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Molecular Mechanics and Dynamics Studies of Polysiloxane Based Hindered Amine Light Stabilizers (HALS)

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ABSTRACT: The conformational preference of a polysiloxane based hindered amine light stabilizer (HALS), UVASIL 299, has been studied. The tetramer is more stable in the cyclic form, and the most stable acyclic conformer is folded-up to resemble a cycle. The molecular dynamics simulations evidence a high degree of flexibility in the cyclic tetramer, as do electron spin resonance (ESR) measurements on oxidized UVASIL. The high miscibility of UVASIL 299 with polypropylene may be due to an intimate interaction between the cyclic tetramer of the light stabilizer and segments of the polymer.

Introduction

Polyolefins are susceptible to light induced oxidative degradation due to the presence in the polymer of fortuitous or deliberately added near-UV light absorbing species such as, e.g. dyes, additives, pigments, oxidation products from processing, etc. The addition of light stabilizers can effectively delay the onset of the polymer photodeterioration.

Hindered amine light stabilizers (HALS) are particularly effective in preventing photooxidation in polymers, and since the first report[1] many different types of HALS have been synthesised, with most commerical products being based on 2,2,6,6-tetramethylpiperidines. HALS reduce photooxidation by acting as free radical scavengers. In one of their now well accepted modes of action,[2] the parent hindered amine >N–H is proposed to act simply as a vehicle to generate a nitroxide radical >N–O$^\bullet$ which then scavenges radicals such as alkyl radicals R$^\bullet$ or polymer macroradicals P$^\bullet$ to form *N*-alkoxy derivatives >N–O(P)R, thus efficiently inhibiting the generation of chain propagating alkyl peroxy radicals. The *N*-alkoxy derivatives may then react with peroxy $RO_2^\bullet$ or other radicals to regenerate, in a cyclic way, the radical scavenger nitroxide (Scheme I). A parallel reaction pathway for regenerating >N–O$^\bullet$ is the oxidation by alkyl, alkoxy, or peroxy radicals of the hydroxylamine, >N–OH, formed by H-atom abstraction by the nitroxide from the polymer backbone.

In general the photostabilizing activity of commercially available HALS considerably exceeds that of stabilizers such as 2-(2-hydroxyphenyl)benzotriazole, 2-hydroxybenzophenone, and nickel complexes. We have recently[3] evaluated the performance of a proprietary new oligomeric HALS, UVASIL 299 (hereafter UVASIL), *1*, having a poly(methylsiloxane) backbone and characterized by a high compatibility with polypropylene. We found that UVASIL when used together with a phenolic antioxidant such as AOX1, *2*, has an additive stabilizing effect on polypropylene, whereas the oligomeric HALS1, *3*, is reported to have an antagonistic effect, as indicated by the decrease in the induction time in the carbonyl index growth test[3] (Scheme II).

Is is reasonable to assume that while the mode of action of the two HALS examined in our study should be basically the same (Scheme I), the difference in the backbone structure might be responsible for the different performances of the two light stabilizers.

Poly(dialkylsiloxane)s in which the repeating unit is $-OSiR_2-$ are indeed endowed with unusual properties such as high dynamic flexibility, low entropy of dilution, excellent thermal stability, and low glass transition temperatures.

Some of these properties may be attributed to the general structural characteristics of the polysiloxanes backbone repeating unit, such as the unusually large Si–O–Si angle, the relatively long Si–O bond, and the small size of the O atoms that, lacking substituent groups, do not introduce unfavorable steric hindrance factors but give rise instead to unusually soft torsional and bending potentials for the Si–O bond.

We thought that the soft polysiloxane backbone, while providing a better flexibility than the carbon counterpart, could result in a tighter interaction with the polyolefins whose structural features match more closely the mean shape of the siloxane polymeric chain and may account for, e.g., the unusually high miscibility with polypropylene.

