Conformational Study of Poly(*p*-phenylene) by Molecular Mechanics Minimization

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ABSTRACT: Molecular mechanics minimizations were performed on alkyl-substituted biphenyls to explore the effect of the position and length of side chains on the planarity of the phenyl rings. This approach was extended to poly(*p*-2,5-di-*n*-alkylphenylene)s. The structural behavior was investigated by systematically modifying the length of the main chain and the side chains. Studies of substituted biphenyls showed that the methyl substituent at 2, 2′, 6, and 6′ positions much affected the torsion angle between the phenyls. The torsion angle decreased and converged to an asymptotic value of ∼70° from trans as the length of side chains was increased in 2,2′,5,5′-tetraalkylbiphenyls. The results of a single poly(*p*-2,5-di-*n*-alkylphenylene) chain clearly showed that the main chain and side chains cooperate on the molecular level to make a stable conformation. Poly(*p*-2,5-di-*n*-alkylphenylene)s with long side chains showed partial ordering of side chains with a plain plate structure, whereas those with short side chains did not show side-chain ordering and had cylindrical, or hairy-rod structure. The onset of side-chain ordering for this single-chain system was found to occur for a sexiphenylene unit with eight carbons in the side chains. The average torsion angles of poly(*p*-2,5-di-*n*-alkylphenylene)s decreased from 89° to 61° relative to trans as the length of side chains was increased from methyl to dodecyl.

Introduction

The relationship between electronic structure and backbone conformation is a fundamental feature of conjugated polymers. A dramatic red shift has been observed for the $\pi-\pi^*$ transition from *cis*-polyacetylene to *trans*-polyacetylene.[1] Color changes have also been observed in poly(3-alkylthiophene)s as the temperature and solvent quality are changed.[2,3] The interpretation has been that torsion in the conjugated chain disrupted π-electron overlap resulting in an electronic localization and that the effective conjugation length was decreased. The conformational changes are accompanied by large spectroscopic changes indicative of a major modification of the polymer electronic structure at the transition. It is well known that conductivity is closely related to the chain planarity of conducting materials.[4] Hence, it is very important to control the planarity for the maximum conductivity. Recently, Ho *et al.* investigated the effect of alkyl side chains on the planarity of the P3ATs' backbone, observing the UV−visible absorption behavior of these polymers.[5] They reported that the absorption maximum increased with increasing length of the side chains. Our investigation is motivated by this cooperation between the side chains and the backbone. In this work, poly(*p*-phenylene) (PPP) was adapted for this calculation because its structure is simple and its data by calculation and experiment are available elsewhere.[4,11,12,14,16]

PPP has been extensively investigated because it is a thermally, oxidatively stable polymer and it is conductive in the oxidized or reduced states. PPPs have been synthesized by various methods ranging from the direct synthesis method from benzene to the Pd-catalyzed polymerization method developed in Mainz.[6−9] Specifically, Wegner's group found a more efficient method of synthesizing PPPs to overcome the difficulty related to the insolubility and infusibility and to increase the degree of polymerization. In these successful modifications of PPPs, flexible side chains were introduced at the 2,5 positions of the *p*-phenylene repeating unit, and the relationship between the lengths of the alkyl side chains and properties were well established.[10] Differential scanning calorimeter (DSC) thermograms indicate that the onset of side-chain ordering occurred at alkyl side-chain lengths greater than six, and isotropic melt transition temperatures decreased considerably with increasing alkyl side-chain length.[11] Vahlenkamp and Wegner reported that PPPs with long alkoxy side chains exhibited a layered phase structure whereas those with short alkoxy side chains had a cylindrical packing structure.[12] The influence of the cooperation between the polar backbone and the nonpolar side chains on the structure formation seems to be evident, but the molecular origin of the observed long spacing and the role of the alkyl side chain in controlling the packing of these systems are still not completely understood.

