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Sensitivity of Imaging Materials to Electron Beam Irradiation

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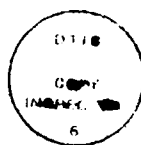
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19. ABSTRACT (Continue on reverse if necessary and identify by block number) A literature review was conducted in order to assess what approaches could be taken to enhance the sensitivity of PERM (processless electron recording media) film to electron-beam irradiation. It was implied that the process for producing the film had been optimized with the current imaging component and that a different imaging component would be required. Among the few imaging compounds capable of being converted from a colorless to a colored product directly upon exposure to an electron beam without further processing are the substituted diacetylenes. The surveyed diacetylene literature revealed little previous work with regard to the electron-beam imaging process. Much of the early work involved thermal, UV, and gamma radiation induced polymerization, primarily in the solid state. Only in the late 70s were soluble diacetylene polymers synthesized, creating the opportunity to study the solution chemistry of diacetylene polymerization. This result produced a wide variety of studies directed toward a better understanding of the structural changes that give rise to the observed chromic effects. Work on electron-beam polymerization of diacetylenes was limited, and other methods had to be used as a guide for the recommendations presented in this report. Among the recommended approaches are: optimizing the film				
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processing techniques to include monomer purity, crystal size, and dispersion quality; maximizing the crystalline packing parameters to reduce crystal lattice deformation and enhance the extent of polymerization; determining the relationship between the effective conjugation length and the molecular weight distribution of the polymerized imaging component; exploring the effect of side chain substitution on enhancing reactivity and providing an additional chromic effect beyond that observed for the skeletal polymerization itself.

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I. INTRODUCTION

The purpose of this report is to summarize the findings of a literature search on the methods of improving the sensitivity of processless electron recording media (PERM™)* film to electron-beam radiation. The film is characterized by the ability to produce very fine grain, blue images on exposure to high energy electrons. The color change is the result of a solid-state polymerization, which converts a monomer crystal into a polymer species that absorbs light radiation in the visible region. This image formation is a chain process in which a single event produces multiple chromophores, which gives PERM™ recording film its high sensitivity. Since further enhancement of the imaging properties of the film is desirable, an investigation of the chemistry of the imaging component in the film was necessary.

Compounds that display chromic behavior of the type described above are the substituted diacetylenes. The primary characteristic of diacetylene compounds that makes them unique for this application is their ability to undergo a crystal-crystal transition in the solid state. In the monomer crystal, the π system of the diacetylene is isolated, and the monomer absorbs at short wavelength between 240 and 280 nm. In the polymer, conjugation extends all along the chain, the excitation energy of the system is lowered, and the polymer absorbs in the visible region between 500 and 600 nm. As a result, the polymerization of diacetylenes is accompanied by a distinct color change from colorless to blue, or in some cases, to blue-red.

Polydiacetylenes have been the subject of a number of experimental studies. The methods used have included both solid- and liquid-state studies, including ultraviolet (UV) and visible absorption, light scattering, resonance Raman spectroscopy, X-ray crystallography, and nuclear magnetic resonance (NMR) studies. The motivation for most of these investigations was the observation that an abrupt color change occurs as one varies the temperature, both when the polydiacetylene is crystalline and when it is in solution. A similar color change has been observed in solution by varying the solvent/nonsolvent ratio, and in the solid state by applying mechanical stresses. The terms thermochromism, solvatochromism, and mechanochromism have been coined to describe these phenomena.

This report reviews the research efforts pertaining to the chemistry of diacetylene compounds, the directions being taken in the field, and attempts to highlight those efforts, which may lead to approaches toward improving the sensitivity of PERM™ recording film to electron-beam radiation.

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II. BACKGROUND

Diacetylenes are unique in that monomer single crystals of suitably substituted derivatives can be converted into polymer single crystals via solid-state polymerization. The diacetylene molecules are arranged in the lattice in a ladderlike fashion, such that the ends of the adjacent triple bond systems approach each other at a distance of less than 5 Å. Polymerization is said to occur by successive tilting of each molecule along the ladder without moving the molecule from its lattice site. Thus, the mode of packing of the side groups and the lattice symmetry are retained throughout the reaction. The concept of a topochemical polymerization reaction in a perfect lattice is shown in Figure 1, while the whole process for a diacetylene stack is shown in Figure 2 [1].

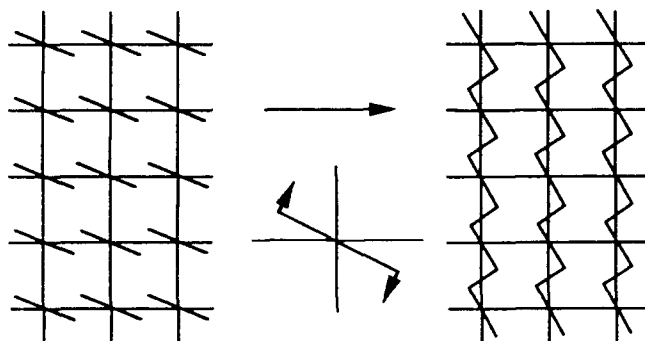


Figure 1. The principal idea of a topochemical solid-state polymerization: a reaction in a perfect lattice.

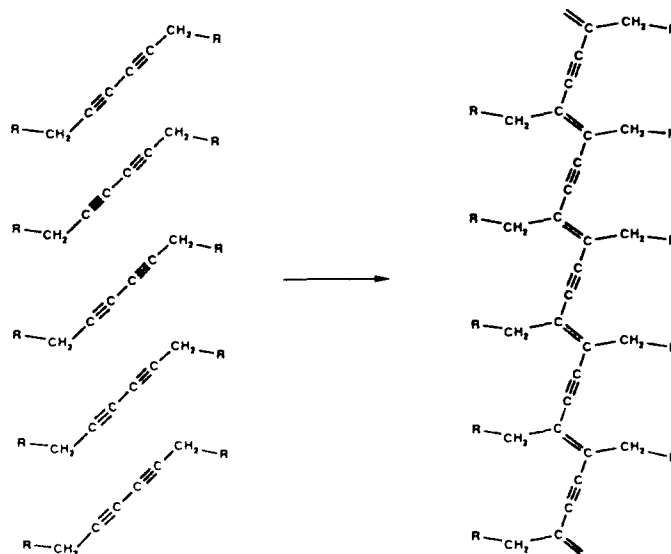


Figure 2. Scheme describing the topochemical polymerization of monomers with conjugated triple bonds ("diacetylenes"); note that the reaction gives rise to a planar, polyconjugated macromolecule.

Although topochemical polymerizations are fairly well understood in terms of their crystallography, very little is known about the kinetics of these reactions in terms of macromolecular aspects, namely, control of molecular weights, molecular distribution, etc. One mechanism of phase transformation, which shows how the lattice symmetry can control the kinetics, is depicted in Figure 3.

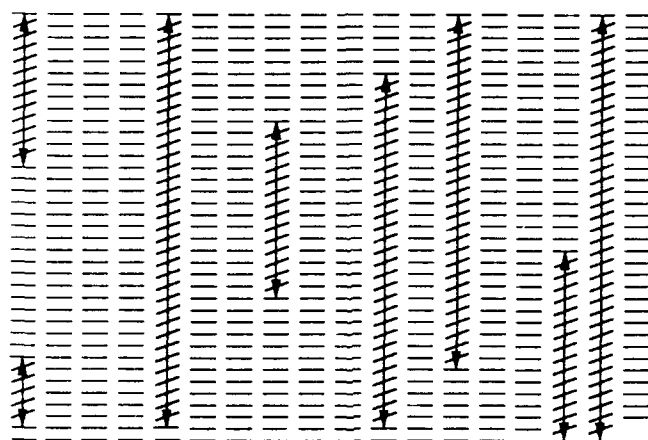
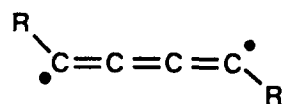


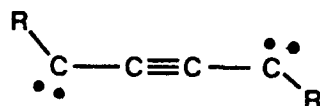
Figure 3. The mechanism of phase transformation during the solid-state polymerization of diacetylenes: polymer chains grow independently from each other, forming a solid solution of extended chains in the otherwise undisturbed lattice.

Intense debate exists as to how the chains are initiated and propagated, and what the causes of chain termination might be. Answers to such questions are being pursued.

For initiation, it appears that a diacetylene converts to a species such as the diradical (DR) or dicarbene (DC), shown below [2]:



DR



DC

The generation and role of these species in chain propagation have been studied extensively. There is, as yet, no definitive conclusion as to the nature of these reactions. Both thermal and radiation induced polymerization are also expected to occur by different mechanisms. In general, however, the solid-state polymerization is believed to proceed via trans-1,4-addition reaction in the crystal lattice leading to the two extreme backbone structures: a mesomeric ene-yne structure or a butatriene structure, as shown in Figure 4 [3].

