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Stereochemical Structure-Property Relationships in Polynorbornene from Simulation

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Single-chain Monte Carlo simulations of polynorbornene were carried out for three stereochemical isomers. These simulations employed custom force field parameters derived from *ab initio* and semi-empirical quantum calculations. The scaling of intrinsic viscosity with molecular weight was determined from these simulations. An unusually large variation in this scaling was obtained, which is attributed to the large degree of steric hindrance inherent in this form of polynorbornene that retains the bicyclo-heptane ring in the backbone. The same scaling was measured for three commercial samples of this polymer produced using three different catalysts. The simulation and experimental results were consistent and the former were used to estimate the stereochemical configuration of the commercial samples. The simulation results for a stereoregular isomer of polynorbornene were also consistent with previous RIS model results. These structure-property relationships extracted from the simulations are potentially useful in the commercialization of polynorbornene for interlayer dielectric applications in electronic packaging.

Introduction

The bi-cyclic variation of polynorbornene is a polymer currently under investigation for a number of applications, including ultra-violet photoresists and interlevel dielectrics in microelectronics applications.[1-6] The 2,3-norbornene monomer undergoes a vinyl-like polymerization that retains the bicyclic conformation in the backbone of the resulting polymer as seen in Figure 1. This is unlike the commonly employed Ring Opening Metathesis Polymerization (ROMP) mechanism which retains only a single ring in the polymer backbone. This polymer is currently being test marketed by the BFGoodrich Company under the trade name Avatrel® dielectric polymer. Polynorbornene has excellent dielectric properties and a cost advantage over other materials currently being used as interlevel dielectrics,[1,7] however, the bicyclic backbone structure makes direct experimental characterization of the polymer microstructure using 2-D NMR difficult.[1,8,9] Therefore, we are currently using a combination of molecular modeling and experiment to characterize the microstructure of this polymer. This work involves the development of the requisite force field to carry out molecular modeling of the polymer. This force field is then used in a number of force field based simulation techniques to determine polymer microstructure and relate it to properties.

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Polynorbornene undergoes 2,3 exo-exo enchainment during polymerization, and a variety of properties can be obtained depending on the polymerization catalyst system used.[1] We hypothesize that different catalyst systems produce different stereochemistries and this gives rise to different properties. It is presumed that the zirconocene catalyst[10,11] produces the highly stereoregular 2,3-erythro di-isotactic polynorbornene, because of the intractable polymer produced from this catalyst. The stereochemistries produced by other catalyst systems are investigated in this work. Comparison of simulation results to experiment is employed to determine the relationship between catalyst system, stereochemistry and microstructure.

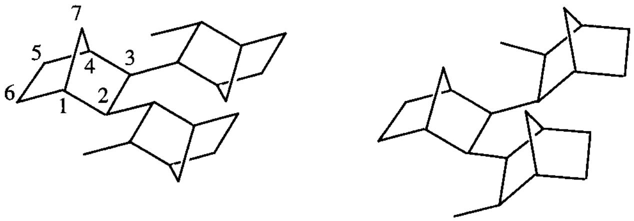

Figure 1. Structure of polynorbornene. The erythro di-isotactic trimer (left) with completely alternating bridgehead carbons and the threo di-syndiotactic trimer (right) with all bridgehead carbons in the same orientation are shown to illustrate extremes in stereochemical variation. Because the cis conformation is the extended form, the di-isotactic polymer has alternating bicyclo-heptane orientations, and the di-syndiotactic form has identical orientations. This is opposite of the isotactic and syndiotactic forms for vinyl polymers. 2D-NMR results from BF Goodrich indicate an exo-exo 2,3 polymerization.

