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Molecular modeling and synthesis of polymers for use in applications requiring a low-k dielectric

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Abstract

As integrated circuits have become more and more complex and with smaller and smaller feature sizes several limitations have become apparent. One of these is the need for low-k dielectric materials as insulating layers. Recent work has reported promising materials for such insulators that include some fluorinated polymers. These dielectric materials were further improved by introducing porosity into the polymer films. One of the key factors in the dielectric constant of a material is its density. As the polarization of the material is related to the number of bonds, the dielectric constant will scale with the density. In this paper a series of molecular modeling calculations were conducted on various fluorine substituted polymers in order to predict their densities. A surprising result of these calculations was the prediction that some of the polymers would have densities less than 1 g/cm^3. One of these polymers was synthesized and the density determined. The calculated density was in extremely good agreement with the experimental density. This paper will present the details of the molecular modeling technique as well as the synthesis and characterization of one of the polymers of interest.

Keywords: Low-k dielectrics; Polymer densities; Molecular modeling

1. Introduction

Over the past several decades there has been ongoing development of advanced ULSI integrated circuits. These devices have reached the point that one of the major limiting factors is the dielectric material separating the metallic connections. It is not uncommon to have devices with 6–7 layers of metallization separated by dielectric material that is less than 1 μm thick. The International Technology Roadmap for Semiconductors [1] has identified the need for dielectric film materials with dielectric constants of less than 2 as a limiting factor in lithographic production of devices at below the 100 nm size range. The ITRS, describes the need for materials with low dielectric constants in order to affect the capacitance (*C*) of the portion of the interconnect relay (*RC*) as transistors become smaller. This effect of reducing the *RC* delay is leading to the introduction of metals with lower resistivity (Cu) and the replacement of SiO_2 as the interlayer dielectric.

Silicon oxide has a dielectric constant of about 4 but is widely used because it exhibits a unique combination of properties including the ability to withstand the rigors of semiconductor manufacturing and exhibits very good thermal and mechanical stability. Further it has become routine to produce thick defect free films of this material. It is clear, however, that the dielectric constant is far too high for the next generation of devices. SiO_2 has been slowly being replaced by organic polymer dielectrics. The progress of this replacement has been slow due to the fact that these polymers cannot match all of the properties of SiO_2. Fluorinated silica glass comes very close to matching the properties of SiO_2, but its k value of 3.6 is only a small improvement over SiO_2 and is not sufficient at below the 130 nm node.

Work conducted by. Zhou, et al. [2] on fluorinated polymers has shown that dielectric constants of ∼2 can be produced. A review of the physical properties of a number of fluorinated polymers by Bruma, et al. [3] also reports low values for the dielectric constant for these type of polymers. Recent work on these materials has shown that even lower dielectrics can be made by forming porous foam films. This is accomplished by

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inducing a phase separation of solvent from the polymer on a microscale with subsequent removal of the solvent to leave voids. The dielectric constant of a material is given by the Debye equation [4] Eq. (1) below;

$$(\varepsilon_r - 1)/(\varepsilon_r + 2) = \rho P_m/M \qquad (1)$$

where M is the molar mass and P_m the relative permitivity is given by Eq. (2);

$$P_m = \frac{N_A}{3\varepsilon_0(\alpha + \mu^2/3KT)} \qquad (2)$$

And where; N_A, Avogadro's number; ε_0, is the permitivity of a vacuum; α, polarizability of the molecule; μ^2/KT, term arises from the thermal averaging of the dipole moments in the molecule under and applied field.

Rearranging the Debye equation we find the following relationship between ε_r and ρ in Eq. (3).

$$\varepsilon_r = \frac{(2\rho P_m/M + 1)}{(1 - \rho P_m/M)} \qquad (3)$$

This shows that the dielectric constant of a material is very sensitive to the density of the material assuming molar mass and relative permitivity remain fairly constant across chemically similar compounds.

