z dwu dialdehydów otrzymano oligomery zawierające ugrupowania azometinowe (O1, O2, O3 i O4, Schematy B i C). Dialdehydy oraz oligomery charakteryzowano za pomocą FT-IR, ¹H NMR i ¹³C NMR (rys. 1—3, tabele 1—3). Metodą chromatografii żelowej (SEC) wyznaczono rozkład ciężarów cząsteczkowych zsyntetyzowanych oligomerów (tabela 5). Ich stabilność termiczną oceniano za pomocą analizy termogravimetrycznej (TGA) oraz różnicowej analizy termicznej (DTA) (rys. 9—11, tabela 4). Stwierdzono, że w temp. 1000 °C ubytek masy oligomerów O1, O2, O3 i O4 wynosił odpowiednio 54,74, 46,27, 54,85 i 53,10 %. We wszystkich przypadkach, w wysokiej temperaturze, w pierwszej kolejności rozrywane są wiązania iminowe (-HC=N-). Na podstawie badań TGA ustalono, że oligomery O2 i O4, zawierające atomy chloru w łańcuchu, charakteryzują się w temp. 1000 °C lepszą stabilnością termiczną niż oligomery O1 i O3 niezawierające atomów chloru.

Słowa kluczowe: oligoazometiny, monomery dialdehydowe, rozkład ciężarów cząsteczkowych, stabilność termiczna.

Polyazomethines (PAMs), known as polyimines of Schiff bases polymers, were prepared for the first time by Adams and co-workers from terephthalaldehyde and benzidine and dianisidine in 1923 [1]. Polyazomethines, which contain -HC=N- bonds in their structures, may exhibit attractive physical properties such as electronic, optoelectronic, nonlinear optical or liquid crystalline properties that make this kind of polymers particularly interesting in materials science [2—6]. Polyazomethines

show also high thermal stability [7], high mechanical strength [8, 9] and ability to form metal chelates [10—12]. Many of these polymers form mesophases during heating [13]. These types materials have low solubility in common organic solvents and high melting temperatures. Due to these reasons, the determination of application areas of them is difficult. However, several approaches have been undertaken to improve the processability of conjugated polyazomethines by introducing of differently substituted benzene rings into the main chains [14, 15], by using monomers containing cer-

^{*)} Corresponding author; e-mail:kayaismet@hotmail.com

tain heterocyclic units such as thiophene [16], oxadiazole, thiadiazole [17–19], pyridine [20], diphenylfluorene [21] and others. Copolymers with phenyl-substituted quinoxaline rings were proved to be very beneficial [22, 23]. In the recent years, the interest in polyazomethines has increased due to their proved capacity to act as good materials; as reagents or supports in various applications. For example, poly(imine)s have been used as reagents to obtain hybrid materials by the linkage of polypyrrole to the backbone of the polymer [24]. Also, some poly(imine)s with dendrimer properties are excellent supports for coordination of metal ions [25]. On the other hand, similarly to polyaniline doping, imine groups, -HC=N- in poly(imine)s, can take protons, yielding cationic backbone that have different anions, which retain interesting properties. Some article in literature mention the protonation of poly(imine)s with heteropolyanion with Keggin structure, which have catalytic properties [26, 27].

This paper presents the syntheses, characterization and thermal properties of some oligoazomethines obtained by simple polycondensation reactions of one of two different aromatic diamines: 2,5-dichloro-*p*-phenylenediamine (DCPDA) and *p*-phenylenediamine (PDA) with two synthesized dialdehydes. The effects of chlorine atoms, in *para* or *ortho* positions in benzene rings in the middle of dialdehydes and ether linkages on oligomer chains were studied.

EXPERIMENTAL

Materials

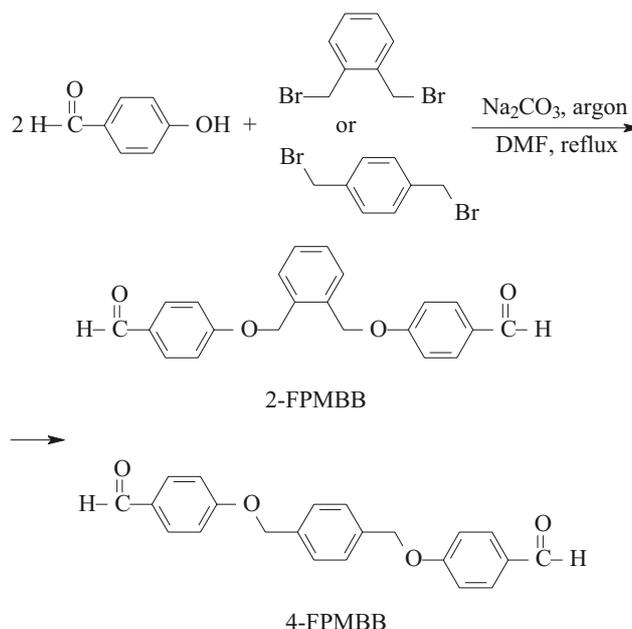
p-Hydroxybenzaldehyde, dimethylformamide (DMF), dimethylsulfoxide (DMSO), anhydrous sodium carbonate (Na_2CO_3), methanol, toluene and *p*-toluenesulfonic acid (PTSA, used as a catalyst), 2,5-dichloro-*p*-phenylenediamine (DCPDA) and *p*-phenylenediamine (PDA) were purchased from Merck Chemical Company (Germany).

p-Xylenedibromide and *m*-xylenedibromide in chromatographic grade were supplied by Alfa Aesar Chemical Company (Germany) and they were used as received.

Dialdehyde monomers syntheses

Dialdehyde monomers, namely 4-((2-[(4-formylphenoxy)methyl]benzyl)oxy)benzaldehyde (2-FPMBB) and 4-((4-[(4-formylphenoxy)methyl]benzyl)oxy)benzaldehyde (4-FPMBB), were synthesized according to the reactions presented in Scheme A and procedure described in literature [28].

p-Hydroxybenzaldehyde (0.740 g, 0.006 mol) dissolved in 30 mL of DMF was added into 250 mL three-necked flask equipped with a condenser and magnetic stir bar.