In general, rigid backbone polymers may have certain preferred molecular conformations such as helix or planar structures, depending on the presence of hydrogen bonds, conjugated bonds, and aromatic rings embodied in the main chain. Chain rigidity comes primarily from intrachain interactions and rotational barriers. Hence, the study of supermolecular structures in rigid backbone polymers should be combined with an investigation of conformations on a single-chain level because the structural and conformational data provide a starting point in the study of the bulk properties of these polymers. The availability of structural data for small molecules has provided precise atomic coordinates, but it is not always possible to obtain such precise information for polymers. Rather, computational techniques offer certain advantages in gaining insight to molecular geometry. The basic approach used is to obtain a particular conformation, to calculate its corresponding energy, and to compare it with the energies associated with conformations that have already been investigated. Using this approach, it is possible to identify the minimum energy, which will hopefully correspond to the global minimum, and thus to the preferred molecular conformation. Such an approach requires a systematic

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exploration of the possible conformational space. The main limitation is that it is extremely demanding of computational resources if there are more than a few sources of conformational flexibility in a molecule. To reduce the computational load, a variety of algorithms and more specific theories have been developed.

In this paper, single-chain conformations of poly (*p*-2,5-di-*n*-alkylphenylene)s are studied using molecular mechanics minimization for the study of the structure−property relationships of conducting polymers. The goals are to elucidate the effect of alkyl side chains on the planarity of the *p*-phenylene backbone and to investigate the structural behavior when the lengths of the main chain and side chains have been changed.

Experimental Section

Location of the global minimum energy conformation of a small molecule is a trivial problem because of the small number of possibilities. The situation becomes more complex with large molecules. Even in a single chain, it is difficult to find the most stable conformation directly because a polymer chain has an enormous number of possible conformations. It is also difficult because algorithms for minimizing the conformational energy lead only to the local minimum that is closest to the starting point rather than to the global minimum that is required. Location of the global minimum energy conformation of a large-chain molecule would be an extremely difficult and uncertain process unless there were simplifying factors. For instance a long-chain alkane would exist preferentially as a zig−zag conformation. In our calculations, the zig−zag conformation of the side chains was used to reduce the number of possible conformations, and investigations was started from the most basic structures of given polymer systems. Alkyl-substituted biphenyl was thoroughly investigated to make a strong basis for further study of alkyl-substituted PPPs. The PPP chain was constructed on the basis of information obtained from biphenyl derivatives. The main-chain length (N_m) and side-chain length (N_s) were changed systematically.

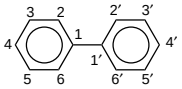
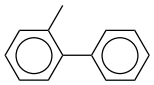
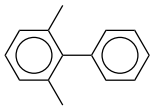
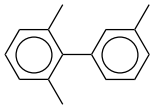
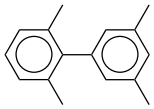
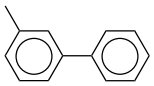
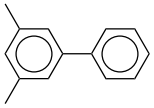
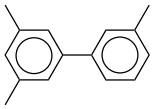
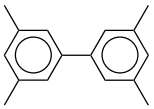
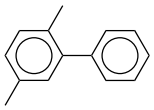
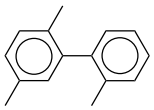
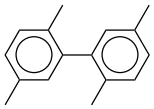
There are two ways of attacking global minimization. In the first, the minimization procedure is allowed to converge on the nearest local minimum. Thermal motion is then simulated by shifting the atoms a given amount in directions corresponding to the normal coordinates. This has the effect of jolting the molecule out of the local minimum and hopefully into another potential well of greater depth. Continual repetition of this process should eventually lead to the global minimum. The second method is to generate a conformation somewhere within the potential well corresponding to the global minimum before energy minimization is commenced. In our calculations, these two ways were tried simultaneously. Many conformations of PPPs were used as the initial condition by systematic changes of torsional angles. Dynamics simulation was applied to a result of molecular mechanics minimization to give a thermal disturbance, and then molecular mechanics minimization was reapplied to the results of the dynamics simulation. This process was repeated many times to get no severe conformation changes.

