Characterization and Photoluminescence Study of Blue and Green Emitting Polyketanils and Their Blends

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Received January 18, 2005; Revised Manuscript Received March 2, 2005

ABSTRACT: The optical and thermal properties of novel polyketanils (PKAX) with structures containing aliphatic and aromatic moieties are reported. It is demonstrated that the photoluminescence (PL) spectra can be modified not only by changing the ratio of conjugated to nonconjugated segment in the polymer main chain but also via acid−base doping involving the protonation of ketimine groups. By combining these two methods, it is possible to precisely tune the emission spectra of polyketanils in the spectral range of 435 to 550 nm. The most electron-rich molecule, PKA3, has the highest HOMO value of 2.26 eV. The protonation of the polymers changes the HOMO/LUMO energy gap of the polyketanils. Additionally, the photoluminescence spectra of the polyketanils in polymer blend with poly(methyl methacrylate) (PMMA) have also been described. The use of bifunctional protonating agent, containing plasticizing groups, for example the 1,2-(di-2-ethylhexyl) ester of 4-sulfophthalic acid (DEHEPSA), in addition to the modification of the luminescent spectra, leads to a lowering of the glass transition temperature and solubilization of the polymers studied. Soluble DEHEPSA complex with the aliphatic−aliphatic polyketanils in organic solvents facilitated their solution spectroscopic (^{1}H, ^{13}C NMR, UV−vis, PL) characterization. The results of this study show that aliphatic−aromatic and aliphatic−aliphatic polyketanils are an interesting class of π-conjugated polymers whose electronic structure and properties can be regulated over a wide range by variation in main chain structure and through protonation or intramolecular hydrogen bonding.

Introduction

Conjugated polymers offer many possibilities in the optoelectronic application such as light-emitting diodes, thin-film transistors, and plastic laser. They are also reliable candidates for the sensory materials. The fluorescent sensor is one of the most desirable technique to detect chemicals because the guest binding event results in the increase or decrease and the wavelength shift of the emission or absorption peak.

The use of noncovalent interactions between molecules possessing the desired complementary structural elements is a crucial synthetic tool due to its great potential in the design of new, highly functional materials. The self-assembly processes of organic systems, driven by protonation may be used to obtain structural variation and specifically physical properties for potential applications of these materials. Protonation is one of the important noncovalent interactions playing a fundamental role in polymer properties as well as in the design of new polymer architectures[1].

Polyazomethines and polyketanils are interesting group of conjugated polymers having carbon−nitrogen double bonded units in the main chain, capable of protonation and complexation. Polyazomethines in the most cases are insoluble in common solvents, and complexation of imine groups improves solubility as was reported by Jenekhe et al.[2] He also observed a bathochromic shift of electronic absorption spectra after complexation polyazomethines with $GaCl_3$ and diphenyl or di-*m*-cresyl phosphate. The reverse behavior was found by Cho et al.[3] Fluorene-based polyazomethines after complexation with sulfonated polystyrene exhibited a hypsochromic shift of the UV−vis spectra in comparison to the pristine ones. However, it is interesting that those polymers after complexation gave a high luminescence in the solution although the pristine polymer did not show luminescence in a solution and film. None or very low intensity of polyazomethines luminescence was also reported in.[4] However polyazomethines with some another fluorophore structure in the polymer chains can exhibit high intensity of luminescence as it was described in.[5] The authors[5] found that changing aprotic solvent (NMP) over formic acid caused hypsochromic shift of emission wave along with decrease of luminescence intensity.

Surprisingly, much less research has been devoted to conjugated polyketanils which are closely related to polyazomethines. To the best of our knowledge, the papers dealing with polyketanils are scarce[6,7] and centered on the preparation aspects rather than on electronic or spectroscopic properties vital for their application in optoelectronic devices. Yet these polymers seem very interesting constituents of new materials suitable for use in polymer electronics, especially in view of a recent discovery that the photoluminescence of conjugated polymers containing basic sites in the main chain can be strongly modified by protonic (acid−base) doping.[8−10]

In this paper, we demonstrate that, by combining chain engineering with acid−base doping (protonation of imine nitrogens), it is possible to precisely control the photoluminescence spectra of polyketanils over the spectral range of ca. 120 nm.

Additionally, the effects of blending the new polyketanils with other polymers, such as PMMA, on PL spectra will also be discussed. Moreover, the use of protonating agent with plasticizing properties, in addition to the modification of the photoluminescence spectrum, results in a significant improvement of the mechanical proper-

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10.1021/ma050102f CCC: $30.25

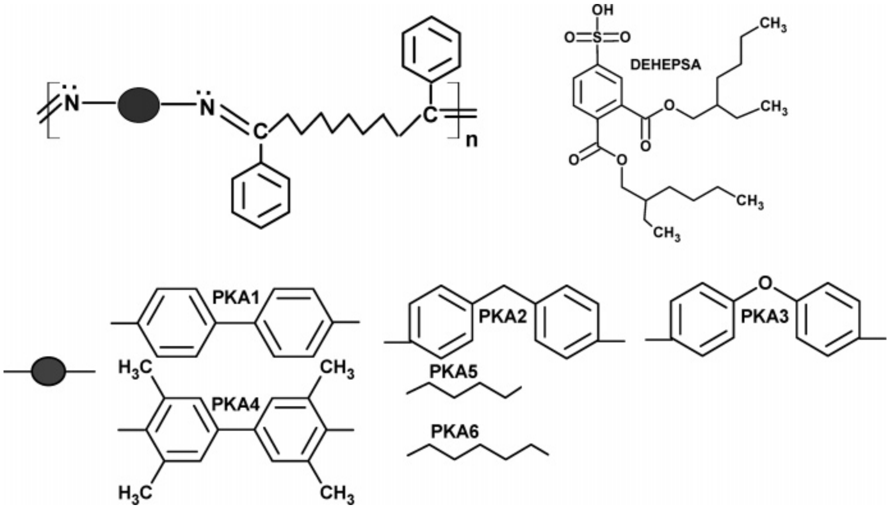


Figure 1. Chemical structure of synthesized polyketanils.

ties of polyketanils due to a significant decrease in their T_g.

