



RADICAL-FORMING POLYAMIDES FOR SELF-DECONTAMINATION COATINGS

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Design and synthesis of thermally stable polyamides with improved solubility based on an asymmetrical aromatic diamine containing phenoxy substituted benzophenone segment was the main objective of this work. These polymers were easily soluble at room temperature in polar aprotic solvents and even in less polar solvents, such as tetrahydrofuran. The polymers showed excellent thermal stability, up to 385 °C, and exhibited glass transition in the range of 225-256 °C. All the polymers emitted an intense blue light upon irradiation with UV light, due to the emission from the benzophenone chromophore. The free-standing films having the thickness in the range of tens of micrometers obtained from these polymers were flexible, tough, and maintained their integrity after repeated bendings. To investigate the radical-forming ability of the polyamides for decomposing surrounding harmful materials, degradation of methylene blue by the polymer films was studied.

INTRODUCTION

Development of self-cleaning or self-decontamination surfaces represent one important way to successfully address the contamination issues. Upon contact with a chemically or biologically hazardous substance, such materials are capable of catalytically degrading said hazardous substance to less toxic or, ideally, non-toxic substances. In this manner, the hazardous substance is continually destroyed by contact with the self-cleaning or self-decontaminating surface. Because no hazardous materials accumulates, there is no need to clean (*i.e.* decontaminate) these self-cleaning or self-decontaminating materials via conventional procedures, e.g. through the treatment with an aqueous soap solution to remove pesticide residue or aqueous bleach or alcohol solution to kill absorbed bacteria.¹⁻⁴

To protect the human body from the contaminated environments, many researchers have been interested in protective finishing on textiles, for example antimicrobial treatments and

novel membranes, which can block outer toxins from penetrating through, as well as achieve comfort, to be employed in protective clothing. On the other hand, radicals tend to undergo fast reactions, since they are highly reactive chemical species possessing at least one unpaired electron. Many chemical processes involve radical reactions, such as the biological reduction of O₂ by antioxidants. Benzophenone chromophoric group, known to undergo light-excitation to n, π* triplet states, are commonly used as photosensitizers in photochemistry. Triplet benzophenone chromophore can abstract hydrogen atom from weak C-H bond or other hydrogen donor to form a ketyl radical and can be readily quenched by oxygen. Because of high reactivity of the formed radicals, the photo-excited benzophenone polymers could decompose certain toxic chemicals and demonstrate antibacterial functions. Therefore, polymers containing benzophenone chromophoric groups could be employed as self-decontaminating materials for protective clothing, when exposed to UV or visible light irradiation⁵⁻¹¹.

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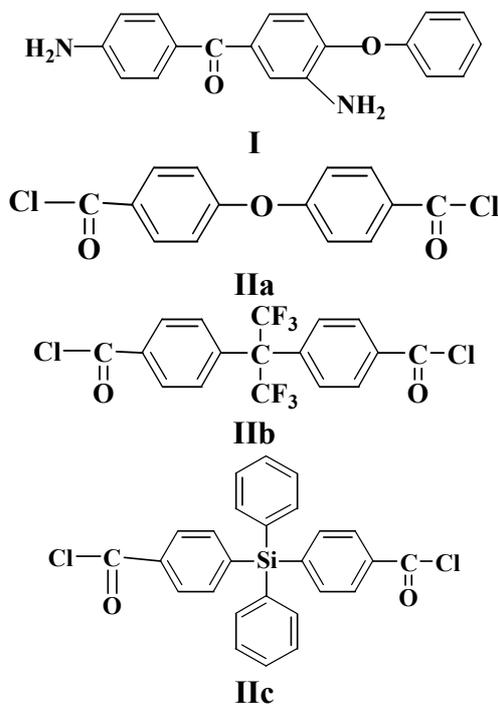
In this study, we report the development of a series of self-decontaminating polymers containing benzophenone moiety that show radical-forming ability and can provide antimicrobial properties and decolourization function to certain dyes. These polymers were synthesized by low-temperature solution polycondensation reactions of an asymmetrical aromatic diamine containing phenoxy substituted benzophenone segment with a diacid chloride containing aryl-ether linkage, hexafluoroisopropylidene groups or diphenylsilane units and were characterized by different methods.

