

ACCESSORY PUBLICATION

Ring Opening Metathesis Polymerization of Polyoctahedral Oligomeric Silsesquioxanes (POSS) incorporated oxanorbornene-5,6-dicarboximide: Synthesis, Characterization, and Surface Morphology of Copolymers

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Solubility of the polymers

The solubility of the linear homo- and copolymers of TFNDI-NPOND I was tested in a variety of organic solvents such as polar, non-polar, polar protic and polar aprotic solvents at room temperature. The results were given in Table S1. The linear homo- and copolymers showed good solubility in polar aprotic solvents such as N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), tetrahydrofuran (THF), dimethylsulphoxide (DMSO), 1,4-dioxane and chlorinated solvents such as chloroform (CHCl₃), dichloromethane (DCM), dichloroethane (DCE) and tetrachloroethane. The 3NPOND I was partially soluble in the case of chlorinated solvents indicating that the increase in the POSS concentration decreases the solubility of the polymers. The HTFNDI and 1NPOND I were highly

soluble in most of the solvents even at ambient temperature. The enhanced solubility of these polymers was attributed by the presence of more number of pendant CF₃ groups in the imide chains and cyclopentyl groups attached to the POSS which decreases the intermolecular interaction between the polymer chains. This leads to good solubility of polymers.

Table S1 Solubility of TFNDI-NPONDI copolymers

| Solvents | Samples | | | |
|--------------------------------------|---------|---------|---------|---------|
| | HTFNDI | 1NPONDI | 2NPONDI | 3NPONDI |
| THF | ++ | ++ | ++ | ++ |
| CHCl ₃ | ++ | ++ | ++ | ++ |
| CH ₂ Cl ₂ | ++ | ++ | ++ | ++/Δ |
| DMSO | ++ | ++ | ++ | ++ |
| DMF | ++ | ++ | ++ | ++ |
| NMP | ++ | ++ | ++ | ++ |
| CH ₂ ClCH ₂ Cl | ++ | ++ | ++ | ++/Δ |
| CHCl ₂ CHCl ₂ | ++ | ++ | ++ | + - |
| DMAc | ++ | ++ | ++ | ++ |
| Acetone | ++ | ++ | + - | + - |

| | | | | |
|--|--------------|----|----|----|
| Toluene | ++/ Δ | -- | -- | -- |
| CH ₃ CN | -- | -- | -- | -- |
| Hexane | -- | -- | -- | -- |
| CH ₃ COOC ₂ H ₅ | ++ | ++ | +- | +- |
| 1,4 Dioxane | ++/ Δ | ++ | +- | +- |

++: Soluble, --: Insoluble, +-, partially soluble, Δ : heating.

Supporting information S2

Contact Angle Measurements

Contact angle was widely used to get information about the nature of surface properties of copolymers. In this study, the surface properties such as hydrophobicity and the polarizability of the polymers were evaluated. The contact angles were measured using ultra pure water and heptadecane. The contact angle values were given in Table S1. Here, the surface energy, polar and dispersion factors were calculated using Young and Fowks equation.^[1]

$$\gamma_{LV}(1 + \cos\theta) = 2(\gamma_L^d \gamma_S^d)^{1/2} + (\gamma_L^p \gamma_S^p)^{1/2} \quad (1)$$

where γ_{LV} is the interfacial tension at liquid/air interface; γ_L^d and γ_S^d are the dispersion factors of the sample for liquid and solid respectively; γ_L^p and γ_S^p are the polar factors of the liquid and sample; θ is the contact angle between the sample and liquid/air interface. The total surface energy γ_{SV} of the samples were estimated using the following relationship,

$$\gamma_{SV} = \gamma_S^d \gamma_S^p \quad (2)$$

The synthesized polymers were composed of polyimide as a hydrophilic part and POSS as a hydrophobic part. It was expected that the morphologies of such polymers would be determined

