

Synthesis and Photoluminescence of Polyketanils with Aliphatic Chains

Danuta SĘK,[†] Agnieszka IWAN, and Henryk JANECZEK

Centre of Polymer Chemistry, Polish Academy of Sciences, 34, M. Curie-Skłodowska Str., 41–819 Zabrze, Poland

(Received August 5, 2002; Accepted October 23, 2002)

ABSTRACT: Novel polyketanils were synthesized *via* the polycondensation of diketones with two aliphatic diamines. The polyketanils were prepared in a one-step polycondensation in the presence of 1, 4-diazobicyclo[2, 2, 2]octane (DABCO) or DABCO and titanium tetrachloride. Thermal and luminescence properties were investigated. Polymers properties have been correlated with the length of aliphatic segments.

KEY WORDS Polyketanils / Ketimine / Thermostable Polymers / Fluorescence Properties /

Several research teams made studies polymers with $-C=N-$ groups in the main chain, *i.e.*, polyazomethines and polyketanils. In contrary to polyazomethines, having hydrogen atom at imine carbon, polyketanils with aliphatic or aromatic substituents at imine carbon have not been widely studied. Previously, a few papers were published concerning synthesis and thermal properties of some polyketanils being the polycondensation products of diketones and diamines.^{1–8} However an increasing interest in polyketanils has been observed last by because of their potential application in optoelectronics.^{9, 10}

The main aim of this work was synthesis a series of new polyketanils and investigations of their photoluminescence and thermal properties. For synthesis five diketones, *i.e.*, *p*-dibenzoylbenzene, *p*-dibenzoyltoluene, *p*-dibenzoylxylene, *p*-disbacoylbenzene and *p*-disbacoyltoluene and two aliphatic diamines, *i.e.*, 1, 6-diaminohexane and 1, 7-diaminoheptane were used.

In the literature the only *p*-dibenzoylbenzene was reported to be used for polymers synthesis.^{1–3}

However, according to the authors' best knowledge there are no works concerning studies of photoluminescence properties of this group of compounds. Spectroscopic studies of polyketanils were carried out for undoped and doped polymers with 1, 2-(di-2-ethylhexyl) ester of 4-sulfophthalic acid (abbreviated as DEHEPSA).

EXPERIMENTAL

Materials

1, 6-Diaminohexane (Merck), 1, 7-diaminoheptane (Merck) were used as laboratory reagents without further purification.

Terephthaloyl chloride (Aldrich), sebacoyl chloride (Aldrich), aluminium chloride (Aldrich), were used without purification.

Solvents: Acetone, benzene, toluene and *m*-cresol were dried and distilled in the usual manner; dimethylacetamide DMA (Aldrich), *p*-xylene (Aldrich), methanol, hexane were used without purification.

The protonating agent (DEHEPSA) was a gift from Prof. A. Pron from CEA in Grenoble.

Measurements

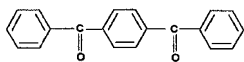
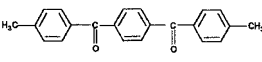
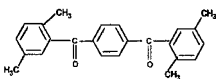
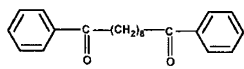
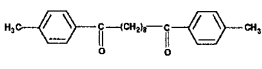
Glass transition temperatures of polymers (sample weight about 20 mg, heating rate of 20 °C min⁻¹) and melting points of diketones (sample weight about 5 mg at a heating rate of 5 °C min⁻¹) were determined on a TA DSC 2010 apparatus using sealed aluminium pan under nitrogen atmosphere (flow rate about 30 mL min⁻¹). Thermogravimetric (TG) analyses were performed on a Paulik–Erdey apparatus at a heating rate of 10 °C min⁻¹ 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. ¹³C NMR spectra were recorded on a Varian Inova 300 Spectrometer using DMSO-*d*₆ as a solvent and TMS as an internal reference. UV-VIS spectra were recorded in DMA solution (conc. 10⁻⁵ mol L⁻¹) using a Beckman Acta M I V. Fluorescence spectra were acquired on a spectrophotometer Fluorolog 3.12 Spex (USA). Gel permeation chromatography (GPC) experiments were carried out on a Spectra Physics 8800 in temperature 35 °C. A differential refractometer Shodex SE61 was used as detector. Tetrahydrofuran was used as the eluent and polystyrene-as standard.

