

4.3.4 Molecular Modeling of the Carbazole-Phenoxy Based Methacrylate Polymer and Ring-Opened Carbazole Epoxide

Molecular modeling is a useful tool for investigating hypothetical structures. Once the ground state minimum energy configuration is found for a hypothetical molecule (which can take many hours), a negative value for the minimum energy configuration means that theoretically, it is possible for that molecule to exist. A positive value for the minimum energy configuration means that, theoretically, the hypothetical molecule would not be able to exist as drawn. The Gaussian molecular modeling program takes into account steric hindrance, ionic repulsions, bond lengths, and other factors. This program does not figure out how to make compounds synthetically, it simply determines, theoretically, whether a conceivable molecule can exist.

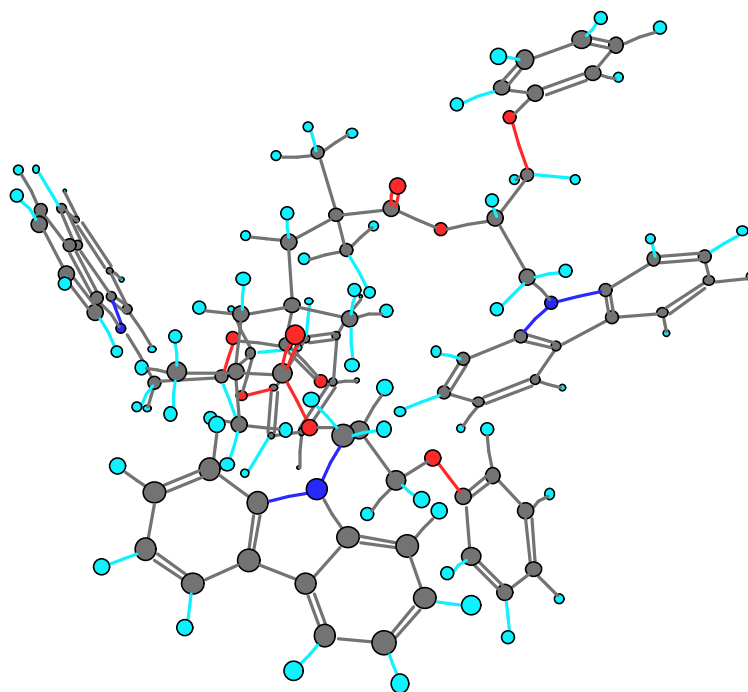
Molecular Modeling using Gaussian 98 software was employed to investigate the ground state minimum energy configurations of the carbazole-phenoxy based methacrylate polymer, and the hypothetical structure of ring-opened carbazole epoxide. Molecular structures were first drawn in ChemDraw 3D, then imported, and energy minimization performed with the semiempirical PM3 method of the Gaussian 98 molecular modeling program. Both the carbazole-phenoxy based methacrylate polymer and the hypothetical ring-opened carbazole epoxide had negative values for the minimum energy configurations, which meant that it was possible for both of these polymers to exist.

Molecular modeling provided some insight into the structures of these compounds, from a Maxwell demon point of view. Figure 4.50 shows the three dimensional, minimum energy configuration of three repeat units of the carbazole-phenoxy based methacrylate polymer. Of interest was how the carbazole and phenoxy rings were arranged around the polymer chain, in a stacked, somewhat helical fashion. Due to the bulkiness and steric hindrance of these large, aromatic substituents, the aromatic groups in the final polymer should be very ordered, perhaps giving the rod-like polymer crystalline attributes. In fact, films of the carbazole-phenoxy based methacrylate

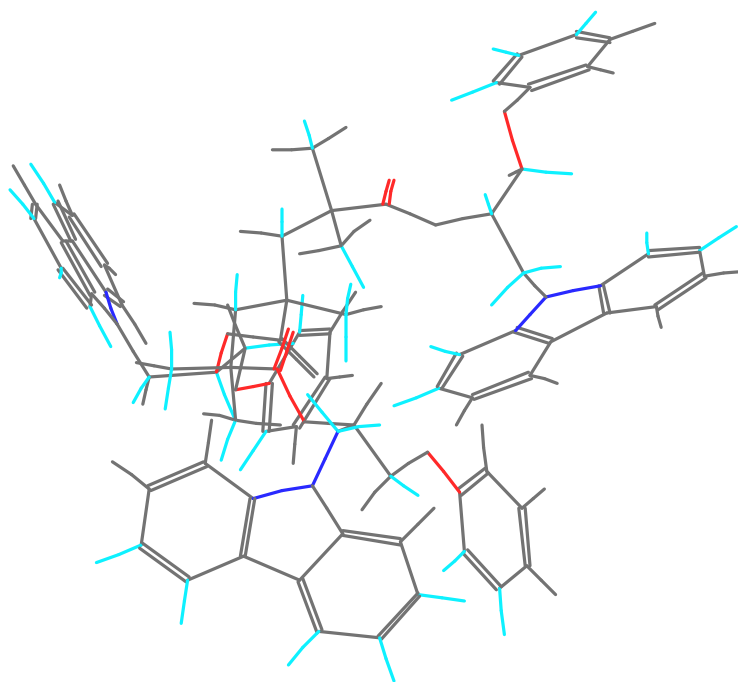
homopolymer were very brittle and shiny. This helical structure, due theoretically to high order from lack of space for the aromatic groups to freely rotate, may provide the final polymer with ring current effects, which could prove extremely useful in electronic applications and in non-linear optics.

