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Hybrid Inorganic/Organic Diblock Copolymers. Nanostructure in Polyhedral Oligomeric Silsesquioxane Polynorbornenes.

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ABSTRACT

Our main approach to the synthesis and study of hybrid organic/inorganic materials involves incorporating nano-size inorganic polyhedral oligomeric silsesquioxane (POSS) clusters into various polymeric resins. A typical POSS cluster is a discrete silicon and oxygen framework solubilzed with organic groups and contains a single reactive site. This lone site of reactivity is used to covalently attach the inorganic macromers pendent to a polymer backbone without causing any crosslinking. This strategy permits the synthesis of melt processable, linear hybrid polymers containing pendent inorganic clusters, and allows us to study the effect these clusters have on chain motion, polymer properties and morphology. The synthesis of norbornenyl-based (POSS) macromers, their ring opening metathesis copolymerizations with varying amounts of norbornene, and analysis of the effect of the pendent POSS group is presented. Ring opening metathesis polymerization permits the easy synthesis of both random and diblock copolymers. Transmission electron microscopy (TEM) clearly images POSS-rich domains against the POSS-free regions. Major differences in polymer morphology are observed as the amount of inorganic POSS is varied, between random and diblock copolymers, as well as between polymers that differ only in the solubilizing cycloalkyl groups on the POSS cluster.

why in parens?

INTRODUCTION

The design of new materials with enhanced properties continues to be a driver for the investigation of hybrid materials. As hybrid materials are copolymers based on inorganic and organic comonomers, they display enhanced properties by bridging the property space between two dissimilar types of materials [1]. A typical hybrid material will contain a crosslinked inorganic phase bound (often covalently) with an organic phase. An alternative approach, that several groups have pursued, is to append well-defined monodisperse silica-like clusters into thermoplastic resins [2-7]. The resulting hybrid polymers are easily processed, yet their physical properties are modified by the effect of the nano-sized inorganic component.

Our research has focused on using well-defined (POSS) (polyhedral oligomeric silsesquioxane) molecules for the inorganic component. Thermoplastics modified with POSS tend to show an increase in glass transition and modulus, a large increase in heat distortion temperature and a reduction in flammability. Changes to the rheological properties appear to

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derive from interaction between POSS groups themselves or with the polymer backbone. Characteristic polymer relaxation times are increased and we have found evidence for retardation of chain motion. Interestingly, the alkyl groups on the POSS cage play a major role in defining the overall effect of the POSS cage (See Figure 1 for a picture of a POSS). The subtle change from cyclohexyl to cyclopentyl groups at the POSS cage renders major differences to the material properties of the hybrid polymer [2].

Recently, we found that TEM images of polynorbornenes containing POSS-norbornyl groups *randomly* distributed throughout the polymer show phase separation on very short length scales and no long range order [8]. We have now synthesized diblock nobornenyl copolymers, which were expected to easily phase separate into POSS-rich and POSS-free polynorbornyl phases, in order to investigate their morphology.

EXPERIMENTAL DETAILS

Polymerizations. The polymers were all synthesized under nitrogen using the ROMP catalyst (Strem Chemicals), $Mo(=CHCMe_2Ph)(2,6\text{-di}^iPrC_5H_3N)(OC_4H_9)_2$, in anhydrous chloroform with various proportions of norbornene and either of the two POSS-norbornenyl derivatives **1a** and **1b** [1c, pp 381]. The reactions were designed to yield polymers with degrees of polymerization of 500 by controlling the ratio of monomers to catalyst. The reactions were terminated by addition of benzaldehyde. To generate random copolymers, the POSS-norbornenes and norbornene were dissolved together in chloroform prior to addition of the catalyst. To synthesize diblock copolymers (see Figure 1), the catalyst was added to a chloroform solution of the POSS-norbornene and, after allowing 30 minutes for polymerization, a solution of norbornene was added to the already polymerized POSS-norbornene. The polymers were precipitated and purified by adding the chloroform solution to a large excess of methanol and collecting the precipitate. This resulted in copolymers isolated in yields over 90 %.

Thermal analysis. The glass transition temperatures were determined using a TA Instruments differential scanning calorimeter (DSC). The temperature corresponding to the midpoint in the heat capacity step-rise is used for this purpose. The second heating run data are used with samples heated at a rate of 10 °C/min (See Figures 2 and 3).

Transmission electron microscopy. TEM micrographs (See Figure 4) were obtained from ultramicrotomed thin sections of films of 0, 10, 30 and 60 wt % POSS-norbornene copolymers cast from para-xylene. Bright field images were obtained using combined mass-thickness and phase contrast with a 120 keV JEOL 1200EX TEM. Due to the high electron density difference between polynorbornene and POSS molecules enough contrast could be obtained without any chemical treatment. Polymer phases rich in POSS appear as dark domains, while the TEM image of polynorbornene containing no POSS is featureless.