Synthesis of Diketones

Synthesis of *p*-dibenzoylbenzene (Friedel–Crafts acylation of benzene with terephthaloyl chloride in the

[†]To whom correspondence should be addressed.

Table I. Properties of diketones

Structure (Code)	mp ^a (°C)	Elemental Analysis		FT-IR (KBr) (cm ⁻¹)
		Carbon (%)	Hydrogen (%)	
		Found (Calcd)	Found (Calcd)	
 (DB)	161	83.56 (83.89)	4.86 (4.93)	3084 (C–H ar. stretch.), 1657 (C=O) , 1595, 1576, 1447 (phenyl ring stretch.), 677, 708, 783, 858 (C–H arom. out of plane deform.), 1070, 1109, 1158, 1270 (1,4-subst. and mono subst. phenyl ring C–H deform.)
 (DT)	192	84.39 (84.05)	5.92 (5.77)	3029 (=C–H stretch.), 2950 (CH ₃), 1651 (C=O) , 1605, 1448, 1401 (phenyl ring stretch.), 691, 737, 822, 860 (C–H arom. out of plane deform.), 925, 1035, 1155, 1272 (1,4-subst. phenyl ring C–H deform.)
 (DK)	119	84.04 (84.18)	6.37 (6.48)	3025 (=C–H stretch.), 2962 (CH ₃), 1659 (C=O) , 1569, 1500, 1451 (phenyl ring stretch.), 695, 747, 826, 843 (C–H arom. out of plane deform.), 949, 1041, 1112, 1157, 1261 (1,4-subst. phenyl ring C–H deform.)
 (DA)	95	81.44 (81.95)	8.19 (8.13)	3037 (C–H arom. stretch.), 2925, 2910, 2845 (C–H aliph. stretch.), 1682 (C=O) , 1605, 1574, 1450, 1406 (phenyl ring stretch.), 1468 (C–H def aliph.), 725, 815 (C–H arom. out of plane deform.), 979, 1069, 1107, 1181, 1212 (mono subst. phenyl ring C–H aliph.), 2859 (–CH ₃)
 (DAT)	101	82.83 (82.24)	8.79 (8.63)	3057 (C–H arom. stretch.), 2931, 2913, 2850 (C–H aliph. stretch.), 1685 (C=O) , 1596, 1576, 1447 (phenyl ring stretch.), 1464 (C–H def aliph.), 689, 736 (C–H arom. out of plane deform.), 975, 1187, 1226 (mono subst. phenyl ring C–H aliph.)

^adetected by DSC method.

presence of aluminium chloride) was carried out as described in the literature.^{1–3} The new diketones were synthesised using the same method, *i.e.*, Friedel–Crafts acylation of toluene or *p*-xylene with terephthaloyl or sebacyl chloride. Recrystallization of the crude compounds was carried out from a mixture of acetone–hexane (1 : 2 v/v).

Polymers Synthesis

High temperature polycondensation was used for preparation of the polymers. A diketone (1 mmol) and a diamine (1 mmol) were heated and stirred in 4 mL of *m*-cresol at 180 °C for 48 h under nitrogen atmosphere in the presence of DABCO (2 mmol) or DABCO + TiCl₄ (2 mmol + 0.5 mmol). The polymer was precipitated into methanol. The product was collected by filtration, purified by Soxhlet extraction with methanol and dried at 150 °C under vacuum for 24 h.

RESULTS AND DISCUSSION

Characterisation of New Diketones

The structures of the diketones were confirmed by elemental analysis and spectroscopy methods (FT-IR, NMR,) and their characteristics are collected in Table I.

Absorption bands in the range of 1650 cm⁻¹–

1685 cm⁻¹ characteristic for carbonyl group in ketone were observed in the IR spectra. In the reaction of terephthaloyl chloride with toluene there are two possibilities of a substitution, *i.e.*, *para* or *ortho* position. Analysis of over-tone region in FT-IR spectrum confirms the substitution at *para* position (absorption bands at 1935 cm⁻¹, at 1817 cm⁻¹, and 1700 cm⁻¹).