RESULTS AND DISCUSSION

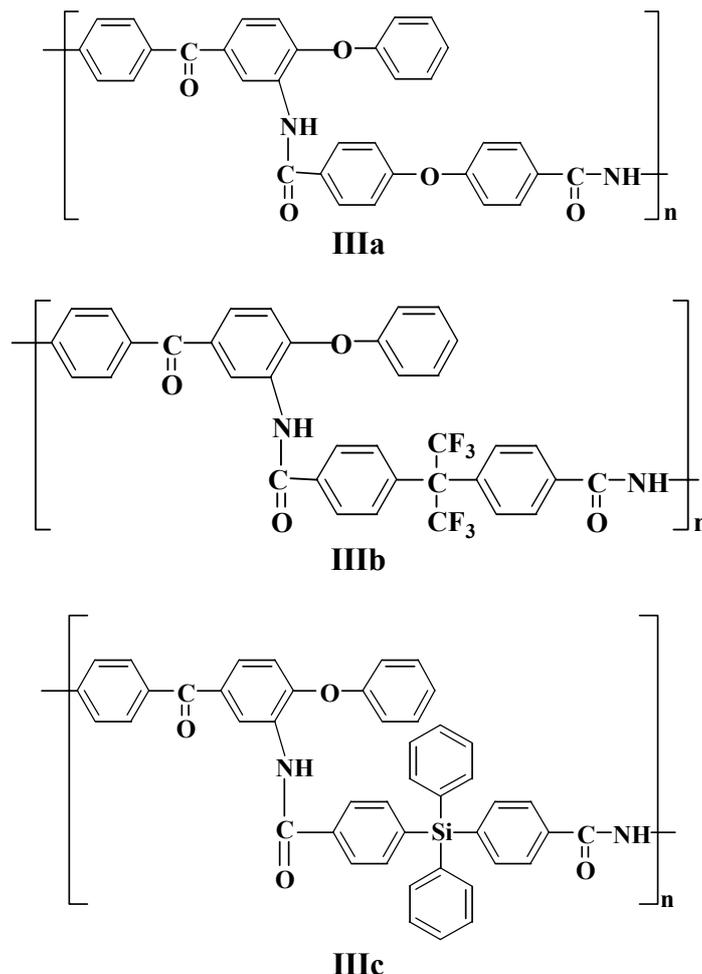
Design and synthesis of thermally stable polyamides showing radical-forming ability based on an asymmetrical aromatic diamine containing phenoxy substituted benzophenone segment was the main objective of this work. For this purpose, an asymmetrical aromatic diamine, namely 3,4'-diamino-4-phenoxybenzophenone (**I**), whose structure is shown in Scheme 1, was successfully prepared by a multi-step reaction. Three aromatic diacid chlorides, **IIa-c**, containing ether, hexafluoroisopropylidene or diphenyl silane groups, whose structures are shown in Scheme 1, were also prepared and used for the synthesis of polymers.

Asymmetrical aromatic polyamides **IIIa**, **IIIb** and **IIIc**, whose structures are shown in Scheme 2, have been synthesized by low-temperature solution polycondensation reaction of equimolar amounts of the asymmetrical aromatic diamine **I** with diacid chlorides **IIa-c** having ether, hexafluoroisopropylidene, or silicon groups, respectively.

The structures of the polyamides were identified by FTIR spectroscopy that provided evidence that all polymers had the correct structure. All the polymers showed characteristic amide group absorptions in the range of 3428-3425 cm^{-1} (NH stretching, wide bands), 1681-1658 cm^{-1} (carbonyl stretching, amide I) and 1519-1529 cm^{-1} (NH deformation, amide II). The absorption peak corresponding to benzophenone carbonyl groups is superposing on amide I band. C-H and C=C linkages in aromatic rings showed absorption peaks at 3068-3066 and 1490-1487 cm^{-1} , respectively. The strong absorption bands in the range of 1257-1234 and 1177-1167 cm^{-1} , more intense in the case of polymer **IIIa**, are due to the presence of aromatic ether stretching. Also, polymer **IIIb** displayed C-F linkage characteristic absorption peaks in the range of 1100-1300 cm^{-1} , while polymer **IIIc** exhibited phenyl-Si typical absorption bands at 1426, 1107 and 698 cm^{-1} .