Figure 4.51 shows the minimum energy configurations for three repeat units of the (conceived) ring-opened carbazole epoxide. Again, of interest was the arrangement of the aromatic groups around the polymer chain in a stacked fashion. This is somewhat analogous to the structure of poly(vinyl carbazole), investigated by Dais, *et al.*²⁵⁹ This polymer would be expected to have properties similar to poly(vinyl carbazole) and the carbazole-phenoxy based methacrylate polymer.

²⁵⁹ Karali, A.; Froudakis, G.E.; Dais, P., *Macromolecules*, **2000**, 33, 3180.



Ball-and-stick Depiction



Stick-only Depiction

Figure 4.50 Minimum Energy Configurations Using Molecular Modeling (Gaussian 98) of 3 Repeat Units of the Carbazole-Phenoxy Based Methacrylate Polymer

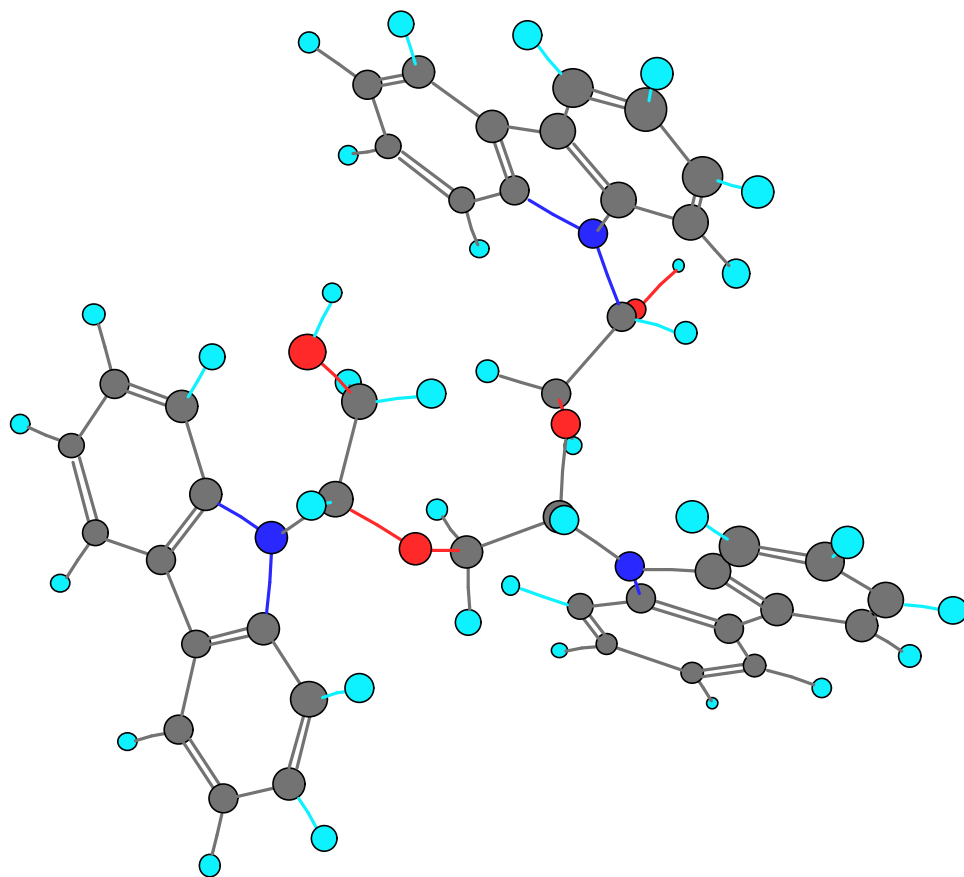
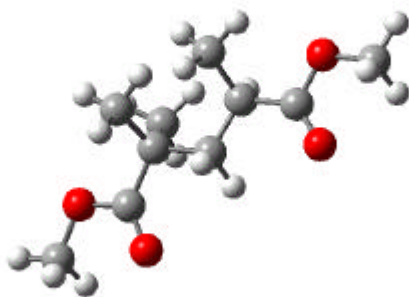


Figure 4.51 Minimum Energy Configurations Using Molecular Modeling (Gaussian 98) of 3 Repeat Units of the Carbazole Epoxide

Molecular modeling provided for a fascinating, three dimensional glimpse into the hypothetical structures of these highly functionalized polymers. If this were to be investigated further, two structures could be drawn for the carbazole-phenoxy based methacrylate polymer, containing five to seven repeat units. One structure would contain the isotactic configuration. The other unit would contain the syndiotactic configuration. Comparing the values generated from the minimum energy configurations would suggest a strong tendency for one configuration to predominate. The syndiotactic configuration would be expected to have a much lower minimum energy value than the isotactic configuration.