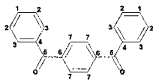
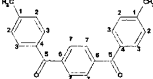
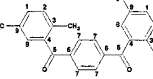
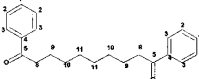
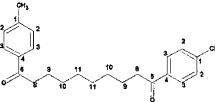
In the ¹³C NMR spectra a peak characteristic for carbon atom in carbonyl group was detected at 194 ppm for diketones DB and DT. In the case of the diketone with methyl group at *ortho* position to carbonyl group (DK) the peak is shifted to 196.9 ppm. In the diketones DA and DAT with aliphatic chain between carbonyl groups, the peak is shifted to 199.2 ppm. Assignments of the remaining absorbance are shown in Table II.

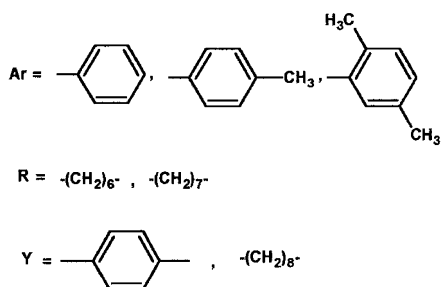
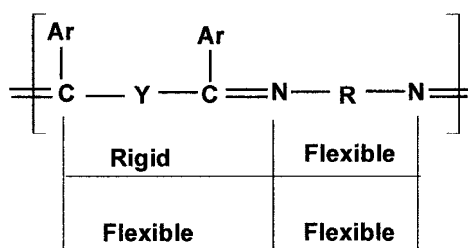
Characterisation of Polymers

Structure of the polymers is presented in Figure 1 and some their properties are listed in Table III.

The polyketanils were soluble in *m*-cresol, DMF, DMA except the polymer DB7. In FT-IR spectra the absorption band in the range 1608–1612 cm⁻¹, being characteristic for –C=N– group along with the absorption due to phenyl ring confirmed structure of the polyketanils. Thermal stability of the polyketanils was investigated by thermogravimetric analysis. These

Table II. ^1H and ^{13}C NMR assignments

Structure	^{13}C NMR (ppm)											
	1	2	3	4	5	6	7	8	9	10	11	CH_3
	132.52	128.21	128.93	136.33	194.84	139.87	129.17					
^1H NMR (ppm)	2Har. 7.71 (m)	4Har. 7.58 (m)	4Har. 7.81 (m)	—	—	—	4Har. 7.87 (s)	—	—	—	—	—
	143.12	128.79	128.75	133.69	194.46	140.05	129.39					20.69
^1H NMR (ppm)	—	4Char. 7.38 (d)	4Char. 7.74 (d)	—	—	—	4Har. 7.84 (s)	—	—	—	—	2 CH_3 2.41 (s)
	130.91	130.53	132.57	137.42	196.93	140.36	129.23	128.23	134.35			19.88 18.53
^1H NMR (ppm)	2Har. 7.26 (m)	2Har. 7.14 (m)	—	—	—	—	4Har. 7.82 (s)	2Har. 7.29 (m)	—	—	—	2 CH_3 2.19 (s) 2.28 (s)
	132.32	127.33	128.15	136.68	199.66			37.54	23.50	28.16	28.24	
^1H NMR (ppm)	2Har. 7.61 (m)	4Har. 7.50 (m)	4Har. 7.94 (m)	—	—	—	—	2 CH_2 2.99 (t)	2 CH_2 1.59 (m)	2 CH_2 1.29 (m)	2 CH_2 1.29 (m)	—
	142.70	128.73	127.48	134.22	199.17			37.43	23.62	28.19	28.25	20.57
^1H NMR (ppm)	—	4Char. 7.30 (d)	4Char. 7.84 (d)	—	—	—	—	2 CH_2 2.94 (t)	2 CH_2 1.56 (m)	2 CH_2 1.28 (m)	2 CH_2 1.28 (m)	2 CH_3 2.36 (s)