There has been considerable recent interest in applying molecular modeling techniques, including molecular dynamics (MD), to the study of equilibrium statistics and conformational dynamics of a series of poly(dialkylsiloxane)s, $-(OSiR_2)_n-$. In the case of poly(dimethylsiloxane), where R is CH_3, the tendency of the linear oligomer to close upon itself after 22 bonds, i.e. when $n = 11$, has been reported.[4] This particular behavior stems from the inequality of the O–Si–O and Si–O–Si bonds and is anticipated for the all-trans (tt) conformations. In our case a mass spectrometry (MS) and high performance liquid chromatography (HPLC) study[5] has indicated that UVASIL tends to adopt a cyclic structure after only ca. 8 bonds ($n = 4$) in keeping with the predictions of the

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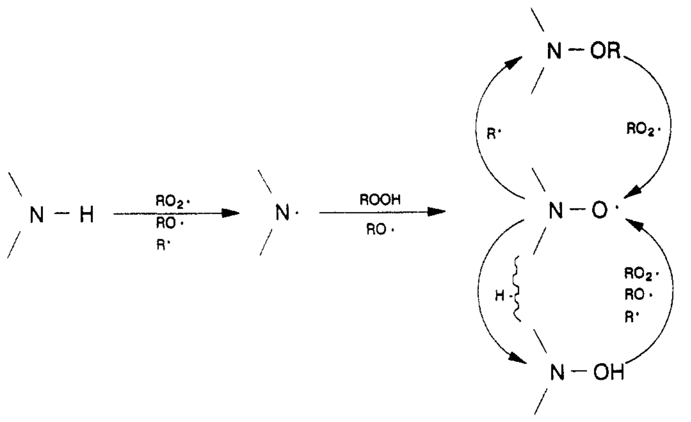
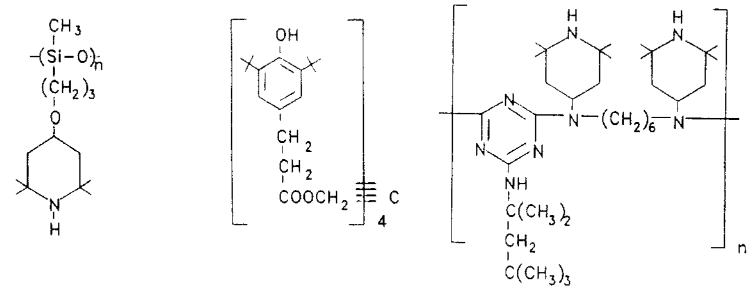
Scheme I



Scheme II



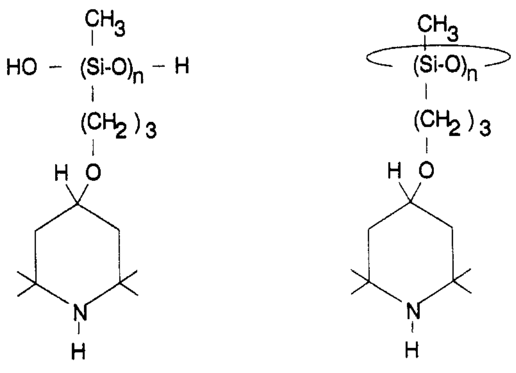
UVASIL 299 AOX 1 HALS 1

1 2 3

theoretical study on poly(dimethylsiloxane) by Mattice et al.,[6] in which gauche (g) conformers were also taken into consideration and shown to be more stable than the all-trans ones (vide infra).

To accurately model the structure and dynamics of UVASIL, it was necessary to have the correct force field parameters and identify the most representative 3D structure, i.e. the oligomer with a given number of repeating units that would fit most or all of the experimental findings, such as, for example, the high physical compatibility with polypropylene.

Experimental data concerning C–Si, Si–O, C–Si–O, Si–O–Si, and O–Si–O parameters cover a fairly wide range of variability, mainly concerning the last two valence angles and the length of the Si–O bond. Recent studies[7,8] have presented a very detailed survey of the experimental X-ray data and analyzed the steric and electronic factors that explain the variability of these valence parameters. A correlation between lengthening of the Si–O bond and widening of the Si–O–Si bond angle in silicon containing ethers has been suggested. The work of Darsey[4] on the conformation of poly(dimethylsiloxane) and of Nicholas and Hopfinger[9] on a new force field for zeolites has also evidenced the high variability of the valence geometry. Another very important observation comes from the extensive MD simulations on substituted polysiloxanes of Mattice and co-workers. They have found[6,10,11] probability distributions of conformers very different from those predicted by Flory et al.[12] which depended on the size of the substituent pendant chains. Due to these findings, our first concern was to obtain a reliable model of the methyl substituted siloxane backbone, mainly for linear and cyclic tetrameric species.



a b

Figure 1. General formulas of linear (a) and cyclic (b) UVASIL299.