Simulation Method

The force field used to describe interatomic interactions is critical to the accuracy of molecular modeling.[12] Preliminary work carried out on polynorbornene using commercially available force fields indicated that these force fields do not provide a good characterization of the material.[8,9,13,14] This most likely occurs because the carbon and hydrogen parameters for these force fields are typically parameterized for simple hydrocarbons. However, the high ring strain and severe steric hindrance in polynorbornene required the development of a new force field. New equilibrium geometry and bonded parameters were derived using a combination of *ab initio* and semi-empirical methods.[13,15] These parameters were used with the non-bonded parameters from the Dreiding2.21[16] force field, to create the resulting force field used in this simulation. The Dreiding2.21 van der Waals parameters were left unchanged because structure is not particularly sensitive to van der Waals parameters for non-polar species.[17] The equilibrium structures, produced from the quantum chemistry calculations, and used to derive the non-bonded parameters, reproduced the IR and Raman spectra of the norbornene monomer and dimers reasonably well.[13-15]

A Metropolis - Monte Carlo[18] simulation incorporating the pivot algorithm[19] followed by energy minimization was used to simulate isolated chains of polynorbornene. The assumption that isolated chains are sufficient to describe the structure of this polymer is justified by the fact that the bulky backbone of the polymer makes the intramolecular interactions much stronger than the intermolecular ones. Starting from an initial extended conformation a random torsional perturbation is applied to one rotatable bond, this is followed by 4000 steps of energy minimization using the BFGS[20] algorithm. No correction was applied for the potential conformational bias, caused by the minimization step, but without the minimization step the acceptance ratio was prohibitively low. Even with the minimization step, the acceptance ratio was approximately 2%. Three different molecular weights of three stereochemical isomers of polynorbornene were simulated: the erythro di-isotactic, and the threo di-syndiotactic isomers as well as a 50/50 statistical mixture of the two (atactic). These three isomers were simulated for 1000 iterations, and resulted in 15-20 accepted structures. This low acceptance ratio casts some doubt on the convergence of these simulations, and we therefore consider the results preliminary. We suggest some potential approaches to improving the acceptance ratio below.

The average radius of gyration as a function of molecular weight can be extracted from the simulations described above. Using the universal viscosity law (below) we may relate the scaling of the radius of gyration with molecular weight to a similar scaling of the intrinsic viscosity $[\eta]$ with molecular weight . At the θ condition, the following proportionality can be derived from the universal viscosity law:

$$[\eta] \propto \left(\frac{< s_o^2 >}{M} \right)^{3/2} M^{1/2}$$

Where M is the molecular weight and $<s_o^2>$ the mean squared radius of gyration. After obtaining the scaling of the $<s_o^2>$ with molecular weight from simulation, it can be substituted into the expression above to predict the scaling with intrinsic viscosity. This result is then compared to the experimentally measured scaling for three polynorbornene samples produced from three different metallocene catalysts. For a random coil the mean squared radius of gyration is proportional to the molecular weight and for a rigid rod it is proportional to the square of the molecular weight. From this we obtain the limits in scaling of intrinsic viscosity with molecular weight at the θ condition.

$$[\eta] \propto M^{1/2} \text{ (random coil)} \qquad [\eta] \propto M^{2} \text{ (rigid rod)}$$

RESULTS AND DISCUSSION

From the Monte Carlo simulations outlined above we obtained the scaling of $<s_o^2>$ with molecular weight for erythro di-isotactic, threo di-syndiotactic and atactic polynorbornene. This scaling was substituted into the universal viscosity law above to estimate the scaling of intrinsic viscosity with molecular weight. Figure 2 contains the plot of the natural logarithm of the simulated intrinsic viscosity with the logarithm of the number of bonds in the chain. The slopes of the best-fit lines pictured in figure 2 provide the scaling of $[\eta]$ with molecular weight. Erythro di-isotactic polynorbornene gives an intrinsic viscosity scaling with molecular weight of 1.91 (rigid rod),