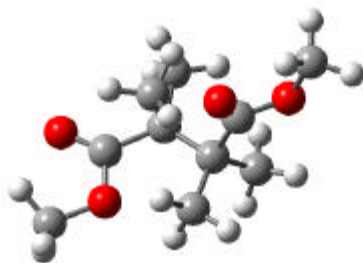
The head-to-head and head-to-tail linkages of the carbazole-phenoxy based methacrylate were investigated (Figure 4.53). As a control, analogous molecular modeling was also performed for the head-to-head and head-to-tail linkages for PMMA (Figure 4.52). For both polymers, the difference between head-to-head and head-to-tail linkages of the ground state minimum energy configuration was minimal, however, the difference between head-to-head linkages for the minimum energy configurations in terms of nuclear repulsion energy was quite significant. The head-to-tail polymerization of PMMA predominates, with about 95 % its structure composed of head-to-tail linkages, and this is with the theoretical nuclear repulsion energy of the head-to-tail structure 82 Hartrees less than the head-to-head structure. The head-to-tail structure of the carbazole-phenoxy based methacrylate polymer was determined to be 296 Hartrees less than the head-to-head structure, in terms of nuclear repulsion energy. One Hartree equals 627.5095 kcal/mole. This is very strong theoretical evidence that the formation of head-to-head linkages in the carbazole-phenoxy based methacrylate polymer would be very unlikely due to nuclear repulsion from steric hindrance. The absence of head-to-head linkages would explain the remarkably high decomposition temperatures observed for the carbazole-phenoxy based methacrylate polymer.



H-T Linkage, 2 Repeat Units

$E(\text{RHF}) = -684.744443974 \text{ A.U.}$

$E_{\text{Nuclear Repulsion}} = 976.95 \text{ Hartrees}$



H-H Linkage, 2 Repeat Units

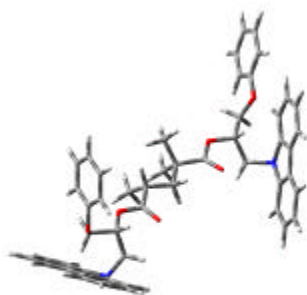
$E(\text{RHF}) = -684.744443974 \text{ A.U.}$

$E_{\text{Nuclear Repulsion}} = 1058.80 \text{ Hartrees}$

$\Delta E(\text{RHF})_{(\text{H-T} - \text{H-H})} = -0.21029 \text{ A.U.}$

$\Delta E_{\text{Nuclear Repulsion}} (\text{H-T} - \text{H-H}) = -82 \text{ Hartrees}$

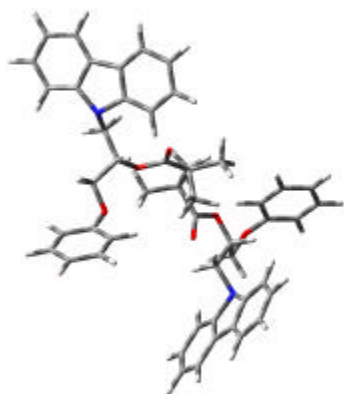
Figure 4.52 Molecular Modeling (Gaussian 98, Ground State Minimum Energy Configurations) for 2 Repeat Units of PMMA



H-T Linkage, 2 Repeat Units

$E(\text{RHF}) = -2465.09663844 \text{ A.U.}$

$E_{\text{Nuclear Repulsion}} = 7723.79 \text{ Hartrees}$



H-H Linkage, 2 Repeat Units

$E(\text{RHF}) = -2464.99550886 \text{ A.U.}$

$E_{\text{Nuclear Repulsion}} = 8019.26 \text{ Hartrees}$

$\Delta E(\text{RHF})_{\text{H-T} - \text{H-H}} = -0.10113 \text{ A.U.}$

$\Delta E_{\text{Nuclear Repulsion}}(\text{H-T} - \text{H-H}) = -296 \text{ Hartrees}$

Figure 4.53 Molecular Modeling (Gaussian 98, Ground State Minimum Energy Configurations) for 2 Repeat Units of PCPM