Theoretical Methods

We performed quantum mechanical ab initio calculations, with geometry optimization, on 1,1-dimethylcyclotetrasiloxane (Figure 2), using two different basis sets, 3-21G and STO-3G. Semiempirical quantum mechanical calculations were performed on this molecule and on octamethylcyclotetrasiloxane, whose structure has been solved by Steinfink et al.,[13] using the MOPAC package with an AM1 Hamiltonian.[14]

The geometrical optimized parameters computed with each of the above methods are reported in Table I along with the X-ray data taken from ref 13. The SYBYL Version 5.41 package[14] running on VAX and E&S PS390 was used for the molecular mechanics (MM2) calculations. We built the same methyl substituted tetramer and added the missing terms to the TRIPOS force field. We have chosen the smallest set of charges obtained from ab initio calculations (i.e. those given by STO-3G) to build the electrostatic part of the pairwise analytical potentials and used, as minimum energy structural parameters, those reported in the fourth column of Table I. The bond stretching, angle bending, and torsional parameters of the

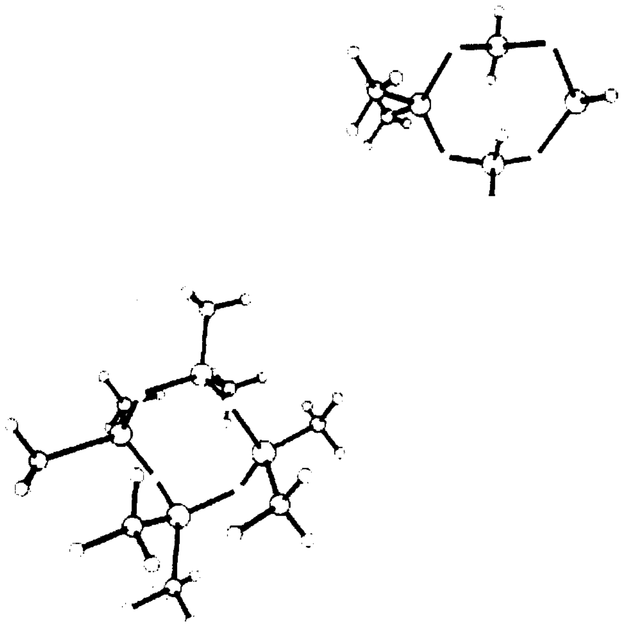


Figure 2. Structure of model compounds 1,1-dimethylcyclotetrasiloxane (upper) and octamethylcyclotetrasiloxane (lower).

Table I. Optimized Values of Geometrical Parameters[a] for Octamethylcyclotetrasiloxane

	AM1	STO-3G	3-21 G	MM2	X-ray[b]
Si–O	1.61–1.65	1.61–1.69	1.66–1.67	1.62	1.65
Si–C	1.83	1.86	1.89	1.85	1.92
Si–O–Si	115–128	130–133	150–158	130–149	142.5
O–Si–O	106–119	108–109.5	106–109.5	106–117	105
C–Si–C	102–109	110.8	108.7	105–112	106

atom	charges			
Si	1.54	0.89	1.65	0.89
O	−0.85	−0.57	−1.08	−0.56
C	−0.63	−0.34	−1.15	−0.34

[a] Bond lengths are in Å; bond angles are in deg. [b] Reference 13.

Table II. Force Field Parameters Used in Molecular Mechanics and Dynamics

Valence Potential Parameters[a]

stretching	equilibrium bond length[b]	stretching constant[c]
Si–O	1.62	597
Si–H	1.40	370
Si–C	1.85	600

bending	equilibrium angle[d]	bending constant[e]
Si–O–Si	149.4	0.18
O–Si–O	109.5	0.02
X–Si–C	110.	0.02
X–Si–H	109.5	0.016

torsion	torsion constant[f]
X–Si–O–X	1.2
X–Si–C–X	1.2

Nonbonded Potential Parameters[a]

atom	van der Waals param[g]	R_o[h]	charge
Si	0.042	2.1	0.89
O	0.160	1.6	−0.57

[a] Potential energy function of ref 15. [b] Å′. [c] kcal/(mol Å^2). [d] deg. [e] kcal/(mol deg^2). [f] kcal/mol. [g] kcal. [h] Å.

analytical expression for the interaction potential[15] are reported in Table II and have been adjusted in order to fit, at the energy minimum, the reported experimental geometry.[13] The new parameters added are Si–O and Si–C stretching, O–Si–O, O–Si–C, Si–O–Si, and C–Si–C bending, and torsions involving silicon atoms.