Experimental Section

1. Materials. 4,4′-Methylenedianiline (Aldrich), 3,3′,5,5′-tetramethylbenzidine (Aldrich), 1,6-diaminohexane (Merck), and 1,7-diaminoheptane (Merck) as well as the following solvents, dimethylacetamide (DMA from Aldrich) and methanol, were used as received. The diketone 1,8-disebacoylbenzene was synthesized using Friedel−Crafts acylation of benzene with sebacoyl chloride in the presence of aluminum chloride and characterized as described in.[11] *m*-Cresol (MC from Aldrich) was distilled prior to its use. 4,4′-Diaminobiphenyl (Fluka) and 4,4′-diaminodiphenyl ether (Merck) were recrystallized from boiling water in the presence of charcoal. 1,2-(Di-2-ethylhexyl) ester of 4-sulfophthalic acid (abbreviated as DEHEPSA) was prepared as described in ref 12.

2. **Characterization Techniques.** The obtained polymers were characterized by the following techniques: elemental analysis (240C Perkin-Elmer analyzer), ^1H and ^{13}C NMR (Varian UNITY Inova 300 spectrometer, $CDCl_3$ solvent against TMS as an internal reference), and FTIR (BIO−RAD FTS 40 A spectrometer, KBr pressed pellet technique).

Molecular weights of the synthesized compounds were determined using size exclusion chromatography (SEC). The determinations were carried out on a Spectra Physics 8800 chromatograph at a temperature of 308 K. A differential refractometer Shodex SE61 was used as detector. Tetrahydrofuran (THF) was used as the eluent and polystyrene (PS) samples of narrow polydispersity as standards.

Glass transition temperatures (T_g) of the synthesized polymers (sample weight of ca. 20 mg, scanning rate of 20 °C·min^{-1}) were determined by differential scanning calorimetry (DSC) on TA DSC 2010 apparatus using sealed aluminum pans under nitrogen atmosphere (flow rate of ca. 30 mL·min^{-1}). Thermogravimetric analyses (TG) were performed on a Paulik-Erdey apparatus at a heating rate of 10 °C·min^{-1} under nitrogen.

UV−vis solution absorption spectra (concentration = 1×10^{-4} mol/L) were recorded using a Hewlett-Packard 8452A spectrophotometer whereas the photoluminescence solution spectra (concentration = 1×10^{-4} mol/L) were registered on a Fluorolog 3.12 Spex spectrometer with a 400 nm excitation line (450 W xenon lamp as the light source).

3. Polymer Synthesis. In a typical preparation 1 mmol of a given diketone and 1 mmol of a diamine were heated and stirred at 180 °C for 24 h under nitrogen atmosphere. The mixture was then cooled to room temperature, scraped, and powdered. The polymers were purified by Soxhlet extraction with methanol and then with acetone and finally dried at 60 °C under vacuum for 24 h.

4. Protonation of Polyketanils. Protonation of polyketanils with DEHEPSA was carried out at room temperature using *m*-cresol as a solvent. DEHEPSA was added to the MC solution of polyketanils studied in the 1:1 ratio with respect to imine nitrogens in order to ensure full protonation of the polymer.

5. Preparation of Polymer Blends. Polymer blends were obtained by dissolving the desired amount of the polymers (PMMA, PKAX) in chloroform to form a homogeneous solution. Films cast on glass were dried in vacuum oven at 60 °C over 10 h.

Results and Discussion

Chemical structures of the polyketanils synthesized in this research and of the protonating agent DEHEPSA are presented in Figure 1 whereas their principal spectroscopic and molecular characteristics are collected in Table 1 and Table 2.

The polyketanils synthesized are novel, except the PKA1 and PKA3 described in refs 9 and 13, respectively.

Aliphatic−aromatic polyketanils (PKA1−PKA4) are only partly soluble in THF to give yellow or orange solutions and a brown solid residue. The molecular weight of the soluble fraction can be estimated by SEC using polystyrene standards and THF as an eluent. The weight-average molecular weight (M_w) is about 4.55×10^3 and number-average molecular weight (M_n) is about 2.55×10^3, giving a polydispersity index of 1.78. The M_n corresponds to an average of four repeat units. As seen from the size exclusion chromatography results, the soluble fraction of the polyketanils has rather low degree of polymerization. However we notice that the soluble fraction has an intermediate molecular weight, while the brown insoluble residue is expected to have a much higher average molecular weight. Similar results were described for Schiff bases.[14]

Additionally polyketanils can be dissolved in such solvents as MC, DMA or chloroform, with the exception of PKA5 and PKA6. Good optical quality films can be obtained by casting from solution on glass, quartz or any other suitable support, however free foils are brittle. The solubilization of the aliphatic polyketanils (PKA5, PKA6) in organic solvents such as MC and chloroform was achieved by protonation of the polymers by Bronsted acid such as DEHEPSA. The success of Bronsted acid protonation and solubilization of aliphatic−aliphatic polyketanils (PKA5, PKA6) in organic solvent has

Table 1. FTIR, Elemental Analysis, TG Data, DSC Characterizations, and Fluorescence Emission Bands of Undoped and DEHEPSA-Protonated Polyketanils

code	FTIR C=N [cm^{-1}]	anal.[a] found/calcd			dec temp [°C][b] RW % T_{10}	T_g[c] (DSC[d]) [°C] before (after) protonation	PL λ_{emis} [nm][e] DMA MC/MC + DEHEPSA
		% C	% H	% N			
PKA1	1623	85.17/86.81	7.62/7.23	6.27/5.96	410	114	485
					35	(10)	525/543
PKA2	1623	85.81/86.78	5.84/7.44	6.86/5.79	380	130	480
					38	(33)	
PKA3	1614	82.33/83.95	6.88/7.00	5.98/5.76	420	124	453
					30	(18)	522/549
PKA4	1625	86.88/86.69	6.27/7.98	5.70/5.32	385	148	476
					42	(29)	522/534
PKA5	1650	84.56/83.58	7.15/9.46	6.70/6.96	360	62	
					21	(22)	−/484
PKA6	1650	82.15/83.65	7.53/9.62	6.23/6.73	370	55	
					20	(20)	−/486

[a] For the calculation, a repeating unit formula of the polymer was used. Some differences in the calculated and found values may be due to the omitting in calculation the end groups. According to FTIR and NMR date in the polymer PKA1, PKA2, PKA3, and PKA4 there are ketone end groups (C=O) and the presence of oxygen in these groups (not taken into account) may cause the discrepancies. Another reason for the differences may be the difficulties in burning these high-temperature polymers. [b] Temperature of 10% weight loss (T_{10}) and residual weight percentage at 1000 °C were determined by TG under N_2 atmosphere. [c] Determined on the second heating scan. [d] Scanning rate: 20 °C·min^{-1}. [e] Fluorescence emission bands (PL) of undoped (in DMA and MC) and DEHEPSA-protonated Polyketanils solutions in MC (MC + DEHEPSA).

facilitated the detailed characterization of their molecular structures by ^{1}H and ^{13}C NMR spectroscopy.