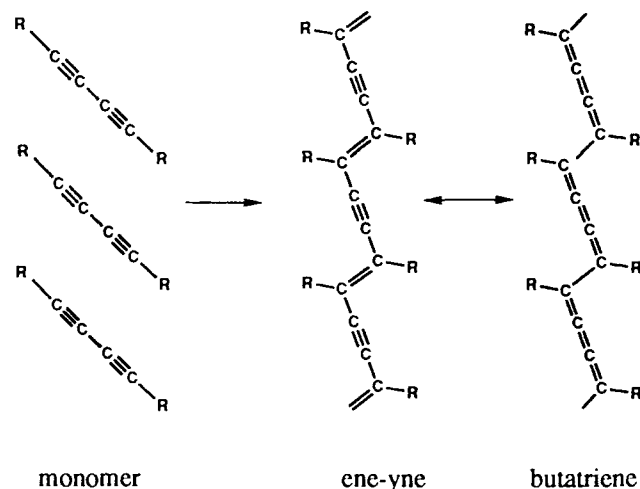


Figure 4. Topochemical solid-state polymerization of diacetylenes.

Although the geometries of the ene-yne and butatriene structures are essentially equivalent, there is general agreement that for high molecular weight polydiacetylenes, the ene-yne structure predominates and that the butatriene structure is absent. For example, crystal structures show that the chain with an alternation of double, single, triple, and single bonds (ene-yne structure) occurs in preference to that with a single and three double bonds (butatriene structure). Calculations also predict the ene-yne structure to be energetically more favorable. Recent results with solid-state ^{13}C NMR provide further evidence for this view [4].

The phenomenon of color changes in these systems has been attributed thus far to one of two hypotheses. One hypothesis is that order disorder transitions in the polymer backbone structure impact the effective conjugation length of the polymer chain. The other hypothesis is that the color changes are linked to an aggregation phenomenon of many different chains, similar or equal to the nucleation of particles in the course of the precipitation or crystallization of conventional polymers from dilute solution. However, this area is quite controversial, and the true reasons for the color changes as yet appear unclear.

Disruption of conjugation in the polydiacetylene molecules can be illustrated by allowing rotation about the single bonds, which serves to break up the conjugation. This operation is depicted in Figure 5 [5].

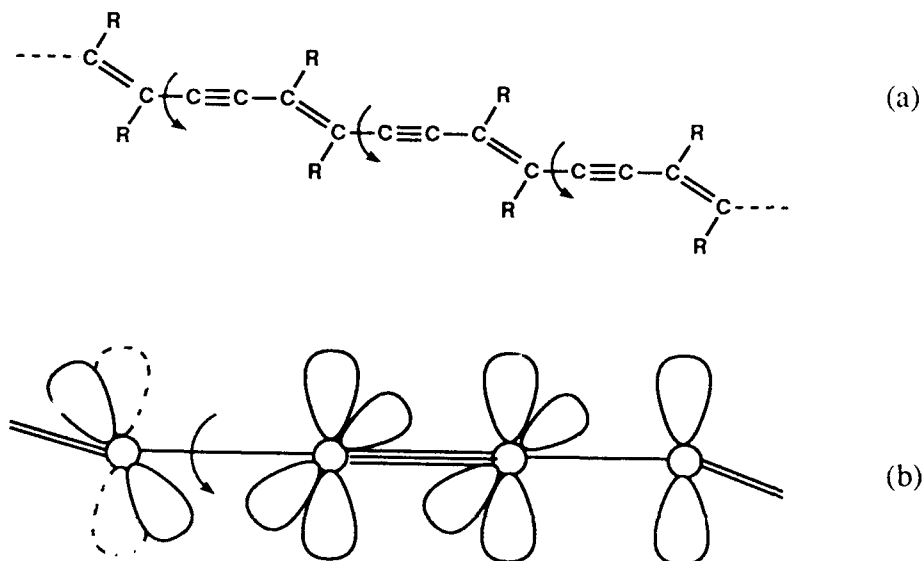


Figure 5. (a) Structure of a substituted polydiacetylene. The letter R represents side chains, and the arrows represent the low energy rotations around single bonds capable of creating disorder in the electronic structure. (b) An enlargement of single bond—triple bond—single bond region of the polymer, showing how the relative orientations of the p orbitals change when a rotation is performed.

Random rotation can result in a variety of conjugation lengths, which contribute to the different colors observed when the polymer is subjected to different stresses. The most general description shows the polymer consisting of (a) a rodlike structure with maximum conjugation length; (b) a random disorder, which is likened to a defect; and (c) a wormlike structure, similar to a continuous curvature or coiled structure [6]. This description is represented in Figure 6.

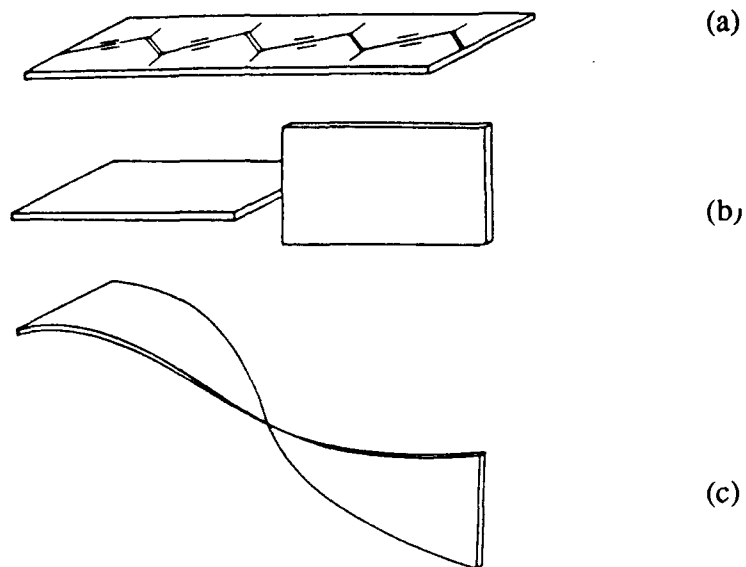


Figure 6. Shape of the PDA chain. (a) Planar structure in the crystal. (b) Two segments in solution in terms of the Kuhn chain (note that adjacent segments are electronically coupled due to bond rotation and that the bond connecting two segments has the character of a local defect). (c) Part of wormlike chain with continuous curvature of the chain skeleton.

With this background, we will focus on those areas of study that may shed some light on the issue of sensitivity while also reviewing progress in the field.

III. DISCUSSION

Disubstituted diacetylenes polymerize in the solid state either upon thermal annealing or upon exposure to high energy radiation such as UV light, X-ray, and γ ray. During polymerization, the crystal structure of the monomer is retained, leading to nearly defect-free single crystals of polymers. The highly conjugated backbone structure of the polymer is responsible for the colors observed. This description has been broken down further to relate the colors observed to an effective conjugation length [7]. Some generalizations regarding the geometries of polydiacetylenes and the colors observed are shown in Table 1. Improved sensitivity would require a defect-free crystal-crystal transition capable of a high effective conjugation length and, therefore, high molecular weight. The conclusions in Table 1 do not address how the distributions of conjugation lengths might affect the color observed or the efficiency of the polymerization.

Table 1. Colors of Polydiacetylene Molecules and Their Conformations

-
- A. Blue Color ($l_c^a > 30$ r.u.^b)
 - 1) Planar and Unstrained
 - 2) Planar and Compressed
 - 3) Planarity Periodically Interrupted
(Planarity > 30 r.u.)

 - B. Red Color (20 r.u. $> l_c > 10$ r.u.)
 - 1) Planar and Stretched
 - 2) Periodically Interrupted
($20 > \text{Planarity} > 15$ r.u.)
 - 3) Slightly Twisted
 - 4) Planar Butatriene Structure
 - 5) Low Concentration of Structural Defects

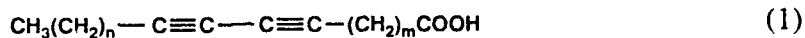
 - C. Yellow Color ($l_c < 6$ r.u.)
 - 1) Highly Nonplanar
 - 2) Highly Stretched
 - 3) Highly Twisted
 - 4) Planarity Periodically Interrupted
(Planarity < 6 r.u.)
 - 5) Isomerization With the Side Groups
 - 6) High Concentration of Structural Defects
-

^a Effective average conjugation length over which the electrons are delocalized.

^b Repeat units.

The review of the literature from 1980 on has revealed little in terms of spectral sensitization of diacetylene polymerization [8]. Photopolymerization of pure diacetylene is restricted to UV or high energy radiation, because the monomeric diacetylene chromophore absorbs in the UV range only. Extending the spectral sensitivity would require substituents that absorb visible light. But, the choice of substituents is limited by steric effects. Since the polymerization of diacetylene occurs in the solid state and is lattice controlled, a substituent acting as a chromophore must not disturb the molecular packing necessary to bring about solid-state reactivity. Thus far, there has been no report of a material specifically synthesized to sensitize the diacetylene polymerization to electron beam radiation.