**Figure 1.** Structure of polymers.

polymers lost 10% weight at temperatures in the range of 330–420 °C in nitrogen. The residue at 1000 °C is between 56–63%. Glass transition temperatures de-

pend on the polymers structure and were observed in the range of 134–305 °C. It was not possible to detect glass transition temperature for the polymer DB7. Generally, polymers obtained from 1,6-diaminohexane have the lower glass transition temperatures than the polymers from 1,7-diaminoheptane and the same diketones. This result is unexpected because in the many polymers those with odd number of (CH_2) groups in the chain exhibit lower T_g than with even ones and a longer aliphatic chain usually lowers temperature of the glass transition. Molecular weights of the polymers from these two diamines and proper diketones differ very little and it cannot be a reason of the various T_g 's. Of course, the glass transition temperatures depend on molecular weights to some extent but the influence of the polymer chemical structure should not differ very much in the case of high or low molecular weight of the polymers. It seems that the different conformations of the polymers chains might be responsible for the observed phenomenon. Polyketanils prepared in the presence of DABCO (Table III) have not high molecular weight (detected by GPC). When a mix-

Table III. Some properties of the new polyketanils (synthesized in the presence of DABCO)

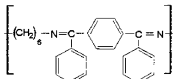
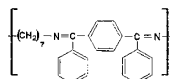
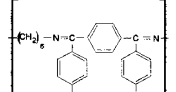
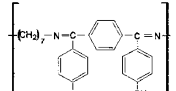
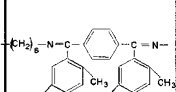
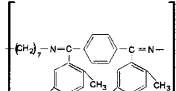
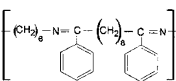
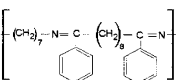
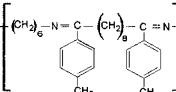
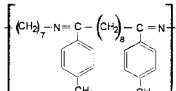
Structure (Code)	T_g (°C)	TG in argon		FT-IR (KBr) (cm^{-1})	M_n (GPC)
		10% weight loss (°C)	Residue at 1000 °C (%)		
 (DB6)	193	420	62	3510, 3386 (N-H stretch in amine end groups), 3029 (C-H arom. stretch.), 2922, 2861 (C-H aliph. stretch.), 1611 (C=N), 1586, 1495, 1416 (phenyl ring stretch.), 1451 (C-H aliph. deform.), 701, 781, 809 (C-H arom out of plane deform.), 1034, 1160, 1247 (1.4 subst. and mono subst. phenyl ring C-H deform.)	2400
 (DB7)	ND	420	63	3028 (C-H arom. stretch.), 2922, 2861 (C-H aliph stretch.), 1611 (C=N), 1588, 1492, 1416 (phenyl ring stretch.), 1452 (C-H aliph. deform.), 702, 781, 811 (C-H arom. out of plane deform.), 1035, 1159, 1246 (1.4 and mono subst. phenyl ring C-H deform.)	—
