Macromol. Symp. **2003**, *199,* 511-521

Aromatic Polymers with Side Oxadiazole Rings as Luminescent Materials in LEDs

Maria Bruma,[*1] Elena Hamciuc,[1] Burkhard Schulz,[2] Thomas Köpnick,[3]*
Yvette Kaminorz,[4] Jenifer Robison[5]

[1] Institute of Macromolecular Chemistry, Aleea Ghica Voda 41A, 6600 Iasi, Romania
Email: mbruma@icmpp.tuiasi.ro; ehamciuc@icmpp.tuiasi.ro
[2] University of Potsdam, FZDOBS, Am Neuen Palais 10, 14469 Potsdam, Germany
[3] Institute of Thin Film Technology and Microsensors, Kanntstr 55, 14513 Teltow, Germany
[4] University of Potsdam, Institute of Physics, Am Neuen Palais 10, 14415 Potsdam, Germany
[5] Tyco Electronics Corporation, Menlo Park, California 94025, USA

Summary: Aromatic polyamides and polyazomethines with side oxadiazole rings have been synthesized by using aromatic diamines containing pendent substituted oxadiazole groups and a diacid chloride having diphenylsilane or hexafluoroisopropylidene, or an aromatic dialdehyde with fluorene unit, respectively. These polymers were easily soluble in amidic solvents. Very thin films which were deposited from polymer solutions onto silicon wafers exhibited smooth, pinhole-free surface in atomic force microscopy investigations. The polymers showed high thermal stability with decomposition temperature being above 400°C. Some of them exhibited blue photoluminescence, in the range of 450-480 nm, making them promising candidates for future use as high performance materials in the construction of light emitting devices.

Keywords: oxadiazole, photoluminescence, polyamides, polyazomethines, thin films

Introduction

Aromatic polymers containing 1,3,4-oxadiazole rings in the main chain are well-known for their high thermal resistance in oxidative atmosphere, good hydrolitic stability, low dielectric constant and tough mechanical properties.[1] There is currently much research directed towards the discovery of new blue light-emitting polymers, with characteristics of high efficiency and high reliability. For such a purpose polyoxadiazoles are of great interest because due to the electron-withdrawing character of the 1,3,4-oxadiazole rings they can facilitate the injection and transport of electrons.[2] But, aromatic polyoxadiazoles are rigid, rod-like molecules and are insoluble in organic solvents and do not have a glass transition (T_g) which makes their processing quite difficult. To improve the solubility and lower the T_g, various approaches have been undertaken such as introduction of flexible side groups on the aromatic rings[3] or bulky moities, such as „cardo“ groups[4] in the main chain. Another way would be the incorporation of oxadiazole rings as pendent groups on a polymer chain.[5]

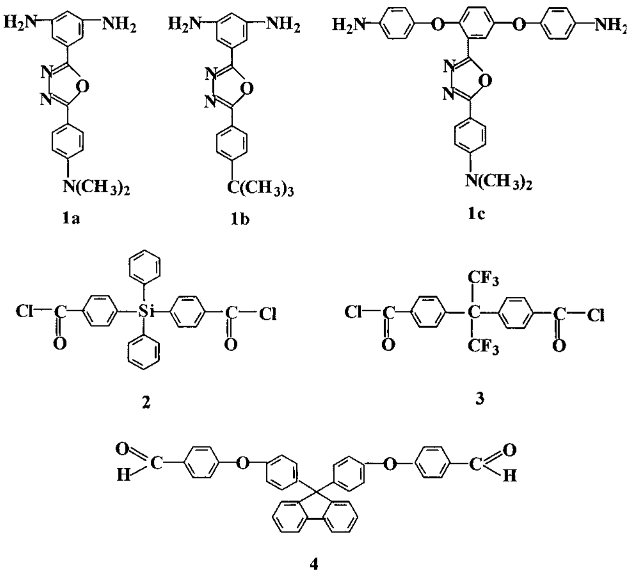
DOI: 10.1002/masy.200350942

Therefore, we considered interesting to make polymers in which the oxadiazole rings are attached as side groups to an aromatic polyamide or polyazomethine backbone. Here we present the synthesis of certain aromatic polyamides and polyazomethines containing the 1,3,4-oxadiazole rings in the side groups; polyamides have the diphenyl silane or 6F units in the main chain, while polyazomethines have fluorene units in the main chain. The properties of these polymers, such as solubility, thermal stability, glass transition, film forming ability and quality of thin films, as well as their photoluminescence ability are discussed.