Early work in polydiacetylenes focused on diacetylene monomers of type (1), below:



where n and m were varied and the electronic effects on the diacetylene moiety were negligible. These compounds were used to prepare Langmuir-Blodgett (LB) monolayers, where the molecules are aligned in a parallel fashion and subsequently polymerized. An example of the spectral changes that occur when polydiacetylene films are thermally annealed is shown in Figure 7, for the LB film of (1), where $n=12$ and $m=8$. The name of this compound is abbreviated to PCDA [9].

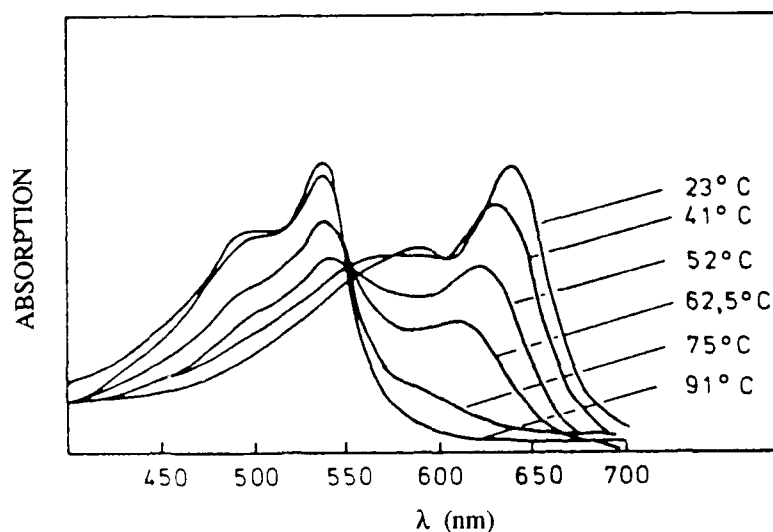
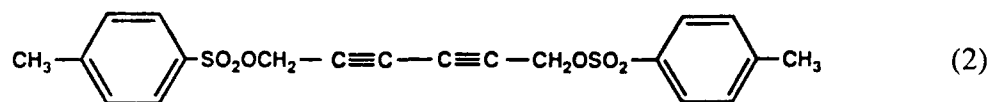


Figure 7. Optical absorption spectra of a partially polymerized multilayer LB film of PCDA polydiacetylene.

For this compound, the color change is an irreversible one from blue to red at about 70°C. The color change could be the result of change in side group packing or shortened conjugation lengths arising from structural disorder.

Original work in this field was restricted to the solid state because the polymers formed were insoluble. Extensive studies were carried out on the ditosylate of 2,4-hexadiyn-1,6-diol (2).



The desirability of this compound was its ability to form the most defect-free crystals of the diacetylenes studied thus far. It was also shown that, in order for solid-state polymerization to take place, the monomer molecules must be aligned such that the intermolecular distance between reacting diacetylene moieties is less than 5 Å. Otherwise, the stresses developed during the crystal-crystal transition from monomer to polymer would terminate continued chain propagation. The general results in Table 1 are consistent with those obtained from work in the solid state at that time.

Studies in solution began in the late 70s with the synthesis of the urethane substituted monomers. The butoxycarbonylmethylene urethane (BCMU) structure is shown as type (3), below:



It was now possible to compare the chromism of these polymers in solution with that in the solid state. For these examples, the thermochromic phase transitions that occur in solution are reversible [10]. The changes in optical absorption for solutions of 3BCMU (n=3, m=3) and 4BCMU (n=4, m=3) are seen in Figure 8.

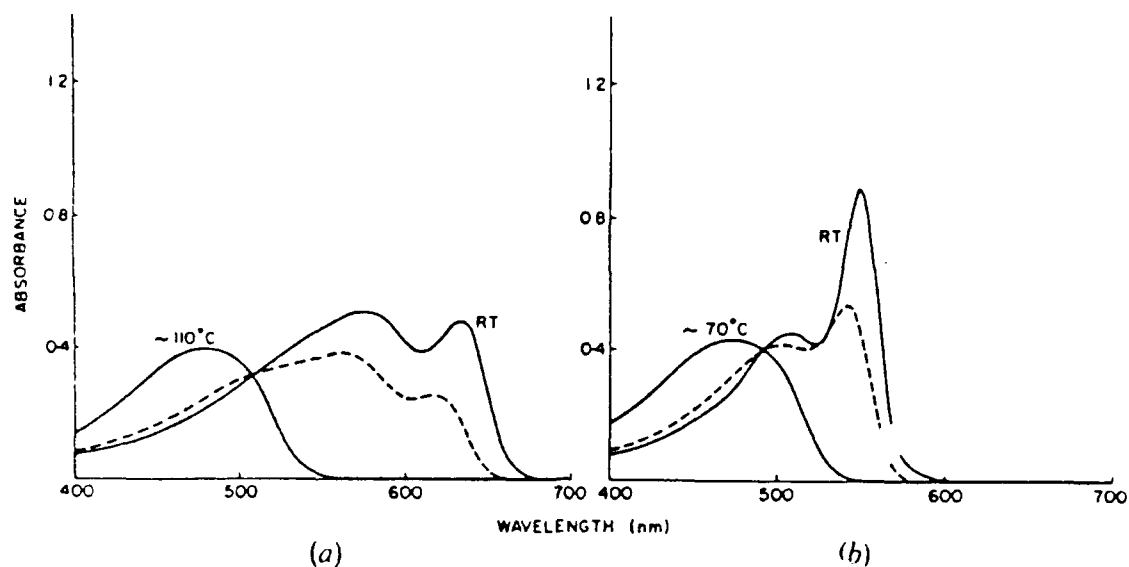


Figure 8. Optical absorption spectra of (a) 3BCMU and (b) 4BCMU polydiacetylene solutions at room temperature and elevated temperatures. The dashed curves are intermediate spectra. The solvent was *o*-dichlorobenzene.

The structural changes responsible for the color changes resulting from thermal annealing are believed to be the same as those resulting from solvatochromism. It was found that solutions of 3BCMU show a color dependence, depending on the solvent/nonsolvent ratio used. At ambient temperature, the chloroform solution is yellow, whereas at a critical concentration of the non-solvent toluene, a blue solution results. Considerable controversy exists as to the exact nature of the transformations responsible for the color changes. However, there seems to be little dispute that the polymer chains are reasonably straight in the blue solution, as the optical absorption spectra are very similar to those in the crystalline form, and that the polymer chains are disordered in the yellow form.

All of the monomers described thus far have a number of methylene groups attached to the diacetylene moiety. As such, there is little influence by the substituent group on the electronic character of the reactive group. Where substituent groups are varied, the results range from rapidly polymerizable to completely unreactive when the monomers are subjected to irradiation.

One example where only a single methylene group separates the diacetylene group from the remainder of the side group is shown in Table 2 [11].

Table 2. Polymerization Behavior of Diacetylenes to UV Radiation in the Frozen State

Structure	R	Activity
$R-CH_2-C\equiv C-C\equiv C-CH_2-R$	CH_3COO-	Inactive
	CH_3O-	Inactive
	$(CH_3)_2N-$	Inactive
	$Br-$	Active
	$Cl-$	Highly Active

It appears that inductive effects of the side group on the diacetylene moiety are responsible for the reactivity. However, there is no information regarding whether these groups create different packing parameters, which could also lead to these differences in reactivity.

The literature reviewed thus far pays little attention to the sensitivity of diacetylenes to radiation other than UV radiation. Much of the work being carried out today is related to the nonlinear optical properties of substituted diacetylenes and their polymers. The ability of these molecules to align in an orderly fashion is a major criterion for the optical properties observed. The synthesis of a wide variety of compounds is being pursued in order to tailor the properties of the molecules to the application of interest [12,13].

Another research area in which efforts are significant is the study of the exact nature of the causes of chromism in polydiacetylenes. Under the general heading of conformational disorder, various research groups are attempting to determine whether chromism is the result of distortion of the polydiacetylene backbone structure with the resultant reduction of conjugation length, or whether the phenomenon is the result of the aggregation of groups of molecules. These studies are expected to be quite important in designing imaging components that might serve to maximize the sensitivity of diacetylene monomers to various forms of radiation.

Many of the studies that are of interest attempt to compare the effect of different diacetylene substitution patterns on the reactivity of the diacetylenes. However, in general, these studies are very selective and do not answer many of the questions that arise concerning the causes of

chromism. These questions include (1) What effect do the substituent groups have on the order and packing of the new diacetylenes in the crystalline state? and (2) What effect do nearby substituent groups have on the reactivity of the diacetylene moiety, independent of the packing parameters?