Scheme 1 – Structures of monomers, **I** and **II**.

Scheme 2 – Structures of polyamides **III** containing benzophenone moieties.

The solubility behavior of these polymers was tested qualitatively in various organic solvents. Due to their amorphous nature, all asymmetrical polyamides were easily soluble at room temperature in polar aprotic solvents (as NMP, DMAc, DMF, and DMSO) and even in less polar solvents such as tetrahydrofuran, which is a convenient and easy accessible solvent. In addition, polyamide **IIIc**, containing diphenylsilane units, was soluble even in chloroform. The organosolubility behavior of the polyamides generally depends on their chain packing density and intermolecular interactions, which are affected by the rigidity, symmetry, and regularity of the molecular backbone. These asymmetrical diamine-based polyamides **IIIa-c** revealed enhanced solubility in comparison with that of the corresponding analogues that are only soluble in strong acids such as H_2SO_4 and, only in some cases, in NMP¹². This improved solubility can be attributed to the resulting three possible dyad microstructures within the polyamide backbone and the molecular chain nonlinearity

caused by the specific phenoxy-bearing diamine. Moreover, the presence in the macromolecular chain of flexible ether linkages, voluminous hexafluoroisopropylidene groups or phenyl substituents and the bending of the chains at silicon atoms make the shape of macromolecular chains to be far from a linear one and thus prevent chains from packing into tight structures through hydrogen bonds between amide groups and lead to a decreased chain–chain interaction, thus allowing the solvent to penetrate among the polymer chains. Their good solubility makes the present polymers suitable candidates for practical applications in spin-coating and casting processes.

The molecular weights of the polymers were measured by gel permeation chromatography (GPC), by using polystyrene standards. The molecular weight values, M_w , are in the range of 103000–492000 Dalton, M_n in the range of 63000–197000 Dalton, and polydispersity M_w/M_n in the domain of 1.43–2.5, a range expected for condensation polymers. It should be noted that gel permeation chromatography measurements by using polystyrene

standards, which have a completely different structure as compared with the present polyamides, provide only a crude estimate of molecular weights and not an accurate evaluation.

The polyamides showed glass transition temperature (T_g) values between 225 and 256 °C. As expected, T_g depended on the structure of the diacid chloride component and decreased with increasing flexibility of the polymer backbones. The lowest T_g of 225 °C observed for polyamide **IIIa**, derived from 4,4'-oxy-bis(benzoyl chloride) (**IIa**), was attributed to the presence of ether linkage that provides a polymer chain with decreased rotational barrier and to the asymmetrical structure that disturbs the dense packing between polymer chains. The polymers showed excellent thermal stability, as expected in case of aromatic polyamides. The initial decomposition temperatures (*IDT*) were about 385-396 °C and the temperatures for 10 % gravimetric loss ($T_{10\%}$), which are important criterion for evaluation of thermal stability, were in the range of 402-431 °C, indicating a high thermal stability. The decomposition of the asymmetrical polyamides **IIIb** and **IIIc** takes place in two steps as shown by DTG curves and by the values of the maximum decomposition temperature calculated from these curves: the first step occurs at 421 °C and 383 °C, and the second at 550 °C and 445 °C, for **IIIb** and **IIIc**, respectively (Fig. 1).

All these polymers possess film-forming ability as shown by casting 10-12% polymer solution onto glass plates. The free-standing films having a thickness of 40-50 μm , were transparent, flexible, tough, and maintained their integrity after repeated bending. These films had a very strong adhesion to

the support and they could be only taken off the plates by boiling in water.