Given the relationship between density and dielectric constant it would be reasonable to expect that if the free volume of a low-k dielectric material could be increased then the dielectric of that material would also improve. It would be extremely useful to have a fast easy method to predict polymer densities prior to committing laboratory resources to synthesis of potential polymers of interest. The calculation of polymer density for dense polymers utilizing molecular modeling has been reviewed by Kremer and Muller–Plathe [5] and reported for selected dense polymers Curco and Aleman [6]. This paper reports the results of molecular modeling of the densities for a series of known density polymers utilizing commercially available software. The method was then followed by the prediction of densities for several fluorine substituted styrenic polymers that have the potential for low-k dielectric constants and low density due to steric hindrance. One of these polymers was synthesized and the density measured and comparisons made between measured and calculated densities. The effect of polarizability of the fluorinated polymers has been ignored in this study and could turn out to effect the dielectric substantially. This however, is thought not to be the case for several reasons. First, fluorines are least polarizable of atoms. Secondly any dipole moments in the family of polymers that were studied tend to be quite small due to the fact that the polymers tend to form helical structures that tend to cancel any dipoles. Thirdly, within the family of fluorinated styrenes the expected difference in permittivity would be very small across the whole family.

2. Experimental

2.1. Materials

The monomer 3,5-bis(trifluoromethyl styrene) was obtained from Aldrich. The inhibitor was removed by using *tert*-butylcatechol as a remover. The solvent, dimethyl sulfoxide, was obtained from Aldrich with 99.9% purity and used as recieved. The nitroxide and initiator azobis isobutyronitrile were obtained from Aldrich and used as received. Styrene, benzene and toluene were purchased from Aldrich and solvents anisole, ethyl acetate, tetra hydrofuran and diethyl ether were purchased from Fischer. All the solvents were used as received.

2.2. Molecular modeling

The molecular modeling was carried out utilizing the commercial Cerius 2 software package. All calculations were atomistic forcefield based and were conducted using the COMPASS forcefield reported by Sun and Ren [7] and Sun [8].. The monomers for all the polymers were produced using the 3D sketcher. The monomers were then assigned charges in the open forcefield setup module and minimized in open forcefield methods module [9–28]. The COMPASS forcefield was utilized in all calculations. The homopolymers were generated using polymer builder. The polymers generated were 10 units in length. The partial charges on the polymers were recalculated and were iterated through several cycles of minimization and molecular dynamics. In Crystal Builder a tetragonal unit cell of 12×12×30 Å was generated and converted to $P1$ symmetry. The polymer of interest was then imported to that cell. In visualizer a 4×4 cell array was created and converted to a super cell. This super cell now containing 16 molecules of the polymer of interest was taken through a series of minimizations and molecular dynamics until a minimum energy was reached. The cycles of molecular dynamics were conducted under NVE (constant moles, volume, and energy) conditions until the last few cycles at which time it was switched to NPT (constant moles, pressure, and temperature) conditions. The dynamics were run at 298 K and 0.1 GPa of pressure with 1000 steps of 0.001 ps per step.

2.3. Synthesis of poly(3,5-(bistrifluoromethyl)styrene)

The synthesis of poly(3,5-(bistrifluoromethyl)styrene) was accomplished as follows. Azobis isobutyronitrile (0.016 g) was dissolved in 5 ml of DMSO placed in a 25 ml round bottom flask with continuous argon purge. Purified monomer (3,5-bis trifluoromethyl styrene) 0.5 ml was injected via syringe into the round bottom flask with continuous argon purging. The round bottom flask was then placed in an oil bath maintained at 95 °C. After 36 h the solution was precipitated into methanol and the precipitate was filtered and dried overnight under vacuum at room temperature.

Table 1
A comparison of calculated densities from molecular modeling and experimentally measured densities for selected polymers

Polymer type	Calc. density (g/cm^3)	Exp. density (g/cm^3)	Delta (%)
P3MS	1.022[a]	1.027	0.49
P3MVCH	0.9213	0.9237	0.260
PtBS	0.929	0.9458	1.776

[a] Average of six separate calculations.

2.4. Density determinations

The density of the synthesized polymer was determined by a simple floatation method utilizing a series of solvents (Table 2) that bracketed the range of density expected for the polymer. The determination was done by placing small pieces of the polymer into the solvents at 25 °C and recording whether or not they floated or sank. This allowed the density to be bracketed to a fairly narrow range of densities.