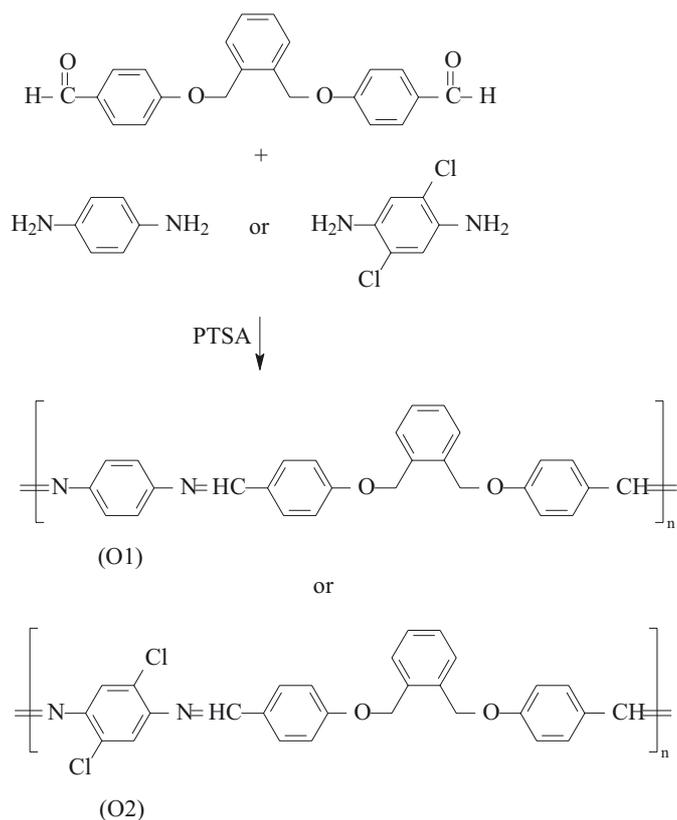


Scheme A. Syntheses of dialdehyde monomers

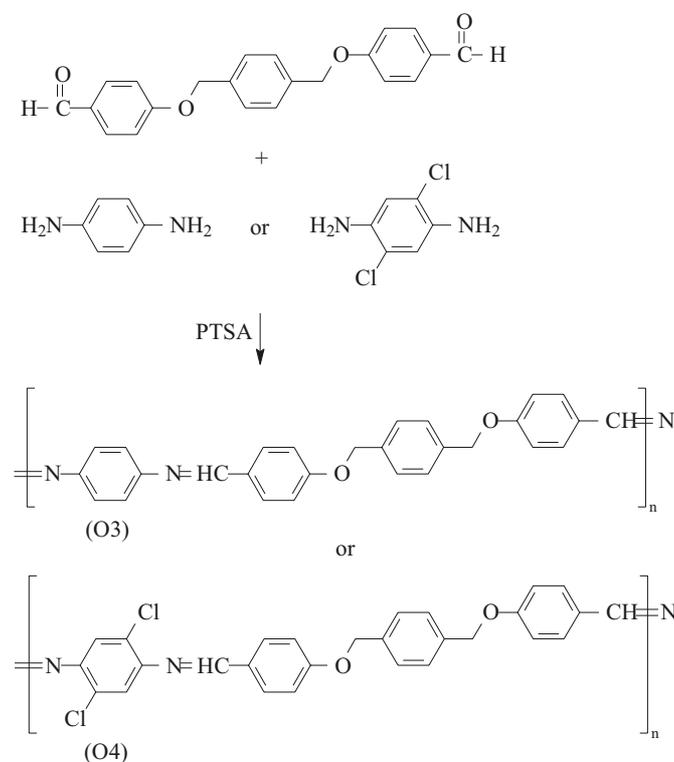
Anhydrous sodium carbonate (0.795 g, 0.0075 mol) was added to the flask. *o*-Xylenedibromide (0.792 g, 0.003 mol, for 2-FPMBB) or *p*-xylenedibromide (0.792 g, 0.003 mol, for 4-FPMBB) was dissolved in 30 mL of DMF and added into the reaction mixture under argon atmosphere. The mixture was heated for 4 h at 150 °C under continuous stirring. After cooling, the product was poured into 250 mL of cold water (approximately 5–10 °C). The precipitate was washed 3 times using 250 mL of water for separation of mineral salts. Then 2-FPMBB or 4-FPMBB was filtered and dried. Finally the products were purified by recrystallization from methanol and dried in vacuum desiccator for 24 h at 60 °C (yields 48.6 % and 29.4 %; melting temperatures: 142–143 °C and 166–167 °C for 2-FPMBB and 4-FPMBB, respectively). Results of elemental analyses are: calculated for 2-FPMBB or 4-FPMBB: C, 76.28; H, 5.23; found: C, 76.14; H, 5.10 for 2-FPMBB and C, 76.15; H, 5.11 for 4-FPMBB.

Syntheses of oligo(azomethine ether)s

PDA (0.162 g, 0.0015 mol) or DCPD (0.265 g, 0.0015 mol) and dialdehyde (0.519 g, 0.0015 mol) were dissolved in 25 mL DMF in a 250 mL three-necked round bottom-flask equipped with a reflux condenser, a gas inlet-outlet, a Dean-Stark trap and a magnetic stirrer. Then 2 mL of toluene (in order to remove water as an azeotrope) and *p*-toluenesulfonic acid as catalyst were added and purged with a stream of argon. Reaction mixture was stirred for 1 h at room temperature and 6 h at reflux under argon atmosphere. After cooling at room temperature, the oligomers were precipitated into methanol, washed with methanol and dried at 60 °C for 3 h in a vacuum oven. The general reactions and the structures of oligomers are given in Schemes B and C.



Scheme B. General reaction for the synthesis of oligo(azomethine ether)s from 2-FPMBB



Scheme C. General reaction for the synthesis of oligo(azomethine ether)s from 4-FPMBB

The yields of O1, O2, O3 and O4 oligomers were found to be 75.62, 91.52, 86.64 and 70.79 %, respectively.

Methods of testing

The FT-IR spectra were recorded by Perkin Elmer Spectrum One FT-IR system using universal ATR sampling (powder form directly usable) accessory within the wavelengths of 4000–650 cm^{-1} .

Elemental analysis was carried out using a Carlo Erba 1106 analyzer.