The open and cyclic forms of octamethyltetrasiloxane were energy minimized. Though not identical, the optimized geometry for the cyclic form is within the experimental range of the X-ray parameters reported by Steinfink et al.[13] for the cycle and in good agreement with that computed by ab initio means. The results of the minimization, for octamethylcyclotetrasiloxane, are reported in the fourth column of Table I.

Having assessed the geometry of the backbone, we then built the monomer of UVASIL and performed energy minimization and a conformational search for the aliphatic pendant chain. The open chain and cyclic tetramers were then further optimized and the minimum energy conformers matched and compared on the computer graphics display (Figure 3).

Molecular Dynamics of UVASIL Tetramers

Molecular dynamics has been used to gain a more quantitative understanding of the flexibility and mobility of both the UVASIL backbone and pendant chains and to evidence their relevance on the HALS properties. MD simulations have been carried out in the Sybyl framework using the same energy and geometry parameters given in Table I. In the case of the acyclic tetramer we performed one run of 10 ps at 400 K to achieve thermalization and then the simulation was continued for another 30 ps at constant temperature (300 K). For the cyclic tetramer we performed, as previously indicated, three different runs, one for each of the three most representative conformers.

Electron Spin Resonance (ESR) Study

We have used an intrinsic spin-label technique to assess the mobility of the piperidino pendants in the UVASIL tetramer by estimating, from the extent of the electron/nuclei exchange interaction, the correlation time and hence the relative mobility of piperidino nitrogen atoms. The N–H groups were oxidized with H_2O_2 in the presence of sodium tungstate,[16] to nitroxyl >N–O• free radicals, and the electron spin resonance (ESR) spectra of toluene solutions (5×10^{-4} mol/mL) were recorded on a VArian E109 ESR spectrometer set at 3200 G and 9.042 GHz and equipped with a variable temperature accessory. The samples were deaerated by ten freeze–pump–thaw cycles. The temperature was varied from 383 to 103 K. The room temperature ESR spectrum of oxidized UVASIL is typical of a polyradical species (Figure 4) undergoing electron exchange. At intermediate temperature values the exchange rate becomes progressively slower, and at 193 K the exchanging species is approaching the slow limit.

Results and Discussion

UVASIL Structure and Properties. The HPLC and MS[5] data indicate that several types of oligomers are present in all the UVASIL samples. The most representative species have from three to eight repeating units and may take both linear and cyclic forms with the tetrameric species having the highest concentration (90% in some of samples). The energy minimization of octamethylcyclotetrasiloxane, reported in the fourth column of Table I, agrees with the X-ray data.[13] The acyclic octamethyltetrasiloxane has a bent geometry and the adjacent Si–O and O–Si bonds prefer, by ca. 4 kcal/mol, alternating gauche$^+$/gauche$^-$ (g^+g^-) states to the all-trans (tt) ones (Figure 5), in keeping with Mattice's[6] report. On the other hand the cyclic tetramer is more stable, by ca. 10 kcal/mol, than the bent pseudocyclic g^+g^- open chain tetramer.