In benzophenones, both phenyls can interact with C=O group through *s* (inductive effect) and *p* (mesomeric effect) bonds. Due to this p-electronic delocalization, the C=O group loses part of its individual character and partially integrates with the phenyls, leading to system stabilization and transfer of the electronic deficiency from the $\text{C}_{\text{carbonylic}}$ atom toward the C atoms of phenylene rings¹³. Such a conjugation is mirrored by the electronic absorption spectrum. Fig. 2 shows the UV-vis spectra of polyamides **IIIa-c** in dilute NMP solutions. UV absorbance in the region of 250-300 nm belongs to the main benzenoid $\pi - \pi^*$ type transition. The $n - \pi^*$ transition is usually found between 300 and 350 nm because of the spin forbidden transition.¹⁴ All the polyamides displayed one strong UV absorption maximum in the range of 274-278 nm, the spectra being quite identical. Polyamide **IIIb** showed an additional shoulder at about 305 nm. Compared with the reference benzophenone data, in which the absorption maximum of benzophenone in heptane localized at 248 nm is attributed to $\pi - \pi^*$ transition, the present polyamides exhibit significantly red-shifted $\pi - \pi^*$ maximal absorption. This is presumably due to the electron delocalization of the chromophoric group resulted from inclusion of benzophenone into the main polymer chains, and so the extended chromophoric conjugation contributed to bathochromic and hyperchromic shifts in UV-vis absorption.¹⁵ The weak absorption peak observed in polyamide **IIIb** may be due to a $n - \pi^*$ transition. The absence of this transition in the other two polymers may account for H bonds between the solute and the solvent.¹⁶

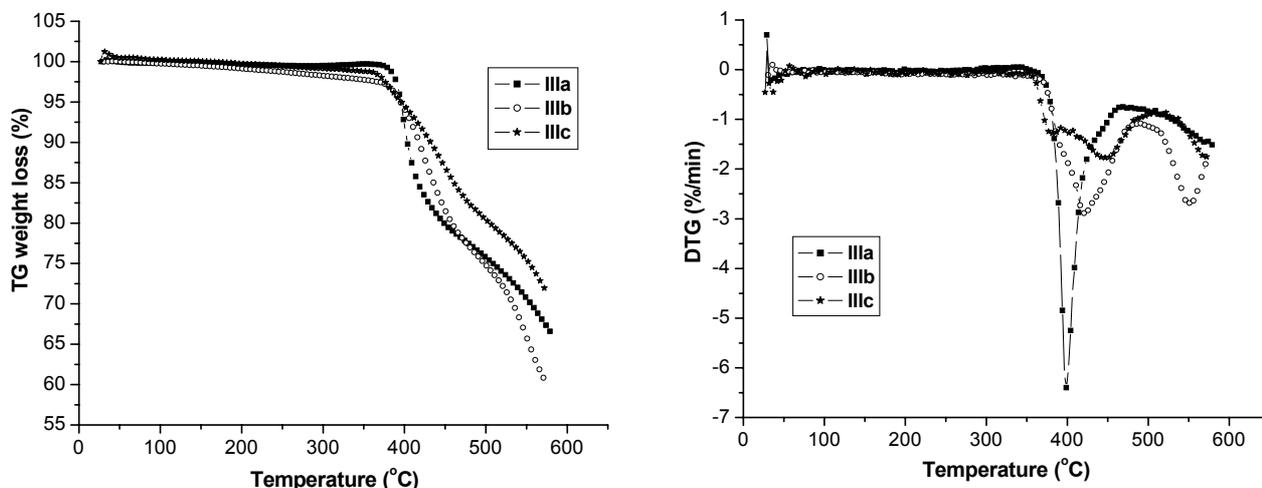


Fig. 1 – TG (left) and DTG (right) curves of benzophenone-containing polyamides **III**.