Experimental

Synthesis of the Monomers

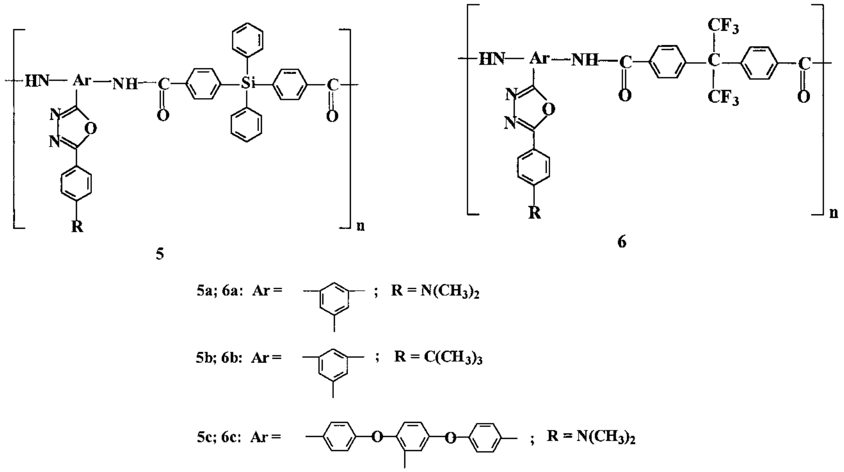
Aromatic diamines, **1**, having an oxadiazole ring in the side group, namely 2-(4-dimethylaminophenyl)-5-(3,5-diaminophenyl)-1,3,4-oxadiazole, 2-(4-tert-butylamino)-5-(3,5-diaminophenyl)-1,3,4-oxadiazole and 2-(4-dimethylaminophenyl)-5-[2,5-bis(*p*-aminophenoxy)-phenyl]-1,3,4-oxadiazole respectively,[6] two diacid chlorides such as bis(*p*-chloro-carbonyl-phenylene)-diphenylsilane,[7] **2**, and hexafluoroisopropylidene-bis(*p*-benzoyl chloride),[8] **3**, respectively, and an aromatic dialdehyde, **4**, having fluorene unit, namely 9,9-bis(p-formyl-phenoxy-4-phenylene) fluorine,[9] have been prepared by published procedures and thoroughly purified, and their structures are shown in Scheme 1.



Scheme 1. Structures of the monomers **1**, **2**, **3** and **4**.

Synthesis of the Polymers

Six polyamides containing 1,3,4-oxadiazole ring in the side group, three of them having silicon in the main chain, **5**, and the other three having 6F in the main chain, **6**, have been synthesized by low temperature solution polycondensation reaction of equimolar amounts of a diamino-oxadiazole **1** with bis(*p*-chlorocarbonyl-phenylene)-diphenylsilane, **2**, or with hexafluoroisopropylidene-bis(*p*-benzoyl chloride), **3**, in NMP as a solvent and with pyridine as an acid acceptor, and their structures are shown in Scheme 2.

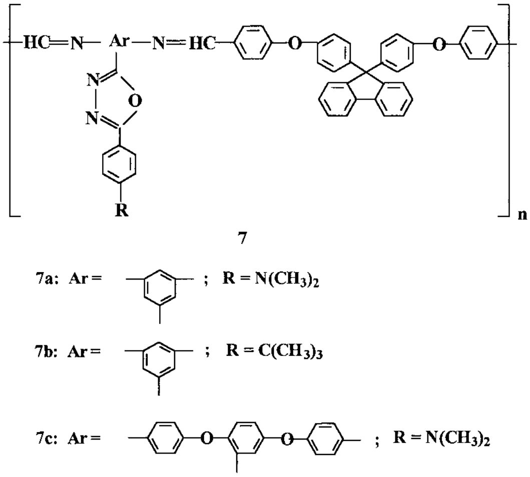


Scheme 2. Structures of polyamides with oxadiazole units in the side group, **5** and **6**.