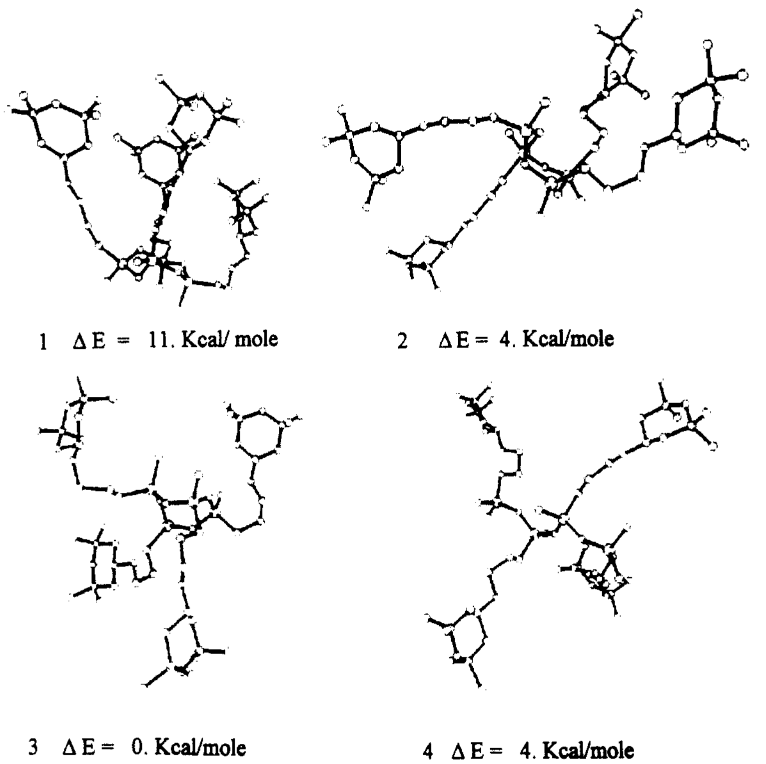

1 ΔE = 11. Kcal/ mole
2 ΔE = 4. Kcal/mole
3 ΔE = 0. Kcal/mole
4 ΔE = 4. Kcal/mole

Figure 3. Most representative conformers of tetrameric UVASIL: (1-3) cyclic forms; (4) folded-up acyclic form.

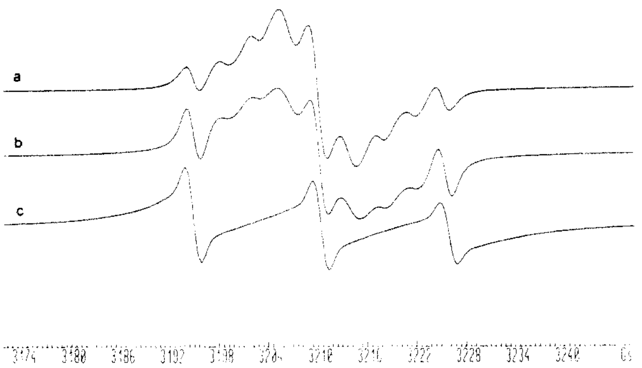
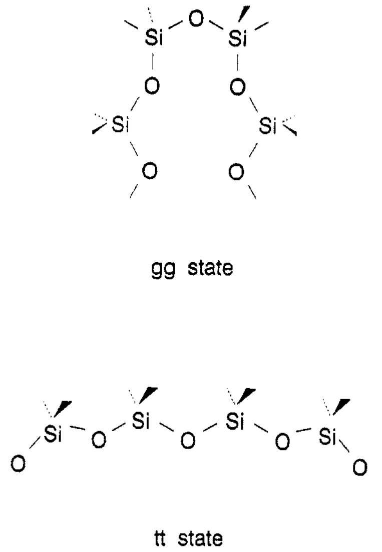


Figure 4. ESR spectra of oxidized UVASIL in toluene (5×10^{-4} mol/mL) at various temperatures: (a) 363 K; (b) 298 K; (c) 193 K.

This extra stability seems to be due entirely to the electrostatic interaction. While this result could be an artifact of our potential, the observed energy drop is consistent with the unpredicted higher stability of octamethylcyclotetrasiloxane and of the cyclic tetrameric form of UVASIL. The polysiloxane backbone of open-chain and cyclic UVASIL tetramers has almost the same shape and volume; i.e. in the linear oligomer the –Si–O– chain is folded so that the four tetramethylpiperidino pendant chains (see Scheme II) are arranged as in the cyclic tetramer. Conformational analysis indicates that conformers with totally different arrangements of the four pendants are characterized by very similar stability, provided that the siloxane backbone adopts the most stable open or cyclic conformation. Figure 3 shows the structure and energy differences of the low-lying conformers of UVASIL tetramers, with the cyclic "calix-like" one, **1**, being the least stable and having each piperidino group equidistant at ca. 10 Å. Of the two other cyclic conformers, the near-planar type **3** has each of the four pendant >N–H groups equidistant from its nearest neighbors. The third cyclic conformer, **2**, characterized by a "two-up" and a "two-down" arrangement of the pendants, has an energy comparable to that of the most stable open-chain tetramer, **4**.



gg state

tt state

Figure 5. Gauche and trans conformations of open-chain octamethyltetrasiloxane. For simplicity's sake only the g^+g^- state of the central Si–O and O–Si bonds is shown.