RESULTS

Polymerization of POSS macromers. Random copolymers of norbornene and either of the two POSS macromers **1a-1b** were prepared by adding a molybdenum catalyst to a well-stirred solution of norbornene and POSS-norbornene. The molybdenum catalyzes a living ring opening metathesis polymerization; the polymerizations were designed to yield polymers with a degree of polymerization of 500. These polymers may be viewed as organic polymers randomly filled with monodisperse inorganic particulates which are covalently bound to the polymer backbone. The synthesis of diblock copolymers containing blocks of polynorbornene and polyPOSS-norbornene (See Figure 1) was achieved by first polymerizing the POSS-norbornene monomers, then adding norbornene to the living polymerization reaction. Addition of benzaldehyde clips the molybdenum catalyst from the chain ends and terminates the polymer chains with a =CHPh group.

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Differential scanning calorimetric characterization. DSC measurements were taken on both the random and the diblock copolymers (See Figures 2 and 3). As expected, the random copolymers show an increase in Tg as the weight % of POSS is increased. The effect on Tg is larger for the cyclohexylPOSS copolymers than for their cyclopentyl analogs. The diblock copolymers only exhibit one Tg for the POSS-free block, as the block of polyPOSS-norbornene has a Tg well above the decomposition of the polymer.

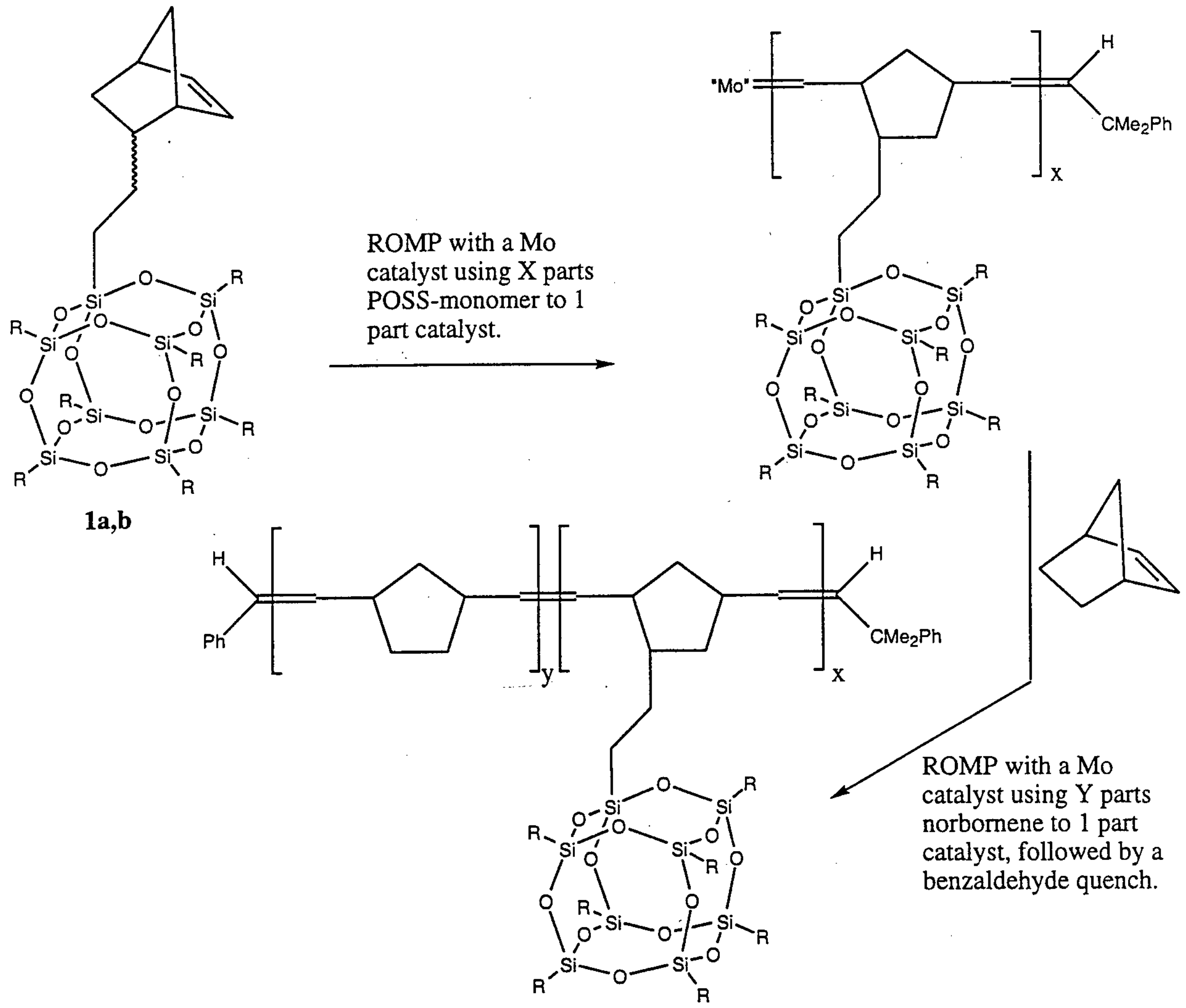

Figure 1. Synthesis of POSS-norbornene diblock copolymers.