In Table 2, ^{1}H and ^{13}C NMR data concerning all aromatic−aliphatic polymers investigated are collected together with the assignment of the registered NMR lines. In particular, the signals in the range of 165−170 ppm (see *C-5*), present in the spectra of all polymers, confirm the existence of the ketimine group carbon atoms. In the case of the ketimine structure two isomers are possible (cis and trans), even though the trans structure is always supposed to be thermodynamically more stable. A splitting of the signals in ^{13}C NMR spectrum seems to confirm the coexistence of the isomers.

The changes in the chemical shift, observed upon the modification of the chemical constitution of the diamine originating subunit of the repeat unit, are consistent with the assignment proposed in Table 2. Thus, the presence of an alkyl spacer between the phenylene groups influences the NMR spectrum to a rather small extent whereas the ether group in the same position induces a significant upfield shift of the signal related to carbon number 13, as expected (compare the ^{13}C NMR data of PKA1, PKA2, and PKA3). A small downfield shift is also observed for carbon number 12. In the case of PKA4, the presence of methyl groups in the ortho position with respect to nitrogen results in a upfield shift of the line related to carbon number 11 and a slightly smaller upfield shift of the line ascribed to carbon number 5.

Most signals were assigned based on well-known proton NMR chemical shift displacements resulting from electron shielding/deshielding of the hydrogen nuclei by the inductive effects or from the diamagnetic anisotropy of various neighboring groups (see Table 2). For example, the inductive effect of the electron-rich ether linkage of the 4,4′-diaminodiphenyl ether (ODA) segment (PKA3) has a shielding effect on the phenyl rings *o*-oxygen protons, thus their shifts to lower frequency (H-12; 7.00 ppm). The induced magnetic field resulting from circulating π-electrons found in the methyl groups has a shielding effect on the aromatic hydrogen atoms of the pendant phenyl ring, consequently shifting them to lower frequency (H-3, 7.40 ppm).

The ^{1}H NMR and ^{13}C NMR spectra of the aliphatic−aliphatic polyketanils (PKA5, PKA6) were obtained also in deuterated chloroform but containing DEHEPSA. In this case a slight complication of the ^{1}H and ^{13}C NMR spectra of the polyketanils was observed in PKA5 and PKA6 due to the partial overlap of the methyl proton or carbon resonances of the polymers with that of the methyl proton/carbon resonances of the protonating agent (1,2-(di-2-ethylhexyl) ester of 4-sulfophthalic acid).

The ^{1}H NMR spectrum of the protonating agent—DEHEPSA—was obtained in deuterated chloroform. The assignments of the chemical shifts of all resonances in the ^{1}H NMR spectrum are given below.

DEHEPSA, ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): 0.91 (m, 12H), 1.31 (m, 16H), 1.68 (m, 2H), 4.25 (m, 4H), 5.50 (s, 1H), 7.74 (d, 1H), 7.99 (d, 1H), 8.17 (s, 1H).

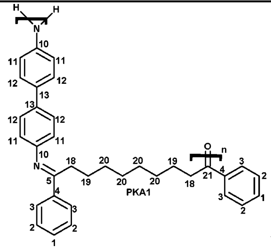
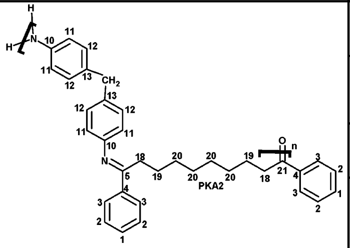
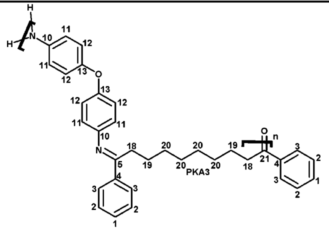
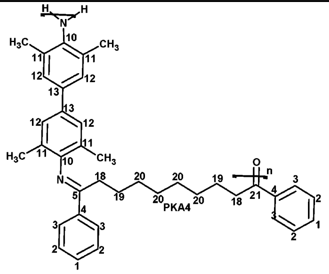
We have here exhibit the strong binding ability polyketanils to DEHEPSA. The doping involves protonation of imine nitrogen in the polymer chain. From the ^{1}H NMR experiments, it is confirmed that the molecular recognition could be attributed to the formation of the complex between polyketanil and DEHEPSA. Protonation effect by DEHEPSA is visibly not only in the shift and the broadening of $-SO_3H$ protons in ^{1}H NMR spectrum (Figure 2, inset) but also in the shift and broadening of NMR lines of methyl, methylene and methine protons in DEHEPSA. ^{1}H NMR spectra of DEHEPSA and PKA6 with DEHEPSA are shown in Figure 2.

Additionally, changes in the ^{13}C NMR spectra of doped polymers PKA5 and PKA6 were observed. The characteristic for aliphatic region ^{13}C NMR spectra of DEHEPSA and PKA6 with DEHEPSA are shown in Figure 3.

It shows new resonance lines in the aliphatic region of doped polyketanil PKA6 at: 22.8, 23.4, 23.7, 38.5, and 38.6 ppm assigned to the four different carbons of the methylene groups. Additionally, the signal about 165 ppm present in the spectra of two aliphatic polyketanils (PKA5, PKA6) confirm the existence of the ketimine group carbon atoms.