During the last 8 ps of the simulation run on the UVASIL cyclic tetramer the N---N distance varies from ca. 8 to 17 Å and is covered in about 4 ps. Moreover in each configuration there is at least one pair of nitrogen atoms at a mutual distance ranging from 7 to 11 Å. The maximum displacement undergone by the >N–H group is of the order of 10 Å. The ESR measurements carried out on the oxidized UVASIL, having >N–O• instead of the original >N–H groups, evidence the presence of a species for which the >N–O• free electron experiences a spin exchange interaction. At high temperature (363 K) the nine-line ESR spectrum is consistent with four equivalent >N–O• groups undergoing fast exchange. Since the exchange time of the electron among nuclei may be calculated,[17] for a hyperfine coupling constant of 16 G, to be on the order of 25 ns, conformational changes faster than a few tens of nanoseconds would mimic an "averaged-out" structure consisting of a nitroxyl free electron that experiences a

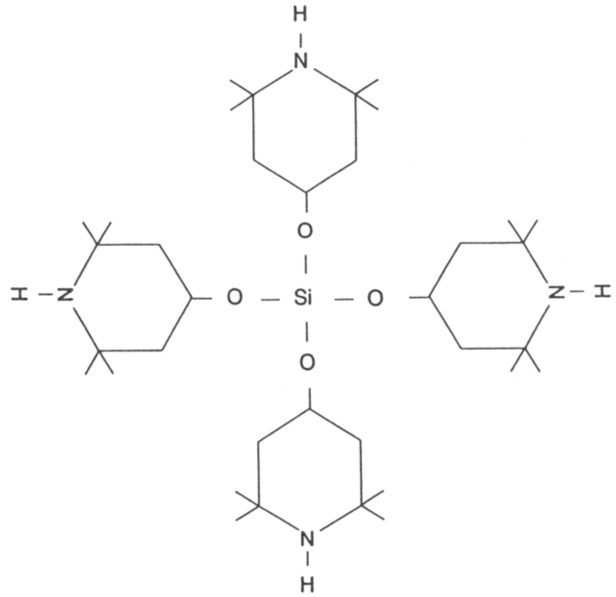


Figure 6. Structure of tetrakis(tetramethylpiperidinyl) orthosilicate.

time-averaged interaction with all four nitrogen nuclei of the piperidino pendants. Actually, the four *N*-oxyl groups are not simultaneously at the closest distance, but rather at least one N···N pair is at the right distance for the exchange to occur. All the side chain pendants move fast enough and without energy barrier, so that the four different pairs would behave as equilvalent. The equivalence of the four piperidinyl-*N*-oxyl groups is progressively removed as the conformation mobility becomes lower by decreasing the temperature. The ESR spectrum at low temperature (103 K) is typical of a randomly oriented free-radical species in a glassy matrix. By contrast, spectra of oxidized UVASIL in a polypropylene matrix reflect a preferential alignment along the polymer backbone even at room temperature. In order to estimate the average >NO•---•ON< distance required for exchange to occur we have used the orthosilicate shown in Figure 6 as a molecular "ruler", since the EPR spectrum of the corresponding oxidized form, in which >N–O• replaces >N–H, has a pattern and hyperfine coupling (nine lines, $a_N = 4$ G)[16] matching very closely that of the oxidized tetrameric UVASIL, although the compound is much less flexible. We built and energy minimized the structure, performed a full conformational search, and obtained an N---N distance ranging between 7 and 10 Å, a result very similar to that of the tetrameric UVASIL species in the closest arrangement. We conclude that the observed electron exchange in the oxidized UVASIL is an intramolecular phenomenon occurring in the cyclic tetrameric species and most likely also in the folded-up linear tetramer and is due to the highly flexible side chains of the highly stable tetrameric form.