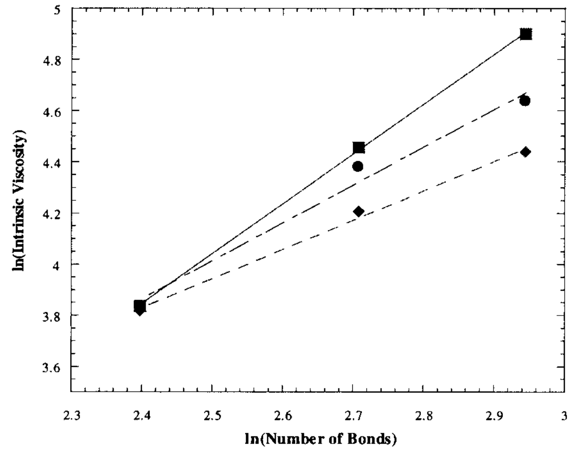

Figure 2. Simulated scaling of intrinsic viscosity with molecular weight. (■) Solid squares represent erythro di-isotactic polynorbornene (slope=1.91). (•) Solid circles represent threo di-syndiotactic polynorbornene (slope=1.20). (♦) Solid diamonds represent atactic polynorbornene (slope=0.71).

threo di-syndiotactic polynorbornene gives an intrinsic viscosity scaling with molecular weight of 1.20 (semi-rigid rod), while atactic polynorbornene gives an intrinsic viscosity scaling with molecular weight of 0.71 (closer to random coil).[21] Based on these results, we suggest the qualitative relationship between the scaling of intrinsic viscosity that is pictured schematically in Figure 3.

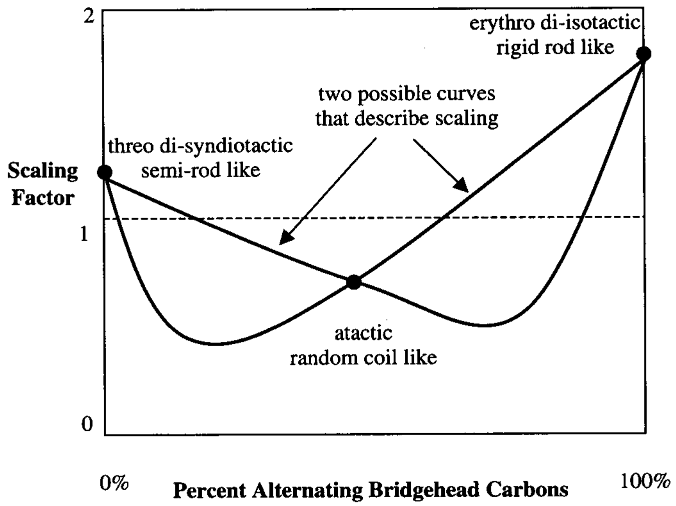

Figure 3. Schematic diagram of the qualitative variation of viscosity scaling with stereochemistry.

Two possible qualitative curves with different symmetries that intersect the three points from the simulations are provided. More stereochemical configurations must be simulated to determine the curve symmetry, but this approximate relationship can be used to estimate the stereochemical structure of three polynorbornenes produced using three different catalysts by the BF Goodrich corporation.

Three molecular weights of two different polynorbornene samples produced with Ni metallocene catalysts were used to determine the scaling of intrinsic viscosity with molecular weight. The BF Goodrich corporation provided these polymers. Viscometry was carried out in 1,2,4-trichlorobenzene at 70°C, which is the θ condition for both of these polymers. Both Pd and zirconocene catalysts have been shown to produce intractable polymers that are only negligibly soluble. These are postulated to be of the erythro di-isotactic form. Given their low solubility, a derivative of the Pd catalyzed polymer with butyl side chains at the 5 or 6 positions on 95% of the monomeric units, that is more soluble was used in the experiments. To obtain a qualitative comparison for this polymer, viscometry on the alkane derivative was performed in the same solvent at the same temperature. Its sparing solubility implies that the solvent swelling effect is small so this may be near the θ condition, however, this was not confirmed as the θ condition for this polymer. We are also assuming that the short hydrocarbon side chains do not effect the conformation significantly because they have a minimal effect on the severe steric hindrance due to the bicyclo-heptane backbone. The results of these viscometry experiments are seen below in Figure 4.