Summary NMR study of the polyketanils we would like to emphasize that contrary to aromatic−aliphatic PKAs, which are soluble in organic solvents, the solubilization of two aliphatic−aliphatic polyketanils (PKA5,

Table 2. Solution ^{13}C and ^{1}H NMR Characterizations of Polyketanils Studied[a]

^{13}C NMR* [ppm] ^{1}H NMR [ppm]								
Structure	**C1** *H1*	**C2** *H2*	**C3** *H3*	**C4**	**C5**	**C10**	**C21**	**CH$_3$** **(CH$_2$)**
 PKA1	**132.85**7 *7.52*	**128.52** *7.45*	**128.02** *7.92m*	**137.03**	**170.14**	**145.95**		
	C11 *H11*	**C12** *H12*	**C13**	**C18** *H18*	**C19** *H19*	**C20** *H20*	**200.60**	-
	120.49 **120.02** **119.95** *6.70*	**127.24** **127.52** *7.20*	**134.45** **134.68**	**38.56** *2.90*	**24.29** *1.6-1.8*	**29.28** *1.2-1.4*		
 PKA2	**C1** *H1*	**C2** *H2*	**C3** *H3*	**C4**	**C5**	**C10**	**200.84**	**40.44**
	132.85 *7.50*	**128.52** *7.40*	**128.00** *7.90m*	**136.96**	**165.98**	**144.39**		
	C11 *H11*	**C12** *H12*	**C13**	**C18** *H18*	**C19** *H19*	**C20** *H20*		
	120.45 **119.98** *6.80*	**127.07** **127.25** *7.20*	**134.25** **134.65**	**38.55** *2.90*	**24.28** *1.6-1.8*	**29.03** **29.26** *1.1-1.4*		
 PKA3	**C1** *H1*	**C2** *H2*	**C3** *H3*	**C4**	**C5**	**C10**	**200.62**	-
	132.86 *7.53*	**128.54** *7.44*	**128.04** *7.92m*	**137.05** **138.10**	**170.80**	**138.20**		
	C11 *H11*	**C12** *H12*	**C13**	**C18** *H18*	**C19** *H19*	**C20** *H20*		
	116.21 *6.70*	**120.30** *7.00*	**146.25**	**38.58** *2.6-2.9*	**24.31** *1.5-1.7*	**29.29** *1.2-1.6*		
 PKA4	**C1** *H1*	**C2** *H2*	**C3** *H3*	**C4**	**C5**	**C10**	**200.59**	**17.78** **18.39** **18.45** **18.62**
	132.85 *7.50*	**128.52** *7.40*	**128.02** *7.40m*	**137.03**	**166.02**	**141.96**		
	C11	**C12** *H12*	**C13**	**C18** *H18*	**C19** *H19*	**C20** *H20*		
	121.84	**126.91** **126.85** **127.44** **126.45** *7.20*	**135.84** **135.64**	**38.56** *2.90*	**24.29** *1.6-1.8*	**29.47** *1.2-1.4*		*2.1-2.4*

[a] The asterisk denotes that the splitting of the signals is due to the presence of the possible isomers (cis and trans).

PKA6) in organic solvents such as chloroform, DMA, and MC was achieved by protonation of the polymers by Bronsted acid such as DEHEPSA. Therefore, a novel feature of the aliphatic−aliphatic polyketanils can be compared to aromatic−aliphatic ones only after protonation of these two groups of the polymers.

Furthermore, FTIR spectroscopic characterization to be presented below provides additional evidence for the ketimine groups in these two polymers.

The presence of ketimine groups is confirmed by FTIR spectroscopy since in each case the band characteristic of the C═N stretching deformations is detected. The FTIR spectra of all the aliphatic−aromatic polymers (PKA1−PKA4) show an intense absorption band at 1614−1625 cm^{-1} (see Table 1), which is characteristic for ketanile linkages [-C═N-]. In addition to the C═N stretching band, a band at 1597 cm^{-1} can be distinguished ascribed to the C═C stretching deformations in the aromatic ring. The position of the ketimine band is shifting toward higher wavenumbers for the polymers with the aliphatic subunits (PKA5, PKA6) and shows an intense absorption band at 1650 cm^{-1} (see Table 1).

FTIR spectroscopy also provides a facile method of elucidating the effect of Bronsted acid protonation on the molecular structures of the polyketanils. As stated previously, the aliphatic polyketanils (PKA5, PKA6) are soluble only after protonation with DEHEPSA. The corresponding assignments of vibrational modes in the FTIR spectra of the pure polymers (PKA1, PKA6) (KBr pressed pellet technique) and its DEHEPSA complex are listed in Table 3.

The absorption of C═N stretch in PKA1 occurs at 1623 cm^{-1} and is of strong intensity. In contrast, the C═N stretch in PKA1/DEHEPSA complex is less intense and is broadening and shifted to higher energy at 1630 cm^{-1}. The shift to higher energy of the C═N stretching band after Bronsted acid protonation is different from that observed in Bronsted acid complexes

