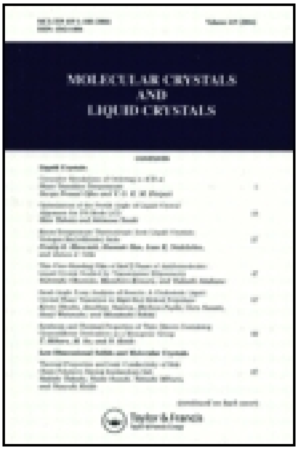

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Structure-Reactivity Relationships in the Solid State Polymerization of Diacetylenes

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Many diacetylenes undergo 1,4-addition polymerization in the solid state. In the course of our work we have discovered several examples in which seemingly minor changes in the constitution of highly reactive monomeric diacetylenes have rendered them inert. The subtlety of the effects, revealed by structural studies, illustrates the stringent packing requirements for solid state polymerization.

Many derivatives of butadiyne (diacetylene) undergo thermal or photochemical polymerization in the solid state. The mechanism for this single-crystal-to-single-crystal transformation, first proposed by Wegner,[1] involves rotation of the butadiyne segment of the molecule concomitant with 1,4-addition along the stack, as shown in Figure 1. During the course of our efforts to synthesize variations of existing polymers, we discovered several instances where slight modifications of highly reactive molecules rendered them totally inert to polymerization. This seemed interesting in its own right and caused us to investigate the structures of several unreactive diacetylenes in order to determine those factors responsible for their inertness.

Baughman[2] has discussed in great detail the packing arrangement the monomers must assume in order for the polymerization reaction to occur. The one essential requirement is that the monomers form stacks, as in Figure 1, such that the potentially reacting carbon atoms be approximately 3.5–4.0 Å apart. In order to fulfill this requirement the molecules within the stack must be slipped relative to one another to the extent that opposite ends of the butadiyne segments in adjacent molecules are essentially in contact. The magnitude of the slippage necessary to accomplish this is such that the

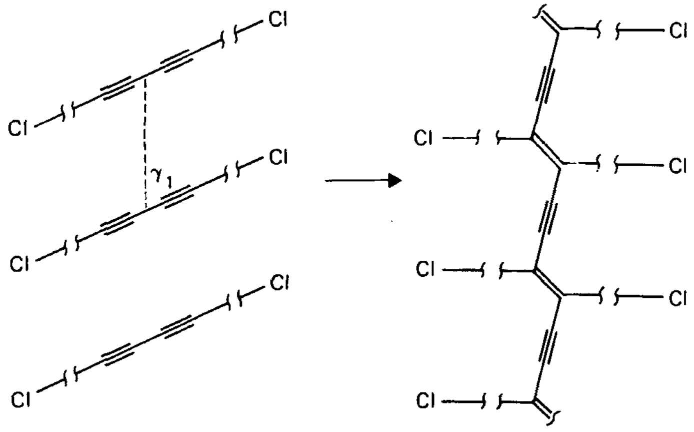

FIGURE 1 Wegner model for solid-state polymerization of diacetylenes.

angle between the molecular axes and the stack axis (an imaginary line connecting the molecular centers) must be on the order of 45°.

The monomeric diacetylene 2,4-hexadiyneylene-1,6-bis(*p*-toluenesulfonate) (Figure 2, X=Y=CH_3), is an extremely reactive molecule, readily polymerizing upon crystallization to give metallic appearing single crystals.[3] In an attempt to modify the electronic properties of the toluenesulfonate (hereafter PTS) polymer, we substituted Cl atoms for the methyl groups and found that in both the mono- (Figure 2, X=Cl, Y=CH_3) and di-substituted (Figure 2, X=Y=Cl) cases the resulting molecules were rendered completely inert to polymerization. The dibromo derivative (Figure 2, X=Y=Br) was also found to be inert, whereas the benzenesulfonate monomer (Figure 2, X=Y=H) was found to be highly reactive. Since the van der Waals radii of Cl and Br are similar to that of a methyl group it seemed clear that the change

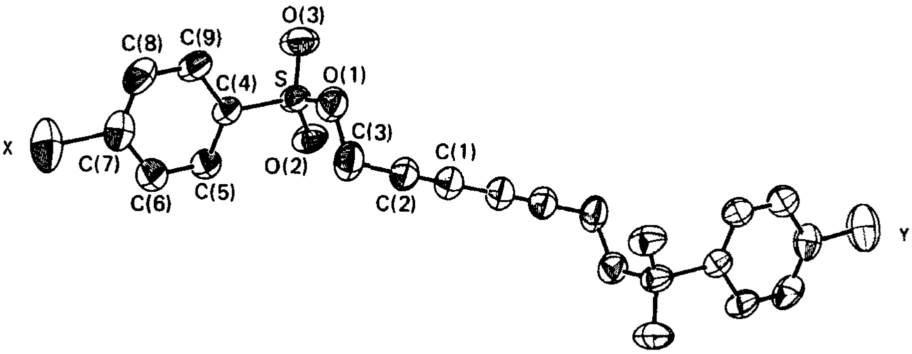

FIGURE 2 Molecular structure of various monomeric derivations of 2,4-hexadiyneylene bis(benzenesulfonate). The substituents (*X*, *Y*) on the aromatic rings are noted in the text.

