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Synthesis and Characterization of Easily Processable Polyaramides Containing Pendent Diamantan Moiety in the Main Chain

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Abstract: Three new polyamides were synthesized by direct polycondensation of 1-6 bis(carboxy methyl diamantan with three different aromatic amines in *N*-methyl 2-pyrrolidone containing lithium chloride using triphenyl phosphate and pyridine as condensing agent. 1-6 bis(carboxy methyl)diamantan was prepared from 1-6 dibromo diamantan and structure was conformed by ^1H and ^{13}C NMR spectroscopy. A comparison of the effect for introducing bulky side group in the diamine contribution was evaluated. This polyamide had inherent viscosity of 0.57-1.18dL/g. It was found that all polyamides were soluble in polar aprotic solvents. Thermal stability of polymer was evaluated by TGA analysis. Molecular weights of all polyamides were determined by gel permeation chromatography. These have been found to be thermally stable up to 400 $^{\circ}\text{C}$ with 1320% weight loss under nitrogen atmosphere.

Keywords: Polyaramides, Diamantan, Synthesis, Polycondensation

Introduction

Aromatic polyamides are a high temperature resistance engineering class polymer which have good thermal stability, good chemical resistance and good mechanical property. Formation of aromatic amides generally carried out by solution polycondensation. Some methods use aromatic diamine that reacts with *di* acid chlorides¹⁻⁶ and other methods use high temperature, where diamines react with aromatic *di*-acids or *di*- acid chlorides as Yamazaki's reaction⁷. Some aromatic polyamide contains intermolecular hydrogen bonding and crystallizes easily. Due to these factors, some polyamides cannot dissolve in most organic solvents and difficult to process. Therefore several attempts has been made to

maintain thermal property and improve solubility.⁸⁻¹⁸ These study include (i) introducing soft segment CH₂ in the main chain of polymer (ii) introducing bulky group in the main chain of polyamide to break the symmetry of the polymer which suppress crystallization (iii) breaking symmetry and structural regularity makes crystallization impossible (iv) forming a three dimensional structure without sharing the same surface and (v) destroying the hydrogen bonding by substituting hydrogen at amide group. Pali *et. al*¹⁹ used low temperature poly condensation of pendent bulky group containing diamines with *di* acid chlorides and found slight increase in solubility with aromatic poly amide chain stiffness. Diamantan is a most general cyclo-aliphatic cage hydrocarbon which contains an extended cage structure made up adamantane structure compound and first time used in polymer in the form of 1-6 diethynyl diamantan monomers which on addition polymerization forms clear thermoset film and have no much use. Charn and Wang²⁰ have prepared aromatic polyamides using Yamazaki reaction and find that solubility increases with increasing extended cage effect in the main chain. Hence structural modification plays an important on the solubility of aromatic polyamides. In this communication, we present the synthesis of 1-6 *bis*(carboxy methyl) diamantan along with three different poly amides based in different aromatic diamines. Also, we have attempted to introduce not only cage type structure but also bulky pendent grouping to the aromatic polyamide main chain. We have synthesized three polyamides based on high temperature poly condensation reaction of 4-4' (9- fluorenylidene) diamines, 4-4' (hexa fluoro-isopropylidene) dianiline, 4-4' diamines benzophenone with 1-6 *bis*(carboxy methyl) diamantane using Yamazaki reaction and studied to understand the influence of thermal property and solubility with the change in structure diamines and *di*-acids.

Experimental

The diamines used for polyamide synthesis are shown in the Table 1. All amines were further purified by vacuum sublimation and all the solvents used were further purified by vacuum distillation. All the chemicals were procured from Alderich chemical company. Diamantan was prepared by three step synthesis from norbornadiene²¹. 1-6, Dibromo diamantan was prepared by the direct bromination of diamantan at ambient temperature²².

Table 1. Characterization of polyamide

Polymer	% Yield	η_{inh} dL /g	Elemental analysis, %			
			C	H	N	
1A	90	1.18	Found	84.01	6.55	4.59
			Cal.	83.77	6.49	4.55
1B	92	1.12	Found	66.10	5.95	4.98
			Cal.	65.78	5.32	4.65
1C	96	0.57	Found	78.02	6.55	5.98
			Cal.	77.50	6.49	5.83

Synthesis of 1-6, Bis(carboxyl methyl) diamantane

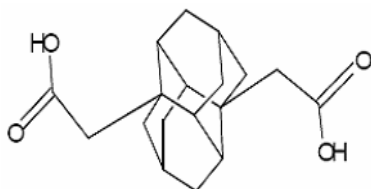
0.8g (0.02mole) of 1-6, *Bis*(carboxyl methyl) diamantan was added to 400mL flask containing 98% concentrated sulphuric acid and stirred thoroughly. About 80 mL of 1-1 dichloro ethylene was then added to the mixture and stirred vigorously at 40⁰ C for six hours. Thereafter the reaction product was poured into flask containing ice and the precipitate was separated by filtration. The product was precipitated through sodium salt and crystallizes from glacial acetic acid /DMF yield=5.010g.

