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Synthesis and Characterisation of Polyketanils with Ether Linkages

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Summary: A series of polyketanils from four diketones with pendant aromatic groups (i.e. dibenzoyl, p-dibenzoylbenzene, p-disebacoylbenzene and trans-1,2-dibenzoylethylene) and two diamines with flexibilizing ether linkages [4,4'-diaminediphenyl ether, 4,4'-(1,3phenylenedioxy)dianiline] has been synthesized using melt polycondensation (180^{0}C, 24h). Spectral and thermal properties of the polyketanils before and after protonation with 1,2-(di-2-ethylhexyl)ester of sulfophthalic acid (DEHEPSA) were investigated.

Keywords: fluorescence, polyketanils (polyketimines), protonation, thermostability

Introduction

In recent years conjugated polymers have been widely studied in regard to their electronic and optoelectronic properties being useful for diverse technological applications. These polymers have various chemical structures of chains and polyenes, polythiophenes, polypyrroles, polyphenylenes, polyphenylenevinylenes and polyaniline can be mention as the main groups. However some interest exhibits also polymers with C=N groups in main chain i. e. polyazomethines (polyimines, poly Schiff-bases) and polyketanils (polyketimines). In contrary to polyazomethines, polyketanils being polycondensation products of diketones and diamines have not been widely studied. However an increasing interest in this group of polymers is observed lastly. Previously, as in the case of the most conjugated polymers, polyketanils were investigated from the point of view of their thermal stability. In several works diacetyl derivatives were used as diketone comonomer. Topchiev et al.[1] condensed 4,4'-diacetyldiphenylmethane and 4,4'-diacetyldiphenylsulphid with 1,4-phenylenediamine. The resulting products melted at about 100^{0}C and their conductivity was in the range of

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$10^{-16} - 10^{-11}$ S/cm. The same results were described in [2]. D'Alelio et al.[3] obtained a few series of polyketanils from 1,4-diacetylbenzene, 4,4'-diacetyldiphenyl-methan, -ether, -sulphid and sulphone and various diamines and investigated their thermal stability. 1,4-diacetylbenzene was also used for condensation with 2-methyl-1,4-phenylenediamine by Morgan et al.[4] while Patel et al.[5] condensed 4,4'-diacetyldiphenylether with different diamines. Polyketanils with phenyl pendant groups were synthesized by Volpe et al.[6-8] using para- and meta- dibenzoylobenzene and diamines. Thermal stability of the polyketanils with naphthalene pendant groups were studied by Sęk.[9] Halo-displacement method was used by Yeakel et al.[10] for synthesis of polyketanils with ether linkages. Linear and cyclic oligomers from 4-aminobenzophenone and dendritic oligomers were synthesized by Yamamoto et al.[11-14] Hall et al.[15, 16] investigated polyquinoneimines obtained in polycondensation reaction of antraquinone and its derivatives with aromatic diamines.

But there are not systematic studies of relationships between structure and properties of the polyketanils and to the our best knowledge no influence of the ketimine group protonation on the polyketanils properties was published.

In this work a series of new polyketanils from four diketones with different cores between ketone groups and two aromatic diamines with flexibilizing ether linkages i.e. 4,4'-diaminediphenyl ether (ODA) and 4,4'-(1,3-phenylenedioxy)dianiline (DODA) was synthesized. Melt polycondensation was used for the polyketanils synthesis. Architecturally diverse π-conjugated structures in the polyketanils provides a basis to establish structure – properties relationships.

Experimental

Materials: 4,4'-(1,3-phenylenedioxy)dianiline (Aldrich), trans-1,2-dibenzoylethylene (Aldrich), dibenzoyl (Aldrich) were used as laboratory reagents without further purification.

4,4'-Diaminodiphenyl ether (Merck) was recrystallized from boiling water in the presence of charcoal.

1,2-(di-2-ethylhexyl)ester of sulfophthalic acid (DEHEPSA) was prepared as described in ref.[17]

p-Dibenzoylbenzene, p-disebacoylbenzene were synthesised using the Friedel-Crafts acylation as described in the literature.[18]

Solvents: m-cresol was distilled; dimethylacetamid DMA (Aldrich), methanol were used without purification.