Finally, there is one area of research that has not received adequate attention: the important relationship between polymer molecular weights and molecular weight distribution and the chromic effects observed. In the early work on polydiacetylenes, the polymers were insoluble and could not be studied by most methods. The extent of polymerization was determined by dissolving unreacted monomer from the solid polymer product. However, this method has been called into question because of the difficulties inherent in the process, and the extent of polymerization may be much less than that observed [14]. Also, low molecular weight components with short effective conjugation lengths that are not soluble will not contribute to the desired photochromic effect. Because of the emphasis on effective conjugation length and therefore on the molecular weights of the products formed, it will be necessary to obtain molecular weight distribution information. With the synthesis of new diacetylene compounds, certain classes of compounds were found to be soluble when polymerized and molecular weight determinations began to be reported. However, the data obtained thus far has not been effectively applied to the chromism question. Further work in this area is expected to produce information that should shed some light on the relationship described above [15].

Controversy exists as to whether chromism is reflected by very high molecular weight species in which there are few defects and the conjugation length is long, or whether there is an assembly of shorter chain lengths that produces the same results. *Ab initio* calculations of conjugation lengths and the expected absorption spectra attributed to the degree of conjugation have been made [16-19]. However, suitable experimental model systems supporting these studies are lacking. It is not yet clear what part molecular weight distribution plays in the resolution/sensitivity scenario.

There is a lack of information directly relating the sensitivity of diacetylenes to electron-beam irradiation. Therefore, pertinent data obtained from the polymerization of diacetylenes by other methods must be considered and applied to the problem at hand. The following section summarizes those factors deemed important and offers guidelines for further study.

IV. FACTORS INFLUENCING DIACETYLENE CHEMISTRY

A. LATTICE EFFECTS

It appears that only those diacetylenes are reactive to irradiation where the geometric change in going from the monomer to the polymer crystal is not too severe. In crystallographic terms, the interplanar distance in the monomer crystal must be of the order of 5 Å, and the tilt angle between the principal crystal axis and the long axis of the diacetylene group must fall within a certain range of values [20]. Thus, a properly designed monomer would have built in to its structure those features that would maximize these crystalline parameters.

An example that may serve to illustrate this structural requirement is the high energy beam irradiation of the LB films formed from pentacosadiynoic acid (12-8 PDA). The LB films were prepared by building up monolayers under different subphase conditions and surface pressures. This approach was taken in order to elucidate the reactivity of LB films as a function of molecular density or arrangement in the film. The films were described as a low density type (A) and a high density type (B). If one assumes that the molecular arrangement of the LB films is maintained during buildup, then the molecules in type A film will be arranged in a somewhat tilted state, while those in type B film will have a more densely packed arrangement. The reactions of these two types of films to irradiation are shown in Figure 9 [21]. The loosely packed configuration shown in Figure 9A is more favorable for 1, 4 addition, while the more vertically oriented configuration in Figure 9B reacts by an alternate mechanism. Spectroscopic analysis showed that polydiacetylene

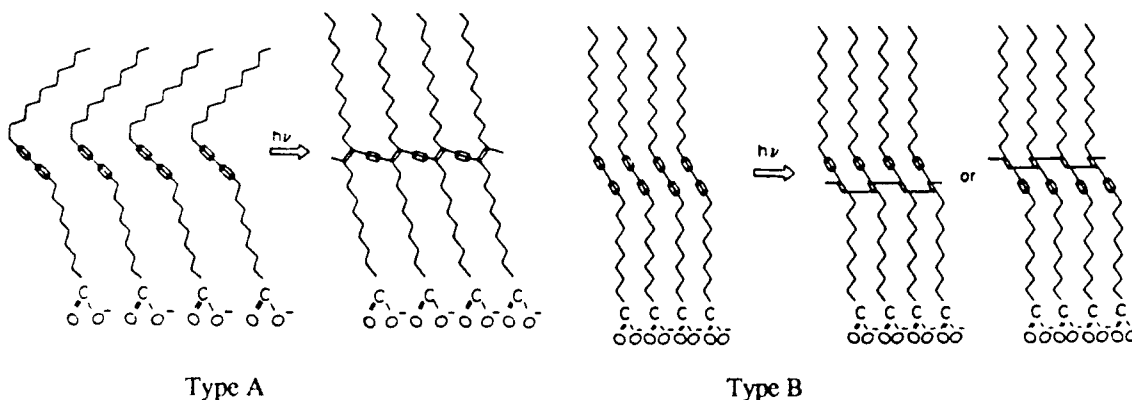
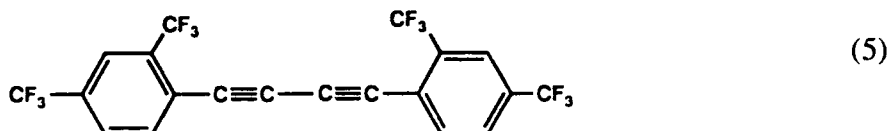
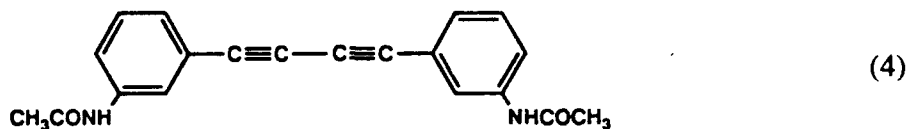


Figure 9. Reactivity of two types of LB films under high energy beam irradiation.

polymerization occurs by X-ray radiation only with type A film, while polyacetylene polymerization occurs only with type B film. The above analysis makes a very strong case for the requirement that proper molecular alignment is necessary for diacetylene polymerization to proceed favorably.

One of the few studies where the side chain participates in the conjugation with the triple bonds in the carbon backbone compared the reactivities of butadiynylenebis(m-acetamidobenzene) (4) and butadiynylenedi[2,4-bis(trifluoromethylbenzene)] (5) to X-ray irradiation.



The fluorinated monomer (5) was not amenable to crystallographic study, since this compound reacts very rapidly under X-ray irradiation to give 100% polymer, even at temperatures as low as 100 K. On the other hand, monomer (4) reacts only slowly in the X-ray beam, and the reaction ceases after about 40% conversion to polymer. The conclusion from this work is that the role of the side chain in the solid-state polymerization of a diacetylene is to act as an anchor, allowing the product to fit in the reacting lattice [22]. Intramolecular effects, both steric and electrostatic, can contribute to this anchoring. Thus far, the part each effect plays in side chain order has not been thoroughly investigated. Model systems can be generated to assess at least the steric contributions that might maximize the lattice order and lay the foundation for predicting the optimum side chain structure.

B. CONJUGATION LENGTH

The effective length L of the potential well of a linear conjugated molecule is known as the conjugation length. This imprecise term is useful in describing the effects that occur when an otherwise perfect conjugated backbone is subjected to mechanical deformation that destroys either the planarity or the regular pattern of bond lengths. With increasing distortion, the conjugation length decreases and, hence, the energy of the electronic excitation increases. A single, long polymer molecule may have a number of regions with varying distortion and conjugation length. In addition to the conjugation length, there is a polarization contribution to the energy, which depends on the density of nuclei and electrons in the vicinity of the polymer backbone. Thus, any change in the molecular packing, such as that caused by thermal expansion, application of hydrostatic pressure, or the occurrence of a phase transition, is likely to alter this energy and, hence, also the color of the conjugated polymer [23]. An example of this mechanochromism is

illustrated by the effect of hydrostatic pressure on the electronic excitation of a polydiacetylene crystal, as shown in Figure 10.

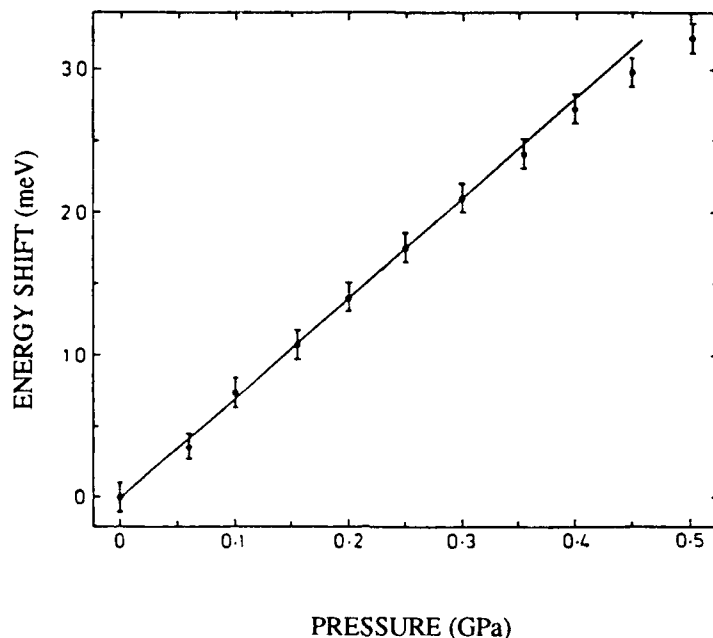


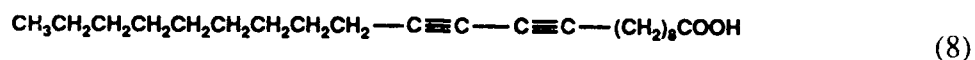
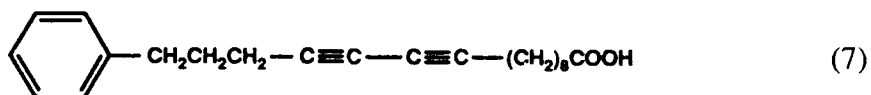
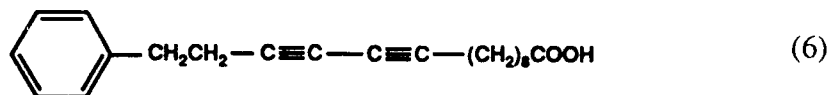
Figure 10. Shift of the 2 eV electronic excitation of a TS polydiacetylene single crystal to lower energy with increasing hydrostatic pressure.