by their unique molecular architectures. The HTFNDI has the lowest contact angle of 91.3° and the addition of POSS units had a major impact on the surface film as evidenced by the change in water contact angle from 91.3 to 104.3° as shown in Table S2. This observation indicates that the hydrophobicity of the materials significantly enhanced the surface free energy of the hybrid copolymers. In the case of heptadecane, contact angle decreases from 31.2 to 18.2° which may be due to the effect of increase in the hydrophobicity of polymers from HTFNDI to 3NPONDI. The surface energy of the film was decreased by the increase in the POSS content (Fig.S1). It was found that the decrease in the surface energy was mainly attributed by the polar component because of drastic decrease in γ_s^p from 14.70 to 3.55 mNm⁻¹. The contribution of dispersion factor γ_s^d was found to be less indicating that POSS was contributing less towards the surface energy of the copolymers. From these observations, we could conclude that the presence of POSS molecule reduces the surface energy of the copolymer structures.

Table S2 Surface energies of TFNDI-NPONDI copolymers

| Samples | $\theta_{\text{H}_2\text{O}}$ | $\theta_{\text{C}_{17}\text{H}_{36}}$ | γ_s^p (mNm ⁻¹) | γ_s^d (mNm ⁻¹) | γ_{sv} (mNm ⁻¹) |
|----------------|-------------------------------|---------------------------------------|-----------------------------------|-----------------------------------|------------------------------------|
| HTFNDI | 91.3 | 31.2 | 14.70 | 23.66 | 38.36 |
| 1NPONDI | 100.2 | 20.1 | 6.52 | 25.85 | 32.35 |
| 2NPONDI | 103.4 | 19.3 | 4.21 | 25.97 | 30.17 |
| 3NPONDI | 104.3 | 18.2 | 3.55 | 26.14 | 29.69 |