Measurements: Glass transition temperatures of polymers (sample weight about 20 mg, heating rate of 20°C/min) were determined on TA DSC 2010 apparatus using sealed aluminium pen under nitrogen atmosphere (flow rate about 30 ml/min). Thermogravimetric (TG) analyses were performed on a Paulik-Erdey apparatus at a heating rate of 10°C/min under nitrogen. For elemental analysis a 240C Perkin-Elmer analyser was used. Infrared spectra were acquired on a BIO-RAD FTS 40 A spectrometer. Measurements of the IR spectra were done using KBr disc. ^{13}C NMR spectra were recorded on a Varian Inova 300 Spectrometer using $CDCl_3$ as a solvent and TMS as an internal reference. Fluorescence spectra were acquired on a spectrophotometer Fluorolog 3.12 Spex (USA) with a 450 W xenon lamp as a light source. Emission spectra were recorded in DMA solution, at conc. 10^{-4} mol/l. Excitation wavelength was 400 nm. UV-VIS spectra were recorded in m-cresol solution using Hewlett Packard 8452A diode array spectrophotometer. Gel permeation chromatography (GPC) experiments were carried out on Spectra Physics 8800 in temperature 35°C. Differential refractometer Shodex SE61 was used as detector. Tetrahydrofuran was used as the eluent and polystyrene - as standard.

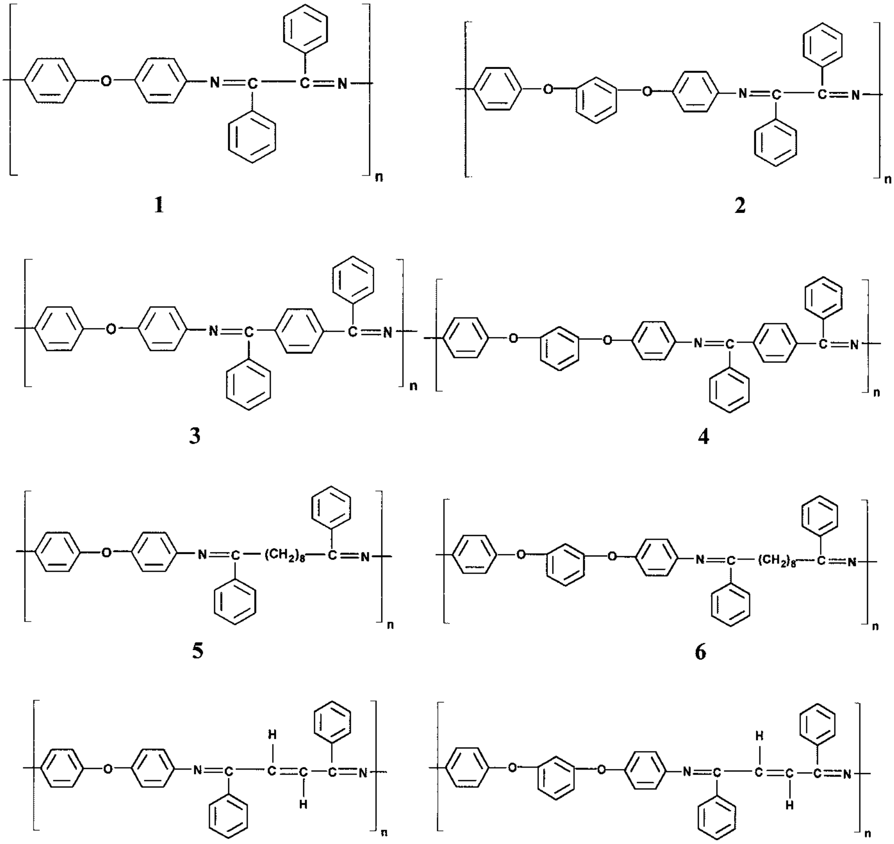
Polymer Synthesis

1 mmol of diketone and 1 mmol of a diamine were heated and stirred at 180°C for 24 hours under nitrogen atmosphere. The mixture was cooled to room temperature, scraped and powdered. The polymers were purified by Soxhlet extraction with methanol and later with acetone and dried at 60°C under vacuum for 24 hours.