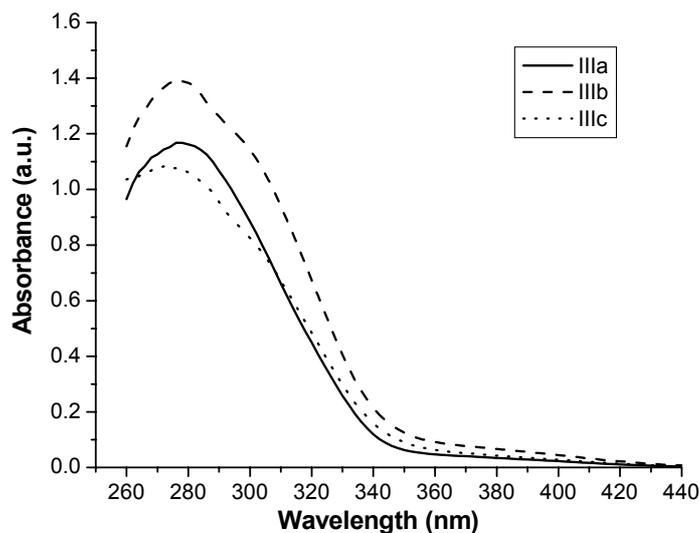
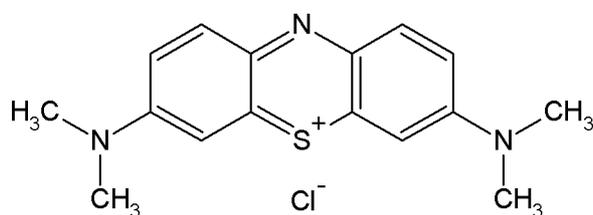


Fig. 2 – UV-vis absorption spectra of the polymers **IIIa-c**.



Scheme 3 – Structure of methylene blue dye.

To investigate the radical activity of the resultant polymer for decomposing surrounding harmful materials, degradation of methylene blue (MB), whose structure is shown in Scheme 3, by the benzophenone-containing polymers **IIIa-IIIc** was observed. This behaviour is given for polymer **IIIa** as representative example. The polymer free-standing film (12 wt%) **IIIa** was immersed in methylene blue/water solution, and the change in colour of methylene blue solutions was measured by UV–VIS spectrometry, as UV illumination time increased, as shown in Fig. 3. Also, the UV spectra of the pure methylene blue/water solution in the presence of polymer **IIIa** before UV illumination was measured and taken as reference. The absorption peaks at 610 and 661 nm characteristic to methylene blue were gradually decreased with the increasing of UV illumination time. In the same time, the absorption peak at approximately 290 nm where the benzophenone chromophore absorbs UV light increases with the increasing of UV illumination time which means that some benzophenone unit were linked to MB after irradiation. It was assumed that the keto-radicals formed in the polymer film under UV light decomposed the chromophoric group of methylene blue. In particular, light absorption by

benzophenone group in the structural unit of the polymer **IIIa** yields first a singlet (n, p^*) excited state, which converts fast through intersystem crossing into a triplet (n, p^*) excited state that is able to abstract an H atom from water. This process can produce α -hydroxyl radicals commonly known as benzophenyl ketyl (BPK) radicals.⁹ The BPK radicals are able to react with methylene blue to form excited methylene blue, which then can be rapidly decomposed under light.

The spectral changes in the UV spectra of methylene blue induced by polyamide film under UV illumination are reflected in the degradation rate values, for which the rate constant k was determined according to equation:

$$\ln(A_0/A_t) = kt$$

where, A_0 and A_t are the values of the absorbance at times t_0 and t , respectively, and k is a rate constant. Accordingly, the k value calculated for this process is $k = 4.32 \times 10^{-3} \text{ s}^{-1}$. The kinetic representation obtained by plotting the logarithm of the reduced absorption against time with a factor of convergence of 97.96%, indicates a first-order kinetic of the degradation of methylene blue by polyamide **IIIa** film (Fig. 4).