The results were generated using the program Cerius[2] version 1.6 and Silicon Graphics IRIS Indigo R4000 series workstation. Universal force field 1.01 was used for energy minimization. Charge equilibrium calculations were also carried out every 50 steps because this calculation is recommended when using Universal force field, and charge equilibrium might be affected by conformation change. RMS value, 0.005 (kcal/mol)/Å, was used for efficient comparison and consistency. The Universal force field used for this study has been previously defined.[13] Generally, choosing the proper force field is the most important parameter governing the accuracy of simulation results.

Results and Discussion

Various configurations of substituted biphenyls were investigated upon changing side-group (methyl) positions and numbers. Torsion angle is the only important intramolecular degree of freedom in the biphenyl structure and was determined by the calculation of the intramolecular potential energy minimum. The calculated results are listed in Table 1. Biphenyl was the most stable when the torsion angle between the phenyl rings was 42° from trans. This is consistent with the results of others.[4,14−16] Both the coplanar and perpendicular conformations are less stable than the 42° torsion angle situation, and the perpendicular conformation is more stable than the coplanar structure. The main reason behind the larger stability of twisted conformation may be found in the balance with the steric hindrance between the hydrogen atoms in the ortho position and the electrostatic interaction between

Table 1. Torsion Angle of Biphenyl Derivatives with Various Methyl Side-Group Positions and Numbers

no.	structure	nomenclature	torsion angle $\lvert\phi - \phi^t\rvert$
1		biphenyl	42
2		2-methylbiphenyl	67
3		2,6-dimethylbiphenyl	86−94
4		2,3′,6-trimethylbiphenyl	80−100
5		2,3′,5′,6-tetramethylbiphenyl	84−96
6		3-methylbiphenyl	42
7		3,5-dimethylbiphenyl	42
8		3,3′,5-trimethylbiphenyl	42
9		3,3′,5,5′-tetramethylbiphenyl	42
10		2,5-dimethylbiphenyl	67
11		2,2′,5-trimethylbiphenyl	82
12		2,2′,5,5′-tetramethylbiphenyl	82

the π-atomic orbitals, which increases the planarity of the compound.

The presence of substituents causes a departure from planarity. When one methyl group is substituted at the 2, 2′, 6, or 6′ position as shown by sample 2 in Table 1, the torsion angle increases to 67°. The angle reaches 86−94° when two methyl groups are substituted at the 2,6- or 2′,6′-positions as shown by sample 3. If the substituents are in any positions other than the 2, 2′, 6, and 6′ positions, the torsion angle remains at 42°. Samples 6−9 show that substituents at 3, 3′, 5, and/or 5′ positions behave similarly and do not influence the torsion angle. These results show that the numbers and sizes of substituents at 2, 2′, 6, and 6′ positions greatly affect the planarity of biphenyl because of the severe steric hindrance between the methyl group and hydrogens in the ortho position. Stolevik and Thingstad[14] reported that the change in torsion angle of biphenyl depends on the size of halogen substituents that are substituted in ortho positions. They calculated the torsional potential curves of 2,2′-dihalobiphenyls and 2,6-dihalobiphenyls. The torsion angle between the two ring planes was found to increase with increasing atomic number of the substituents. Bastiansen and Samdal[16] studied the barrier of internal rotation in non-ortho-halogen-substituted biphenyl derivatives from electron diffraction data: the torsion angle for the non-ortho-substituted biphenyl derivatives was 44.3° and seemed to be slightly influenced by substitution in the meta and para positions. Our results were consistent with those results reported by Stolevik and Bastiansen.

2,2′,5,5′-Tetramethylbiphenyl as shown by sample 12 in Table 1 is significant when the repeating unit of PPPs with side chains has the substituents at 2 and 5 positions. This structure has a relatively large torsion angle of ∼82°, which is not good for maximum conductivity. Brédas *et al.* reported that the substituents that do not cause torsion angles larger than 40° along the chain are generally quite acceptable.[4] These results imply that the electronic properties are not drastically modified with respect to the coplanar situation over a torsion angle of ∼40°, and that it is essential to reduce the torsion angle for maximum conductivity.