3. Results and discussion

In ongoing research into low-k dielectrics several fluorine substituted styrene polymers have shown promise. In order to potentially lower the dielectric further, substitution of more and bulkier groups were postulated as ways to increase the specific free volume of the polymers and lower their densities. The original polymer that showed promise was poly(3-fluoromethyl styrene). It was of interest to see if additional groups added on to the ring would increase the free volume further. It was, therefore, surmised that poly(3,5-difluoro-methylstyrene) would have a substantially lower density. The densities of a number of substituted styrene polymers and hydrogenated analogues have been reported Gehlsen et al. [29]. In order to validate the molecular modeling technique for calculating densities, several of these known compounds were utilized as benchmarks. It must be pointed out that the calculations were carried out with as little experimental data on the polymers as possible. No data on crystal structures were sought from the literature which for most of these compounds does not exist since many are amorphous.

The polymers that were modeled which have experimentally determined densities include poly(3-methlstyrene) (P3MS), poly(3-methylvinylcyclohexane) (P3MVCH), and poly(4-*t*-butylstyrene) (PtBS). The first series of calculations involved P3MS. In this work, six separate calculations were performed to determine the precision and accuracy of the method. In each case the polymer was generated and taken through minimization/dynamics and placed in a different size starting unit cell. The densities calculated in those six models resulted in densities of 1.0399, 1.0105, 1.0229, 1.0301, 1.0084, and 1.0191 g/cm^3 for the P3MS. The average density for this series yields a density of 1.022 ± 0.005 g/cm^3.. This average is in very good agreement with the experimental value of 1.027 ± 0.0006 g/cm^3.. The experimental value lies within one sigma of the calculated value. The largest difference in any one simulation between the calculated and experimental numbers is 1.8%. The calculation of six different models for a single compound yielded very good precision and accuracy. However, these calculations are very time consuming and since the goal is to develop a fast method for density prediction in the balance of this paper only single model calculations are utilized. Based upon the series of six separate models it would appear that this approach should yield densities that are less than 2% away from the true value. This is an acceptable level of accuracy for the calculation of densities for low-k dielectrics since large changes in density are being sought. For other applications, suites of calculation can be employed to reach the desired level of accuracy. Table 1 contains a compilation of the calculated and experimental densities for the three polymers that have had accurate experimentally determined densities.

As can be seen the predicted densities are on average within two percent of the experimentally determined values, which is consistent with the level of accuracy determined in the first suite of calculations on P3MS. The densities in all cases are slightly lower than the observed densities. This could be an artifact of the way that the calculations were conducted. There are several factors that could potentially improve the results. The largest error is most likely occurring at the boundary between cells at the juncture of the *ab* plane. This is where the termini of the polymer chains meet and where the mismatch is potentially the greatest. This could potentially be improved by simply increasing the polymer length such that the volume of this mismatch is small relative to the total cell volume. The second and most likely smaller error arises from the fact that a finite number of polymer chains were utilized. The addition of more chains in a larger cell would help in improving the accuracy by statistically allowing the polymers to form the mosaic in the cell more efficiently. As was shown earlier a suite of separate calculations can also improve the accuracy. The trade off is in accuracy versus time to complete the computations. If accuracy greater than 1% is needed the longer computing time may very well be warranted. In the case of this study the level of accuracy was quite acceptable. The very worst agreement was seen in the PtBS and was still only 1.78%, which again is consistent with the earlier suite of calculations. In this particular polymer it is apparent that the bulky *t*-butyl group tends to limit the ability of the polymers to slide relative to one another and, therefore, contributes more severely to the mismatch at cell edges. As an example Fig. 1 gives a graphic representation of the final density cell for P3MS. In order to check the affect of tacticity on density a calculation of density for atactic P3MS was carried out and yielded a value for the density of 1.014 which is 1.2% lower than the observed value and well within the error seen in earlier calculations on an isotactic polymer.