IR(KBr) 2918, 2850 cm⁻¹ (CH₂, CH), 1420 cm⁻¹ (OH), 1685 cm⁻¹ (C=O).

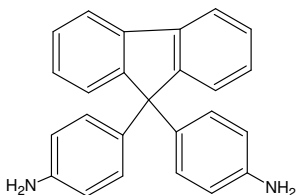
CHN analysis C₁₈H₂₄O₄ cal C 71.05% H 7.95%; Found C 71.15% H 7.97% ¹H NMR (300MHz,

DMSO d₆) 2H(δ =10.5),4H(δ =1.81),4H(δ =2.08),8H(δ =1.65), 4H(δ =1.83), 2H(δ =1.99),
¹³C NMR (75MHz,DMSO d₆) δ =26.9(C-9,4), δ =34.8(C-5,13), δ =38.1(C-3,8,10,14),
 δ =40.5(C-1,6), δ =45.4(C-2,7,11,12), δ =46.8(C-17,15), δ =178.6(C-16,18)

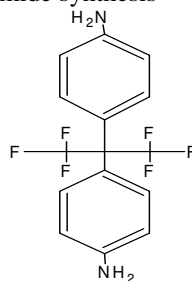
Reactant used for polyamide synthesis



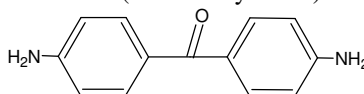
1-6, Bis(carboxyl methyl) diamantan



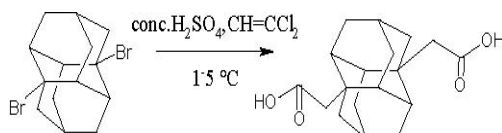
4-4'-(Hexafloro isopropylidene) dianiline (B)



4-4'-(9-Fluorenylidene) diamines (A)



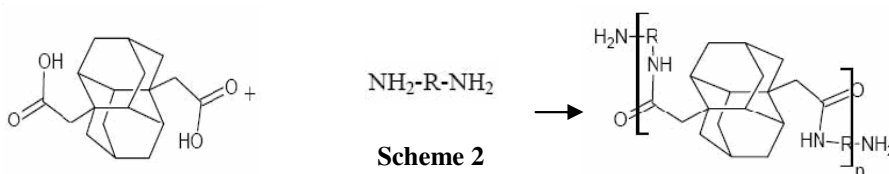
4-4' Diamines benzophenones (C)



Scheme 1

Polymer synthesis

2m mole(0.608g) of 1-6,Bis(carboxyl methyl) diamantan ,4mmole of triphenyl phosphate 15mL of pyridine ,20 mL of *N*-methyl 2-pyrrolidone(NMP) and 0.5g of lithium chloride and 2.5mmole of 4-4'-(9-fluorenylidene) diamines was heated under constant stirring at 130 °C for ten hours in a reflux assembly. The resultant solution was poured to one liter capacity beaker containing 900 mL of methanol and finally the fibrous white precipitate was washed through methanol and water. The yield was almost quantitative and inherent viscosity 1.18 dL/g was found for this polymer at 0.5g/dL concentration at ambient temperature in the presence 5% w/v lithium chloride in dimethyl acetamide (DMAc).Presence of amide group is conformed IR spectrum of the polymer on KBr which shows absorption band at 3332 cm⁻¹ and 1663 cm⁻¹. Elemental analyses of polymers are tabulated in Table 1.



Scheme 2

Where R = Pendent bulky group diamine

All other polymers were synthesized by the same method.

Polymer characterization

For all the polyamides Infra red spectra were obtained using Fourier transformed infrared spectroscopy (Nocolet 380) taking 64 scan per sample using 2%w/w polyamides in KBr. Inherent viscosity of polyamides were measured with Ubbelohde viscometer No.75. The inherent viscosity was determined at a concentration of 0.5g/dL at 30 °C in DMAc solvent. Elemental analyses were carried out in elemental analyzer Heraeus Carlo Erba 1180. Thermogravimetric analysis was carried out in TGA -7, Perkin Elmer thermo gravimetric analyzer, under nitrogen atmosphere at heating rate of 10 °C per minute between 50 and 600 °C. Gel permeation chromatography (GPC) analysis were conducted on polyamide solution in DMAc. The analyses were performed using distilled DMAc containing 0.1M LiBr. Chromatography was performed on high performance liquid chromatograph (HPLC) Waters-510 equipped with a UV detector and three ultrasryragel/PL gel column (size 500,1000,& 100000 Å⁶) connected in series in order to increasing pore size at flow rate of 1.0 mL/min. The columns were calibrated with polystyrene (PS) standard and standard of poly *m*-phenylene isophthalamide with molecular weight 1000 to 310000 g/mol using five point calibration curve.