Similarly, three polyazomethines having 1,3,4-oxadiazole ring in the side group, **7**, have been prepared by polycondensation at 20-80°C of equimolar quantities of a diamino-oxadiazole **1** with 9,9-bis(p-formylphenoxy-4-phenylene) fluorene **4**, by using NMP as a solvent. The structures of these polyazomethines are shown in Scheme 3. The resulting polymer was separated from solution by precipitation in water, followed by washing with water and ethanol and drying in oven at 120°C.

Preparation of Polymer Films

1g of a polymer was dissolved in 10 mL NMP. Half of the solution was cast onto glass plates and were dried in an oven at 80°C, 110°C, 140°C, 170°C and 210°C for 15 minutes each. Transparent homogeneous films resulted, which were stripped off the plates by immersion in hot water. These films had a thickness of 20-30 μm. The other part of polymer solution was dilluted with NMP to 1% concentration and was used to deposit very thin films, in the range of tens of nanometres, onto silicon wafers, by a spin-coating technique, at a speed of 5000 rotation/min. These films, as-deposited, were gradually heated to 210°C in the same way as described earlier to remove the solvent, and were used for atomic force microscopy (AFM) investigations.



Scheme 3. Structures of polyazomethines with side oxadiazole rings, 7.

Measurements

Infrared spectra were recorded with a Nicolet Magna FTIR spectrometer in transmission mode. The thermogravimetric analysis (TGA) of the precipitated polymers was performed with a Seiko RTG 220 thermobalance, operating at a heating rate of 5°C/min, in air. The glass transition temperature (T_g) of the precipitated polymers was determined with a Seiko differential scanning calorimeter DSC 6200. Model molecules for a polymer fragment were obtained by molecular mechanics (MM^+) by means of the Hyperchem program, version 4.0.[10] The surfaces of the very thin films as-deposited on silicon wafers were studied by atomic force microscopy (AFM) with a SA1/BD2 apparatus (Park Scientific Instruments) in the contact mode. For photoluminescence (PL) measurements the polymer was spin-coated on a silicon substrate from NMP solution and heated afterwards to remove the solvent. A UV lamp peaking at 365 nm was used as excitation source. For recording the PL spectra, the emitted light was transfered by an optical fiber to an Insta Spec CCD detector used with an

MS 257 monochromator from L.O.T. Oriel Instruments. All PL spectra were corrected for the sensitivity of the detector.

Results and Discussion

Aromatic polyamides **5** and **6** containing the 1,3,4-oxadiazole ring in the side group and silicon or 6F units in the main chain were prepared by polycondensation reaction of aromatic diamines having pendent oxadiazole ring with a diacid chloride incorporating the diphenyl silane or 6F group (Scheme 2). Aromatic polyazomethines having the 1,3,4-oxadiazole ring in the side group **7** and fluorene unit in the main chain were prepared by polycondensation reaction of the diamines containing pendent oxadiazole ring with a fluorene-containing dialdehyde (Scheme 3). The expected structures of the polymers **5**, **6** and **7** were confirmed by IR spectra as follows. The strong absorption bands which appeared in the spectra of polymers **5** and **6** at 3400-3440 cm^{-1} and 1660-1670 cm^{-1} were attributed to amide groups. The absorption band at 1600 cm^{-1} in the spectra of the polymers **7** was assigned to –CH=N- groups. In the spectra of polymers **V** the absorption peaks at 1425-1430, 1105-1110 and 700 cm^{-1} were attributed to silicon-phenyl bonds. In the spectra of polymers **6** the absorption peaks at 1210 cm^{-1} were assigned to 6F groups. All the polymers exhibited broad absorption at 3060 cm^{-1} which was characteristic to CH aromatic bonds; the IR bands at 960-970 cm^{-1} and 1020 cm^{-1} were assigned to oxadiazole rings. The absorptions at 2920-2960 cm^{-1} were due to methyl groups.