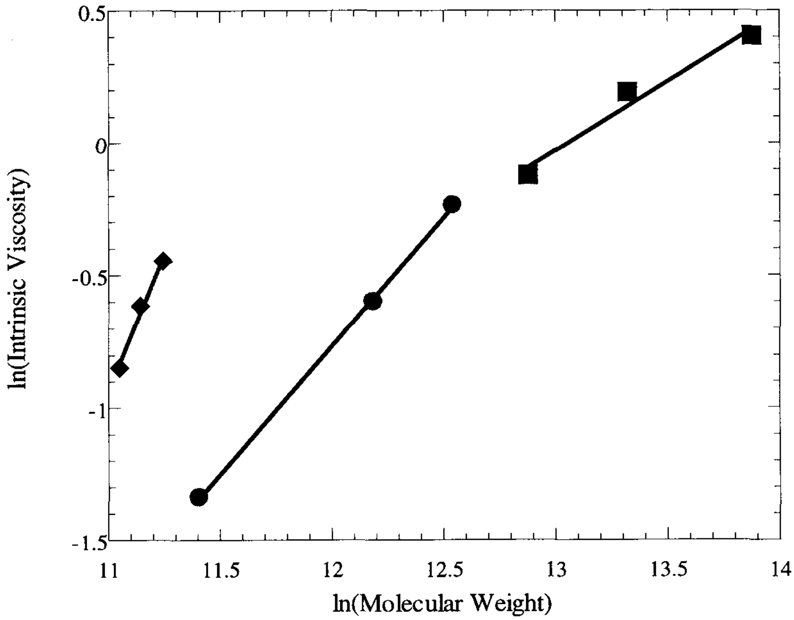

Figure 4. Experimental scaling of intrinsic viscosity with molecular weight. (♦) Solid diamonds represent polynorbornene prepared using a Pd catalyst (slope=2.0). (•) Solid circles represent polynorbornene prepared using Ni(1) catalyst (slope=0.97). (■) Solid squares represent polynorbornene prepared using Ni(2) catalyst (slope=0.53).

Comparison of the simulation and experimental results suggest that the polynorbornene produced with the Pd catalyst appears to have a high percentage of erythro di-isotactic configuration. The first Ni catalyst, labeled "Ni(1)" in Figure 4, appears to be moderately stereoregular, but it could contain a higher percentage of either alternating bicyclo-heptane orientations (more di-isotactic) or same side orientations (more di-syndiotactic). The other Ni catalyst "Ni(2)" is somewhere in the atactic region. However, the Pd catalyst comparison is only qualitative given the nature of the experimental sample.

Although we are currently running additional simulations to improve the convergence of these simulations, a self-consistency check can be made on the erythro di-isotactic configuration. Previously an Rotational Isomeric States[22,23] (RIS) model was developed, for this stereochemical configuration. The details of this model are discussed elsewhere.[13-15] RIS models assume that only short range interactions exist in the material.[22,23] However, the bulky nature of the bicyclo-heptane backbone group makes long range intramolecular effects significant. This was manifested in large differences between the torsional energy maps for different sized oligomers. The torsional energy map of the polynorbornene heptamer was generated by minimizing all but the two internal torsional degrees of freedom using the molecular modeling program CERIUS2.[24] At the heptamer level, an RIS self-consistent two-dimensional energy map was obtained, that suggested the stereoisomer of polynorbornene was dominated by a helical conformation. A Monte Carlo simulation of the heptamer using the Boltzmann Jump algorithm[24] in CERIUS2[24] also confirmed that the helical conformation dominates the backbone conformation of erythro di-isotactic polynorbornene. This RIS model, in its traditional matrix generator scheme,[22,23] was used to calculate the scaling of radius of gyration with molecular weight.