The bond lengths along the backbone are said to remain almost constant. The force exerted on the ends of the polymer chains is almost exactly balanced by the squeezing effect that results from the pressure on the side groups. Thus, the lowering of the energy in Figure 10 results primarily from the increased density of the side group packing. Therefore, the influence of the side group geometry and side group contribution to electron density in the diacetylenes must both be considered in the resulting chromic effects in the polymer formed.

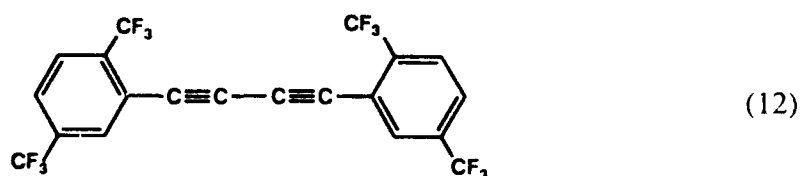
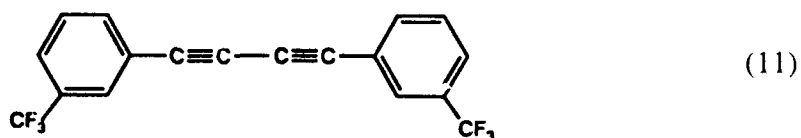
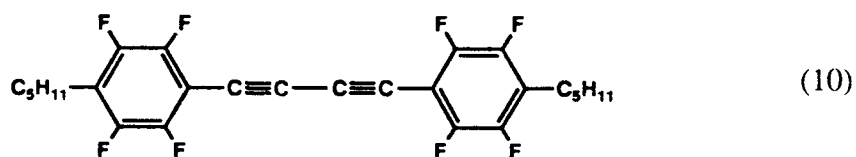
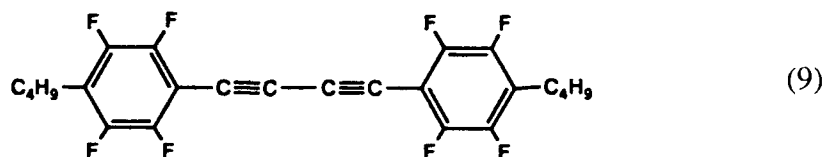
C. SUBSTITUTION PATTERNS

In a study of compounds (6)-(8), where the number of methylene groups on the substituent containing the carboxyl group is kept constant while the other substituent is varied, the results of xenon lamp irradiation of LB films alone or as equimolar mixtures are essentially the same. That is, the mixtures produced copolymers, indicating that varying the chain length of one substituent

group had little effect on the packing parameters, even with the presence of the terminal aromatic group. No quantitative polymerization data were obtained for this system [24]. The compounds are shown below:

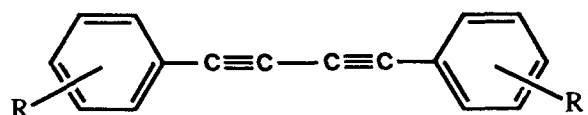



In an example that compared fluorine-substituted aromatic rings that were directly bonded to the diacetylene group, ^{60}Co γ irradiation resulted in 99% conversion to polymer. Of the examples shown below, compound (12) displayed an exceptionally high crystalline quality [25].



Another report on some novel unsymmetrically substituted diacetylenes shows how apparent small differences in substitution patterns can affect different methods of polymerization. In Table 3, although all compounds were polymerized in the solid state, no explanation was given as to the different reactivity of compound III when compared to compounds I and II [26]. These are essentially positional isomers with little stereochemical difference. More information is needed regarding these effects.

Table 3. Solid-state Polymerization of Unsymmetrically Substituted Diphenyldiacetylenes



	R	R'	Solid-state polymerization		
			Heat	UV	Visible
I	4 -NO ₂	2' -OCH ₃		√	√
II	2 -NO ₂	2' -OCH ₃		√	√
III	4 -NO ₂	2' -OH	√		
IV	2 -NO ₂	4' -N=CH  OCH ₃	√	√	

Further work on the solid-state polymerization of unsymmetrically substituted diacetylenes also found some interesting variations. In Table 4, with the exception of monomer (12), diacetylenes (3)-(14) were found to polymerize in the crystalline state upon thermal annealing or exposure to light, UV, or γ irradiation [27].

Table 4. Structures and Properties of Diacetylenes (3) - (15) and Related Compounds^a

$R^1-OCH_2-C\equiv C-C\equiv C-CH_2O-R^2$					
	R^1	R^2	solvent ^b	M.P./°C	Polym.
(1a)	<i>p</i> -MeC ₆ H ₄ SO ₂	= R ¹		96	(+)
(1b)	<i>p</i> -MeOC ₆ H ₄ SO ₂	= R ¹		120	(+)
(1c)	<i>p</i> -MeC ₆ H ₄ SO ₂	<i>p</i> -FC ₆ H ₄ SO ₂		71	(+)
(1d)	<i>p</i> -CF ₃ C ₆ H ₄ SO ₂	= R ¹		105	(-)
(1e)	<i>p</i> -ClC ₆ H ₄ SO ₂	= R ¹		102	(-)
(2)	H	H		113	^c
(3)	PhCH ₂ -NHCO	H	tl	69	(+)
(4)	PhCH ₂ -NHCO	= R ¹	tl/an	140	(+)
(5)	PhCH ₂ -NHCO	Ph-SO ₂	ie/dm	71	(+)
(6)	PhCH ₂ -NHCO	<i>p</i> -MeC ₆ H ₄ SO ₂	et/me	68	(+)
(7)	PhCH ₂ -NHCO	<i>p</i> -CF ₃ C ₆ H ₄ SO ₂	an/al	99 ^d	(+)
(8)	PhCH ₂ -NHCO	<i>p</i> -FC ₆ H ₄ SO ₂	dm/me	90	(+)
(9)	PhCH ₂ -NHCO	<i>p</i> -ClC ₆ H ₄ SO ₂	an/al	87	(+)
(10)	PhCH ₂ -NHCO	<i>p</i> -MeOC ₆ H ₄ SO ₂	ie/dm	75	(+)
(11)	PhCH ₂ -NHCO	<i>p</i> -NO ₂ C ₆ H ₄ SO ₂	ie/dm	98	(+)
(12)	PhCH ₂ -NHCO	<i>p</i> -NO ₂ C ₆ H ₄ NHCO	ea/dm	146	(-) ^e
(13)	PhCH ₂ -NHCO	<i>p</i> -MeC ₆ H ₄ SO ₂ NHCO	ea	168	(+)
(14)	PhCH ₂ -NHCO	<i>S</i> -PhCH*(Me)NHCO	dm/al	73	(+) ^f
(15)	<i>S</i> -PhCH*(Me)NHCO	= R ¹	al	120	(-)

^aSatisfactory ¹H n.m.r. spectra (200.13 MHz) and combustion analyses (C, H) have been obtained for all new compounds (3)-(15): m.p.s were measured on a Kofler hot bench and/or by differential scanning calorimetry (d.s.c.).

^bal: ethanol; an: acetone; dm: dichloromethane; ea: ethyl acetate; ee: diethyl ether; ie: di-isopropyl ether; me: methanol; tl: toluene.

^cSee ref. 11.

^dAnother unreactive crystal modification was occasionally observed (m.p. 100°C).

^eUnreactive on thermal annealing and γ -ray exposure.

^fProbably incomplete polymerization.

It should be noted that the symmetrical compounds, (1d) and (1e), are unreactive, while their corresponding unsymmetrical compounds, (7) and (9), containing the benzylurethane group, polymerize readily. Even from these data, no clear-cut explanation of the reactivities in these compounds is apparent. Unfortunately, there is no comparable information on the extent of polymerization in these systems. This would be very important in elucidating which substituent groups have the greatest impact on polymerization of those compounds where the substituent group is not actually in conjugation with the diacetylene group.