All these polymers are soluble in polar amidic solvents such as N-methylpyrolidinone NMP, dimethylformamide (DMF) and dimethylacetamide (DMAc). Their improved solubility as compared with that of conventional aromatic polyamides, poly(arylene-oxadiazole)s and aromatic polyazomethines can be explained by the presence of pendent groups which disturbe the packing of macromolecular chains and thus facilitate the diffusion of small molecules of solvent which leads to better solubility. In addition, the voluminous diphenyl silane, 6F or fluorene units in the main chain introduce more flexibility and consequently make the shape of the macromolecules to be far from a „rigid rod“, as evidenced by molecular modelling (Figure 1 and Figure 2). The good solubility makes the present polymers potential candidates for practical applications in spin-coating and casting processes.

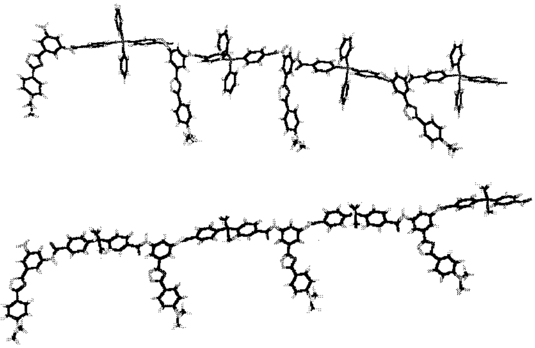


Fig. 1. Models of two polyamides **5a** (top) and **6a** (bottom).

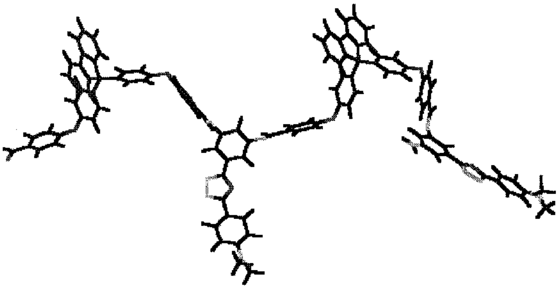


Fig. 2. Model of the polyazomethine 7**a**.

All these polymers possess film-forming ability. Thin transparent films having a thickness of tens of micrometres which were prepared by casting technique were tough and flexible. Also, very thin coatings having thicknesses of tens of nanometres have been deposited onto silicon wafers. The quality of such films as-deposited on silicon substrates was studied by AFM. The films exhibited very smooth surfaces over large scanning ranges (1-100 μm). The values of root mean square (rms) roughness calculated from the AFM data lie in the range of 6-12 Å being of the same order of magnitude as that of the highly polished silicon wafers which were used as substrates. This means that the deposited films are very smooth and homogeneous. They do not show any pinholes or cracks and are practically deffectless. The films had strong adhesion to the silicon wafers. These qualities are very much required when such films are used in microelectronic devices.[11] A typical AFM image is shown in Figure 3.

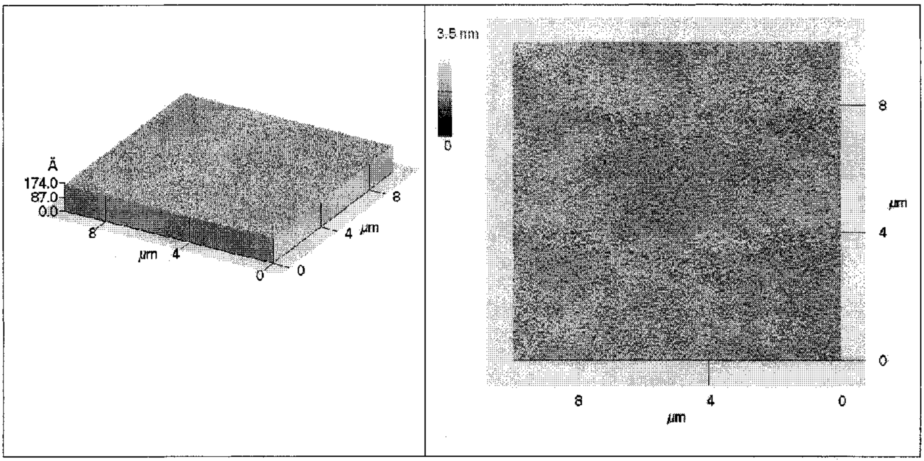


Fig. 3. AFM image of a film made from polymer **5a** (left: side view; right: top view).