Monomers and oligomers were characterized by ^1H NMR and ^{13}C NMR spectra [Bruker AC FT-NMR spectrometer operating at 400 and 100.6 MHz, respectively, and recorded at 25 $^\circ\text{C}$ with use of deuterated dimethyl sulfoxide (DMSO) as a solvent]. Tetramethylsilane (TMS) was used as internal standard.

Thermal data were obtained using a Perkin Elmer Diamond Thermal Analysis. Thermogravimetric (TG) and differential thermal analysis (DTA) measurements were made in the range of temperature 20–1000 $^\circ\text{C}$ (under N_2 atmosphere with heating rate 10 $^\circ\text{C}/\text{min}$).

Size exclusion chromatography (SEC) analyses were performed at room temperature using dimethylformamide/methanol (4/1 v/v) as eluent at a flow rate of 0.4 mL/min. A refractive index detector was used. The instrument (Shimadzu 10AVp series HPLC-SEC system) was calibrated using a mixture of polystyrene standards [Polymer Laboratories; the peak molecular weights (M_p) between 162 and 19 880] using GPC software for the determination of the number-average molecular weight (\overline{M}_n), weight-average molecular weight (\overline{M}_w) and polydispersity index (PDI) values of the polymer samples. For SEC investigations a Macherey-Nagel GmbH & Co. (100 \AA and 7.7 nm diameter loading material) 3.3 mm i.d. \times 300 mm columns and a refractive index detector at oven temperature 30 $^\circ\text{C}$ were used.

UV-Vis spectra of oligomers were measured using Perkin Elmer Lambda 25 apparatus and the absorption spectra were recorded in DMSO solvent.

RESULTS AND DISCUSSION

Solubility of oligomers

O1, O2, O3 and O4 oligomers were from opaque yellow to orange powder forms and they were completely soluble in DMSO and some mono and diprotic acids such as H_2SO_4 , HCl and HNO_3 . All oligomers were insoluble in hexane, heptane, CH_2Cl_2 , CHCl_3 , CCl_4 , methanol, ethanol, acetonitrile, benzene, toluene, acetone, diethyl ether and ethyl acetate.

FT-IR spectral data of dialdehyde monomers and oligo(azomethine ether)s

The spectra of dialdehydes are shown in Figure 1, whereas corresponding spectral data are listed in Table 1. Dialdehyde monomers have similar spectra and show characteristic signals for aldehyde group in 1670–

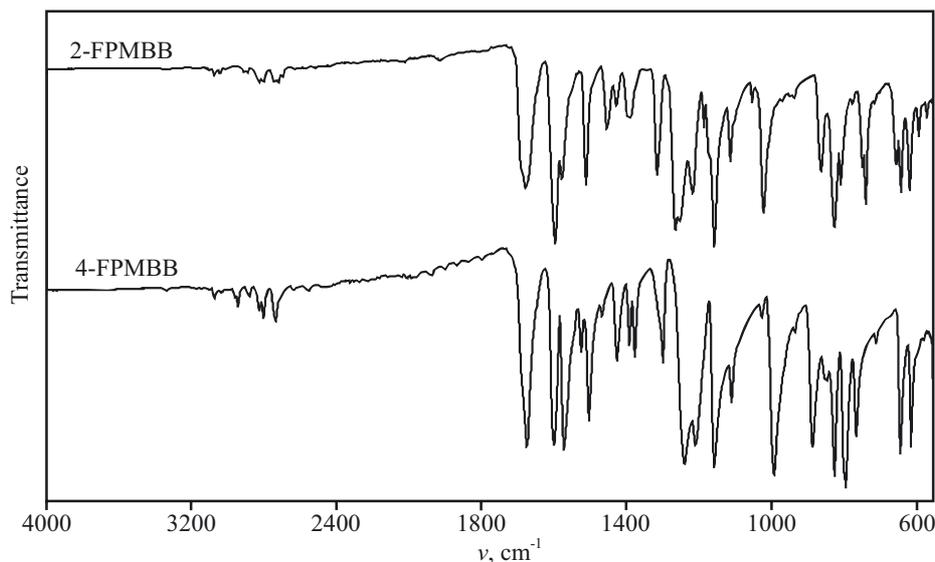


Fig. 1. FT-IR spectra of 2-FPMBB and 4-FPMBB dialdehydes

1700 cm^{-1} . Although weak absorption peaks appeared in the ranges of 3200–2650 cm^{-1} and 2650–1900 cm^{-1} , the strong absorption peaks appeared in 1700–1000 cm^{-1} and they domain attributed to C-C and C-H vibrations. In FT-IR spectra of dialdehyde monomers, aliphatic C-H vibration exerted by $-\text{OCH}_2$ groups were observed in 2800–2900 cm^{-1} . Furthermore, characteristic aldehyde $-\text{C}=\text{O}$ vibration for a carbonyl group was observed at 1670–1680 cm^{-1} .

Table 1. FT-IR spectral data of dialdehydes

Dialdehyde	Wave number, cm^{-1}				
	$-\text{HC}=\text{O}$	C-O-C	$-\text{C}=\text{C}-$	Ar-CH	Aliphatic-CH
2-FPMBB	1678	1265	1597, 1578, 1511	3074	2828
4-FPMBB	1674	1240	1600, 1574, 1505	3077	2882

Table 2. FT-IR spectral data of oligomers

Oligomer	Wave number, cm^{-1}						
	OHC-	HC=N-	-C-O-C-	C=C	Ar-CH	Aliphatic-CH	C-Cl
O1	1619	1600	1237	1573–1509	3048	2875	—
O2	1622	1598	1239	1575–1508	3063	2878	751
O3	1618	1602	1244	1573–1508	3053	2860	—
O4	1619	1599	1243	1569–1508	3074	2868	791

Figure 2 and Table 2 indicate FT-IR spectra and data of O1, O2, O3 and O4 compounds, respectively. There are different and significant changes in the spectra of oligomers compared with the spectra of dialdehydes.