D. REACTIVITY

The lattice packing of reactive diacetylenes is most conveniently displayed using the monomer separation and tilt angles (d and γ). Crystal structure data for both reactive and unreactive compounds were used in a comparison of the lattice packing of diacetylene monomers and their solid-state reactivity. This comparison showed that a reasonable criterion for reactivity is that the reacting (1 and 4') carbon atoms must be separated by less than 0.4 nm [28]. The rate of polymerization is strongly influenced in these cases but not the occurrence of solid-state reactivity. Since the close packing of monomers is determined by the van der Waals radius of the diacetylene carbons, the values of d and γ for reactive packing must lie within the shaded area of Figure 11.

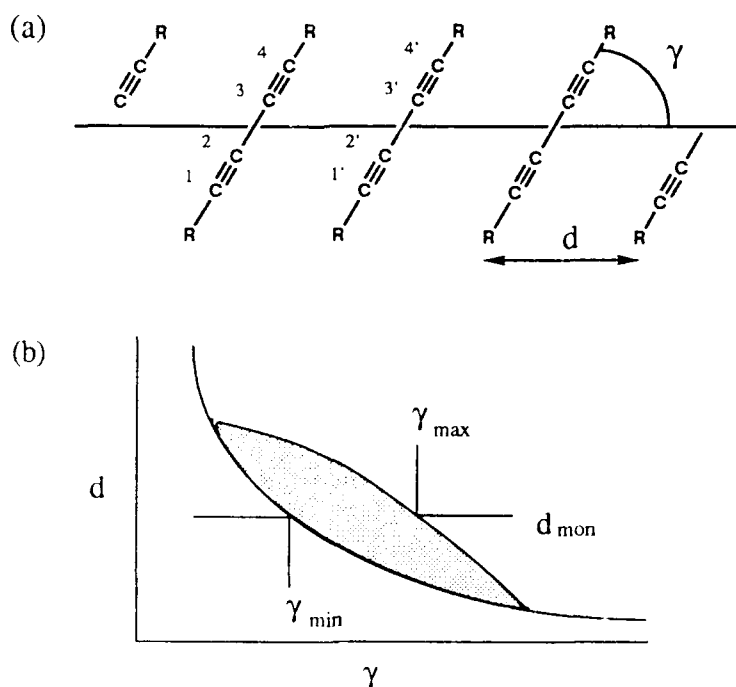


Figure 11. Solid-state polymerization of diacetylenes.
(a) Monomer array in crystal lattice.
(b) Reactive packing (shaded area) shown in terms of d and γ .

Thus, for any given monomer of separation, d , there is a range of values from γ -min to γ -max, which allows solid-state polymerization to occur. The arrangement shown in Figure 11a presupposes an extended conformation of the diacetylene molecule. For monomers with bulky end groups, the flexibility of the monomer molecule can result in a compact molecular structure in the crystal. The side groups then impede the reaction, in contrast to the situation in reactive monomers, where the side group interactions bring the diacetylene moieties into the desired reactive contact.

In a series of monomers based on esters of 2,4-hexadiyn-1,6-diol, substitution on the terminal benzene ring is shown to have a marked effect on the molecular conformation and packing. The members of the series studied are shown in Figure 12.

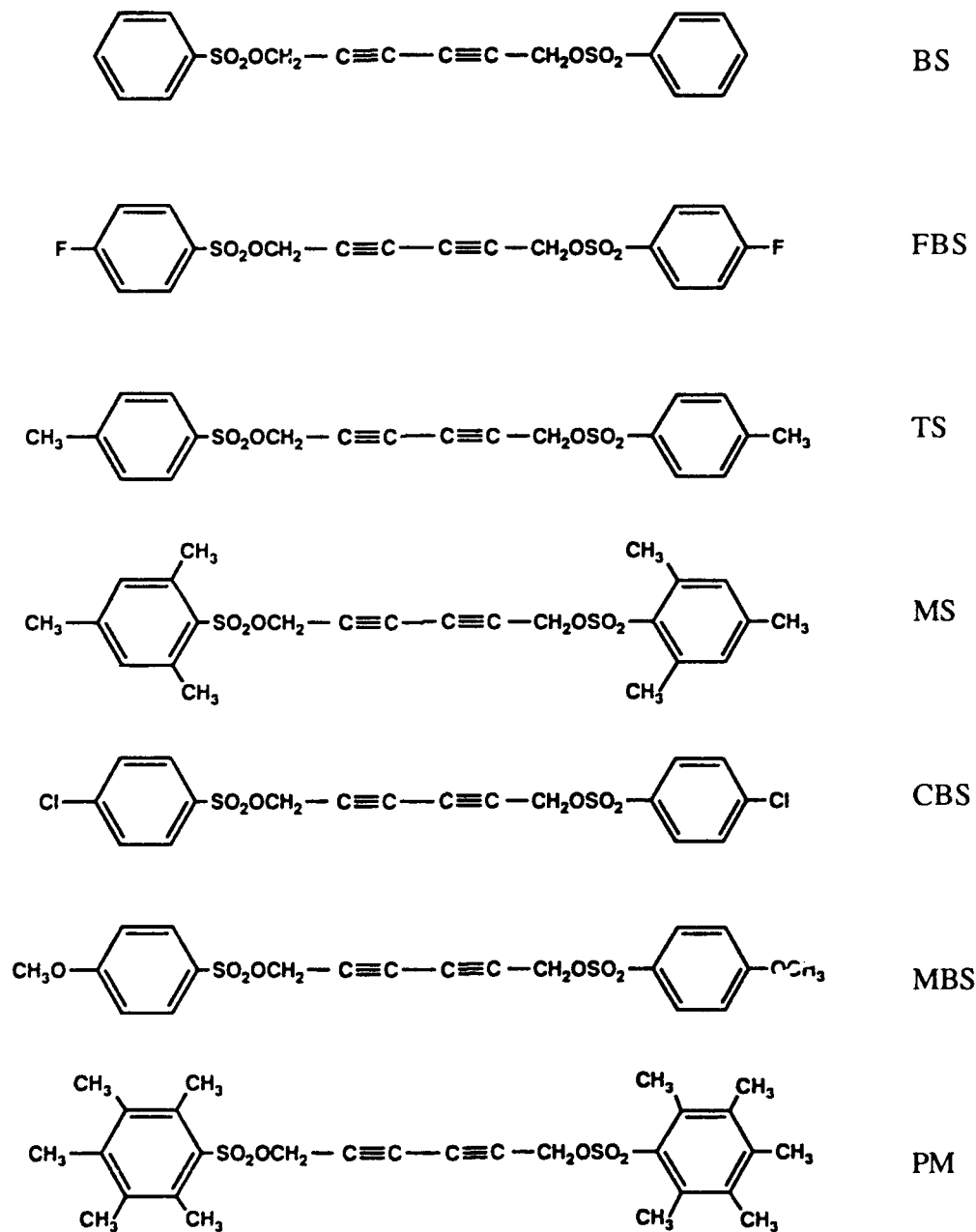


Figure 12. Structures of bisbenzenesulfonate-substituted (BS) diacetylenes.

In Figure 12, the compounds differ only in the substitution on the benzene ring. The values of d and γ determined for the monomers in Figure 12 and their relationship to the solid-state reactivity of these compounds are shown in Table 5.

Table 5. Lattice Packing of BS Related Monomers

Monomer	d (nm)	γ min	γ max	γ	Reaction
BS	0.528	40°	49°	45.2°	Yes
FBS	0.515	41°	50.5°	44.8°	Yes
TS	0.515	41°	50.5°	43.4°	Yes
MS	0.547	37°	46°	66.3°	No
CBS	0.503	42°	51°	66.7°	No
MBS	0.580	36°	43°	60.9°	No
PM	0.645	32°	35°	68°	No

The monomers BS, FBS, TS, MBS, and CBS are found to have the same conformation in the crystalline state. Of these, the values for BS, FBS, and TS fall within the guidelines for packing and reactivity shown in Figure 11. However, for MBS and CBS, the molecular tilt is too great for reactivity. Unlike the previous five monomers, MS and PM adopt different conformations. However, the tilt angle found for these monomers is also too great for reactivity. This study shows how sensitive the lattice packing is to small changes in substitution patterns [28].

One must note, however, that the data on reactivity are not accompanied by characterization of the polymers formed to include extent of polymerization. It may be that there is an optimum d and γ , which produce an ideal lattice packing, where solid-state polymerization can proceed with minimum volume change. This should result in the maximum extent of polymerization in a series of this type. A vivid example of how the crystal-crystal transition is easily accommodated in diacetylene polymerization is seen in the projection of the crystal structure of the monomer, bis-*p*-toluenesulfonate ester of dodeca-5,7-diyne-1,12-diol, on top of the crystal structure of the corresponding polymer (PTS-12) [1]. As shown in Figure 13, the side groups are able to maintain their relative position while the diacetylene moiety adjusts with little overall lattice stress.