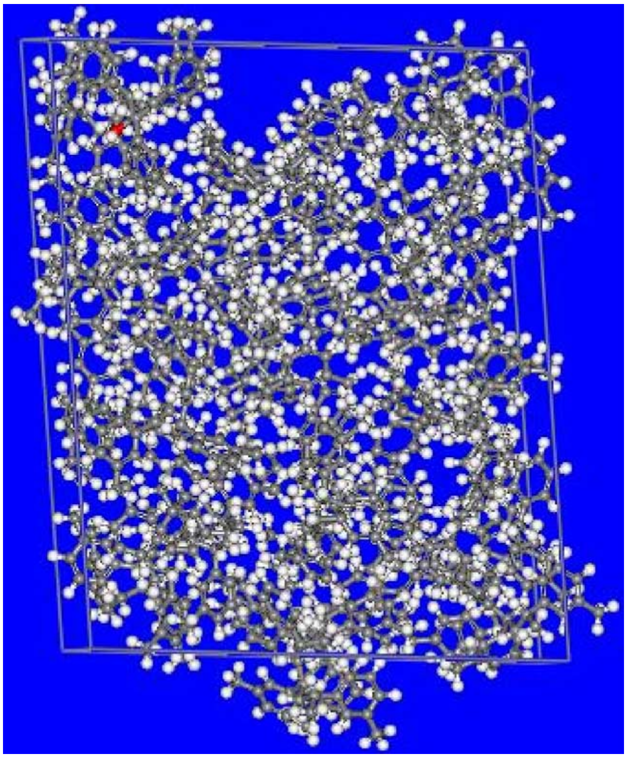

Fig. 1. Molecular model for the densified super cell for P3MS (grey balls are carbon and white represents hydrogen atoms) (for interpretation of the reference to colour in this legend, the reader is referred to the web version of this article).

The first fluorinated polymer that was utilized to model density was poly(3-fluoromethylstyrene) (P3FMS). The molecular modeling of this polymer yielded a density of 1.33 g/cm^3. This seems to be a reasonable density if compared to the unfluorinated analog. If intermolecular repulsions are ignored and only the hydrogen atoms on the methyl are replaced, a density of 1.497 g/cm^3 would be predicted. This seems unreasonably high since the repulsions due to the fluorine atoms is well known to be greater than that of hydrogen due to the higher partial charge on fluorine. It would appear then that the value of 1.33 g/cm^3 that is calculated is indeed reasonable. This density is in line with what is observed for various common fluorinated polymers and would not give any advantage in dielectric due to density. A graphical representation of the densified cell for this polymer is given in Fig. 2. The figure clearly shows a larger specific free volume than seen for the unfluorinated analog given in Fig. 1.

It was next decided to add a second fluoromethyl group to the benzene ring at the five position to potentially increase the steric hindrance of the benzene ring and potentially increase the free volume of the polymer (PD3FMS). The molecular modeling of this polymer gave a predicted density of 0.975 g/cm^2, which was quite surprising. This result if true could lower the dielectric constant by approximately 30% assuming constant permittivity between the two polymers. Fig. 3 is a picture of the final densified cell for this compound. The increase in free volume in the cell is very apparent as