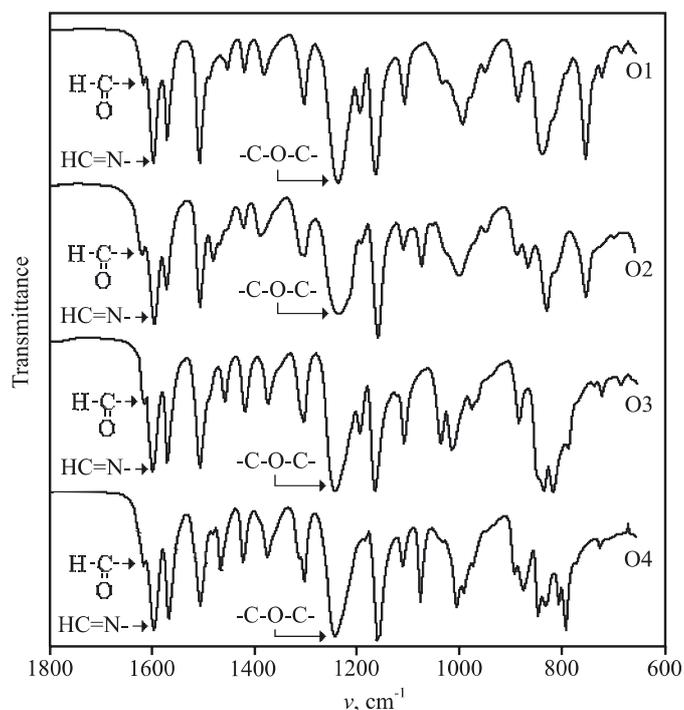


Fig. 2. FT-IR spectra of O1, O2, O3 and O4 oligo(azomethine ether)s

The aldehyde peaks were not clearly disappeared at the FT-IR spectra but their small vibrations were about 1610–1625 cm^{-1} . The signals at 1595–1605 cm^{-1} clearly show the azomethine ($-\text{HC}=\text{N}-$) link during the oligomerization.

^1H NMR and ^{13}C NMR spectra of dialdehyde monomers and oligo(azomethine ether)s

Dialdehyde monomers were characterized by ^1H NMR and ^{13}C NMR spectra. The protons and carbons

positions of monomers are listed in Table 3. The chemical shifts of 2-FPMBB and 4-FPMBB were shown in Figures 3–6.

Table 3. Positions of signals in ^1H NMR and ^{13}C NMR spectra of dialdehydes

Dialdehyde	^1H NMR δ , ppm
2-FPMBB	9.89 (s, 2H, -CHO), 7.84 (d, 4H, Ar-H _a), 7.09 (d, 4H, Ar-H _b), 7.54 (d, 2H, Ar-H _d), 7.44 (t, 2H, Ar-H _e), 5.28 (s, 4H, Ar-CH ₂ -O-)
4-FPMBB	9.88 (s, 2H, -CHO), 7.87 (d, 4H, Ar-H _a), 7.10 (d, 4H, Ar-H _b), 7.49 (d, 4H, Ar-H _d), 5.18 (s, 4H, Ar-CH ₂ -O-)
	^{13}C NMR
2-FPMBB	190.71 (C1), 129.00 (C2), 133.14 (C3), 115.00 (C4), 163.57 (C5), 68.43 (C6), 134.29 (C7), 130.43 (C8), 129.43 (C9)
4-FPMBB	190.69 (C1), 129.86 (C2), 131.86 (C3), 115.29 (C4), 163.47 (C5), 70.70 (C6), 135.83 (C7), 127.70 (C8)

In the ^1H NMR spectra of oligo(azomethine ether)s, the five types of signals were observed. The azomethine