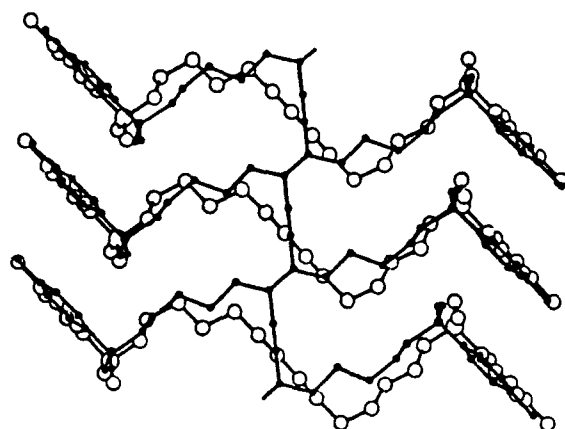


Figure 13. A projection of the crystal structures of PTS-12 monomer and polymer on top of each other.

With the aid of Chem3D, a molecular modeling software program from Cambridge Scientific Computing, Inc., one can visualize the spatial relationships involved in the chemistry of the diacetylenes described in this report. In Figure 14b are shown four molecules of 12-8 PDA assembled in a three-dimensional perspective, as would be observed in a monomolecular layer of an LB film. Flanking this view are both a side view (14a) and a front view (14c). All structures are drawn to mimic the monomer separation distances and tilt angles, which provide the proper geometry for chain propagation in diacetylenes. On polymerization, the linear chain structure is

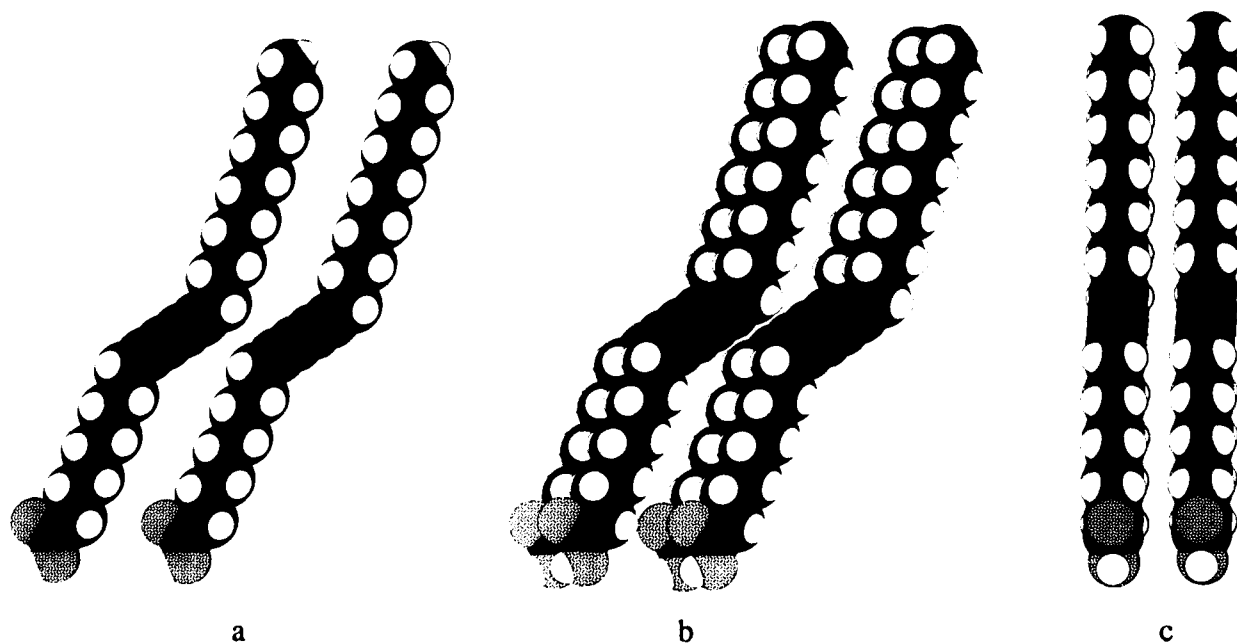


Figure 14. Molecular models of LB simulation of a group of four 12-8 PDA monomers.

formed and is represented in Figure 15 as a chain-terminated hexamer. Figure 15a represents the

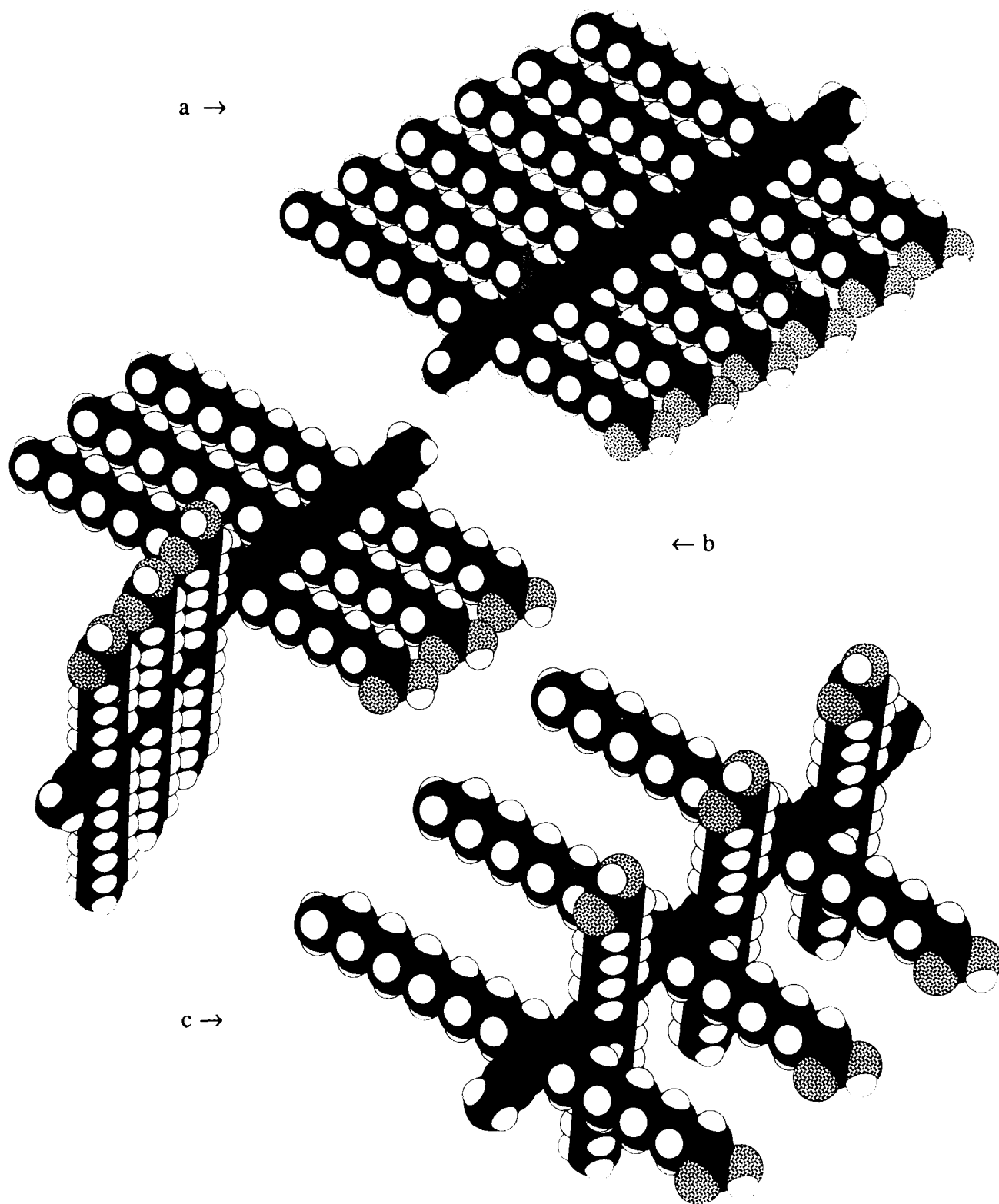


Figure 15. Space-filling molecular models of methyl-terminated 12-8 PDA hexamer.

planar defect-free structure of a polydiacetylene fragment of 12-8 PDA. In Figure 15b, a single defect that reduces conjugation length is shown as a 90° rotation about the single bond connecting sp and sp² carbon atoms in the backbone. An extreme case of alternating 90° rotations along the backbone is shown in Figure 15c, which represents multiple distortions. This would serve to eliminate any chromic effect. With this modeling program, one can design accurate diacetylene monomer and polymer structures and determine energy minimization values for molecules in close proximity. With information such as this, one could predict the molecular architecture required for optimizing the lattice parameters in the solid-state polymerization of diacetylene monomers.