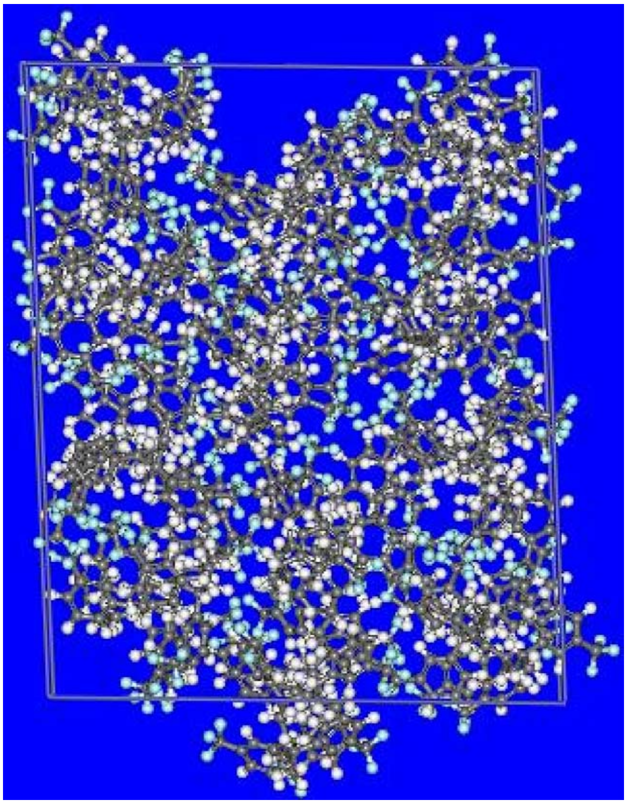

Fig. 2. Molecular model of the densified super cell for P3FMS (grey balls are carbon, white represents hydrogen, and light blue represents fluorine atoms) (for interpretation of the reference to colour in this legend, the reader is referred to the web version of this article).

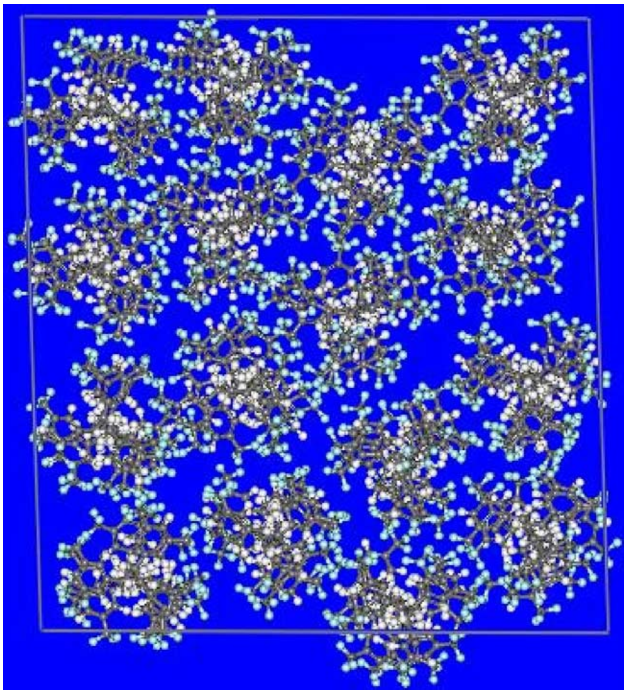

Fig. 3. Molecular model of the densified super cell for PD3FMS (grey balls are carbon, white represents hydrogen, and light blue represents fluorine atoms) (for interpretation of the reference to colour in this legend, the reader is referred to the web version of this article).

Table 2
Table showing the solvents and their densities used for density measurements

Solvents	Density (ρ) (g/cm^3)	Float/sink
Diethyl ether	0.713	S
Toluene	0.865	S
Benzene	0.874	S
Tetrahydrofuran	0.889	S
Styrene	0.909	S
Ethyl acetate	0.922	S
Methyl methacrylate	0.936	S
Anisole	0.995	S
Water	1.00	F

compared to the P3MS and P3FMS models. This was sufficiently surprising that it was decided to synthesize this polymer and measure its density.

The density of the synthesized polymer was determined by floatation in a series of known density solvents. The solvents used and their densities are provided in Table 2.

The experimentally determined density was found to be approximately 0.99 g/cm^3.. This is approximately 1.6% higher than predicted by modeling which is very consistent with observations made earlier.

In order to determine some of the factors that cause these changes in density the molecular models for polystyrene, P3FMS, and PD3FMS were examined in more detail. Fig. 4 contains minimized models of short segments of the three polymers with views parallel to the backbone and normal to the backbone. When viewing the three polymers normal to the backbone it is clear that the angle of the ring relative to the backbone changes radically due to the successive substitution of the fluoromethyl groups. The angle formed by the ring with the backbone is approximately 35, 55, and 75° for PS, P3FMS, and P3DFMS, respectively. The molecular modeling program was further used to measure the energy barrier to rotation of the ring in each polymer.