in reactivity upon halogen substitution must be a result of the electronic properties of the halogen atoms rather than a bulk steric effect. Structural investigations of both the mono- and di-chloro derivatives were undertaken to determine the cause of the unreactivity.

The mono- and di-chloro substituted compounds are isostructural. The first crystallizes in the triclinic space group $P1$ or $P\bar{1}$ with cell constants $a = 8.961(2)$, $b = 11.223(3)$, $c = 5.051(2)$ Å, $\alpha = 100.22(1)$, $\beta = 90.41(1)$, and $\gamma = 95.14(1)^\circ$. The dichloro compound[4] crystallizes in $P\bar{1}$ with cell constants $a = 8.941(1)$, $b = 11.170(1)$, $c = 5.030(2)$ Å, $\alpha = 100.81(1)$, $\beta = 19.19(1)$, and $\gamma = 94.19(1)^\circ$. In both cases there is one molecule per unit cell. At the present time the space group of the mono-chloro derivative seems to be $P\bar{1}$, with the Cl and CH_3 sites being randomly interchanged so as to yield the required center of symmetry. Although the intensity statistics do not clearly reveal the presence or absence of a center, the structure has refined better assuming random disorder. In any case, this has little to do with the explanation for its inertness.

The reason for the unreactivity of the chloro-substituted compounds is evident from inspection of the molecular packing, shown in Figure 3. The molecules pack in stacks along the short crystallographic axis, in a manner similar to that required for polymerization. Although the configuration of

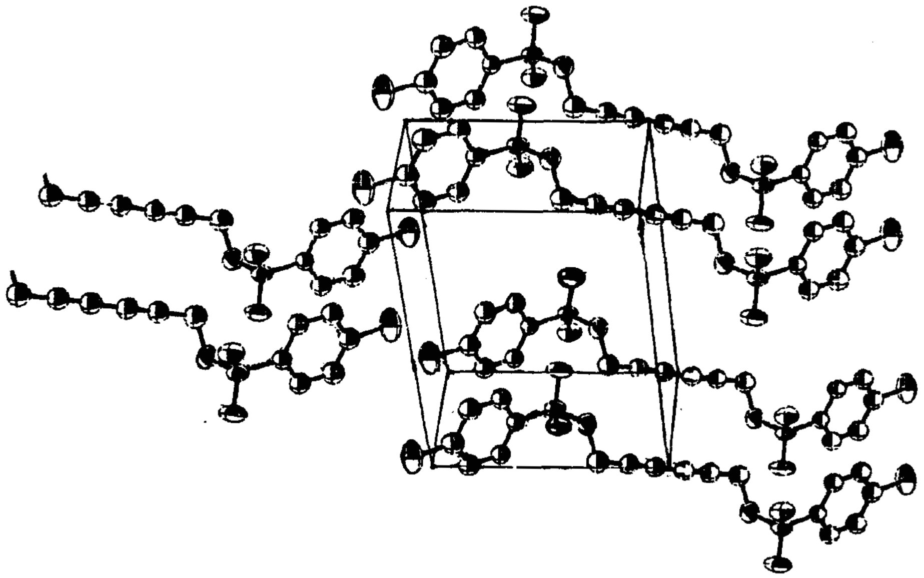

FIGURE 3 The packing arrangement of the mono- and di-chloro derivatives of 2,4-hexadiyneylene bis(benzenesulfonate). The molecules form stacks along the short crystallographic axis.

the individual molecules is quite similar to that of the PTS monomer,[5] the arrangement of the molecules within the stacks is slightly different. As mentioned above, this is the critical factor in determining the reactivity. In the case of the PTS monomer, the angle between the stacking and molecular axes is ~45°, resulting in approximately van der Waals contact between the potentially reacting carbon atoms and, consequently, high reactivity. In the case of the halogen-substituted compounds, the molecules are forced into a slightly more eclipsed arrangement, with the angle between the stacking and molecular axes being ~70°. The resulting distance between the reactive carbon atoms of almost 5 Å is too great to allow the occurrence of polymerization.