The thermal stability of the polymers was evaluated by thermogravimetric analysis (TGA). All these polymers exhibited high thermal stability with insignificant weight loss up to 350°C. The polyamides **5** and **6** begin to decompose (IDT) in the range of 409-425°C. The temperature of maximum decomposition rate is in the domain of 426-522°C (Table 1).

Table 1. Properties of the polyamides containing side oxadiazole groups.

Polymer	IDT a) (°C)	T_{max} b) (°C)	T_g (°C)	Photoluminescence	
				Maximum (nm)	Half width (nm)
5a	413.7	479.4	275.8	475	102
5b	425.2	454.5	Not detected		
5c	409.3	429.8	151.6	460	114
6a	420.3	521.7	Not detected	480	108
6b	417.2	428.1	Not detected		
6c	411.2	425.9	153.6	465	106

a) Initial Decomposition Temperature = Temperature of 10% weight loss.
b) Temperature of maximum rate of decomposition.

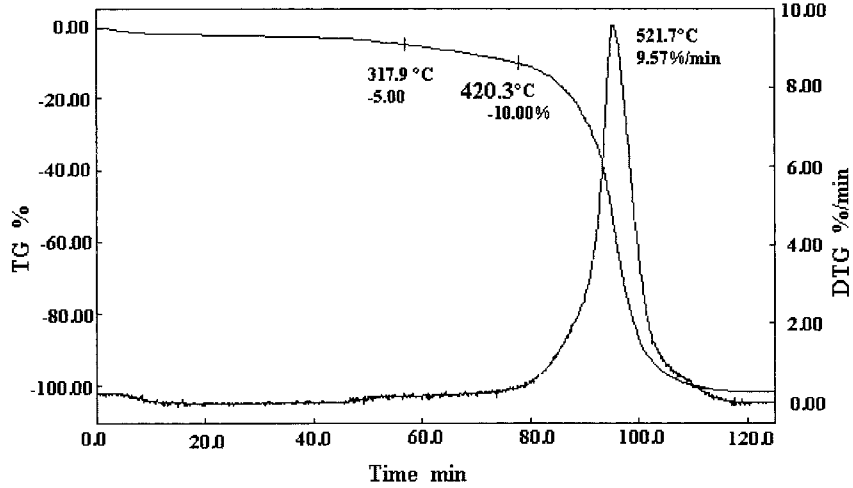


Fig. 4. TG and DTG curves of the polymer **6a**.

The polyamides **5b**, **6a** and **6b** did not exhibit a glass transition when heated to 320°C in DSC experiments. The other polyamides did show a glass transition, in the temperature range of 151-276°C. As expected, the polymers **5c** and **6c**, which contain some ether linkages in the main chain, have lower T_g, in the range of 151-154°C, due to the increase in flexibility of polymer backbone determined by these ether bridges. It can be noticed that there is a large „window“ between the glass transition and decomposition temperature of these two polymers (**5c** and **6c**) which makes them attractive for thermoforming processing.

The light emitting ability of these polymers was evaluated on the basis of photoluminescence spectra. The polyamides **5a**, **5c**, **6a** and **6c** containing the dimethylamino substituent in the *para*-position of the chromophoric diphenyl-1,3,4-oxadiazole unit show intensive blue emission with the maximum between 460 and 480 nm (Table 1). Also, the polyazomethines **7a** and **7c**, containing fluorene units and dimethylamino substituents in *para* – position of the diphenyloxadiazole moiety show blue photoluminescence, in the range 450-480 nm. In contrast to other diphenyloxadiazole side chain polymers such as polymethylmethacrylate derivatives,[5,12] in the present polymers parts of the main chain are conjugated and therefore influence the luminescent behavior. The coupling bond of the side to the main chain influences the luminescence behavior significantly. The half width of the luminescence is around 100 nm, being in the usual range observed for other polymeric emission materials, and does not change significantly with the chemical structure of the present polymers. Typical photoluminescence spectra of polyamides with side oxadiazole groups are shown in Figure 5, while those of polyazomethines with side oxadiazole groups are shown in Figure 6.