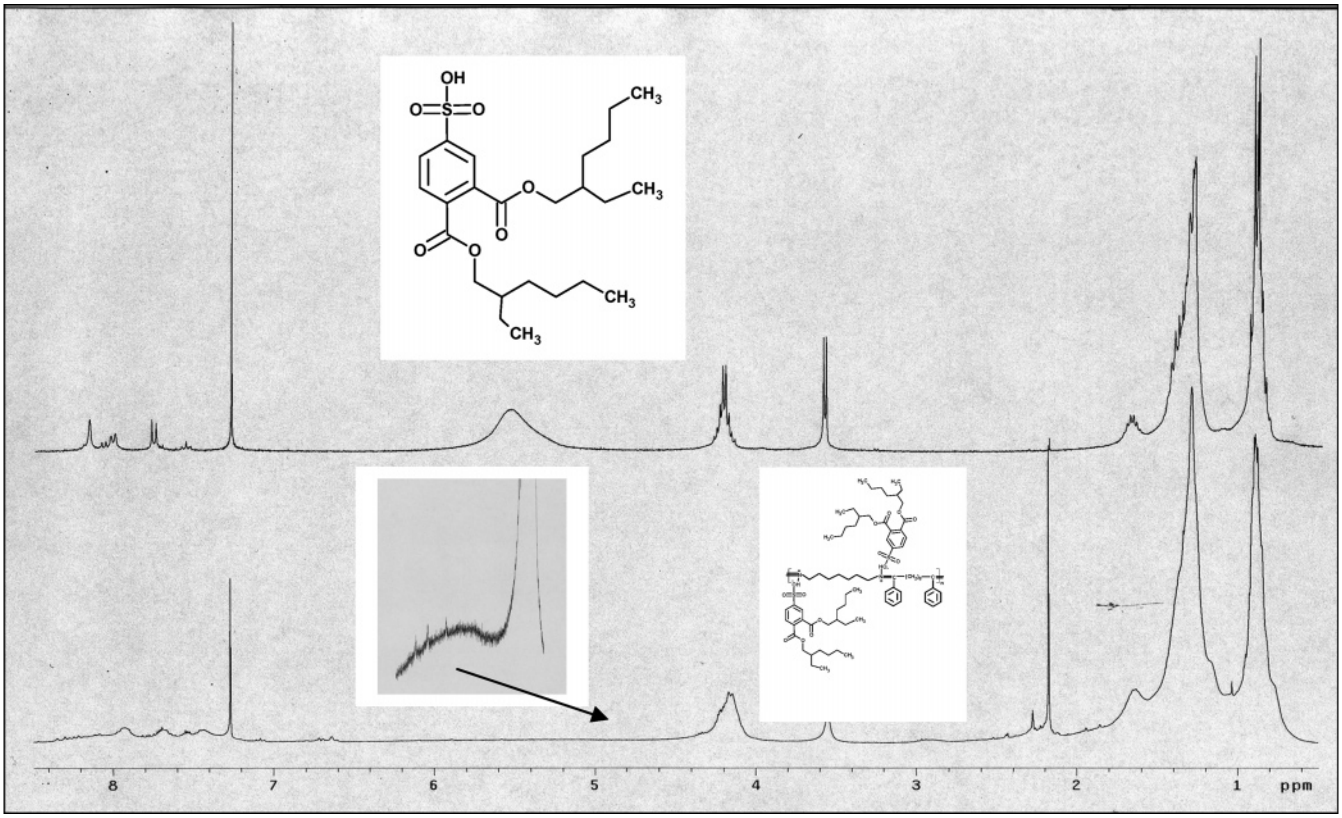


Figure 2. ^{1}H NMR spectra of the DEHEPSA and doped PKA6 ($CDCl_3$ solvent).

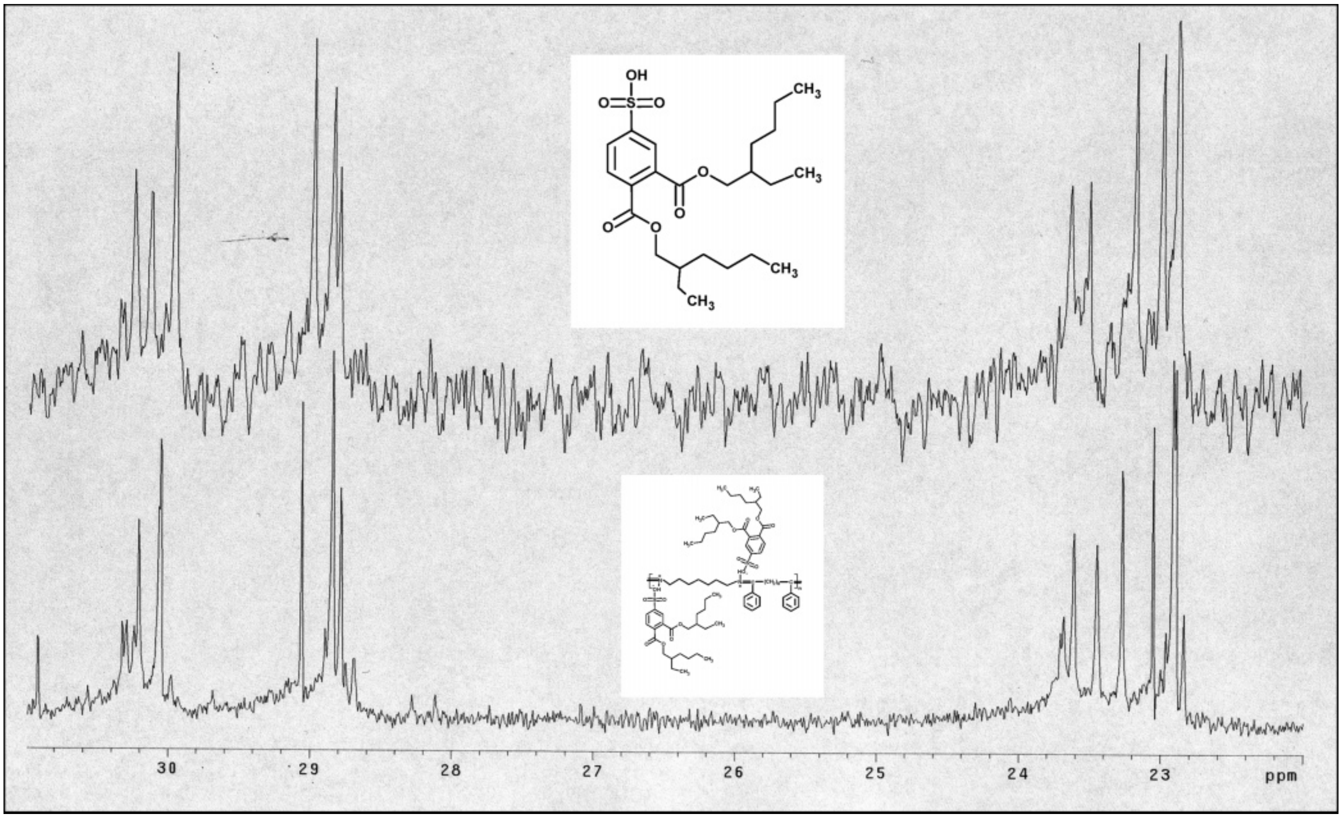


Figure 3. ^{13}C NMR lines of the aliphatic groups of DEHEPSA and doped PKA6 ($CDCl_3$ solvent).

of nonconjugated polymers such as aliphatic−aliphatic polyketanils (PKA5, PKA6). In this case the characteristic C═N stretching band in the PKA6/DEHEPSA complex is only a little shifted to a higher frequency. This part of our work needs additional investigations.