Molecular mechanics minimizations were also performed on alkyl-substituted biphenyls to establish the effect of side-chain length on the torsion angle of the 2,2′,5,5′-tetraalkylbiphenyl. Figure 1 shows the torsion angle variance of a stable conformation of 2,2′,5,5′-tetraalkylbiphenyl with side-chain length N_s. The structure with the methyl side groups has the largest torsion angle, 82°. As the side-chain length increases, the torsion angle decreases slightly, and it goes to a limiting value of ∼70°. The torsion angle does not change over the alkyl side-groups of length six. In other words, side chains longer than hexyl do not increase the torsion angle between the phenyl rings. This implies that the torsional force by the steric hindrance between side chains and hydrogens in the ortho-position and the attraction force by π conjugation and side-chain interactions are equilibrated over hexyl side chains. The torsion angle decreases as the side-chain length becomes larger than a methyl group, which means that the steric hindrance between alkyl side chains and hydrogens in the ortho position is dominated by the interaction between the first methylene group of the alkyl side chain from the main chain and the hydrogens in the ortho position of the adjacent phenyl ring. An interesting property of PPPs with long flexible side chains is

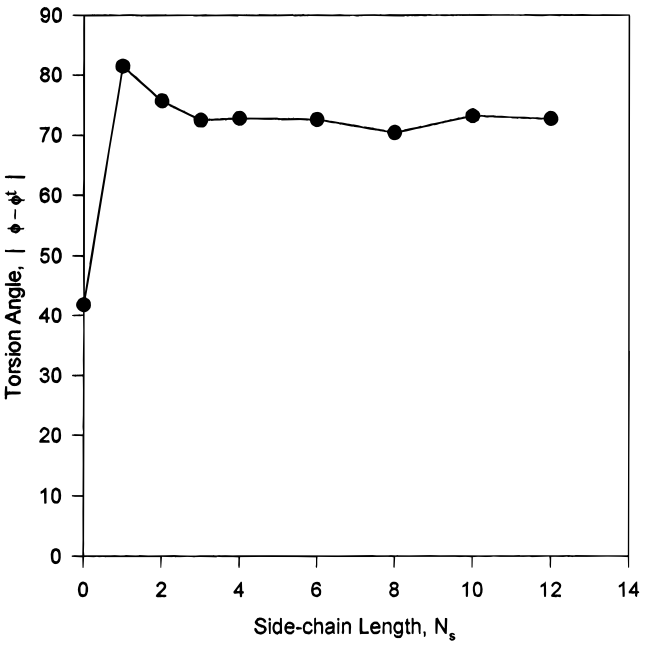


Figure 1. Torsion angle (în deg) between the phenyl rings of 2,2′,5,5′-tetra-*n*-alkylbiphenyls with the length of alkyl side chain, N_s.

the ability to form layered structures, which are characterized by a segregated structure in which the rigid main chains are separated from the flexible side chains. The distance between the layers is defined by the length of the alkyl side chains. Depending on their length, the side chains in the layers are able to form hexagonal paraffinic crystalline structures. Although it is known that the formation of the layered structure is due to the cooperation of the stiff main chain and flexible side chains, the interplay between main chains and side chains and the role of the flexible side chain in controlling the morphology are still not completely understood on the molecular level.

The single-chain conformation of poly(*p*-2,5-di-*n*-alkylphenylene)s is studied to elucidate the effect of alkyl side chains on the planarity of the backbone of PPPs and to investigate the structural behavior with a systematic change in the main-chain length, N_m and the side-chain length, N_s. Figure 2a shows a stable conformation of poly(*p*-2,5-di-*n*-hexylphenylene) ($N_m = 12$, $N_s = 6$) with torsion angles between the phenyl rings and with disordered side chains. The repulsion from the polar backbone directs the adjacent side chains to space out individually to obtain the stable conformation. The torsional force overwhelms a possible attraction force between the side chains and dominates the entire chain shape. The spatial distribution of the side chains along the polymer main-chain is shown in Figure 2b. It can be observed that the shape of this polymer chain is the cylindrical or "hairy-rod" shape. This result is exactly the same as that of Vahlenkamp and Wegner[12] who proposed, on the basis of X-ray and DSC data, that PPPs substituted with short alkoxy side chains are packed in a cylindrical packing. The diffractograms of PPPs with short side chains did not fit the model of a layerlike structure, and DSC measurements also suggested that PPPs with short side chains do not crystallize in the same manner as those with longer ones. Our calculations show that the PPPs with shorter side chains than hexyl revealed disordered side chains, whereas the PPPs with longer a side chain than octyl show side-chain ordering clearly. Figure 3 shows a stable conformation