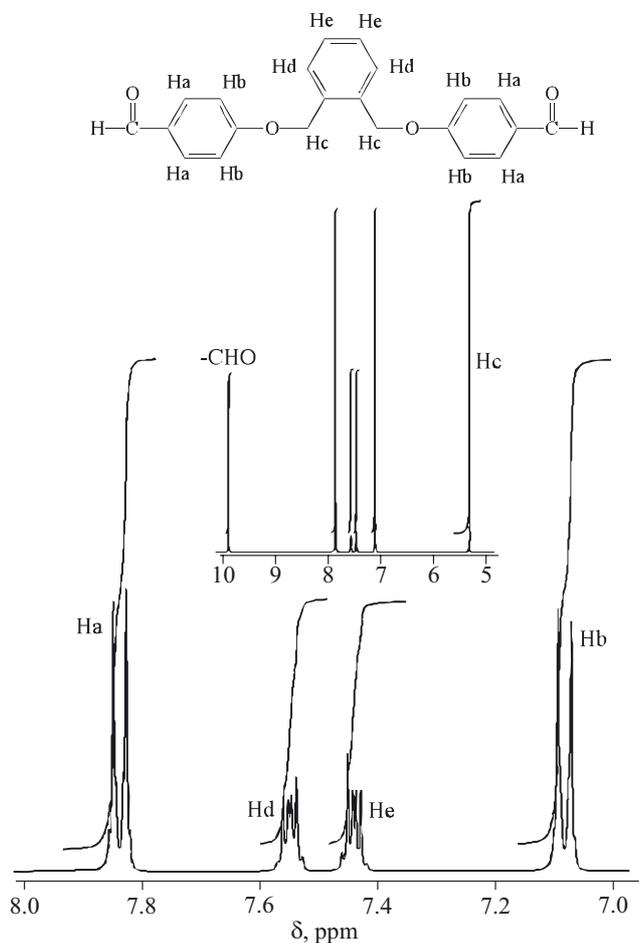


Fig. 3. ^1H NMR spectrum of 2-FPMBB

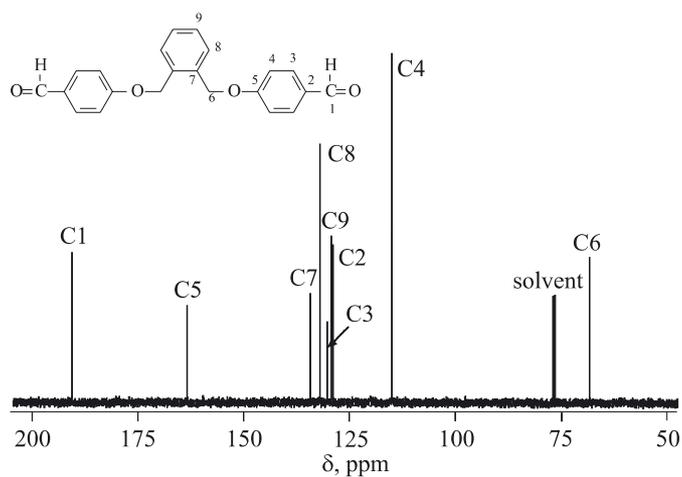


Fig. 4. ^{13}C NMR spectrum of 2-FPMBB

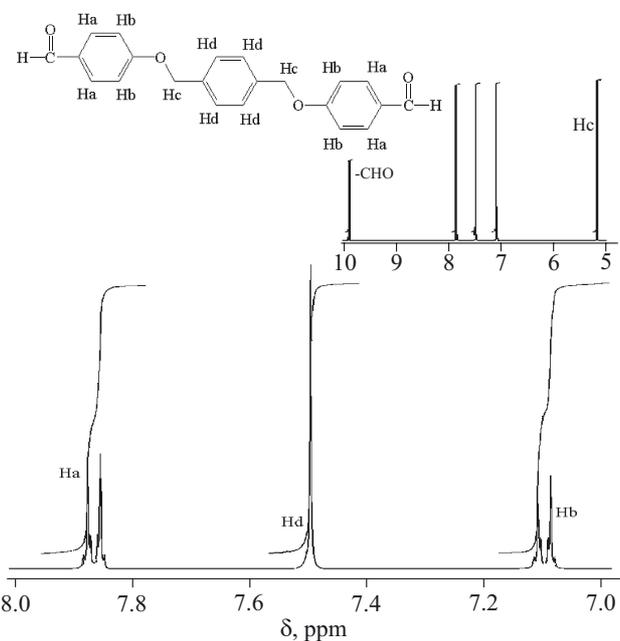


Fig. 5. ^1H NMR spectrum of 4-FPMBB

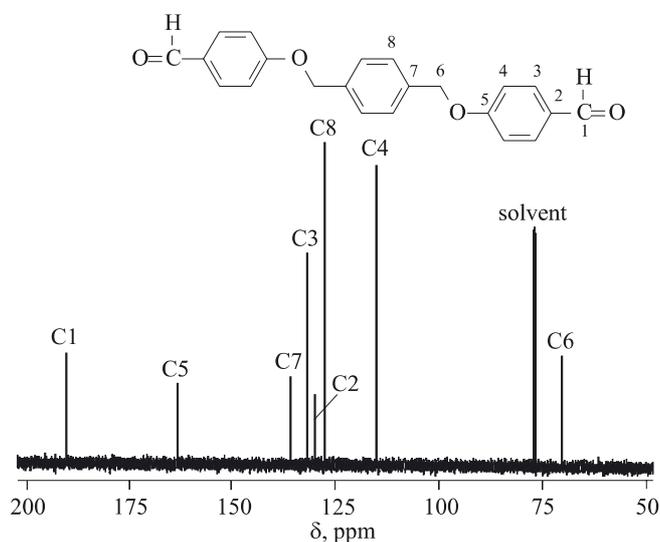


Fig. 6. ^{13}C NMR spectrum of 4-FPMBB

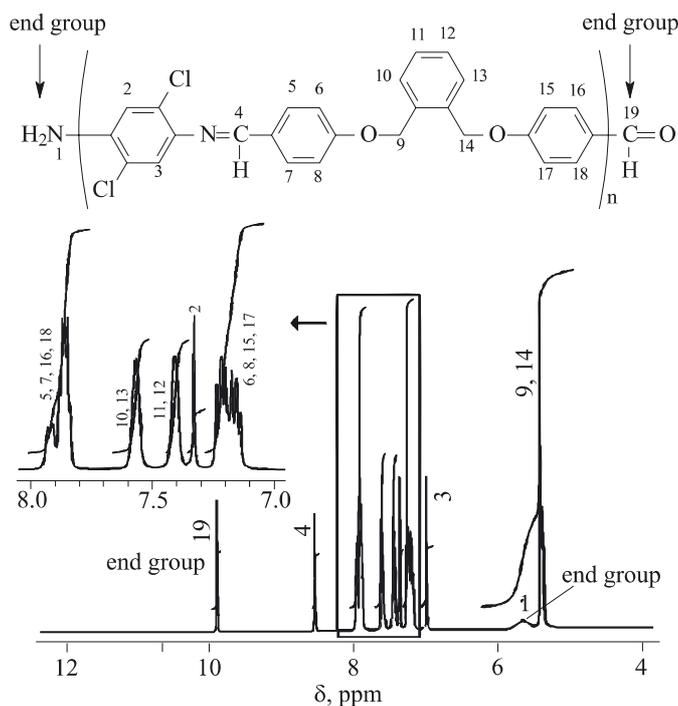


Fig. 7. ^1H NMR spectrum of O2 (all number demonstrate the protons in the main chain of O2)

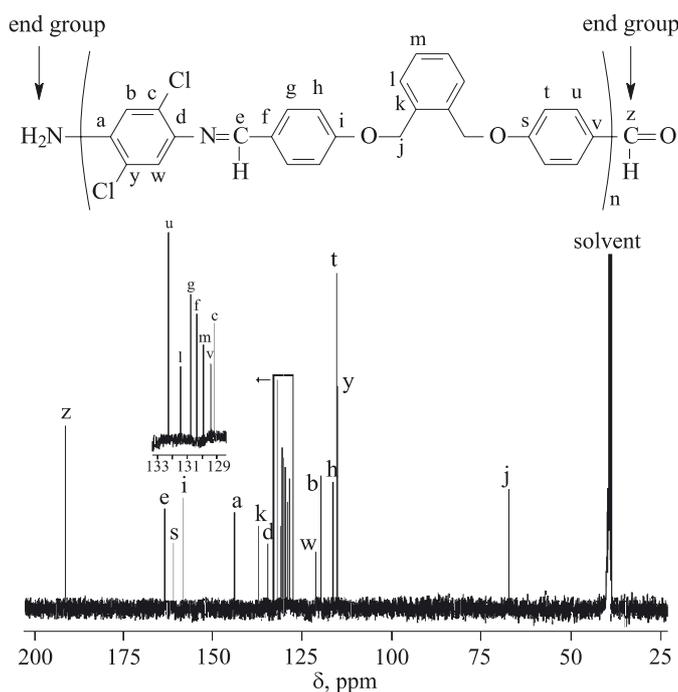


Fig. 8. ^{13}C NMR spectrum of O2

(-HC=N-) protons were seen as a singlet at about 8.68–8.92 ppm, the multiplet aromatic protons at about 6.50–8.20 ppm, the singlet at 5.25–5.35 ppm aliphatic (-O-CH₂-) protons, amine end group protons at about 5.62–5.65 ppm and aldehyde end group at about 9.84–10.00 ppm. The ratio values of the integrals corresponding to aliphatic versus aromatic protons and azomethine protons agree with the proposed structure.