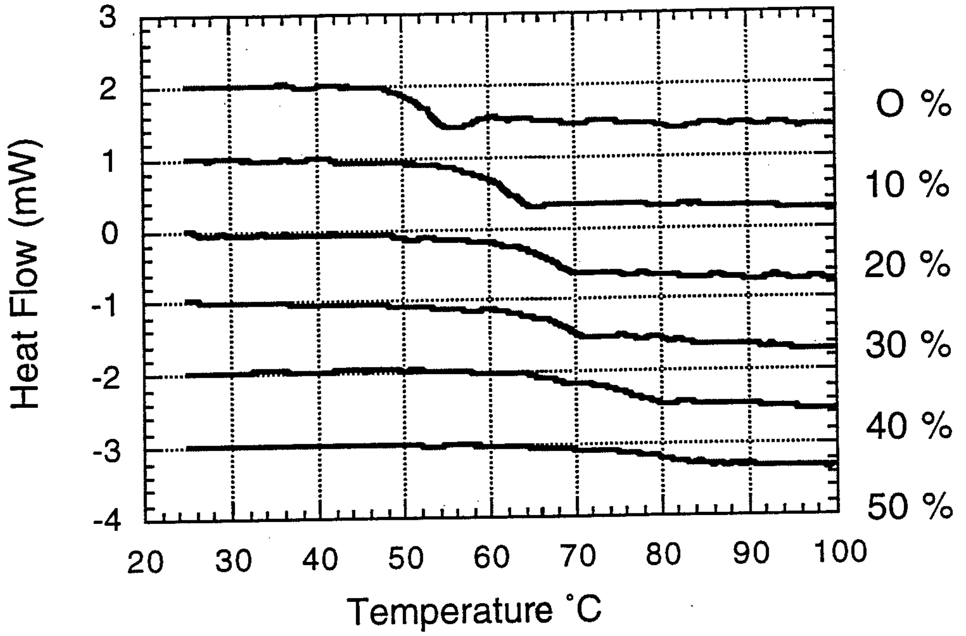

Figure 2. *DSC traces for a series of random copolymers made from monomers of norbornene and cyclohexylPOSS-norbornene (0 to 50 weight %). A single Tg that increases with POSS content is observed.*

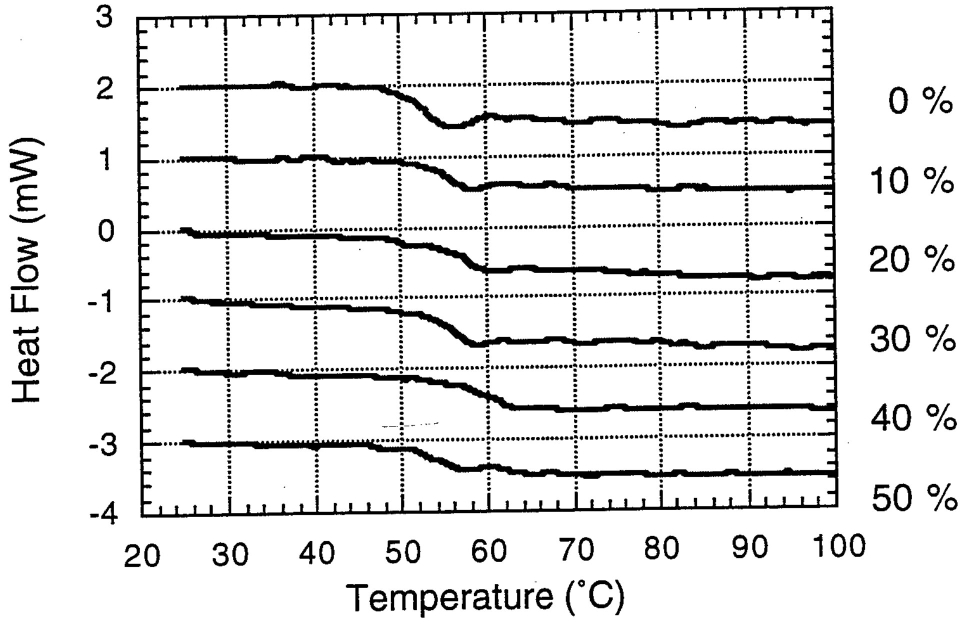

Figure 3. *DSC traces for the series of diblock copolymers made by sequentially polymerizing monomers of norbornene and cyclohexylPOSS- norbornene (0 to 50 weight %). Only the Tg for the POSS-free polynorbornene block is observed.*

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