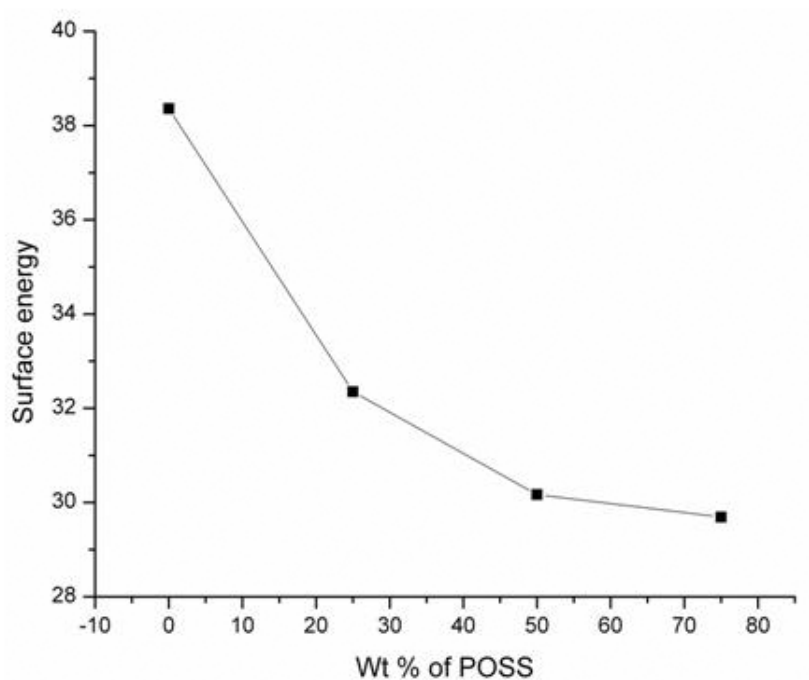


Figure S1 Surface free energy Vs POSS

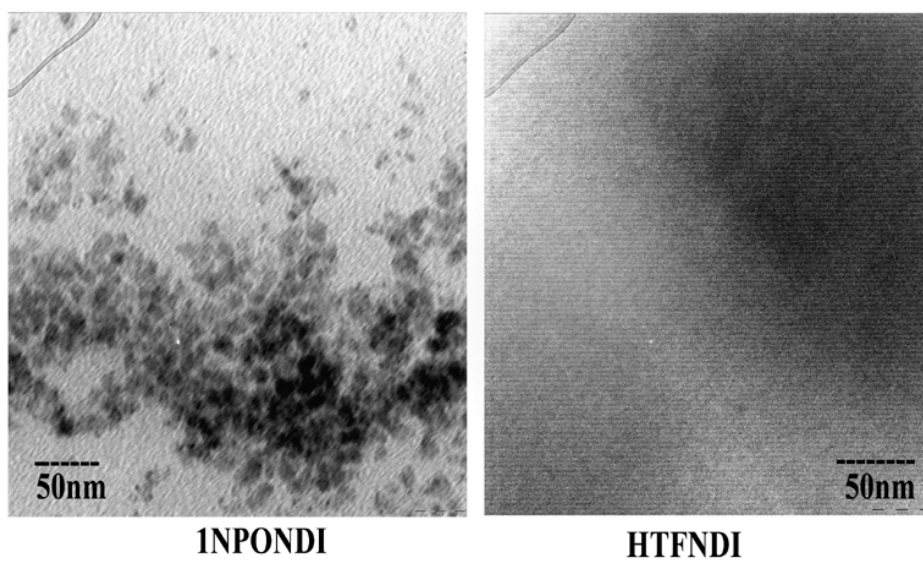


Figure S2 TEM images of TFNDI-NPONDI copolymers

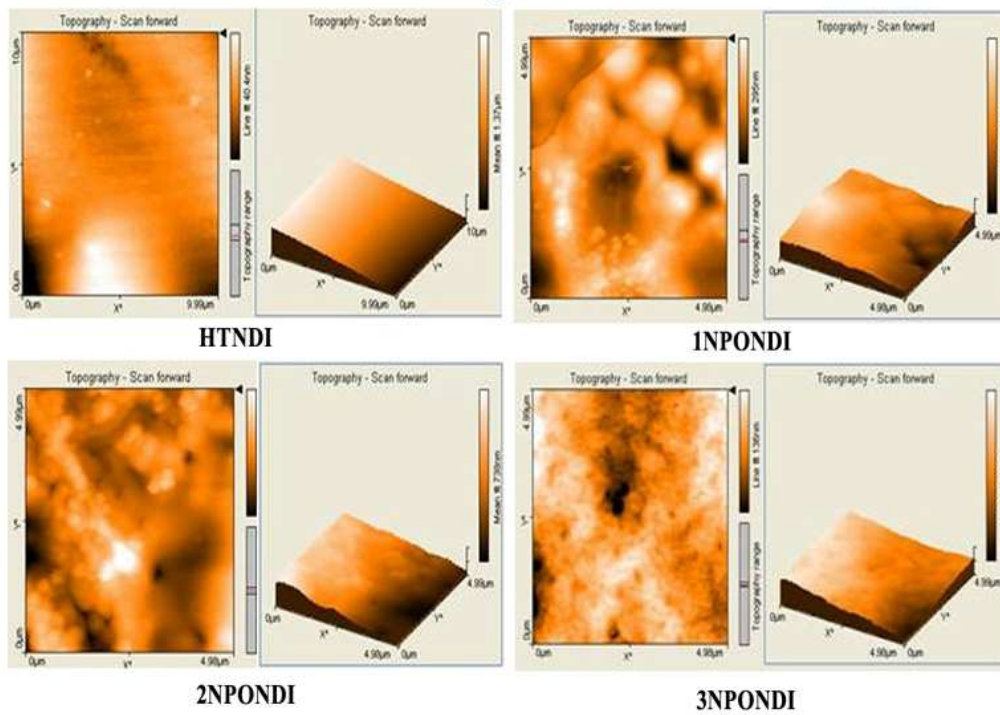


Figure S3 AFM images of all polymers

[1] Maxwell, C.; Treatise on Electricity and Magnetism, vol. 1, Oxford University Press London, 1873.