^1H NMR spectrum of O2 is given in Figure 7. In the ^1H NMR spectrum of O2, five types of signals were assigned to: azomethine (-NC=N-) proton singlet at 8.68 ppm, the multiplet aromatic protons at 7.0–8.0 ppm, the singlet aliphatic (O-CH₂-) protons at 5.32 ppm, amine end group protons at 5.62 ppm and aldehyde end group at 9.84 ppm, respectively. ^{13}C NMR spectrum of O2 is given in Fig. 8. In the ^{13}C NMR spectra of O2, peak values of specific azomethine carbon (-HC=N-) and (-O-CH₂-) linked to aromatic ring were observed in 163.63 and 68.01 ppm, respectively. The aldehyde and amine vibrations of end groups were observed in FT-IR and in ^1H NMR spectra. According to ^1H NMR spectra, the -CHO and -NH₂ peak values were observed in 9.86 and 5.62 ppm, respectively.

Thermal analyses

The thermal degradation of O1, O2, O3 and O4 was studied by TGA, DTG and DTA analyses under N₂ atmosphere and thermal analyses results and the curves are given in Table 4 and Figures 9–11, respectively. These results showed that 20 and 50 % weight losses had occurred in the temperature range of 366–858 °C, 441–824 °C and 402–801 °C, for O1, O3 and O4, respectively. Oligoazomethines have the onset temperature range from 314 to 374 °C. The TGA curved the major weight loss at 335–850 °C, and the residual weight of oligomers remaining at 1000 °C was in the range of 45.15–53.73 %. This variation in weight loss was due to the differences in the structures of symmetrical and unsymmetrical groups (*para* position or *ortho* position in benzene ring in the middle of dialdehydes) of oligomers and the chlorine atoms in the oligomer chain. TGA data indicated that chlorine containing O2 and O4 exhibited higher thermal stability in comparison with the other ones (O1 and O3). According to DTA data, the oligomers showed one exothermic peak in the range of 321–392 °C. It can be clearly seen that the phenyl ring position has smaller contribution to the thermal decomposition than the existence of the chloride group in the main

Table 4. Thermal decomposition values of O1, O2, O3 and O4 oligo(azomethine ether)s

Compound	TGA				% of carbine residue at 1000 °C	DTA T_{exo}^e °C
	T_{on}^a °C	T_{max}^b °C	T_{20}^c °C	T_{50}^d °C		
O1	331	343, 467	366	858	45.26	340
O2	314	323	335	—	53.73	321
O3	374	385, 491	441	824	45.15	392
O4	337	356, 490	402	821	46.90	356

^{a)} Onset temperature. ^{b)} Maximum weight loss temperature.

^{c)} 20 % weight loss temperature. ^{d)} 50 % weight loss temperature.

^{e)} Temperature of exothermic peak.

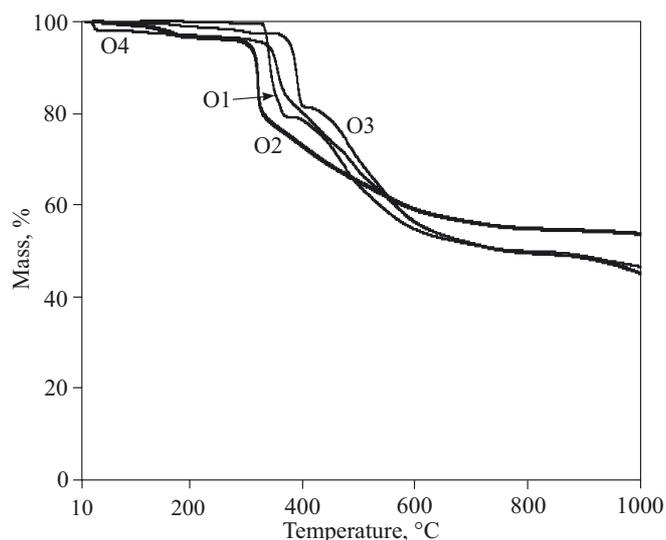


Fig. 9. TGA curves of O1, O2, O3 and O4 oligo(azomethine ether)s

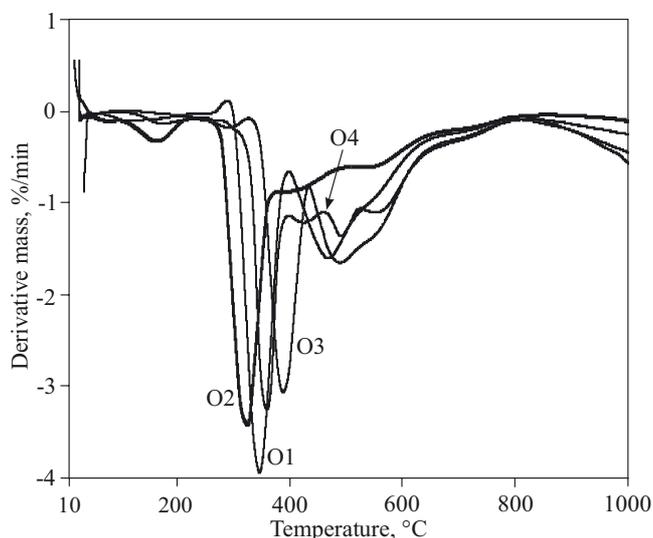


Fig. 10. DTG curves of O1, O2, O3 and O4 oligo(azomethine ether)s

chain of the oligomer. Based on similar structures of oligomers, one may assume that, due to the high temperature, the azomethine (-HC=N-) linkage is the first breaking unit, in all cases.

