

Fully Aliphatic Polyimides- Influence of adamantane and siloxane moieties

Chang Sik-Ha,* Il Kim, Anu Stella Mathews

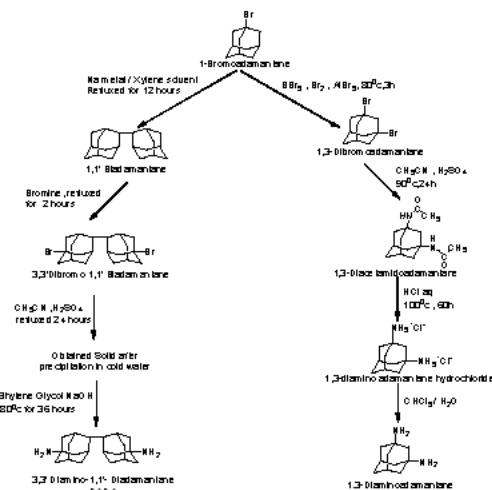
Department of Polymer Science and Engineering, Pusan National University, Busan, Korea
csha@pusan.ac.kr

Introduction

Polyimides (PI) possess excellent thermal, mechanical and electrical properties and thus have found immense applications in technologies ranging from microelectronics to high temperature matrices and adhesives to gas separation membranes¹. Fully aliphatic and alicyclic polyimides (API) are currently being considered for their applications in optoelectronics and inter-layer dielectric materials thanks to their higher transparencies and lower dielectric constants, compared to aromatic polyimides.² Nevertheless, polyimides derived from aliphatic monomers are most suited for applications that have less-stringent thermal requirements. Previous studies revealed that adamantane (tricyclo [3.3.3.1.1] decane), a rigid alicyclic compound composed of three cyclohexane rings in chair conformations,³ is the most salutary alicyclic candidate for incorporation into aliphatic polyimides to enhance thermal stability without sacrificing their high transparency, solubility and low dielectric constants. Recently, silicon containing aromatic polymers have attracted much scientific and technological interest due to their superior permeability and adhesive ability between substrates and polyimides together with low dielectric constant⁴. In this work, we wish to discuss how adamantyl group and siloxane moieties influence the basic properties of aliphatic polyimides (APIs), by synthesizing various fully aliphatic polyimides and polyimide-siloxanes (APISiO).

Experimental

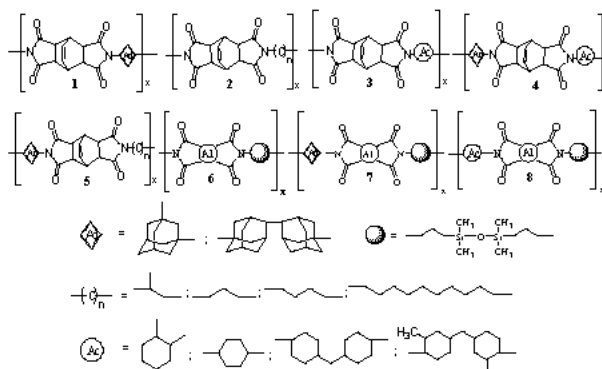
Monomer Synthesis: 1, 3-Diaminoadamantane (DAA) and 3, 3'-diamino-1, 1'-diadamantane (DADA) were synthesized, as shown in scheme 1, starting from 1-bromoadamantane^{5,6} and purified through vacuum sublimation.



Preparation of APIs and APISiOs through One-Step Polymerizations: Equimolar amount of the dianhydride was added slowly to diamine in m-cresol preheated to 60°C. The solution is then heated to 100°C for 12 hours followed by 150°C for 4 hours and 200°C for 48 hours and was precipitated in methanol and dried at 60°C. Co-polyimides contained 1:1 ratio of aliphatic diamines and / or adamantyl diamines and/or APTMS. Structures of APIs and APISiOs synthesized are given in figure 1.

Film Casting: A 5-7 wt % solution of polymer in chloroform was prepared and was poured into a Petri dish. The casting films were dried in an oven at 40°C for 6 hours without vacuum and for another 6 hours with vacuum, and the resulting films samples were dried at 80°C for 6 hours and then at 100°C for 10 hours. To perform the dielectric constant and transparency measurements, the solutions of

polymers were spin-coated onto clean ITO glass and quartz plates, respectively, and then subjected to the heating cycle.



Results and discussion

Structural Analysis. ¹H NMR and ¹³C NMR spectra confirmed the successful formation of co-polyimides containing aliphatic and adamantyl or siloxane units.²⁹ Si-MAS NMR supported the chemical addition of siloxane units to polyimide backbones. Structural characteristics of the polymers obtained by IR analysis confirms the earmark absorption bands of imide group around 1780 (C=O symmetric stretching), 1720 (C=O asymmetric stretching), 1380 and 730 cm⁻¹ (C-N-C bond and the imide ring deformation) for all samples.

Physical Properties. The polyimides which contained only aliphatic units, **2**, had thermal and mechanical properties inferior to other ones due to the highly flexible backbone. Addition of adamantane improved those properties to certain extent. The combination of alicyclic and adamantane moieties in the backbone i.e. polyimides **4**, gave appreciable properties. Without having to incorporate expensive fluorine compounds into their structures, the copolyimides of alicyclic and adamantyl diamines exhibited dielectric constants as low as 2.34 ~ 2.56, while possessing enhanced solubilities and transparencies. Even the commercialized polyimide, Kapton has ϵ value around 3, together with the demerits in that they are insoluble in organic solvents and are highly colored. On the other hand, our co-polyimides, **4**, shows superior properties like low dielectric constant together with excellent solubility in common organic solvents and high transparency c.a. 90%. The synthesized APISiOs with M_n ca. 5200~47000 possess T_g as high as 270°C, 10% weight decomposition ranging from 353-476°C, ϵ values 2.47 - 2.68 and tensile strength 99 - 121 MPa along with excellent solubility in common solvents. Si and adamantane moieties attributed shoulder to shoulder for the lower dielectric constants of adamantyl based APISiOs which makes them a strong competent among technologically significant materials.

Conclusions

We synthesized a series of fully aliphatic polyimides through polyaddition / polycondensation reactions. The organic-soluble APIs and APISiOs that we prepared exhibited low dielectric constants and appropriate thermal and mechanical stability. Thus they have potential for applications in micro- and optoelectronic devices.

Acknowledgements

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