In this part of our work, we proposed the spontaneous polyketanil condensations of an aliphatic diamine with aliphatic diketone, leading to a previously undescribed new kind of cyclic polyketanils with interesting luminescence properties. To our surprise, “full” aliphatic

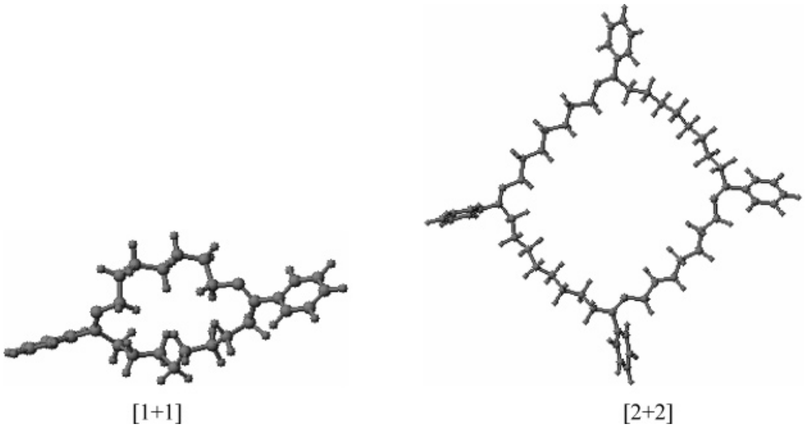


Figure 4. Molecular simulation of the [1 + 1] and [2 + 2] cyclic aliphatic–aliphatic polyketanils.

Table 3. FTIR Selective Bands of Undoped and DEHEPSA-protonated Polyketanils PKA1 and PKA6

	FTIR (KBr) [cm^{-1}] (selective bands)				
code	C=N str	out-of-plane C–H band	methylene C–H str	C=C asym str	O–C=O
PKA1	1623	695 753 818	2926 2853	1597	
PKA1/DEHEPSA	1630	693 820	2927 2856	1598	1723
PKA6	1650	699 755 862	2929 2855	1598	
PKA6/DEHEPSA	1652	700 770 852	2930 2860	1599	1727

polyketanils (PKA5, PKA6) were insoluble in organic solvent, which could be explained by cyclic formation (see Figure 4). Molecular structure of the polyketanils cycle by simple simulation (ACDChem) was studied. The simulation of the aliphatic–aliphatic polyketanils (one diamine with one diketone, 1 + 1) shows a molecule in a four-leaf-clover-like pattern. On the other hand, when we use for simulation two diamines and two diketones units (2 + 2) to form cyclic polyketanils, a molecule in a kitelike pattern was observed.

Our preliminary hypothesis was confirmed by ^{1}H, ^{13}C NMR spectroscopy. In ^{13}C NMR spectrum we not observed carbonyl end group in the polyketanils structure. Additionally, in ^{1}H NMR spectrum, the amine end group was not detected. Different behavior for aromatic–aliphatic polyketanils was observed. In this case the end groups were observed (carbonyl groups at about 200 ppm, –*C21*–, shown in Table 2, while the amine groups were at about 3.6 ppm).

The shift of C=N stretching band in FTIR spectrum to high absorption frequency in the DEHEPSA–polyketanil complexes can be rationalized by a redistribution of electron density from the π-electron system of the conjugated polymer. This also means that significant changes in the emission spectra can be expected on protonation.

The color of the polyketanil family of conjugated polymers is governed by the presence of two types of chromophore groups in their macromolecules, namely the aromatic rings and the ketimine groups (see Figure 1).

The UV–vis spectra of all the polymers show one absorption peaks at around 270–320 nm and the shoulder at around 350–380 nm. The second absorption band is not well-defined. The former was assumed to be the π–π* transition in the benzene component of the structures, and the latter is due to the conjugated ketanile linkage. Figure 5 shows the electronic absorption spectra of the polyketanils PKA1, PKA2, PKA3, and PKA4.

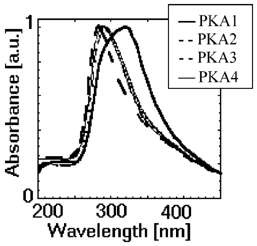


Figure 5. Solution UV–vis spectra of PKA1, PKA2, PKA3, and PKA4.

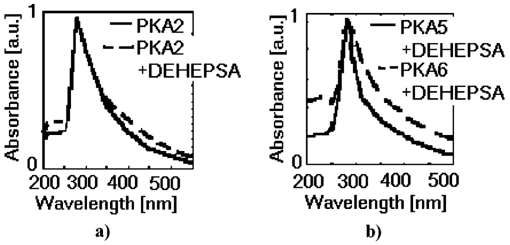
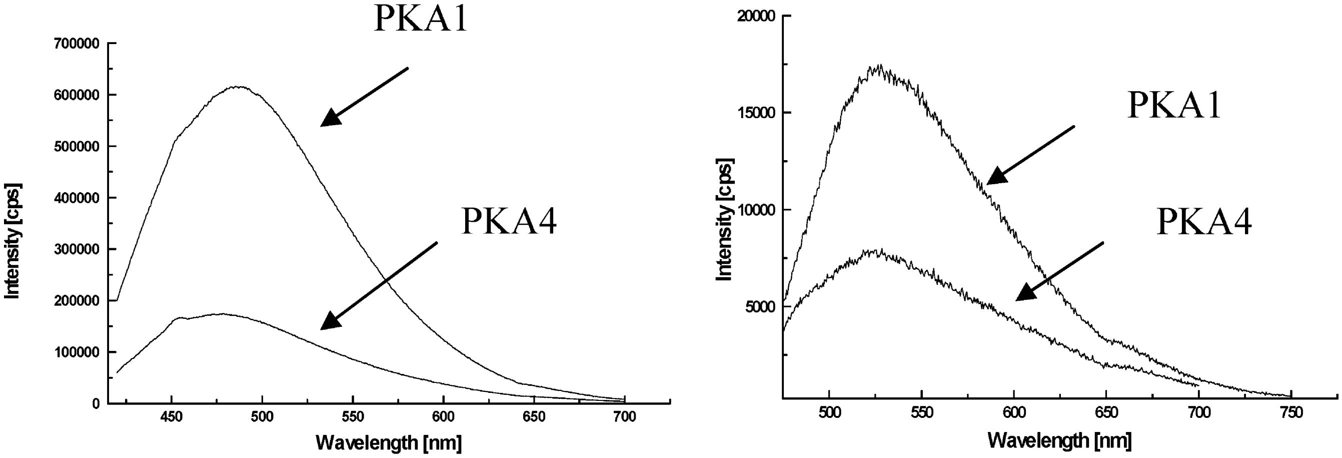