 (DT6)	162	370	62	3510, 3386 (N-H stretch. in amine end group), 3029 (C-H arom. stretch.), 2922, 2861 (C-H aliph stretch.), 2950 (-CH3), 1608 (C=N), 1586, 1497, 1416 (phenyl ring stretch.), 1452 (C-H aliph. deform.), 691, 737, 809, 862 (C-H arom. out of plane deform.), 952, 1034, 1160, 1248 (1.4 subst. phenyl ring C-H deform.)	2400
 (DT7)	304	370	63	3510, 3344 (N-H stretch. in amine end group), 3029 (C-H arom. stretch.), 2921, 2859 (C-H aliph. stretch.), 2950 (-CH3), 1609 (C=N), 1584, 1496, 1417 (phenyl ring stretch.) 1454 (C-H aliph. deform.), 691, 737, 810, 863 (C-H arom. out of plane deform.), 953, 1034, 1160, 1247 (1.4 subst. phenyl ring C-H deform.)	2500
 (DK6)	250	370	54	3510, 3381 (N-H stretch. in amine end group), 3028 (C-H arom. stretch.), 2922, 2861 (C-H aliph. stretch.), 2962 (-CH3), 1611 (C=N), 1586, 1497, 1416 (phenyl ring stretch.) 1452 (C-H aliph. deform.), 689, 737, 808, 862 (C-H arom. out of plane deform.), 951, 1033, 1158, 1260, 1294 (1.4 subst. phenyl ring C-H deform.)	1600
 (DK7)	305	355	56	3511, 3382 (N-H stretch. in amine end group), 3029 (C-H arom. stretch.), 2923, 2860 (C-H aliph. stretch.), 2962 (-CH3), 1611 (C=N), 1586, 1497, 1416 (phenyl ring stretch.) 1454 (C-H aliph. deform.), 689, 737, 811, 863 (C-H arom. out of plane deform.), 953, 1034, 1160, 1247, 1295 (1.4 subst. phenyl ring C-H deform.)	2700
 (DA6)	134	330	48	3509, 3371 (N-H stretch. in amine end group), 3027 (C-H arom. stretch.), 2924, 2858 (C-H aliph. stretch.), 1612 (C=N), 1583, 1498, 1416 (phenyl ring stretch.) 1449 (C-H aliph. deform.), 699, 736, 809, 862 (C-H arom. out of plane deform.), 949, 1158, 1247 (mono subst. phenyl ring C-H deform.)	1600
 (DA7)	187	335	53	3509, 3377 (N-H stretch. in amine end group), 3028 (C-H arom. stretch.), 2925, 2858 (C-H aliph. stretch.), 1612 (C=N), 1584, 1498, 1421 (phenyl ring stretch.) 1450 (C-H aliph. deform.), 699, 736, 809, 862 (C-H arom. out of plane deform.), 948, 1159, 1248 (mono subst. phenyl ring C-H deform.)	1900
 (DAT6)	155	350	50	3509, 3375 (N-H stretch. in amine end group), 3026 (C-H arom. stretch.), 2923 (C-H aliph. stretch.), 2858 (-CH3), 1608 (C=N), 1585, 1499, 1422 (phenyl ring stretch.) 1452 (C-H aliph. deform.), 733, 810, 862 (C-H arom. out of plane deform.), 949, 1181, 1248 (mono subst. phenyl ring C-H deform.)	1500
 (DAT7)	222	355	49	3509, 3349 (N-H stretch. in amine end group), 3028 (C-H arom. stretch.), 2924 (C-H aliph. stretch.), 2859 (-CH3), 1608 (C=N), 1585, 1497, 1419 (phenyl ring stretch.) 1454 (C-H aliph. deform.), 737, 810, 863 (C-H arom. out of plane deform.), 952, 1181, 1248 (mono subst. phenyl ring C-H deform.)	1500