Fig. 5 is a plot of the rotational barriers for each polymer normalized to zero for the minimum energy position and the angle zero set to that minimum position. It can be clearly seen that not only has the angle of the ring relative to the backbone changed but also the barrier to rotation of that ring from its equilibrium position is increased with the substitution of the fluoromethyl groups. A further effect can be seen in Fig. 4 when the polymers are viewed parallel to the backbone of the polymers. The rotation of the ring away from the backbone is also accompanied by the slight twisting of the backbone. This results in polymers that are more difficult to pack together as more substitution on the ring occurs.

In order to see if even bulkier groups would continue this trend calculations were carried out on poly(4-*t*-fluorobutylstyrene)

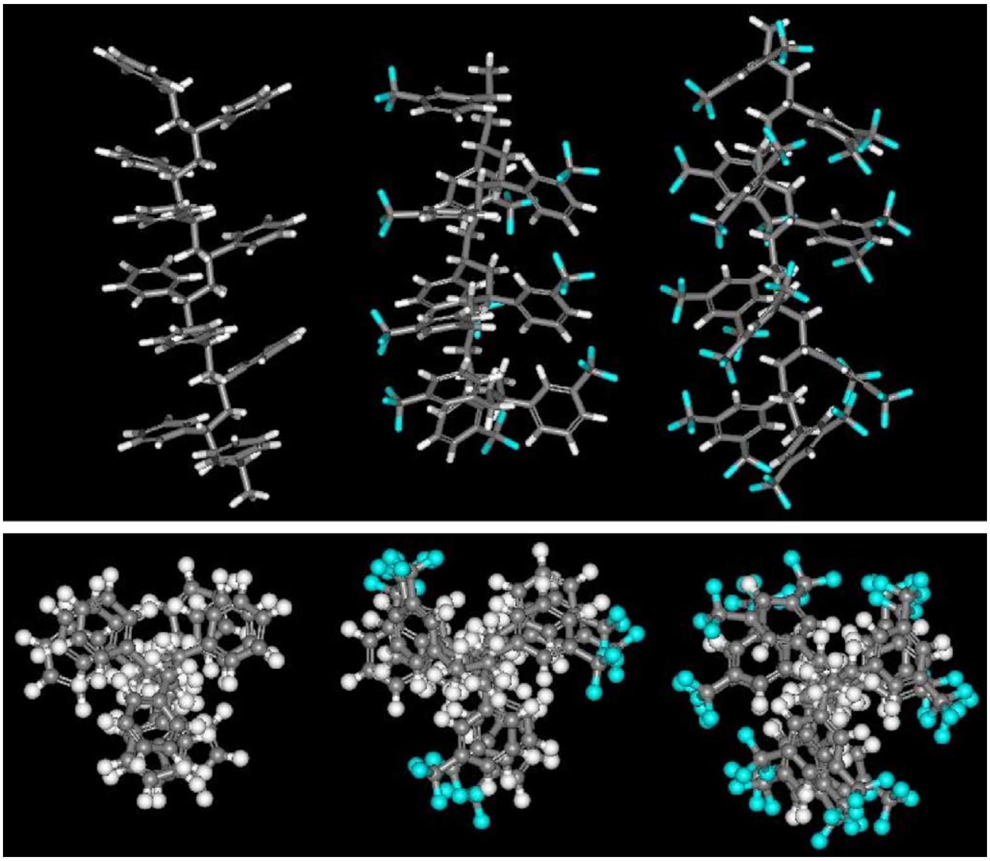

Fig. 4. Molecular models of three polymer segments illustrating the effect of substituent on ring configuration (grey balls are carbon, white represents hydrogen, and light blue represents fluorine atoms) (for interpretation of the reference to colour in this legend, the reader is referred to the web version of this article).