Results and Discussion

Scheme 2 shows the route for synthesis used in this work based on Yamazaki phosphorylation reaction. The infrared spectra of the polyamide obtained shows the characteristic bands for the amine group between 3270 cm⁻¹ and 3332 cm⁻¹ (-NH) and the carbonyl group at 1662 cm⁻¹ (C=O). The solubility of the three polyamides were tested in different solvents using 0.1g of polymer in 5mL of solvent. Dimethyl sulphoxide (DMSO), dimethyl acetamide (DMAc), Dimethyl formamide (DMF), benzene (Bz), tetrahydro furane(THF), pyridine (Py), conc. H₂SO₄ and *N*-methyl 2-pyrrolidone (NMP) were used. Almost all polymers were soluble in polar aprotic solvents. Solvents such as THF and Bz are unable to dissolve polyamides. These are also soluble in pyridine, but partially soluble in DMSO. Solubility data in different solvents are given in Table 2. Inherent viscosity η_{inh} were found ranging from 0.57 to 1.18. Values of Inherent viscosity η_{inh} are comparable to the values of other aromatic polyamide. Films forming capacity was found in all polyamides and film was prepared by casting from their DMAc solution containing 1% LiCl. Film was found colorless and strong. Thermal properties of polymers are summarized in the Table 4. Representative TGA curves are given in the Figure 1 as supporting information. Fluorene substitution in the diamines moiety increases the stability of the polyamide as compared with carbonyl group. However, hexafluoro polyamide have slightly higher decomposition temperature than fluorine containing polyamide, but all these polyamides with stand from 375 to 390 °C without mass loss and 20% mass loss occur at 400 °C. The same trend was observed by Cassidy *et.al.* in poly ester synthesis with hexafluoro substitution²³. Mass loss of the polyamides obtained at 400 °C ranges between 13-20% as shown in Table 4. The mass loss of the polyamides containing fluorene moiety is less compared with hexa-floro polyamide whereas carbonyl polyamide has maximum weight loss. This is due to fluorene group has the number of phenyl group/maximum stabilization energy and hence have maximum stability. GPC analysis conforms that high molecular weight polyamides are obtained by this method. These polymers are found to be soluble in most of common solvents and can be process in relatively easy way by solvent evaporation method. Further analysis and possible application of this polymer system is under development.

Table 2. Solubility of polyimides

Polymer	NMP	DMF	Py	DMAc	Bz	THF	Con.H ₂ SO ₄
IA	++	++	++	++	--	--	++
1B	++	++	++	++	--	--	++
1C	++	++	++	++	--	--	++

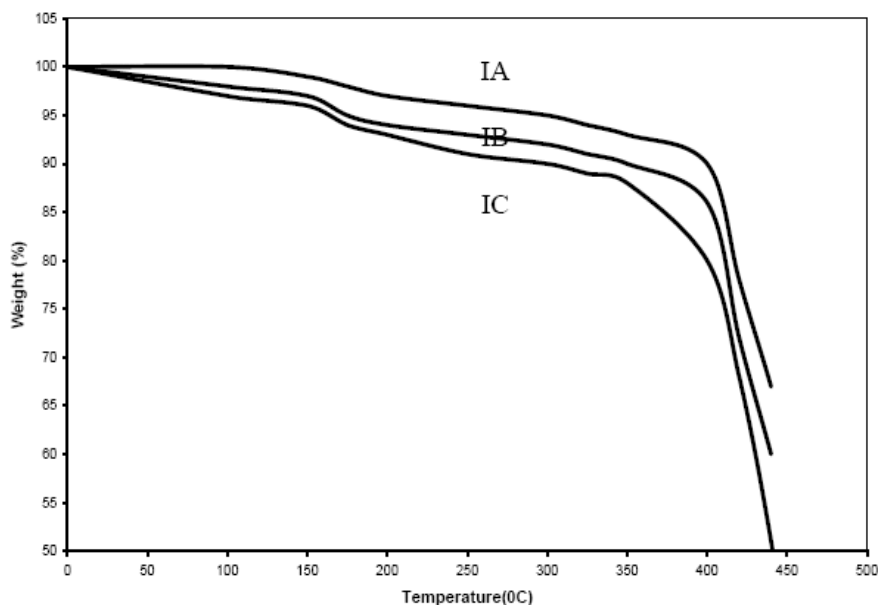
+++ soluble, ++= partially soluble,-- = insoluble

Table 3. Molecular weight (GPC analysis)

Polymer	η_{inh} dL/g	Mw (PS)	Mn (PA)	Mw (PA)	Mw/Mn
IA	1.18	290720	62000	142000	2.3
1B	1.12	298250	56000	112000	2.0
1C	0.57	72780	21000	40000	1.9

Table 4. Thermal properties

Polymer	Decomposition temperature, °C	η_{inh} dL/g	% Mass loss at 400 °C
IA	388	1.18	13.0
1B	390	1.12	16.2
1C	375	0.57	19.1

**Figure 1.** TGA graph of all polymers with 1-6 bis(carboxymethyl) diamantan

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