Table IV. Influence of the catalysts on M_n and T_g of the polyketanils

Code	Dabco		Dabco : TiCl ₄ (2 : 0.5)	
	T_g (°C)	M_n (GPC)	T_g (°C)	M_n (GPC)
DK6	250	1.6×10^3	ND	2×10^6
DK7	305	2.7×10^3	349	1.7×10^5
DA6	134	1.6×10^3	ND	7.5×10^5
DA7	187	1.9×10^3	302	1.2×10^5

Table V. Maximum emission band wavelength of the polyketanils before and after doping

Polymer (code as in Table II)	Photoluminescence (nm)	
	Undoped	Doped with DEHEPSA
DB6	474	519
DT6	501	504
DT7	525	501
DK6	486	494
DK7	536	516
DA6	473	475
DA7	494	488
DAT6	484	485
DAT7	507	478

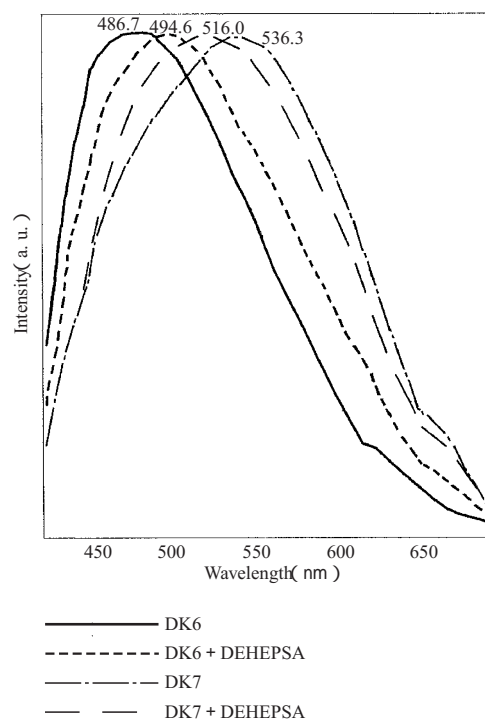
ture of DABCO + TiCl₄ was used as catalyst polymers with higher molecular weight and higher glass transition temperature were obtained. Table IV shows the influence of the catalysts on T_g and M_n for selected polymers.

But the last catalytic system exhibits inconvenience because of the difficulty of titanium derivative traces removing.

In UV VIS spectra of the polyketanils in DMA solution strong absorption band in the range of 270–280 nm and weak (broad and with low intensities) at 345–370 nm were detected. For polyketanils (as in Table III) photoluminescence was detected. Measurements were done in DMA solution (conc. 10^{-4} mol L⁻¹) for undoped and doped polymers with DEHEPSA (ratio: 2 mol DEHEPSA for 1 mol of polymer). Emission spectra of the polyketanils have very similar shape. In Table V the values of the maximum emission band wavelength are collected.

Undoped polyketanils obtained from 1,7-diaminoheptane exhibit maximum emission band in the range of 494–525 nm. The values for the polymers prepared from 1,6-diaminohexane there are between 473–501 nm. The emission bands of the polyketanils synthesized from diamine having odd number of (CH₂) groups and the all diketones are bathochromic shifted in comparison to the polymers from the diamine with even (CH₂) groups.

Doping of the polyketanils with DEHEPSA influ-

**Figure 2.** Emission spectra of the polymer DK6 and DK7 before and after doping.

ences on the emission wavelength in different way.

The polyketanils synthesized from 1,6-diaminohexane and all the diketones after doping exhibited a little bathochromic shift in comparison to the undoped ones. The bigger shift was observed only for the polymer DB6. On the other hand the polymers from 1,7-diaminoheptane and all the diketones after doping with DEHEPSA showed hypsochromic shift of the emission band in comparison with undoped ones.

Figure 2 shows the emission spectra of DK6 and DK7 before and after doping, as an example.

Intra and inter molecular interactions can influence on photoluminescence. Possible reason of the different behaviour of the polyketanils with aliphatic chains after protonation with bulky DEHEPSA molecule can be the different configurational interactions between the polymer chains with odd and even (CH₂) groups.

To the authors' best knowledge no works concerning study of photoluminescence of polymers with imine groups (polyazomethines, polyketanils) in the main chains after protonation have been published. Therefore additional investigations have to be done to solve problem and the work is in progress.

CONCLUSION

A series of new polyketanils was synthesised using different diketones and two aliphatic diamines. The

polyketanils exhibit high thermal stability and their glass transition temperatures depend on the structure of monomers. It was unexpected that the glass transition temperatures of the polyketanils synthesized from 1,7-diaminoheptane (in the presence DABCO as catalyst), *i.e.*, having odd number of (CH₂) groups are higher than the T_g of the polymers from 1,6-diaminohexane. The structure of the diamine influences also on the photoluminescence emission band. Undoped polyketanils obtained from 1,7-diaminoheptane exhibited bathochromic shift of the emission band in comparison with the polymers obtained from 1,6-diaminohexane. Doping of the polyketanils with 1,2-(di-2-ethylhexyl)ester of 4-sulfophthalic acid (DEHEPSA) caused very little bathochromic shift of the emission band in the case of polyketanils from 1,6-diaminohexane while for the series of polymers from 1,7-diaminoheptane – a hypsochromic shift was observed in comparison with the undoped polymers.

Acknowledgments. The authors are grateful to Dr. Z. Mazurak for detected of PL spectra and Dr. J. Kasperczyk for NMR measurements and discussion.

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