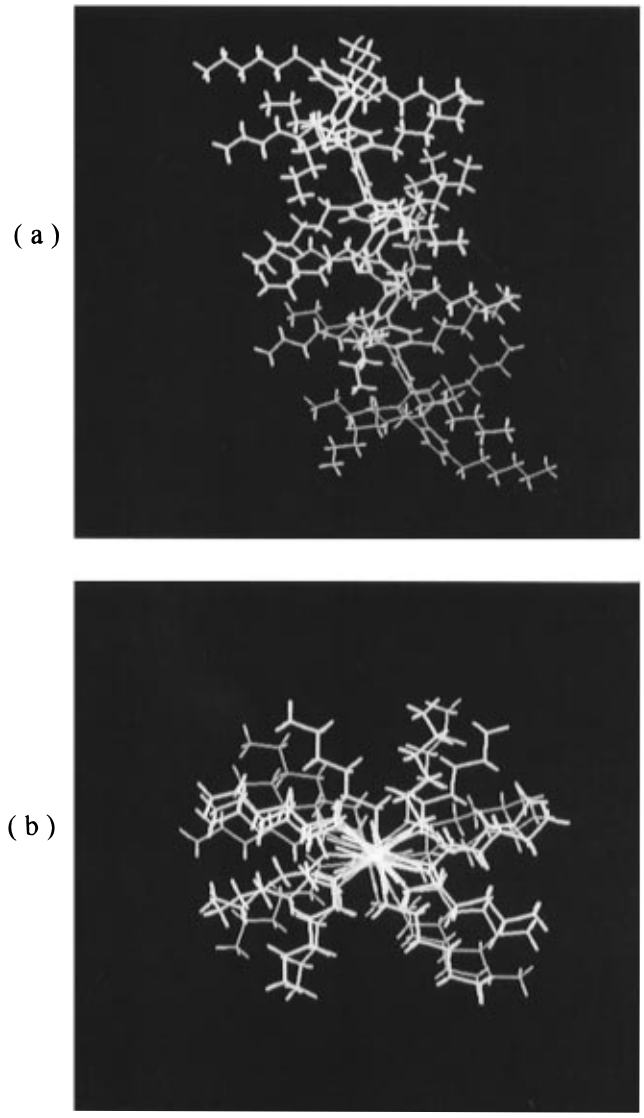


Figure 2. A stable conformation of poly(*p*-2,5-di-*n*-hexylphenylene) ($N_m = 12$, $N_s = 6$): (a) side view; (b) main-chain axis view.