The results clearly indicated that erythro di-isotactic polynorbornene chains behave like rigid rods, where a ratio of end-to-end distance to radius of gyration is around 10 (this ratio is 12 for a rod and 6 for a gaussian coil).[25] The RIS states and energies were then used to set up starting structures for MM/MD simulations in periodic boundary conditions using CERIUS2.[24] Three starting structure were generated for subsequent MM/MD simulations. Each of the starting structures consisted of four chains, each with a degree of polymerization of 30. These initial guess structures were subjected to 3000 steps of MM, followed by 10ps of NVT MD, followed by 1000 steps of MM. The structures obtained at the end of these simulations were then used to generate a wide angle x-ray diffraction (WAXD) pattern for erythro di-isotactic polynorbornene. Good comparison was obtained between the simulated and experimental WAXD patterns. The WAXD diffraction patterns obtained for these polymers were of fairly low resolution and are currently being remeasured. However, the simulated WAXD patterns did contain the characteristic split in the low angle amorphous diffraction. This was also observed by Kaminsky in zirconocene catalyzed poly(norbornene).[11] The scaling of intrinsic viscosity with molecular weight can be obtained from this model for very large molecular weights. These RIS calculations and the Monte Carlo results discussed here are compared in Figure 5. A scaling exponent of 1.85 was obtained from the RIS calculations, which is similar to the value of 1.91 from the Monte Carlo calculations at the lower molecular weight.

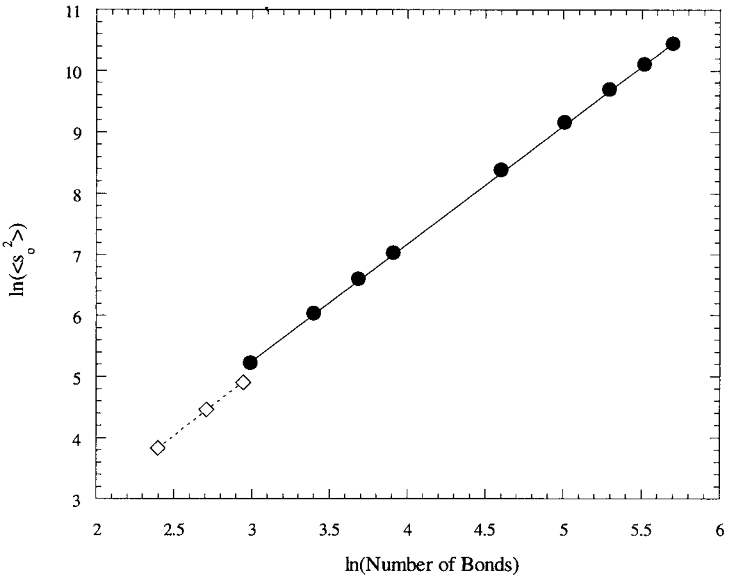

Figure 5. Comparison of Monte Carlo results for erythro di-isotactic polymer (diamonds) and RIS calculations for the same stereochemical isomer (filled circles).

Conclusions

Three stereochemical isomers of polynorbornene were simulated using a single-chain Monte Carlo algorithm. These simulations showed a large variation in the scaling of intrinsic viscosity with molecular weight. This is, most likely, due to the large degree of steric hindrance in the polynorbornene backbone. Despite the low acceptance ratios of the simulations, the results for one of the stereoregular isomers were consistent with previous RIS calculations. We are planning to incorporate some configurationally biased moves in the

Monte Carlo scheme[26,27] to improve the convergence of these simulations. This same intrinsic viscosity scaling was measured for three commercial samples of polynorbornene from BF Goodrich prepared using three different metallocene catalysts. The simulation results allowed the estimation of the stereochemical configurations for the three commercial samples of polynorbornene, which is otherwise difficult to directly determine. This protocol appears promising for further characterization of structure-property relationships in other commercially important derivatives of polynorbornene to be used in the electronic packaging market.

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