Results and Discussion

Structure and Properties of the Polyketanils

Structures of the polyketanils (Fig. 1) were confirmed by spectral and elemental analysis (Table 1).



1 **2** **3** **4** **5** **6** **7** **8**

Fig. 1. Structure of the polyketanils.

Table 1. Structure and characteristic of the polyketanils.

No	**Elemental anal. Found (calcd) [%]**			**FTIR C=N [cm^{-1}]**	**UV-VIS [nm]**	**Fluorescence** Emission band [nm]**	**GPC**		**Tg (DSC) [^{0}C]**	**TG in argon**
	C	**H**	**N**				**Mn**	**Mw (MWD)**		Temp of 10% weight loss [°C] (Residue at 1000^{0}C [%])
1	82.33 (83.42)	4.82 (4.81)	7.20 (7.49)	1610	350	**415**	977	1852 (1.9)	145	420 (40)
2	81.33 (82.40)	4.82 (4.72)	5.63 (6.01)	1608	345	425	926	969 (1.0)	70	420 (38)
3	85.07 (85.31)	4.98 (4.92)	6.16 (6.22)	1609	360	**420**	2381	3319 (1.4)	137	500 (58)
4	83.33 (84.11)	4.75 (4.83)	5.05 (5.16)	1606	350	421	3010	3995 (1.3)	118	430 (46)
5	82.55 (83.95)	6.88 (7.00)	5.98 (5.76)	1614	~350*	**453**	1316	2877 (2.1)	124	420 (30)
6	82.90 (83.04)	6.44 (6.57)	4.45 (4.84)	1611	~350*	462	1889	3551 (1.9)	65	390 (29)
7	83.24 (84.00)	4.94 (5.00)	6.61 (7.00)	1610	385	**442**	1091	2312 (2.1)	133	380 (40)
8	82.77 (82.93)	4.86 (4.88)	5.39 (5.69)	1609	385	444	1119	2047 (1.8)	108	420 (38)

*broad with low intensity

**conc. = 10^{-4}mol/l in DMA, exc. = 350 nm

In FTIR spectra an absorption band in the range of 1608 – 1614 cm^{-1} confirmed the presence of C=N bond. At a little shorter wavelength absorb the polyketanils from dioxydianiline than from oxydianiline and the proper diketones. As a matter of fact the C=N absorption band is very closed to the C=C in aromatic ring absorption being observed at 1590 – 1596 cm^{-1} and in some cases these two bands are not good separated but clearly visible. Fig. 2. shows the FTIR spectrum of the polyketanil from oxydianiline and p-dibenzoylbenzene as an example.

An absorption band at 1660 cm^{-1} suggests the presence of ketone groups being at the end of the polymer chains. In ^{13}C NMR spectra of the polyketanils a signal in the range of 166-169 ppm confirms the presence of carbon atom in ketimine group. A low intensity signal observed at 191 ppm (No 7 and 8) and at 198 – 200 ppm (for remain polyketanils) is due to the carboyl carbon atom being end group of the polymer chain.