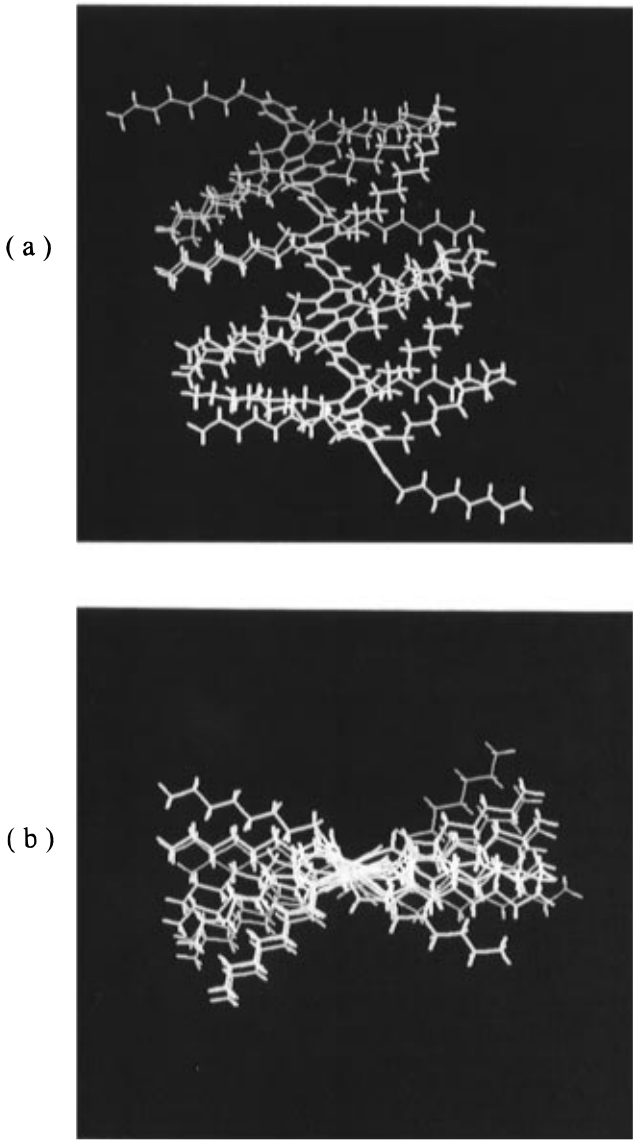


Figure 3. A stable conformation of poly(*p*-2,5-di-*n*-octylphenylene) ($N_m = 12$, $N_s = 8$): (a) side view; (b) main-chain axis view.

of PPP with octyl side chains ($N_m = 12$, $N_s = 8$). The side chains began to order partially, and the structure of the entire chain changed from a cylindrical rod to a plain plate. A stable conformation of poly(*p*-2,5-di-*n*-dodecylphenylene) ($N_m = 12$, $N_s = 12$), shown in Figure 4a, shows the side-chain ordering and plain structure more clearly. Although the torsion angles are not even, they are reduced in the region in which side-chain ordering takes place. This result shows that the torsion angles can be controlled by side-chain crystallization: the torsion angles are reduced as the crystallinity of the side chain increases. This result also shows that up to six carbons at the beginning point of some side chains from the main chain were deformed to accommodate efficient side-chain ordering. This side-chain ordering implies that the attraction force between two adjacent side chains is stronger than the main-chain torsional force. Figure 4b shows that poly (*p*-2,5-di-*n*-dodecylphenylene) has a narrower spatial distribution of side chains which is called a plain plate. This result is also consistent with the results of Vahlenkamp and Wegner, who confirmed that the PPPs with long alkoxy side chains exhibit a layered structure.[12]

Several configurations [$(N_m, N_s) \mid 2 \leq N_m \leq 12, 0 \leq N_s \leq 12$] were investigated to understand the cooperational needs for side-chain crystallization. The results are presented in Figure 5. There is no side-chain ordering if the side-chain length is shorter than hexyl regardless of the main-chain length or if the main-chain length is shorter than sexiphenylene regardless of the side-chain length. That is, the onset of side-chain crystallization for the single-chain system was found to occur for sexiphenylene in the backbone and alkyl side groups of length eight. The window $\{N_m \geq 6 \cap N_s \geq 8\}$ is the region showing the side-chain crystallization. These results of side-chain crystallization are consistent with the DSC side-chain melting data of Wegner *et al.*[11] It is very interesting to observe that the torsional forces dominate the cooperation when the backbone is shorter than sexiphenylene. Thus, even side chains with 12 carbons are not able to crystallize in a tetraphenylene unit. And vice versa, it is also interesting that a long main chain, for example, octaphenylene, with shorter side chains like hexyl are not crystallizable.