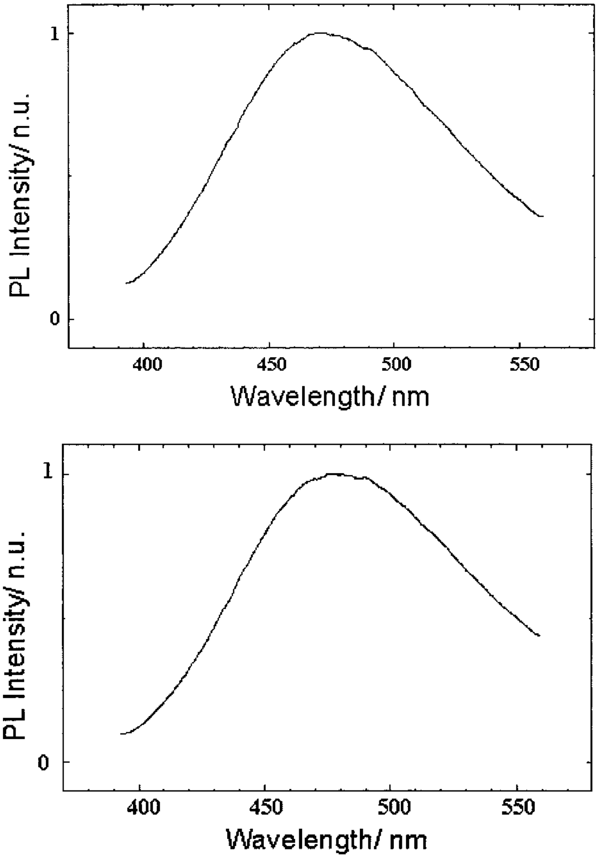


Fig. 5. Photoluminescence spectra of polyamides containing side oxadiazole rings, **5c** (top) and **6c** (bottom).

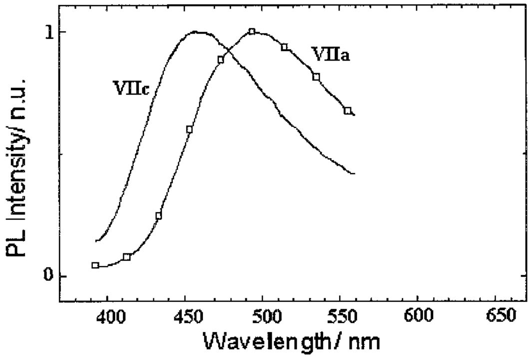
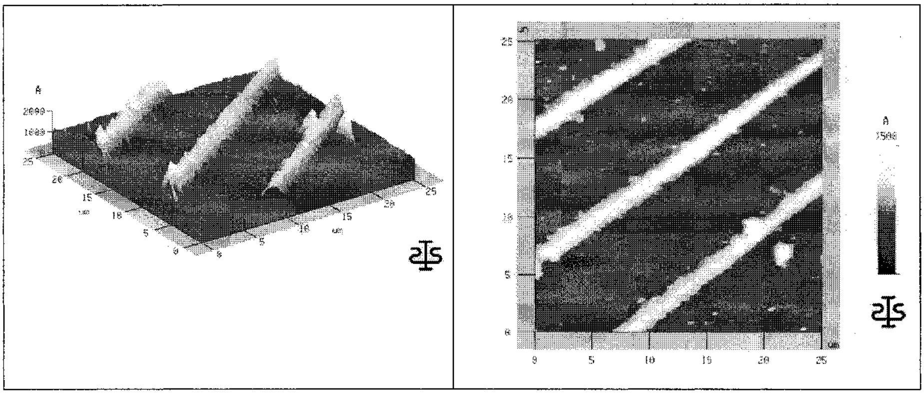


Fig. 6. Photoluminescence spectra of polyazomethines containing side oxadiazole rings, **7a** and **7c.**

Very thin films deposited from polyazomethines containing fluorene units 7 were investigated for use as negative resist materials in electron-beam litography. Fine structures could be designed by electron-beam irradiation follwed by development. A typical AFM image of a such structured film is shown in Figure 7.