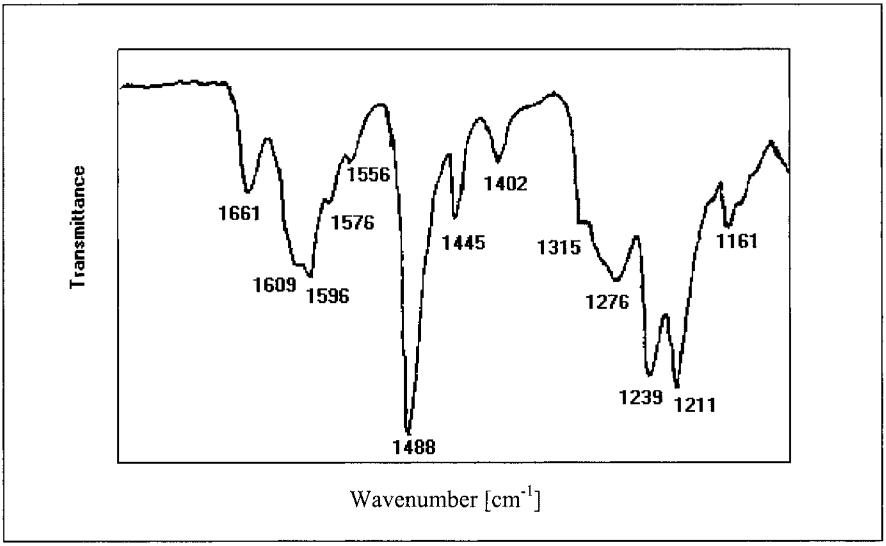
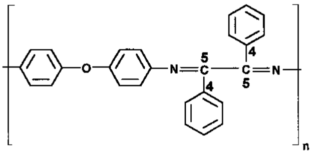
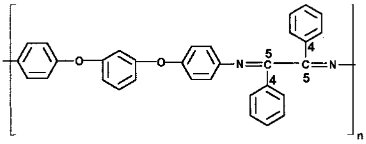
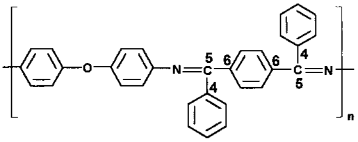
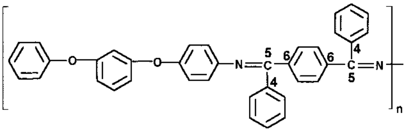
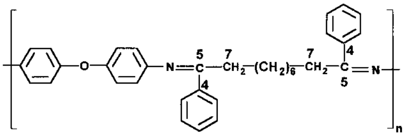
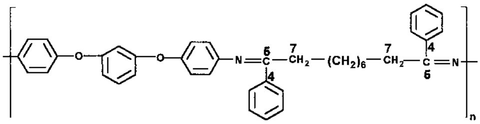
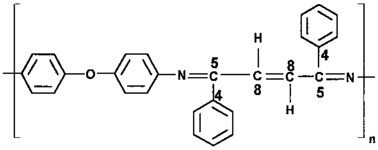
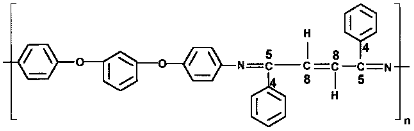


Fig. 2. FTIR spectrum of the polyketanil No 3.

But in the case of ketimine structure the presence of cis and trans isomers is possible even through the trans structure is always supposed to be thermodynamically more stable. A splitting of some signals in ^{13}C NMR spectrum can confirm the presence of isomers. It concerns mainly signals of the quaternary carbon atoms being directly bonded to ketimine carbon. As the diketones used have the different center cores between the carbonyl group the most informative there is the signal from the carbon atom of pendant phenyl rings. Some results are presented in Table 2.

In the polyketanils synthesized from oxydianiline and p-dibenzoylbenzene (No 3 in Table 2) splitting of the signals resulting from the carbon atoms of the pendant benzene rings (4) and the central ring (6) directly connected with ketimine carbon atom (5) confirms the presence of the isomers in the polymer chains. In the spectrum of the polymer from the same diketone and dioxydianiline (No 4) for these carbon atoms the singlets were observed, probably due to existence of the only one isomer. For the other polyketanils investigated the ^{13}C NMR spectra

Table 2. Chemical shift of carbon atoms directly bonded to ketimine carbon atom.

No	Structure	Signal of carbon atom [ppm]				
		4	5	6	7	8
1		134.56 134.76 135.04 137.01	163.89 163.96 165.75 166.27	-	-	-
2		134.32 134.60 135.05	166.46	-	-	-
3		136.02 136.50 137.20 137.50	167.74	138.01 138.60 139.34 139.65	-	-
4		136.53	166.96	137.70	-	-
5		137.05 138.10	170.80 170.78	-	38.58	-
6		136.97	160.26 160.28	-	38.56	-
7		138.94 138.95 139.08 139.11	169.08	-	-	123.70
8		134.32 134.72 135.82 138.42	169.00 169.05 169.20 169.30	-	-	123.74

confirmed the presence of the isomers (detailed study of the whole spectra will be published separately).

Molecular weights of the polyketanils were detected by GPC method. Values of the Mw and Mn are low indicating a formation of oligomers especially in the case of the most stiff diketone used for polycondensation. Never the less these materials form transparent films but some of them are rather brittle. The polyketanils synthesized by melt polycondensation are soluble in many solvents as m-cresol, THF, DMA, chloroform.