Figure 6 shows the average of 11 consecutive torsion angles of the poly(*p*-2,5-di-*n*-alkylphenylene)s with main-chain length, $N_m = 12$, as the side-chain length is varied. A stable conformation of PPP has an average torsion angle of 41.2° which is the same as that of biphenyl. In

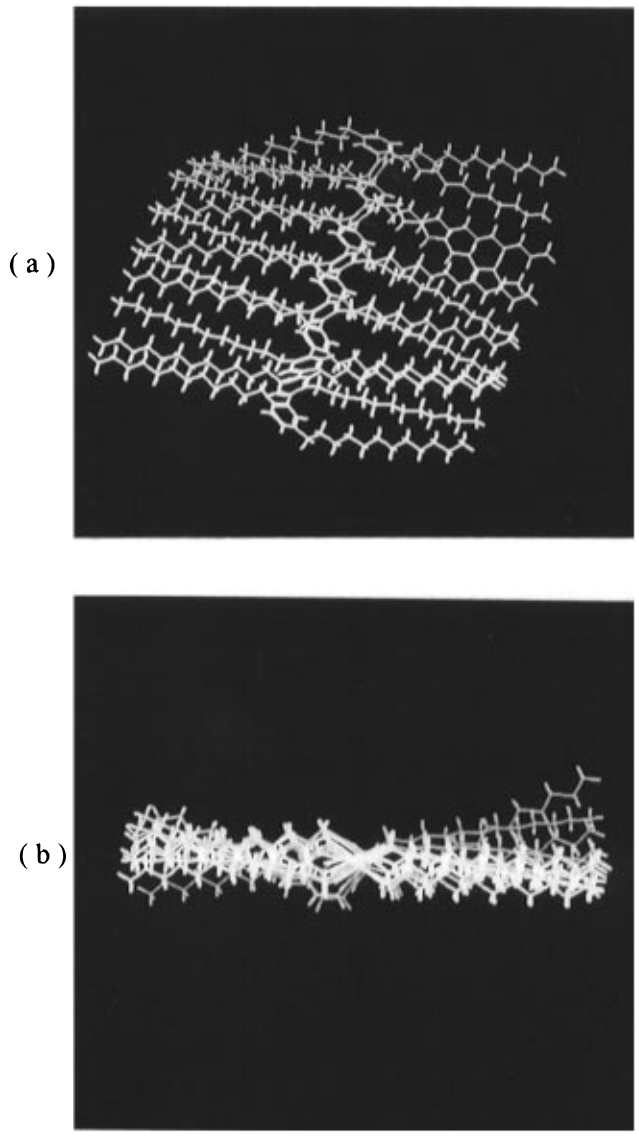


Figure 4. A stable conformation of poly(*p*-2,5-di-*n*-dodecylphenylene) ($N_m = 12$, $N_s = 12$): (a) side view; (b) main-chain axis view.

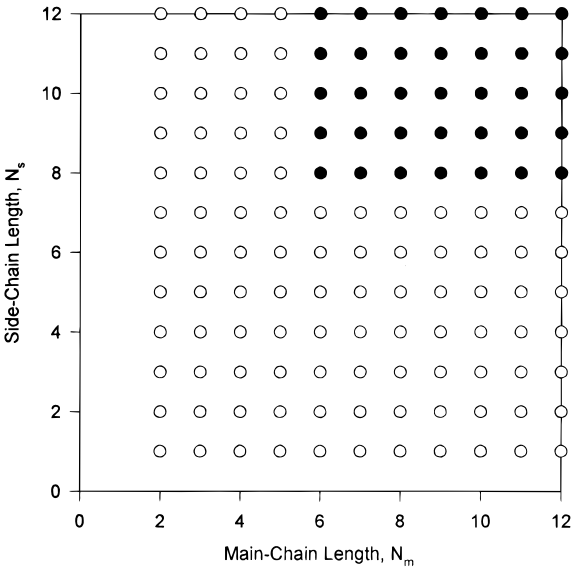


Figure 5. A window showing the side-chain ordering: (●) Ordering; (○) no ordering.