Spin-coating:	5 % polymer solution in NMP; 5.000 rpm/30 s
Substrate:	Silicon, hydrophile (H_2SO_4/H_2O_2 4/1, 120 °C, 30 min)
Pre-bake:	80, 110, 140, 170, 200 °C (20 min each temperature)
Electron-beam:	700 $\mu C/cm^2$; 10 kV (30 s)
Development:	30 s NMP, 30 s iPrOH, 1 min H_2O_2 (ultrasonic bath)

Fig. 7. AFM image of a structured film deposited from polyazomethine **7a** (left: side view; right: top-view).

Conclusions

The incorporation of 1,3,4-oxadiazole rings as side groups into an aromatic polyamide or polyazomethine backbone, together with certain flexible bridges such as diphenyl silane or hexafluoroisopropylidene in the case of polyamides, or together with voluminous fluorene units, in the case of polyazomethines, in the main chain, gave soluble polymers which could be easily processed into thin films from solutions, while maintaining a high thermal stability. Some of these polymers did exhibit a glass transition, with a large interval between the glass transition and decomposition temperature, which may be advantageous for their processing by thermoforming techniques, as well. The very thin coatings which were deposited onto silicon wafers showed a strong adhesion to the substrates and a smooth, homogeneous surface, practically deffectless. The polyamides containing the dimethylamino substituent in the para position of the diphenyl-oxadiazole side groups, as well as related polyazomethines containing fluorene unit in the main chain showed intensive blue photoluminescence, being promissing candidates for future use in light emitting devices. Potential applications in optoelectronics, microelectronics or other related advanced fields are forseen.

Acknowledgements

It is a pleasure to acknowledge the financial support provided to MB and EH by the AiF (Arbeitsgemeinschaft industrieller Forschungsvereinigungen) in Germany and Ministry of Education and Research in Romania. Our warm thanks also go to Burkhard Stiller for performing the AFM investigations.

[1] B. Schulz, M. Bruma, L. Brehmer, *Adv. Mater.*, **1997**, *9*, 601.
[2] Q. Pei, Y. Yang, *Adv. Mater.*, **1995**, *7*, 559.
[3] Z. Peng, Z. Bao, M. Galvin, *Adv. Mater.*, **1998**, *10*, 680.
[4] A.T. Shermukhamedov, A. Oktai, *Uzb. Him. Zh.*, **1989**, *3*, 69; *Chem. Abst.*, **1989**, *111*, 165357 v.
[5] E. Greczmiel, P. Posch, H. W. Schmidt, P. Strohriegel, *Macromol. Symp.*, **1996**, *102*, 371.
[6] M. Bruma, E. Hamciuc, B. Schulz, T. Kopnick, Y. Kaminorz, J. Robison, *J. Appl. Polym. Sci.*, in press.
[7] M. Bruma, B. Schulz, T. Kopnick, R. Dietel, B. Stiller, F. Mercer, V. N. Reddy, *High Perform. Polym.*, **1998**, *10*, 207.
[8] M. Kane, L. A. Wells, P. E. Cassidy, *High Perform. Polym.*, **1991**, *3*, 191.
[9] K. H. Park, T. Tani, M. Kakimoto, Y. Imai, *Macromol. Chem. Phys.*, **1998**, *199*, 1029.
[10] Hypercube Inc. (Ontario), *Hyperchem,* Version **1994**, 4.0.
[11] N. Xu, M. R. Coleman, *J. Appl. Polym. Sci.*, **1997**, *66*, 459.
[12] Y. Kaminorz, B. Schulz, L. Brehmer, *Synth. Met.*, **2000**, *111/112*, 75.