Thermal properties of the polyketanils depend on the diketone and the diamine structures as is shown in Table 1. Glass transition temperatures are higher for the polyketanils synthesized from oxydianiline (No 1, 3, 5, 7) than from dioxydianiline (No 2, 4, 6, 8) and the proper diketones. When structures of the diketones are considered one can see that the presence of aliphatic chain caused lowering of the polymers Tg as it was expected. Direct connection of the ketanil groups increases the glass transition temperatures of the polyketanils synthesized from dibenzoyl (No 1 and 2). Comparable values of Tg exhibit polyketanils obtained from oxydianiline and diketones having as a central core phenyl ring (No 3) or carbon-carbon double bond group (No 7). But it is necessary to mention that glass transition temperatures depend also, to some extent, on molecular weight. Our polymers having low molecular weights are probably in the region where Tg may vary with molecular weights. Never the less the found structural relations fit the common rules concerning the influence of stiffness of mer units on glass transition temperatures. And from this point of view the relation for the our materials seems to be true. It is necessary to mention that the polycondensation conditions were not optimized in respect to the diketones used having probably different reactivity.

Results of thermogravimetric analysis show that the polyketanils are thermally stable up to about 400°C.

For the polyketanils photoluminescence was detected in DMA solution. Emission waves were observed in the range of 415 – 460 nm in dependence on the polymer structures (Table 1).

In all the polyketanils synthesized from oxydianiline the emission was observed at a shorter wavelength than for the dioxydianiline independence of the diketone structure. On the other hand if the diketone structure is taking into consideration, the emission at the shortest wavelength exhibits the poliketanil from dibenzoyl while the polyketanils with aliphatic chain in the macromolecules emit light at longer wavelength than the remain ones.

Properties of the Polyketanils after Protonation with 1,2-(di-2-ethylhexyl)ester of Sulfophthalic Acid (DEHEPSA)

Nitrogen atom in ketimine group having free electron pair can be protonated by protonic acids and complexed by Lewis acids. These treatments may influence on electrons delocalization along the polymer chain.

In this work the 1,2-(di-2-ethylhexyl)ester of sulfophthalic acid (DEHEPSA) was used as a protonating agent. But this compound plays a double role i. e. protonates ketimine nitrogen atom and acts as a plasticizer. The protonation effect can be detected as a change of the UV – VIS spectra of the polymers along with the change of color.

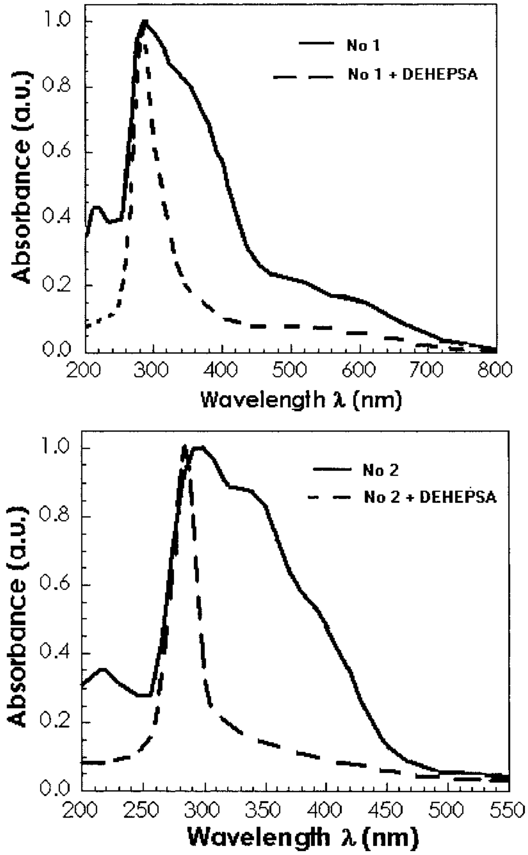


Fig. 3. UV – VIS spectra of the polyketanils No 1 and 2 befor and after protonation.