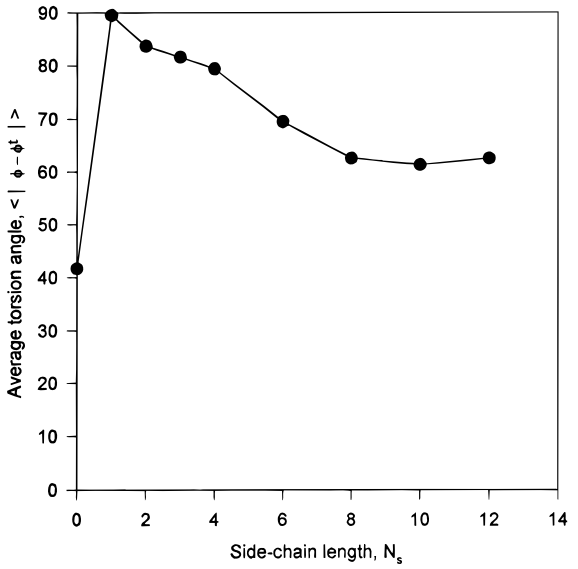


Figure 6. Average torsion angle of poly(*p*-2,5-di-*n*-alkylphenylene)s ($N_m = 12$) with the length of alkyl side chains.

the case of short side chains such as methyl, ethyl, propyl, and butyl, the average torsion angle was larger than that of biphenyl with the same corresponding side chains because each repeating unit has two sites of side-chain interaction, and the torsional force between phenyl rings exceeds the interaction force between side chains. Hence, these materials have the tendency toward forming cylindrical structures. To the contrary, the average torsion angles of PPP with long side chains decreased as the side-chain length was increased. PPP with a side chain longer than octyl had torsion angles of ~60°, which is 10° less than that of biphenyl with corresponding side chains. These torsion angles decreased because the side-chain interactions overcame the torsional force. The side-chain ordering became possible when the attraction force between the side chains was superior to the torsional force between the phenyl rings. Poly(*p*-2,5-di-*n*-hexylphenylene) had an average torsion angle of 69.5°, which was almost the same as that of 2,2′,5,5′-tetrahexylbiphenyl. Poly(*p*-2,5-di-*n*-hexylphenylene) is considered to exist in the boundary region of cylindrical and plain plate structures. All of these results indicate that the torsion angles of PPPs can be controlled by the side-chain conditions in a limited range, but it is inherently difficult to reduce the torsion angle below 40° in a single-chain state. The angle can be reduced more in the ordered region of bulk state by the interchain interaction and packing effects. Although further studies are needed to specify the bulk state of PPPs, the results of the molecular mechanics minimization calculation for a single chain provide a limiting case to predict the microstructure of rigid polymers in the molecular level.

Conclusions

Molecular mechanics minimization was applied to alkyl-substituted PPPs. We have studied the variance of torsion angles as a function of the side-chain length, N_s, and the structural behavior of a single chain. In the biphenyl case, the substituent's position plays an important role in the torsion angle change. The substituents at 2, 2′, 6, and 6′ positions dominate the planarity of biphenyl because of the severe steric hindrance between the methyl groups and hydrogens in the ortho-position. As the side-chain length of 2,2′,5,5′-tetraalkylbiphenyl increases, the torsion angle decreases slightly and converges to an asymptotic value

of ∼70°. This indicates that the steric hindrance is determined by the interaction of the first methylene group of the alkyl side chains from the main chain and the hydrogen in the ortho-position. Poly(*p*-2,5-di-*n*-alkylphenylene)s exhibit the window showing side-chain crystallization as a function of side-chain length and main-chain length: the onset of side-chain crystallization for a single-chain system was found to occur for sexiphenylene in the backbone and alkyl side groups of length eight. It was also revealed that PPPs with long alkyl side chains have a plain plate shape supporting a layered structure in the bulk state, whereas those with short side chains have a cylindrical shape supporting a cylindrical packing in the bulk state. The average torsion angles of poly(*p*-2,5-di-*n*-alkylphenylene)s decreased from 89° to 61° as the length of the side chain was increased from methyl to dodecyl. The torsion angles of PPPs with side chains longer than octyl were ∼60°, which was 10° less than that of corresponding biphenyls.

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