O1, O2, O3 and O4 formed carbines residue at high amounts 45.26, 53.73, 45.15, and 46.90 %, respectively, at

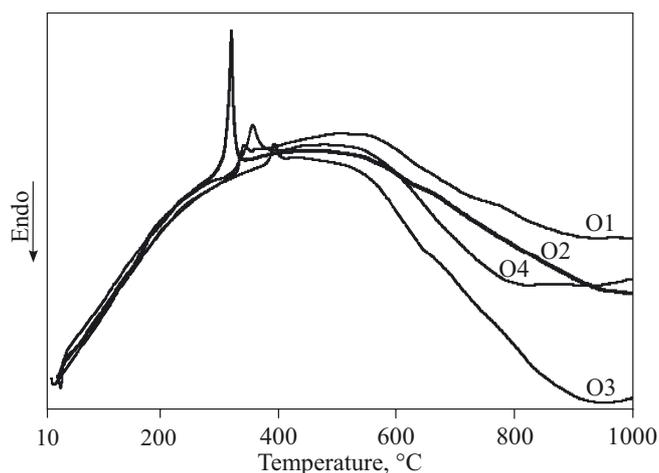


Fig. 11. DTA curves of O1, O2, O3 and O4 oligo(azomethine ether)s

1000 °C because of long band systems. Oligomers demonstrated higher resistance to high temperature. Also, the initial degradation temperatures of O2 and O4 were higher than of O1 and O3 oligomers. Figures 9—11 showed the degradation of oligomers is only one step process. Data presented in Table 4 suggest that these oligomers have good thermal stability (the starting weight loss temperatures for all oligomers are situated within the range 300—400 °C). The thermal decomposition behaviors of oligomers were similar.

Molecular weight distributions of oligomers

SEC analyses results of oligo(azomethine ether)s were given in Table 5. Two peaks were observed in the chromatograms for all oligomers obtained. First peak corresponds to low-molecular weight fraction (I) and the other one to high-molecular weight fraction (II).

According to SEC analyses \overline{M}_n , \overline{M}_w and *PDI* values of the low-molecular weight fraction (I) were found to be 650—750, 850—900 and 1.33—1.308 respectively. For the high-molecular weight fraction (II) of O1 \overline{M}_n , \overline{M}_w and *PDI* were found to be 2550, 2700 and 1.097 respectively, while in the case of other oligomers 6600—8300, 8700—9350 and 1.123—1.417, respectively.

It was stated that for O2 the content of high-molecular weight fraction reached value 47 %, while for O1, O3 and O4 was equal only to 7, 3 and 5 %, respectively.

Table 5. Number-average molecular weight (\overline{M}_n), weight-average molecular weight (\overline{M}_w) and polydispersity index (*PDI*) values of O1, O2, O3 and O4 oligo(azomethine ether)s

Oligo-mer	Total			Fraction I				Fraction II			
	\overline{M}_n	\overline{M}_w	<i>PDI</i>	\overline{M}_n	\overline{M}_w	<i>PDI</i>	weight fraction, %	\overline{M}_n	\overline{M}_w	<i>PDI</i>	weight fraction, %
O1	450	500	1.111	750	850	1.133	93	2550	2700	1.097	7
O2	1750	2400	1.371	700	900	1.286	53	6600	9350	1.417	47
O3	450	550	1.222	650	850	1.308	97	7750	8700	1.123	3
O4	550	650	1.182	700	850	1.214	95	8300	9350	1.127	5

According to SEC results, the second fractions of O1, O2, O3 and O4 contain approximately 5–6, 12–18, 15–17 and 17–20 repeated units, respectively. It can be clearly considered from the SEC analyses results, the first fractions were mostly in dimeric forms, while the second fractions were in oligomeric forms.

Optical properties

The UV-Vis absorption spectra of oligomers obtained are given in Figure 12. The optical band gap (E_g) values of oligomers were calculated from their absorption

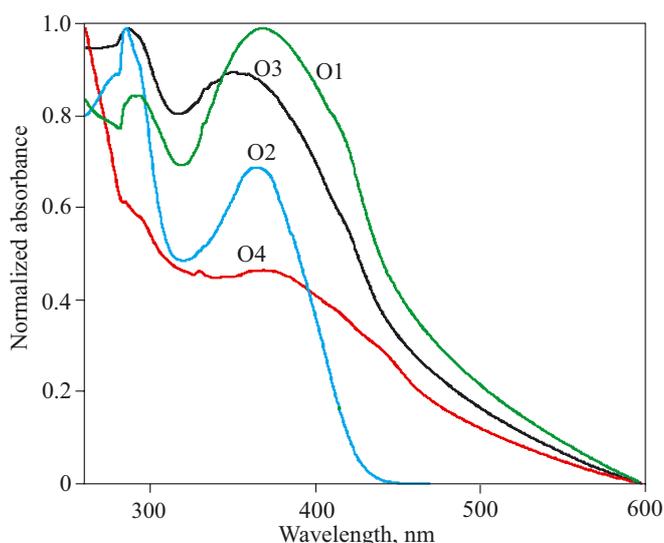


Fig. 12. UV-Vis absorption spectra of O1, O2, O3 and O4 oligo(azomethine ether)s

edges by method described in literature [29–31]. Wavelength corresponding to maximum of absorbance (λ_{max}) and optical band gap (E_g) values of O1, O2, O3 and O4 were found to be 367, 366, 350 and 368 nm and 2.55, 2.94, 2.58 and 2.46 eV, respectively. The E_g value for O2 oligomer containing chlorine atoms was higher than for other oligomers.

CONCLUSIONS

New oligo(azomethine ether)s were synthesized in the reaction of *p*-phenylenediamine or 2,5-dichloro-*p*-phenylenediamine with novel dialdehydes named 4-((2-[(4-formylphenoxy)methyl]benzyl)oxy)benzaldehyde and 4-((4-[(4-formylphenoxy)methyl]benzyl)oxy)benzaldehyde. The FT-IR spectra showed the presence of the absorption band corresponding to the azomethine (-HC=N-) linkage about 1595–1605 cm^{-1} . The sharp and strong peaks are occurring at 1240–1265 cm^{-1} in the spectra of oligomers due to the asymmetrical and symmetrical vibrations of the ether linkage.