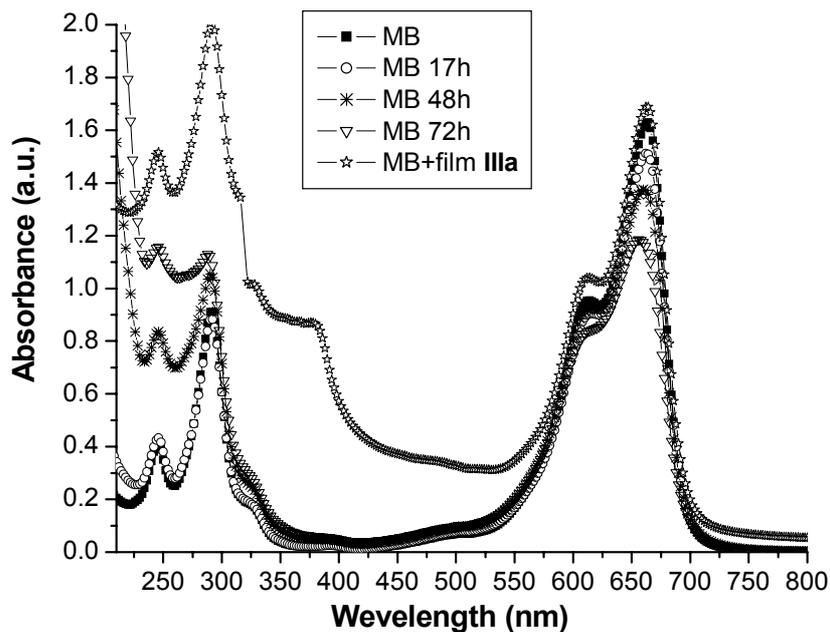


Fig. 3 – UV–VIS spectra of methylene blue/water solution in which polymer film **IIIa** was immersed, with the increasing of UV illumination time.

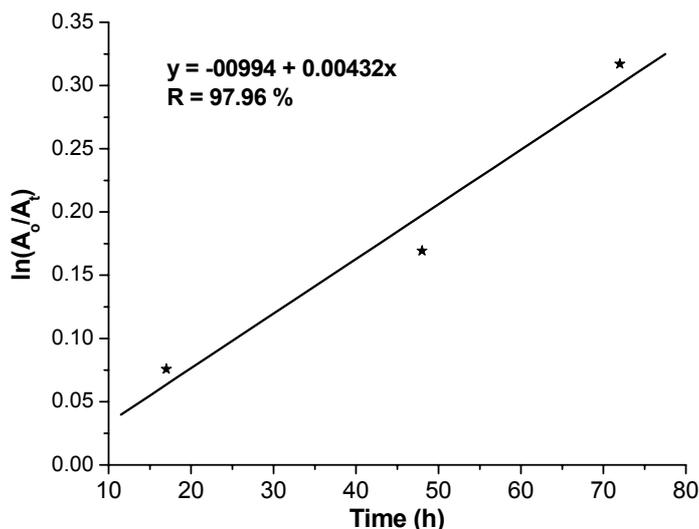


Fig. 4 – Kinetic evaluation of the degradation of methylene blue by polyamide **IIIa** film under UV irradiation.

EXPERIMENTAL

Monomers

3,4'-Diamino-4-phenoxybenzophenone (**I**) was prepared by a sequence of reactions starting from 4-nitrobenzoyl chloride. The Friedel Crafts reaction of 4-nitrobenzoyl chloride with chlorobenzene gave 4'-nitro-4-chlorobenzophenone which underwent the nitration using $\text{KNO}_3/\text{H}_2\text{SO}_4$ as nitrating agent to give chloro-substituted dinitrobenzophenone. The highly activated chlorine atom in 3,4'-dinitro-4-chlorobenzophenone was replaced with a phenoxy group by using aromatic nucleophilic substitution reaction. The reduction of the resulting dinitrocompounds containing phenoxy group, by

using SnCl_2/HCl as the reducing agent, gave the corresponding diamine¹⁷.

The ether bridge-containing diacid chloride, namely *4,4'-oxy-bis(benzoyl chloride)*, **IIa** was prepared by treating the corresponding 4,4'-oxybis(benzoic acid) with excess thionyl chloride at reflux, in the presence of *N,N*-dimethylformamide as catalyst¹⁸.

4,4'-Hexafluoroisopropylidene-bis(benzoyl chloride) (**IIb**) was prepared by treating the corresponding 4,4'-hexafluoroisopropylidene-bis(benzoic acid) with excess thionyl chloride at reflux¹⁹.