V. SUMMARY

This summation has emphasized the importance of lattice effects, conjugation length, and substitution patterns on the reactivity of diacetylene monomers to various forms of polymerization techniques. It seems clear that an ideal set of crystal packing parameters, coupled with the formation of defect-free crystals, would provide the optimum geometry for efficient polymerization to take place. Substitution patterns not only provide the basis for which these conditions are met but also can play a role in the relative reactivity of the monomers to the thermal and radiative means of polymerization that are desired.

Although the mechanisms of polymerization of the diacetylenes are generally understood, much remains to be learned. Characterization techniques are beginning to reveal significant data on the structure of these compounds in solution. These data will provide important information on the effect of molecular weight and molecular weight distribution on the optical properties of polydiacetylenes. It is important that the extent of polymerization and the resulting polymer structure be determined. Detailed property data resulting from electron-beam polymerization of diacetylene monomers are virtually nonexistent. Therefore, studies of the polymerization processes for diacetylenes by other means must be used for comparison. Those studies have been outlined here and will be referred to in the following section.

VI. RECOMMENDATIONS

The approaches outlined below address those areas of study that have not received attention with respect to the sensitivity question. Many of these approaches derive from the extensive research conducted under UV polymerization. Similar work may already be in progress in related areas. Further research in these areas will be essential in order that the effect of structural properties of polydiacetylenes on their optical properties be fully understood.

A. PROCESSING

It will be assumed that all of the obvious film processing techniques that are necessary to maximize the sensitivity of the currently used system have been evaluated, i.e., the crystal size, the monomer purity necessary to provide defect-free crystals, and the quality of the dispersions that are a key part of the film. It has also been shown that some diacetylenes can exist as polymorphic structures. Thus, certain crystal structures of the same compound have been found to be polymerizable, while others are unreactive. In our own work on imaging the 12-8 PDA molecules by scanning tunneling microscopy, we have found that the microstructures of crystals formed from acetone, heptane, and 1-butanol are quite different. Therefore, it is important that crystallization rates be carefully controlled and that the crystalline state of the monomer be well characterized. Beyond the optimization of these processes, the direction of any effort points to the selection of the imaging component.

B. CRYSTALLINE PACKING PARAMETERS

In crystallographic terms, the interplanar distance in the monomer crystal must be of the order of 5 Å, and the tilt angle between the principal crystal axis and the long axis of the diacetylene group must fall within a certain range of values. It is possible to design a monomer that would have built in to its structure those features that would maximize these crystalline parameters. From the available crystallographic data and with the use of sophisticated molecular modeling programs, it is conceivable to construct an ideal model monomer by the application of energy minimization features designed to reduce the effect of volume changes in the crystalline lattice during polymerization. Controlling the geometry of the molecule is expected to enhance the extent of polymerization and ensure that all the monomers will be reacted. In addition to optimizing the crystalline parameters to match the reaction coordinates, an increase in optical absorption can be realized by increasing the number of chromophores per unit volume in the medium. The chromophore, in the case of the 12-8 PDA, is the conjugated π -system of the polymeric backbone,

which forms a pseudo one-dimensional energy band structure that absorbs strongly in the red region of the visible spectrum. The density of the chromophores can be increased by reducing the size of the side groups. This approach has the advantages of providing a higher optical absorption density and a more efficient way of converting the deposited energy to initiating polymerization. The enhancement of conversion efficiency comes about from a probabilistic argument. That is, the energy that is normally absorbed and dissipated by the side groups will be available for initiating chemical reactions. This approach presupposes that the monomer physical properties will have a minimal impact on the film dispersion processes.

C. CONJUGATION LENGTH

It has yet to be determined experimentally what effective conjugation lengths are required to produce the desired chromic effect. If such information were known and the molecular weight distribution necessary to produce the chromic effect was determined, then monomers could be designed to optimize these parameters. In this way, it may be possible to devise a system that serves to short-circuit itself after some minimum degree of polymerization. This short-circuiting might be accomplished by copolymerization of suitably substituted diacetylenes where steric control predominates. A mixture of monomers that have different absorbing characteristics when polymerized may also be employed. This approach can allow the enhancement of sensitivity not only by increasing the absorption strength but also by widening the absorption bandwidth of the chromophore. Spreading the absorption strength of the chromophores over a wide spectral range allows more light to be absorbed and provides a more neutral color.

D. SUBSTITUENT ENHANCEMENT

Enhancing the reactivity of the diacetylene group can be accomplished by using substituents that are in close proximity to the reactive site and capable of inducing polarization in that group. Appropriate symmetrical substitution can serve to either increase or decrease the electron density about the diacetylene group inductively without being in conjugation with that group. In addition to this mode, side chain substitution can also serve to maintain planarity by engaging in remote interactions such as hydrogen bonding, which is observed in the urethane substituted diacetylenes. These remote interactions have the potential for reducing defects that can alter the effective conjugation lengths described previously. It is also possible to introduce into the side chain active groups that are capable of participating in charge transfer complexation that is assisted by the polymerization. This would function as an additional mode of sensitivity enhancement to that occurring during diacetylene polymerization. However, due to the requirements of close packing,

it would appear that the enhancement would be negligible in the transition from monomer to polymer.

E. MULTIPLE CHROMOPHORES

A two-step approach in which the initial diacetylene polymerization is followed by an additional intramolecular interaction that enhances the absorption further might be considered. This would undoubtedly be a complex undertaking but has considerable merit. In this approach, a substituent group could be designed that is not in conjugation with the diacetylene moiety in the monomer but is able to undergo a rearrangement as a second-stage reaction, which brings it in conjugation with the developing polydiacetylene chromophore.

F. SENSITIZATION

Little work has been done regarding the concept of electron sensitization in these systems. At this stage, this approach would be considered a long-range project. Sensitizers for use in UV polymerizations are well known, and an example of sensitizing diacetylene monolayers has been reported. However, such sensitizers must also conform to the crystalline packing parameters outlined previously in order to be effective. In any event, a systematic study of molecular sensitivity to electron beams would have to be undertaken to make this approach viable.

G. DIACETYLENES AS SUBSTITUENTS

In all of the systems studied thus far, the diacetylene group is at the core of the monomer structure, and the substituent groups provide the physical properties that dictate the choice of the monomer for the application of interest. A radical approach would be to design a prepolymer molecule in which the diacetylene group acts as a substituent. Thus, the prepolymer would consist of a flexible backbone chain in which the diacetylene substituents are located at the necessary intergroup distances that would allow chain propagation to take place. The reaction would occur among the side chains, and the proximity of the diacetylene groups would be controlled by the flexible backbone. This is an example of a comb-type polymer, which is common in silicone chemistry and is being applied in other classes of polymers for a variety of applications.

The recommendations outlined here describe areas that have not been addressed systematically. Research in diacetylene compounds is accelerating with respect to a strong interest in their non-linear optical properties. There has been little focus on the questions that are the subject of this report. A number of these areas are ripe for pursuit and are essential to an understanding of the

chemical and physical nature of the polydiacetylene system. Further work is strongly suggested in those areas deemed viable in contributing toward advances in the materials science and technology of imaging systems.

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TECHNOLOGY OPERATIONS

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Electronics Technology Center: Microelectronics, solid-state device physics, VLSI reliability, compound semiconductors, radiation hardening, data storage technologies, infrared detector devices and testing; electro-optics, quantum electronics, solid-state lasers, optical propagation and communications; cw and pulsed chemical laser development, optical resonators, beam control, atmospheric propagation, and laser effects and countermeasures; atomic frequency standards, applied laser spectroscopy, laser chemistry, laser optoelectronics, phase conjugation and coherent imaging, solar cell physics, battery electrochemistry, battery testing and evaluation.

Mechanics and Materials Technology Center: Evaluation and characterization of new materials: metals, alloys, ceramics, polymers and their composites, and new forms of carbon; development and analysis of thin films and deposition techniques; nondestructive evaluation, component failure analysis and reliability; fracture mechanics and stress corrosion; development and evaluation of hardened components; analysis and evaluation of materials at cryogenic and elevated temperatures; launch vehicle and reentry fluid mechanics, heat transfer and flight dynamics; chemical and electric propulsion; spacecraft structural mechanics, spacecraft survivability and vulnerability assessment; contamination, thermal and structural control; high temperature thermomechanics, gas kinetics and radiation; lubrication and surface phenomena.

Space and Environment Technology Center: Magnetospheric, auroral and cosmic ray physics, wave-particle interactions, magnetospheric plasma waves; atmospheric and ionospheric physics, density and composition of the upper atmosphere, remote sensing using atmospheric radiation; solar physics, infrared astronomy, infrared signature analysis; effects of solar activity, magnetic storms and nuclear explosions on the earth's atmosphere, ionosphere and magnetosphere; effects of electromagnetic and particulate radiations on space systems; space instrumentation; propellant chemistry, chemical dynamics, environmental chemistry, trace detection; atmospheric chemical reactions, atmospheric optics, light scattering, state-specific chemical reactions and radiative signatures of missile plumes, and sensor out-of-field-of-view rejection.