Thermal stability of oligomers was found to be high due to the aromatic groups in the oligomer backbones.

According to TG analyses, O2 showed the highest thermal stability at 1000 °C. In all cases, the imine (-HC=N-) linkage is the first breaking group at high temperature. It can be seen from TG analyses that oligo(azomethine ether)s containing chlorine atoms (O2 and O4 samples) have higher thermal stability than O1 and O3 oligomers. It can be understood that chlorine atoms, not ether linkages affect the thermal decomposition of oligomer chains most. Because of electro negativity of chlorine atoms the electron density on azomethine linkages (-HC=N-) was decreased. So, the influence of temperature during thermal decomposition is firstly concerned this bond. That is why the onset temperature of O1 is higher than of O2 and of O3 is higher than of O4 oligomer.

ACKNOWLEDGMENT

The authors thank TUBITAK Grant Commission for a research grant (Project No TBAG-107T414).

REFERENCES

- Adams R., Bullock R. E., Wilson W. C.: *J. Am. Chem. Soc.* 1923, **45**, 521.
- Grigoras M., Catanescu C. O.: *J. Macromol. Sci. Polym. Rev.* 2004, **C44**, No. 2, 1.
- Yang C. J., Jenekhe S. A.: *Chem. Mater.* 1991, **3**, 878.
- Yang C. J., Jenekhe S. A., Vanherzeele H., Meth J. S.: *Chem. Mater.* 1991, **3**, 985.
- Yang C. J., Jenekhe S. A.: *Chem. Mater.* 1994, **6**, 196.
- Yang C. J., Jenekhe S. A.: *Macromolecules* 1995, **28**, 1180.
- Marvel C. S., Hill W. S.: *J. Am. Chem. Soc.* 1950, **72**, 4819.
- Morgan P. W., Kwolek S. L., Pletcher T. C.: *Macromolecules* 1987, **20**, 729.
- Wojtkonski P. W.: *Macromolecules* 1987, **20**, 740.
- Marvel C. S., Tarköy N.: *J. Am. Chem. Soc.* 1958, **80**, 832.
- Marvel C. S., Bonsignore P. V.: *J. Am. Chem. Soc.* 1959, **81**, 2668.
- Rudzinski W. E., Guthrie S. R., Cassidy P. E.: *J. Polym. Sci., Part A: Polym. Chem.* 1988, **26**, 1677.
- Barbera J., Oriol L., Serrano J. L.: *Liq. Cryst.* 1992, **12**, 37.
- Lee K. S., Won J. C., Jung J. C.: *Macromol. Chem.* 1989, **190**, 1547.
- Park S. B., Kim H., Zin W. C., Jung J. C.: *Macromolecules* 1993, **26**, 1627.
- Wang C., Shieh S., LeGoff E., Kanatzidis M. G.: *Macromolecules* 1996, **29**, 3147.
- Saegusa Y., Sekiba K., Nakamura S.: *J. Polym. Sci., Part A: Polym. Chem.* 1990, **28**, 3647.
- Saegusa Y., Takashima T., Nakamura S.: *J. Polym. Sci., Part A: Polym. Chem.* 1992, **30**, 1375.
- Saegusa Y., Koshikawa T., Nakamura S.: *J. Polym. Sci., Part A: Polym. Chem.* 1992, **30**, 1369.

20. Misra M., Das D., Padhi K. B., Panigrahi A. K., Mohanty A. K.: *J. Macromol. Sci., Pure Appl. Chem.* 1998, **35**, 867.
21. Park K. H., Tani T., Kakimoto M., Imai Y.: *Macromol. Chem. Phys.* 1998, **199**, 1029.
22. Hamcium C., Hamcium E., Ronova I. A., Bruma M.: *High Perform. Polym.* 1997, **9**, 177.
23. Bruma M., Schulz B., Töpnick T., Dietel R., Stiller B., Mercer F., Reddy V. N.: *High Perform. Polym.* 1998, **10**, 207.
24. Arsalani N., Geckeler K. E.: *React. Funct. Polym.* 1997, **33**, 167.
25. Yamamoto K., Higuchi M., Shiki S., Tsuruta M., Chiba H.: *Nature* 2002, **415**, 509.
26. Stochmal-Pomarzańska E., Quillard S., Hasik M., Turek W., Proń A., Łapkowski M., Lefrant S.: *Synth. Met.* 1997, **84**, 427.
27. Łuźny W., Stochmal-Pomarzańska E., Proń A.: *Synth. Met.* 1999, **101**, 69.
28. Li C. H., Chang T. C.: *J. Polym. Sci., Part A: Polym. Chem.* 1990, **28**, 3625.
29. Kaya I., Koyuncu S., Çulhaoglu S.: *Polymer* 2008, **49**, 703.
30. Colladet K., Nicolas M., Goris L., Lutsen L., Vanderzande D.: *Thin Solid Films* 2004, **7**, 451.
31. Kaya I., Bilici A.: *Polimery* 2007, **52**, 827.
Received 25 I 2008.

Call for candidates for the AVK innovation award 2009

The AVK — Industrievereinigung Verstärkte Kunststoffe e.V. (Federation of Reinforced Plastics) is now requesting nominations for this year's annual AVK innovation awards in the categories 'industrial applications', 'environment' and 'university research'.

The objective of the innovation awards is to provide solutions to state-of-the-art technological issues by means of composites and thermosets, to highlight the achievements of our industry in the field of environmental protection and to encourage university research into composites and thermosets. Not least, it is hoped that these innovation awards will serve as a source of motivation for specialists active in these fields.

The prizes will be awarded at the

International AVK Conference on October 26-27, 2009, to be held in Stuttgart in conjunction with the COMPOSITES EUROPE Trade Fair (October 27-29, 2009).

Applications for the 2009 innovation awards may be submitted in the following categories:

- **Industrial applications**
- **Environment**
- **University research**

The deadline for the submission of the application papers is **April 20, 2009**.

Further details and objectives may be obtained under: www.avk-tv.de/innovationaward.php