The silicon-containing diacid chloride, namely *bis(p-chlorocarbonyl-phenylene)-diphenylsilane*, (**IIc**) was prepared by a multi-step reaction²⁰. First, *p*-bromotoluene reacted with

lithium to give *p*-tolyl-lithium which further reacted with diphenyl-dichlorosilane to produce bis(*p*-tolyl)-diphenylsilane. The later was oxidized with chromium oxide in a mixture of sulphuric acid and acetic anhydride and gave the corresponding bis(*p*-carboxy-phenylene)-diphenylsilane which was further treated with excess thionyl chloride at reflux to result in bis(*p*-chlorocarbonyl-phenylene)-diphenylsilane.

Polymers

New asymmetrical aromatic polyamides **III** have been synthesized by low-temperature solution polycondensation reaction of equimolar amounts of the asymmetrical aromatic diamine **I** with diacid chlorides **IIa-c** having ether, hexafluoroisopropylidene, or silicon groups, respectively, using *N*-methylpyrrolidinone (NMP) as a solvent and with pyridine as an acid acceptor. The relative amounts of monomers and NMP were adjusted as to have a solid content of 14-15 %. The resulting aramides were isolated from the reaction mixtures by precipitation into water and washing with plenty of water and extraction with ethanol in a Soxhlet apparatus for 1 day in order to remove the unreacted monomers and oligomers and the high boiling solvent.²¹

Preparation of polymer films

Films of polymers **III** were prepared by casting a polymer solution of 10-12% concentration in NMP onto glass plates, followed by gradual heating from room temperature up to 210°C, and kept at 210°C for 1h. Transparent coatings resulted having strong adhesion to the glass support. The resulting films were stripped off the plates by immersion in boiling water. They were kept in boiling water for further 2 h, followed by drying in oven at 110°C. These films had the thickness in the range of 40-50 µm and were used afterwards for various measurements.

Measurements

The infrared spectra of the polymers were recorded on FT-IR Bruker Vertex 70 Spectrophotometer in transmission mode, by using KBr pellets.

Average-molecular weights were measured by means of gel permeation chromatography (GPC) using a PL-EMD 950 evaporative mass detector instrument. Polystyrene standards of known molecular weight were used for calibration and dimethylformamide as the mobile phase.

The thermal stability of the polymers was investigated by thermogravimetric analysis (TGA) using a STA 449F1 Jupiter derivatograph (Netzsch), operating at a heating rate of 10 °C/min, in nitrogen atmosphere, from room temperature to 700 °C. The onset on the TG curve was considered to be the beginning of decomposition or the initial decomposition temperature (*IDT*). The temperature of maximum rate of decomposition which is the maximum signal in differential thermogravimetry (DTG) curves was also recorded.

The glass transition temperature (*T_g*) of the precipitated polymers was determined by using a Pyris Diamond DSC Perkin Elmer calorimeter. Approximately 3 to 8 mg of each polymer were crimped in aluminium pans and run in nitrogen with a heat-cool-heat profile from room temperature to 380 °C at 10 °C/min. The mid-point temperature of the change in slope of the DSC signal of the second heating cycle was used to determine the glass transition temperature values of the polymers.

The UV-vis absorption spectra of polyamides were registered with Specord M42 apparatus by using very diluted polymer solutions in NMP (approx. 10⁻⁵ M). The UV-vis spectra of methylene blue were registered by using water solutions of 10⁻³ M concentration.

CONCLUSIONS

New thermally stable polyamides with improved solubility based on an asymmetrical aromatic diamine containing phenoxy substituted benzophenone segment were obtained. All polyamides were easily soluble at room temperature in polar aprotic solvents and even in less polar solvents such as tetrahydrofuran. These polymers showed excellent thermal stability, up to 385 °C, and displayed glass transition temperature in the range of 225-256 °C. All the polyamides displayed one strong UV absorption maximum in the range of 274-278 nm due to the main benzenoid $\pi - \pi^*$ type transition in benzophenone chromophoric group. These benzophenone-containing polyamides were cast into thin, transparent and flexible films that showed radical-forming ability under UV irradiation. The polymer films decomposed methylene blue dye, and is expected to show antibacterial activity, under UV irradiation. Further work is needed to evaluate the antimicrobial activity of these polymers by illumination under black light blue (BLB) light, which could initiate radicals in polymers. Applications as coating materials for self-decontamination membranes in various fields of these polyamide films are foreseen.

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