Although the more eclipsed mode of packing assumed by the halogen-containing materials is probably the result of many different nonbonded interactions, one of them appears to be dominant. The feature of the structure shared by both the mono- and di-chloro compounds, but not completely by the PTS monomer, is an intrastack interaction (to some degree dipolar) between the halogen atoms and the next aromatic group along the stack. This would tend to pull adjacent rings together, thereby yielding a more eclipsed configuration. To the extent that the interaction is dipolar it would presumably be weakened when methyl groups are substituted for the halogen atoms, thereby allowing the molecules to slip into a configuration that is amenable to polymerization. The fact that replacement of just one of the methyl groups in the PTS monomer by a halogen atom is enough to bring about inertness beautifully illustrates the subtle effects of molecular packing on solid state reactivity and suggests the difficulty of predicting whether or not a given diacetylene will polymerize.

The tremendous change in reactivity brought about by slight structural modifications in the benzenesulfonate series of compounds caused us to wonder whether the unreactivity exhibited by other classes of diacetylenes might also be the result of such subtle effects. In a study of the reactivity of diphenyldiacetylene derivatives with polar or hydrogen-bonding substituents, Wegner[6] found that those derivatives with the substituents in the *ortho* or *meta* positions of the phenyl rings were more reactive than those substituted in the *para* position. This was ascribed to the inability of the *p*-substituted compounds to undergo the dynamic shearing action needed for polymerization. Another explanation for this, different in the sense that the effect is static rather than dynamic, is that the dipolar or hydrogen bonding interaction between groups along the stack forces the molecules to crystallize in an eclipsed or nearly eclipsed configuration when the substituent is in the *para* position, thereby maximizing the interaction. As noted in the above discussion of the chloro compounds, this configuration is inert. Molecular models show that when the substituent is in the *ortho* or *meta* position, however, the hydrogen bonding interaction is just as strong, and perhaps even *enhanced*, when the molecules are slipped relative to each other, thereby rendering them highly reactive. This is probably not true of the *o*- and *m*-substituted compounds when the substituent is the $—NO_2$ or $—NH_2$ group. In these cases, the substituent is smaller and more rigid, leading to stronger interactions when the molecules are eclipsed than when staggered. We are not surprised, then, that Wegner found the *o*- and *m*-substituted $—NO_2$ derivatives to be only slightly more reactive than their *p*-substituted analog and all three of the nitro derivatives to be less reactive than those derivatives containing hydrogen-bonding substituents in the *o*- and *m*-positions. To determine the validity of these arguments, we have begun structural studies of several key compounds and present the first of our results here, the structure of di(p-nitrophenyl) butadiyne.

The compound crystallizes in the tetragonal space group $I4_1/amd$[7] with cell parameters $a = b = 7.088(1)$ and $c = 26.785(5)$ Å. The four molecules in the unit cell, required to possess C2v symmetry, do not crystallize in stacks as required for polymerization but, instead, pack in interpenetrating, sinusoidally stacked arrays of molecules running parallel to the *a* and *b* axes, as shown in Figure 4. The long axis of the molecule is perpendicular to these chains. Thus the inertness of this molecule is due to a gross packing effect rather than to an effect such as described in the preceding paragraph. However, because of the high symmetry of the individual molecules this may be,

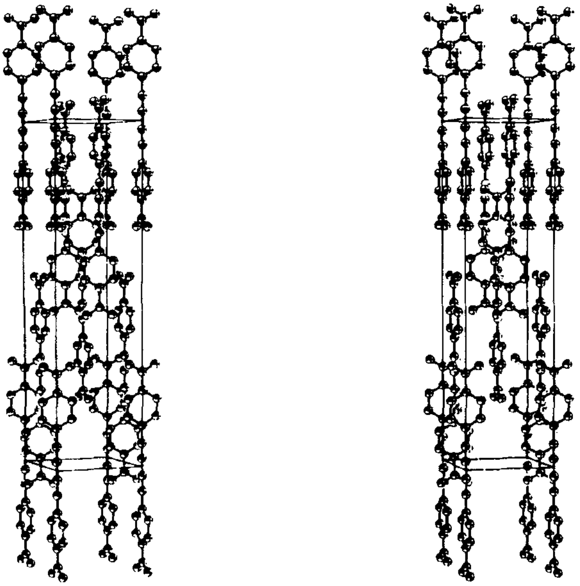

FIGURE 4 Stereographic representation of the molecular packing of di(p-nitrophenyl) butadiyne.

and probably is, a special case. When the molecules are less symmetric, such as those containing the various amido groups investigated by Wegner, the above rationale may prove to be valid. It may also prove to be valid for the less symmetric *o*- and *m*-substituted nitro derivatives, which we expect to crystallize in a nearly eclipsed configuration. The above points are currently being investigated.

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