Polymer–UVASIL Interaction. As mentioned in the Introduction, UVASIL is highly compatible with polypropylene with miscibilities exceeding 1:1 (w/w). In a preliminary attempt we took a rodlike strand of polymer consisting of 16 monomeric units arranged in a 3.10 helix as in the isotactic polymer. This preliminary model has been chosen since the persistence vector computed by Yoon and Flory[18] converges to its limit value for a chain of 16 units or greater, which indicates no directional correlation with the initial pair of bonds. The assembly between the most stable cyclic and linear tetramer of UVASIL and the polymer was done by a sort of docking process with energy minimization; i.e. first a model with a reasonable interaction energy was built and then relaxed over all degrees of freedom, including the translation of one molecule with respect to the second, for both forms of UVASIL and the polymer model. The resulting interaction complex for the cyclic form is reported in Figure 7 as seen from the top (a) and the side (b). The interaction energy, expressed as the total energy of the complex minus the internal energy of each of the components, is −9.1 kcal/mol for the linear and −16.2 kcal/mol for the cyclic UVASIL. The internal energy of the latter isolated molecule is almost identical to the one in the complex. We note that the length of the two compounds is roughly the same and that UVASIL is still in its preferred arrangement, i.e. having a cyclic or folded structure for the backbone. The two outer piperidino pendants are encompassing the polypropylene and run parallel to helical axes, whereas the other two pendants surround the polymer and have their piperidino amino group at distances varying from 13 to 14 Å. The polymer fits quite well between the two aliphatic chains to which the piperidinyl groups are attached. This good geometrical fit does not tell us much about the protection mechanism, but it may explain why the two compounds are so highly compatible. This preliminary study is clearly only one possible way of describing the polymer–UVASIL interaction and encourages us to continue with the molecular modeling approach to search for structure–function correlations and the understanding of the features deter-

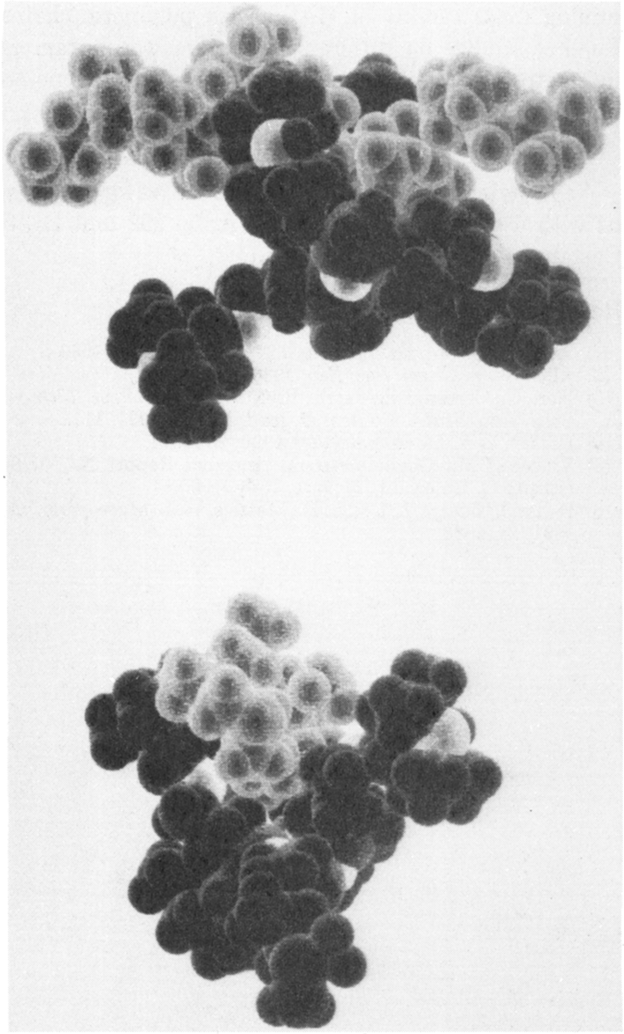


Figure 7. Side (a, top) and top (b, bottom) view of the complex between polypropylene (gray) and cyclic tetrameric UVASIL (black).

mining the assembly of HALS with polymeric chains. Further studies on different oligomers, e.g. hexamers, interacting with polymers other than polypropylene are now in progress.

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