Figure 6. Solution UV–vis spectra of PK2 before and after protonation with DEHEPSA in MC (a) and doped with DEHEPSA PKA5, PKA6 (b).

PKA1 exhibits a red shift in $\lambda_{\max}$ compared to the another polymers. As seen in Figure 5 the introduction of a methylene spacer between the phenylene rings (PKA2); i.e., the transformation of PKA1 into PKA2 results in a the biggest hypsochromic shift of the absorption band.

Effects of Bronsted acid protonation of the imine nitrogens on the electronic structure of the all polyketanils were explored through optical absorption spectroscopy and luminescence spectroscopy. Parts a and b of Figure 6 show the electronic absorption spectra of the 1:1 DEHEPSA:C=N complex of the polyketanils.

A major feature of the absorption spectra of the aliphatic–aromatic polyketanils after protonation (Figure 6a) is their red shift from those of the pristine polymers. One interesting observation from the electronic spectra date of Figure 6b is that the aliphatic–aliphatic polyketanils PKA5 and PKA6 after protonation with DEHEPSA absorb light at shorter wavelength in comparison with the aliphatic–aromatic ones (PKA1–



a) b)

Figure 7. Photoluminescence (PL) solution spectra of PKA1 and PKA4 in DMA (a) and MC (b).

PKA4). It is probably an effect of shorter conjugation of π-electrons in the aliphatic−aliphatic polymers units.

Molecular structure of organic compounds is the main factor responsible for luminescence, therefore the emission persists when fluorophore molecules are in solid or in solution even though its intensity may be different. However, it is necessary to emphasize that luminescence detected in solution is strongly dependent on a solvent nature mainly its refractive index and dielectric constant and also on a possibility of interaction between solvent−fluorophore molecules as for example H-bonding formation.

In contrast to the absorption spectra, the emission spectra are well-defined. Solvatochromism is manifested in the photoluminescence spectra of the polyketanils. The photoluminescence (PL) of polyketanils in DMA and MC solution were investigated. In DMA solution the polymers emit light in the blue-green region. The emission maxima in MC solution are red shifted relative to those in DMA solution (see Table 1). The Stoke shift in this system can be clearly seen. The peak wavelength of the exciplex emission for polyketanils is shifted to longer wavelength with increase in the solvent refractive index ($n^{20}{}_{\mathrm{D}} = 1.5400$ for MC, $n^{20}{}_{\mathrm{D}} = 1.4380$ for DMA). In addition, the shape of the emission spectrum changes significantly, and the emission intensity is much lower in MC than in DMA solution (Figure 7).

This behavior clearly indicates that MC is not an inert solvent and strongly interacts with the polymer chain modifying its conformation toward higher planarity. This can occur via hydrogen bonds formation between imine-type nitrogen atoms of polyketanils which are hydrogen bonding acceptors and the hydroxyl group of MC which is a good hydrogen bonding donor.[9,10]

However, it is necessary to emphasize that the photoluminescence intensity in DMA significantly increases by a factor even as large as 35.

Improvement of emission band intensity is also the polymer structure dependent. First we notice that in DMA solution the polyketanil in which short conjugated segments are separated by long aliphatic spacers (PKA1) in their base form, exhibits the highest photoluminescence intensity of all polymers studied. It was found that photoluminescence intensity in DMA solution increases in the order 4,4′-diaminodiphenyl ether < 4,4′-methylenedianiline < 3,3′,5,5′-tetramethylbenzidine < benzidine, being the diamine monomers in the polyketanils.

Table 4. Photoluminescence of Undoped and DEHEPSA-Protonated Polyketanils Blend

code	PL λ_{emis} [nm][b]	E [eV]
PKA1	435	2.85
doped PKA1[a]	507	2.45
PKA4	504	2.46
doped PKA4[a]	436	2.84

[a] Polymer protonated with DEHEPSA. [b] Photoluminescence of polymer blend.

The MC-solution PL spectra of doped polyketanils have a broad emission band at 534−549 nm, which are significantly red-shifted from the corresponding undoped polymers which have a peak at 522−525 nm (Table 1). It should be also noted that the protonation generally influences not only the emission wavelength but also the intensity of the photoluminescence.[9,17] However, in our cases we did not observed this behavior what attributed to the low degree of conjugation in the polymer chain. The luminescence intensity of the polyketanils in MC and in MC + DEHEPSA solutions were comparable.

The success of Bronsted acid protonation and solubilization of aliphatic−aliphatic polyketanils (PKA5, PKA6) in organic solvent has facilitated the characterization of their molecular structures by photoluminescence spectroscopy. The photoluminescence date for MC solution of polymers PKA5 and PKA6 after protonation under 400 nm excitation wavelength are shown in Table 1. The emission spectra of PKA5 and PKA6 after protonation showed one maximum at 484, 486 nm, respectively, and are blue shifted relative to the another polyketanils (see Table 1).

Additionally, we have studied the emission spectra of free transparent foils obtained by casting chloroform solution of polyketanils PKA1 and PKA4 with a nonemissive polymer, PMMA (see Table 4). The concentration of PKA in PMMA in foil was 1×10^{-4} mol/g.