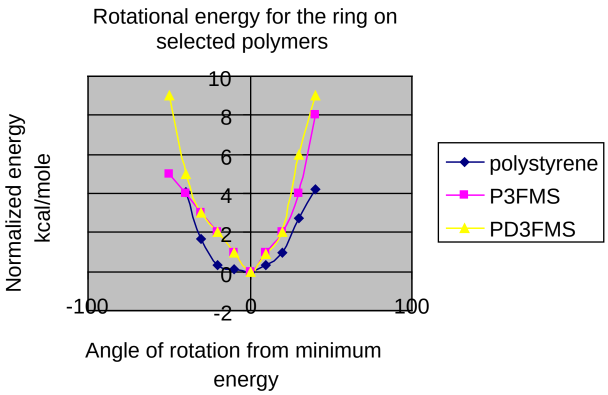

Fig. 5. Energy of rotation of the benzene ring relative to the polymer backbone for selected polymers.

(P4tFBS). The P4tFBS compound was chosen for further molecular modeling, since the analog PtBS gave the lowest experimental density of all the styrene derivatives reported in the literature by Gehlsen et al. [29]. The results of these calculations predict a density of 0.80 g/cm^3. This is even a lower density and would have an even greater impact on the dielectric constant. Fig. 6 contains a graphic representation of the final densified cell for P4tFBS.

Energy calculations conducted on this polymer indicates that the energy of rotation of the benzene ring in this polymer is almost identical to that for polystyrene. This would indicate that steric hindrance within the polymer is not responsible for the high free volume and low density. It would appear instead that the density arises from the tremendous bulkiness of the tertiary butyl group and the large electrostatic repulsion due to the fluorines that largely cover the surface of the polymer.

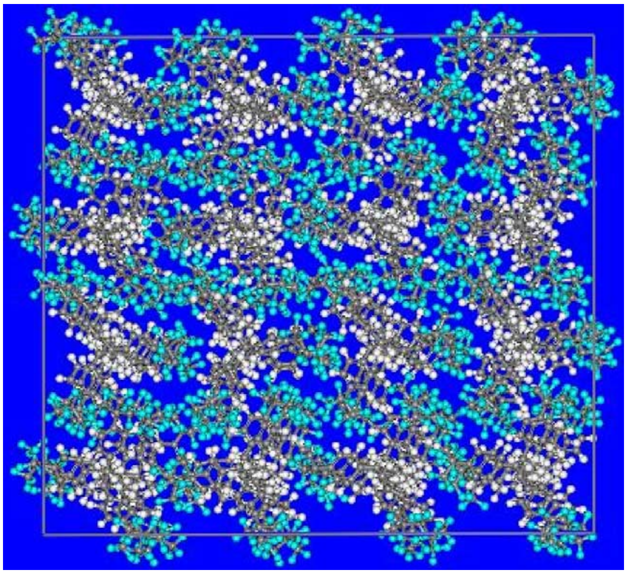

Fig. 6. Molecular model of the densified super cell for P4tFBS (grey balls are carbon, white represents hydrogen, and light blue represents fluorine atoms) (for interpretation of the reference to colour in this legend, the reader is referred to the web version of this article).

4. Conclusions

The commercial software performed very well in predicting densities of polymers which have very accurately experimentally determined densities. The accuracy of these calculations is a function of the number of times the calculations are done. With a single calculation accuracy in the range of 2% can be observed. Suites of six calculations yielded 0.5% accuracy. In single calculations tacticity did not yield densities that were significantly different. In most cases the calculated densities were slightly below the experimentally observed densities. This may simply be an artifact of the construct utilized in the calculations as discussed in the paper.

This method was utilized to predict the density of a hypothetical polymer. The density that was predicted was lower than expected. The polymer was later synthesized and its density measured. The agreement was within the 2% range seen in earlier calculations.

It appears that this method can be very useful in predicting polymer densities in a rapid and accurate way. This unusually accurate prediction of densities may not apply to all classes of polymers since the styrenic polymers tend to be fairly rigid and linear due to bulky side groups. It would be reasonable to expect that for a very flexible polymer such as polydimethylsiloxane that this method may not work as well and may actually yield higher densities and lower free volumes than the observed values.

A final prediction of an unusually low density for polystyrene substituted at the 4th position with a fluorinated tertiary butyl group awaits experimental verification.

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