Fig. 3 shows the UV – VIS spectra of the polyketanils synthesized from dibenzoyl and the diamines (No 1 and 2) before and after protonation. After protonation the absorption band at about 360 nm being responsible for π - π^* transition in ketimine group is not visible. The polymers after protonation change the color to the dipper tone (light brown to brown, yellow-green to brown, respectively).

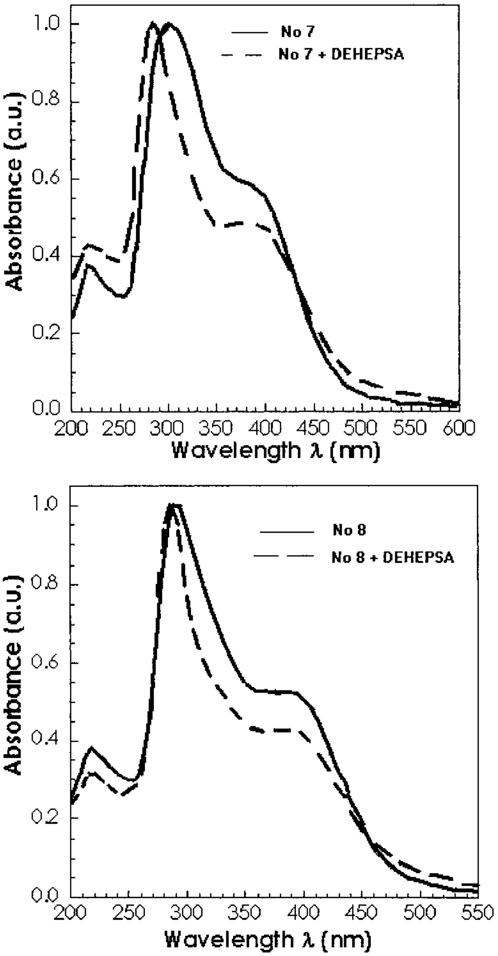


Fig. 4. UV – VIS spectra of the polyketanils No 7 and 8 befor and after protonation.

For the polyketanils from diketone with –C=C- double bond (No 7 and 8), decrease of the absorption intensity at about 385 nm is observed after protonation along with a little higher absorption above 450 nm (change the color from yellow to orange after protonation) (Fig. 4).

In the spectra of the polyketanils with aliphatic chain, asymmetrical absorption band above 300 nm is not structurized. After protonation the narrowing of the band is seen and the absorption is higher at a longer wavelength (about 360 nm). No influence of the diamine structure on the spectra shapes was observed.

Changes in the intensity and shapes of the UV – VIS spectra of the polymers investigated after protonation with DEHEPSA confirm that some delocalization of electrons in the polymers chains took place. Optical spectra before protonation confirmed also the difference in π - electron delocalization in dependence on the polymer structure (Table 1). For example a red (batochromic) shift of 35 nm in λ max was observed while going from the polymer synthesized from oxydianiline and dibenzoyl (No 1) to the one obtained from trans-1,2-dibenzoylethylene (No 7). On the other hand maximum absorption bands of the polyketanils from dioxydianiline and the all diketones exhibited a little blue (hipsochromic) shift in comparison to the ones from oxydianiline.

As it was said before 1,2-(di-2-ethylhexyl)ester of sulfophthalic acid works as a plasticizer. The films after protonation were much more flexible than the virgin ones. Also the glass transitions were observed at lower temperatures. For example the Tg of the polyketanil from oxydianiline and trans-1,2-dibenzoylethylene (No 7) decreased from 133°C to 32°C after protonation while for the polymer from the same diamine and dibenzoyl (No 1) the glass transition temperatures decreased from 145°C to 30°C.

Conclusion

Relationship between structure of a series of soluble polyketanils synthesized from four diketones and diamines containing ether linkages and their thermal and optical properties was investigated.

It was found that the polymers, even if they have rather low molecular weights, exhibit high thermal stability. The polymers emit light in the range of 415 – 460 nm. Protonation of the ketimine groups with 1,2-(di-2-ethylhexyl)ester of sulfophthalic acid (DEHEPSA) caused changes in the UV-VIS spectra that may indicate the changes in delocalization of electrons in the polymers chains. The protonation compound used acted also as a plasticizing agent and caused the lowering of the glass transition temperatures of the polymers.

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