Our preliminary data on the luminescence spectra of blended polyketanils in the solid-state show that PKA1 and PKA4 exhibit the photoluminescence band maximum at 435 and 504 nm, respectively. For the polyketanil PKA4 blend, this value is intermediate between the photoluminescence maxima recorded for the polymer in DMA and MC solutions. In the case of the PKA1 blend, the maximum of the photoluminescence band at 435 nm is hypsochromically shifted not only with respect to the spectrum measured for MC solution (525 nm) but also as compared to the band registered in DMA solution (485 nm).

The solid-state PL spectra of doped polyketanils (PKA1, PKA4) blended with PMMA have the emission band at 507 and 436 nm, respectively, which are significantly red/blue-shifted from the corresponding undoped blended polymers (see Table 4). Moreover, the emission intensity in the solid-state of the doped polyketanils PKA1 and PKA4 blends is higher than in the undoped polyketanil blends.

The observed photoluminescence shifts when going from DMA solution to MC solution and finally to the solid-state in blend clearly indicate that this property is principally governed by local conformation of the polymer chain and interaction between the polymer chains and environment.

Taking into account the chemical constitution of polyketanils studied here, one may expect that they should exhibit a rather low thermal stability especially those with aliphatic subunits. The same arguments apply to their glass transition temperature *T*g. However, the polymers PKA1 and PKA3 are rather stable, and their thermal degradation starts at about 420 °C. The greater flexibility of the polymer chain afforded by the inclusion of an oxygen atom between two phenylene rings in the polymer backbone increases the ability of the polymer chain to pack, hence increasing the thermal stability of polymer PKA3 due to increased intermolecular interactions. Polymers PKA2 and PKA4 are less stable and degradation starts at about 380 °C. The insoluble polymers PKA5 and PKA6 are less stable than another polyketanils. These polymers lost 10% weight at temperatures in the range of 360−370 °C in nitrogen. The residue at 1000 °C is around 20%.

The DSC curves recorded with repeated heating−cooling cycles allowed the evaluation of T_g values of the synthesized polyketanils in the range 55−150 °C (see Table 1). It is obvious that they depend on the structure of the polymers. A shift in the glass transition was observed in the following order: PKA4 > PKA2 > PKA3 > PKA1 > PKA5 > PKA6. The glass transition temperature (T_g) of the polyketanil synthesized from 3,3′,5,5′-tetramethylbenzidine (PKA4) is higher than the value found for the polymer from benzidine. This phenomenon was also observed for polyketanils prepared from *p*-dibenzoylbenzene or *trans*-1,2-dibenzoylethylene and different diamines[9,10] and for polyimides synthesized from diamines with methyl group at ortho position to amine group.[15,16] The explanation of this behavior may be a hindered rotation caused by the presence of the substituents which causes the polymer chain to be more stiff. All synthesized polymers give similar DSC profiles with no melting endotherms and a clear T_g. These findings clearly indicate their amorphous nature. The results of TG and DSC studies are summarized in Table 1.

As evidenced by DSC measurements the plasticizing effect of DEHEPSA is very pronounced and leads to a drastic lowering of the T_g in all polymers studied (see Table 1). This effect is of crucial importance because it improves mechanical properties of the polymer changing brittle films into flexible ones. Therefore, 1,2-di(2-ethylhexyl) ester of 4-sulfophthalic acid (DEHEPSA) is bifunctional and acts simultaneously as a Bronsted acid and as a plasticizing agent. The protonating diester is in fact a simple derivative of di(2-ethylhexyl) phthalate—the most popular industrial plasticizer of PVC.

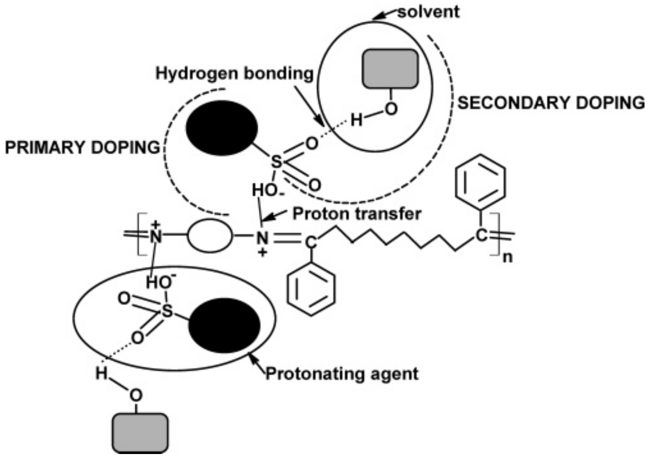


Figure 8. Interaction between the polyketanil chains, protonating agents, and MC solution.

Concluding Remarks

In this paper, we present the results of new group of conjugated polymers − aliphatic polyketanils containing nitrogen atoms in the main chain being doped with 1,2-(diethyl-hexyl)sulfophthalic acid ester (DEHEPSA).

The work elucidates the effect of protonating agent DEHEPSA on the photoluminescence emission, glass transition temperature, and solubility of polyketanils with aliphatic−aromatic and aliphatic−aliphatic chains. Thus, DEHEPSA, in association with polyketanils, should play a triple role: (i) It should modify the electronic properties of these polymers and by consequence alter their photoluminescence as an effect of the imine sites protonation. (ii) It should lower their glass transition temperature because of the presence of plasticizing groups in the DEHEPSA molecule. (iii) It should solubilize the polyketanils in organic solvent, by protonation of the polymers.

Structure of the dopant creates new type of supramolecular comb-shaped architectures in which the lateral groups—anions of sulfophthalic acid residue are ionically bonded to the main chain via protonation of ketimine nitrogen atoms. However, it should be mentioned that there is also the possibility of interaction between oxygen of sulfonic groups of DEHEPSA being ionically bonded to polyketanil chains and MC hydroxyl groups and well-defined supramolecular structures can be formed.[9,10,17,18−24] In Figure 8, possible interactions are presented.

Therefore, DEHEPSA can be treated as a primary dopant while MC is a secondary dopant.

Acknowledgment. The authors thank Prof. A. Proń and Dr. P. Rannou from CEA in Grenoble, France, for fruitful discussions and a gift sample of DEHEPSA.

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MA050102F