Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Increased Amine Surface Density of an Aminosilylated Molecular Layer Through Hyperbranching

Sung Ju Cho [a] , Hong Jin Kim [a] & Joon Won Park [a]

[a] Department of Chemistry, Division of Molecular and Life Science, Pohang University of Science and Technology, San 31, Hyoja-Dong, Nam-Gu, Pohang, Korea, 790-784

Version of record first published: 24 Sep 2006

To cite this article: Sung Ju Cho, Hong Jin Kim & Joon Won Park (2001): Increased Amine Surface Density of an Aminosilylated Molecular Layer Through Hyperbranching, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 371:1, 71-74

To link to this article: http://dx.doi.org/10.1080/10587250108024690

Mol. Cryst. and Liq. Cryst., 2001, Vol. 371, pp. 71-74

Increased Amine Surface Density of an Aminosilylated Molecular Layer Through Hyperbranching

SUNG JU CHO, HONG JIN KIM and JOON WON PARK*

Department of Chemistry, Division of Molecular and Life Science, Pohang University of Science and Technology, San 31, Hyoja-Dong, Nam-Gu, Pohang, Korea 790-784

An aminosilylated substrate was treated with aziridine to prepare hyperbranched polymers on solid supports. It is observed that the primary amine on the substrate is able to initiate the ring-opening polymerization of aziridine. Measuring the thickness of the film and absolute density of the primary amine functionality shows that a very highly branched poly(ethyleneimine) is formed since the primary amine functional group on the very top surface increased dramatically from 3.6 amines/nm^2 to 66-78 amines/nm^2. Atomic force microcopy shows that the polymerization is rather regular laterally and that the morphology of surface has not changed significantly after the polymerization.

Keywords: aziridine; hyperbranched polymer; surface polymerization.

INTRODUCTION

Aminosilylated surfaces find numerous applications in immobilization of biologically interesting molecules and inorganic catalysts.[1] In all these applications, the surface density of the reactive amine group is a primary factor determining the surface property. We have attached aziridine on the aminosilylated surface in order to increase the molecular number density via hyperbranching.

EXPERIMENTAL

An aminosilylated substrate was immersed in a dichloromethane solution (20

mL) of aziridine[2] (0.2 mL) and a catalytic amount of acetic acid. The solution was heated to reflux for 24 h under nitrogen. The resulting substrate was thoroughly washed with copious dichloromethane and sonicated in methanol three times. The washed substrate was dried *in vacuo* at room temperature. Atomic force microscope image were obtained in the non-contact mode.

RESULT AND DISCUSSION

Substrates were treated with (3-aminopropyl)diethoxymethylsilane to make a reactive primary amine functional groups on the surface. The thickness of the self-assembled layer was 8 Å, and the surface density of functional group was 3.6 amines/nm^2. After reaction with aziridine in an inert atmosphere, the thickness of film increased up to 77 Å in 24 h. Considering the reactivity between aziridine and the primary amine, it is obvious that the ring-opening has occurred to form poly(ethyleneimine) hyperbranched polymer on the surface (Fig 1).

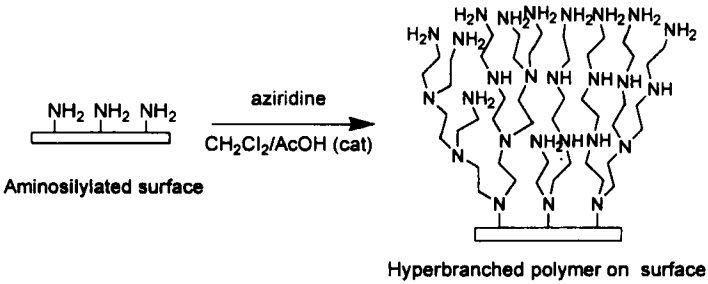


FIGURE 1. Formation of a hyperbranched polymer on a solid support using aziridine

A reliable way to estimate the degree of branching is to determine the surface density of the end groups, i.e., the primary amines. As shown in Fig 2, absorbance at 284 nm due to 4-nitrobenzalimine is evident when the primary amine is converted to the imine.

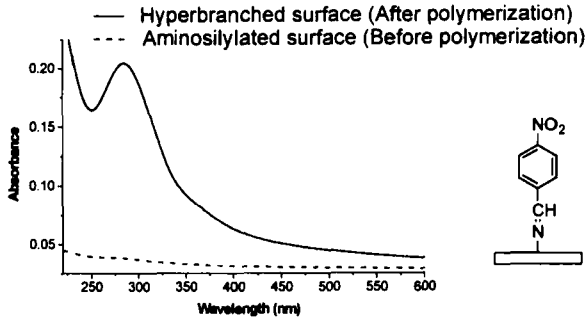
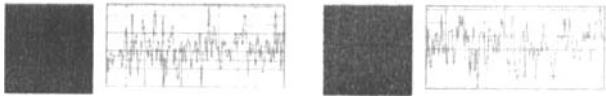


FIGURE 2. UV-Vis spectra of imine-formed surface before and after polymerization

Due to the increased number of primary amines after the polymerization, the absorbance increased sharply. The absolute density of the amine group was determined by hydrolyzing the imine with a known amount of water.[3,4] It is found that the density of the primary amine increased to saturation in 24 h (78 amines/nm^2, Table 1). This observation definitely shows that the branching is operative. Otherwise, a constant surface density will be obtained regardless of the chain growth. The AFM image shows (Fig 3) that the hyperbranched surface is slightly rougher than the aminosilylated one. However, the overall morphology of both surfaces displays similar structures when examined at the surface height.

TABLE 1. Physical Properties of the Film Before and After Polymerization

Sufaces	Contact Angle (°)	Thickness (Å)	Absolute Density (number of Amine/nm^2)
after aminosilylation	62 (± 2)	8	3.6
after polymerization	62 (± 2)	77	78



(a) (b)

FIGURE 3. Atomic Force Microscope (AFM) Images (2.0 μm x 2.0 μm) of (a) aminosilylated surface and (b) polymerized surface

The higher increase of the density indicates that the length of the polymer chain must vary. Irregular polymer chain lengths give a rough surface rendering a higher surface density than that of the monodispersive surface.

CONCLUSION

It is demonstrated that an aminosilylated layer can be converted to a new layer of poly(ethyleneimine) by reaction with aziridine. Particularly, the absolute number density of the primary amine group on the very top surface increases dramatically by the branching process, yet the morphology of the surface does not change significantly.

Aknowledgement

Student fellowships of the Brain Korea 21 are greatly acknowledged, and also the work is supported by the Korea Foundation of Science and Engineering (1999-2-122-002-4).

References

[1] A. Ulman, "An Introduction to Ultrathin Organic Films from Langmuir-Blodgett to Self-Assembly", Academic, New York (1991)

[2] P. Dauban, L. Dubois, M.E.T.H. Dau, and R.H. Dodd, *J. Org. Chem.* **60**, 2035 (1995).

[3] J.H. Moon, J.W. Shin, S.Y. Kim, and J.W. Park, *Langmuir*, **12**, 4621 (1996).

[4] J.H. Moon, H.J. Kim, K.-J. Kim, T.H. Kang, B. Kim, C.-H. Kim, J.H. Hahn, and J.W. Park, *Langmuir* **13**, 4305 (1997).